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A CONTRIBUTION TO THE TEXTILE CREASE RESISTING PROCESS

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NILS LANDQVIST

GÖTEBORG 1958

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1958

In the present dissertation, the parts 1—8 and 10 are a summary of the following papers:

I. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 595–612. (See Appendix.)
II. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 867–892.
III. Landqvist, N. *Acta Chem. Scand.* **11** (1957) 776–779.
IV. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1127–1142.
V. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1459–1465.
VI. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1466–1470.
VII. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1471–1476.
VIII. Landqvist, N. *Acta Chem. Scand.* **11** (1957) 780–785.
IX. Landqvist, N. *Acta Chem. Scand.* **11** (1957) 786–791.
X. Landqvist, N. *Acta Chem. Scand.* **10** (1956) 244–248.
XI. Landqvist, N. *Acta Chem. Scand.* **11** (1957) 792–803.
XII. Landqvist, N. *Svensk Kem. Tidskr.* **69** (1957) 524–532.

Till alla dem, som genom intresse, inspiration och arbete möjliggjort denna avhandlings tillkomst, framför jag mitt varma tack.

N. L.

Introduction

The textile crease resisting process highly improves the utility of rayon and cotton dress fabrics, and accordingly, it is one of the important methods of the textile finishing industry. However, many of its vital parts are based on the empirical knowledge of the people running the finishing plants. An increasing amount of papers regarding these subjects have been published during the past few years, and many of them will help the textile finisher to understand and control the process much better than before.

Among the different chemicals used for the process, the urea-formaldehyde resins still remain the most important group, mainly due to their cheapness and since they can be synthetized from simple and easily available chemicals: urea and formaldehyde. These precondensates are probably the only finishing agents of this kind which are produced within the finishing plants to any considerable extent.

The application of crease resisting resins to cellulose fabrics does not yield solely favourable results: crease resistance, decreased swelling, increased wet strength etc.; at the same time a number of undesirable effects appear, and the main result of their occurance is a deterioration of the wear properties as compared with the untreated samples. This means that the practical limit of the improvements is determined by the magnitude of the undesirable effects. Thus, one of the important problems of the textile finishing is to get a more favourable relation between the improvements and the wear properties.

The present thesis deals with the application of urea-formaldehyde resins to cellulose fabrics.

The parts of the process which have been considered are: The synthesis of the urea-formaldehyde precondensate, with special reference to the kinetics and equilibria of the reactions involved, and under conditions which are suitable for the production of the precondensates within the textile finishing plant. The search for a more favourable relation between the desirable and undesirable effects of the application of these urea-formaldehyde resins to cellulose fabrics represents the second section of the main problem; on spun rayon fabric the effect of presteaming and the use of glycine as a curing catalyst and on cotton fabrics the influence of a weft tension applied during the premercerization, are studied.

The Experimental Methods

1. The pH measurements[1])

A differential measuring method for correcting the alkaline error in pH measurements by means of glass electrodes when the activity of the sodium (or other) ion is unknown, has been described by the present author[1]. The principle is that the measurements are made with two glass electrodes of different, but known, alkaline error functions. From the difference in measured pH for the two electrodes, $pH_1 - pH_2$, the alkaline error, Δ pH, for each can be found from a predetermined diagram, representing

$$pH_1 - pH_2 = f\,(\Delta\, pH_1) = g\,(\Delta\, pH_2)$$

The theoretical background of this metod is connected with the glass electrode alkaline behaviour. A number of theoretical treatments have been applied to this problem[2-11], but their alkaline error equations are not in agreement with experimental data.

In the present treatment, the following physical model is used, including the assumptions that the $Si\,O_4$ — network of the glass is regarded as containing three dimensional interstices, offering room for metal ions, such as Na^+ and Ca^{2+}. When the electrode surface is brought in contact with water, the network on the surface and to some depth into the glass will pass into a swollen state, the aforesaid metal ions will be dissolved to a great extent, and replaced by H^+ or H_3O^+ ions. In this way, the surface layer is substantially free from other cations, and consists of silicic acid. The silicic acid is then able to take part in ion exchange reactions, so that all states from complete H^+ saturation to a more or less mixed composition of H^+ and other cations are possible. Under these conditions, it may be anticipated that the adsorption energies, *i. e.* the forces between the adsorbed ions and the adsorption sites, will be dependent on the state of adsorption, so that the energy will not be the same if

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[1]) This part is a summary of paper I.

an adsorbed ion has identical or dissimilar ions as neighbours on the surrounding adsorption sites. This seems to be reasonable, as the degree of »energy saturation» of each adsorption site may influence the surrounding sites with regard to their available adsorption forces. As we are dealing with a network, *i. e.* a kind of a large molecule, the state of the internal resonance energies can to some extent be compared with that of a polybasic acid. However, in the case of glass, the effect is more complex, as the glass is a solid acid, where the electrical forces outside the molecule have a large influence on the activity of the adsorbed ions.

Bolzmanns' energy distribution law is used for the mathematical treatments on this model. It is also assumed that the number of cation adsorption sites of the surface layer is constant, and that the interaction between the adsorbed ions can be expressed as the sum of contributions of pairs of nearest neighbours[12]. The latter assumption can be compared with experimental results, and they are found to fulfil its requirements.

The general glass electrode alkaline error equation, which is derived by means of this treatment, and exemplified by Na^+ and valid for two univalent ions, can be written:

$$\frac{1}{q}\log/1-\exp\left(-p\,F\,\Delta\,E/R\,T\right)/=pH_{\text{measured}}+\log a_{Na^+}+C$$

The constants p and q refer to the interactions between the adsorbed ions and C to the sodium ion adsorption energy. The equation is found to be in a good agreement with experimental data.

2. The polarography of formaldehyde¹)

Despite the fact that the polarographic determination of formaldehyde is a well-established analytical process, only simplified mathematical treatments have been given for the formaldehyde polarographic current.

It has been assumed that only the dehydrated formaldehyde is able to take part in the electrode reaction[12—15], and briefly, we have the following picture of this reaction: When the equilibrium between formaldehyde and methylene glycol is disturbed by the reduction of the former at the electrode surface, the aldehyde deficiency is com-

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¹) This part is a summary of paper II and partly of paper IV.

pensated by dehydration of the glycol, and the rate of dehydration determines the limiting current. If the rate of dehydration is small in comparison with the diffusion of formaldehyde, the latter rate determines the limiting current. If the rate of dehydration is high, the current is still determined by a rate of diffusion, but in this case the diffusion is that of methylene glycol. However, if the rates of dehydration and diffusion are of the same order, both are of importance.

The equilibrium between dehydrated formaldehyde and methylene glycol is highly in favour of the latter substance, as is found from spectrophotometrical measurements.

The system of general electrode reaction equations is obtained as follows:

$$\left(\frac{\partial C_{HCHO}}{\partial t}\right)_{\text{diffusion}} = D\frac{\partial^2 C_{HCHO}}{\partial x^2} + \frac{2x}{3t}\frac{\partial C_{HCHO}}{\partial x}$$

where x is the distance from the electrode surface.

Since

$$\left(\frac{\partial C_{HCHO}}{\partial t}\right)_{\text{catalysis}} = k_2 C_{HO \cdot CH_2 \cdot OH} - k_1 C_{HCHO}$$

we obtain

$$\frac{\partial C_{HCHO}}{\partial t} = D\frac{\partial^2 C_{HCHO}}{\partial x^2} + \frac{2x}{3t}\frac{\partial C_{HCHO}}{\partial x} + k_2 C_{HO \cdot CH_2 \cdot OH} - k_1 C_{HCHO}$$

and correspondingly:

$$\frac{\partial C_{HO \cdot CH_2 \cdot OH}}{\partial t} = D\frac{\partial^2 C_{HO \cdot CH_2 \cdot OH}}{\partial x_2} + \frac{2x}{3t}\frac{\partial C_{HO \cdot CH_2 \cdot OH}}{\partial x} -$$

$$k_2 C_{HO \cdot CH_2 \cdot OH} + k_1 C_{HCHO}$$

Initial conditions: $t = 0,\ x > 0$: $C_{HO \cdot CH_2 \cdot OH} = C^*_{HO \cdot CH_2 \cdot OH}$, $C_{HCHO} = C^*_{HCHO}$.
Boundary conditions: $t < 0, x = 0$: $C_{HCHO} = 0$, $(\partial C_{HO \cdot CH_2 \cdot OH}/\partial x) = 0$.
(No flux of $HO \cdot CH_2 \cdot OH$ at the electrode surface.)

where k_2 is the dehydration and k_1 is the hydration rate constant of the electrode reaction

$$HCHO + 2\,H_2O + 2\,e = CH_3OH + 2\,OH^-$$

Further, $D \sim D_{HCHO} \sim D_{HO \cdot CH_2 \cdot OH}$.

This equation system can be solved by means of a method[16] previously applied to similar problems.

When only the rate of methylene glycol dehydration determines the limiting current, this current is related to the electrode properties as follows:

$$i_k = \text{constant } m^{2/3} t_1^{2/3}$$

where i_k = limiting current, m = flow of mercury and t_1 drop time.

When the current is determined solely by the rate of diffusion of the dehydrated aldehyde or of the methylene glycol, the corresponding equation can be written:

$$i_d = \text{constant } m^{2/3} t_1^{1/6}$$

When mixed conditions exist, *i. e.* both dehydration and diffusion are of importance, more complicated relationships appear. They can be obtained when the previously mentioned treatment is extended, and by means of comparisons between the limiting currents at two different heights of the mercury reservoir, the equilibrium constant between two substances with an electrode behaviour as exemplified by methylene glycol and dehydrated formaldehyde can be calculated. In the present case, although with a moderate accuracy, were figures obtained which were of the same order as found from spectrophotometrical measurements.

Further, the rate of methylene glycol dehydration can be calculated from the limiting currents. The equation which can be used in the pH range 7—11 and 20 °C without any appreciable error, is:

$$k_2 = 0.7 \cdot 10^{-3} (i)^2 / C^2_{(HCHO)_a} m^{4/3} t_1^{4/3}$$

where k_2 = dehydration rate constant, $\sec^{-1}$; i = limiting current, μA; $C_{(HCHO)_a}$ = analytical formaldehyde concentration; m = mercury flow, mg/sec; t_1 = drop time, seconds.

When polarography is used for the determinations of unreacted formaldehyde in urea-formaldehyde reaction mixtures, several problems have to be considered.

Since at increasing formaldehyde concentrations increasing polarographic maxima appear, a maximum suppressor ought to be used. Among the well-known substances which are effective in this respect, only gelatin seems to be suitable. The half-wave potential of formaldehyde is comparatively high, and this means that interferences with the cation of the supporting electrolyte decrease the accuracy of the determinations. This disadvantage can be reduced when Li^+ salts are used. Since the polarographic current of formaldehyde increases with increasing pH, a high pH value of the supporting electrolyte would be favourable. However, at increasing pH values, the rates of the urea-formaldehyde reactions increase, and corresponding to this, a more pronounced time dependency of the limiting current appears. During the reduction of formaldehyde to methanol, hydroxyl ions are produced at the electrode surface increasing the limiting current in a more or less uncontrolable way and also disturbing the urea-formaldehyde reactions. Thus, a good buffer capacity of the supporting electrolyte is required.

When all these problems are considered, a solution containing 0.10 M Li_2CO_3 + 0.12 g/l gelatin at pH 9.50 was found to be a suitable composition for practical purposes.

3. The determination of urea and methylol ureas of the reaction mixtures¹)

A comparatively selective colour reaction between urea and *p*-dimethylaminobenzaldehyde and its application for spectrophotometrical determinations of urea has been described previously[17], [18].

The same reagent also produces a colour reaction with mono- and dimethylol urea.

When the samples of the ureas are added to methanol solutions of the reagent, disturbances from hydrolysis and also from continuing reactions in the presence of formaldehyde are avoided.

When the initial concentrations of urea and formaldehyde are known, the concentrations of the components of a reaction mixture can be determined from a spectrophotometrical measurement, when combined with a determination of the unreacted formaldehyde.

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¹) This part is a summary of paper III.

The Synthesis of the Urea — Formaldehyde Precondensates

4. The kinetics of the mono- and dimethylol urea formation and hydrolysis reactions[1])

The kinetics of the basic urea-formaldehyde reactions have been studied by a number of previous authors[19−31]. However, some of the experimental methods used do not allow any accurate determinations of the unreacted formaldehyde, used for the rate constant calculations.

In the present study, such conditions are selected, which are of interest in connection with the preparation of urea-formaldehyde precondensates for the textile crease resisting process. Also in this case the reactions were followed by means of determinations of the concentration of free formaldehyde of the reaction mixtures. The polarographic metod was used. Buffer substances were included in the reaction mixtures in order to maintain a constant pH value during the reaction and also in order to investigate their influence on the reaction rates.

The urea-formaldehyde reactions at equal concentrations of the reactants do not obey a simple second order reaction rate relationship. When the experiments are carried out with an excess of urea, side reactions do not disturb, and the rate constants can be determined.

The reaction between monomethylol urea and formaldehyde is described by a second order relationship, considering the hydrolysis of the reaction product.

The hydrolysis of monomethylol urea cannot be described by any simple reaction rate equation. However, the rate constants can be determined by means of a graphical extrapolation method.

The hydrolysis of dimethylol urea is in accord with a reaction rate equation which also considers the reaction between liberated monomethylol urea and formaldehyde, and reaction rate constants are calculated from this relationship.

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[1]) This part is a summary of papers V—VII, and partly of paper IV.

In summary, the following general observations are made:

The concentration of the reactants does not affect the rate constants to any considerable extent.

A linear relationship is present between the reaction rate constants and the buffer concentrations at a constant cationic strength.

No simple relationship exists between the catalytic contribution of hydroxyl ions and their activities.

A very low catalytic effect is present in the case of borate buffers.

5. **Studies of the reaction rates and equilibria at formaldehyde-urea molecular ratios in the range 1.4—2.0**[1])

The formaldehyde-urea molecular ratios of the precondensates used for the textile crease resisting process are within the range 1.4—2.0. Under the reactions carried out in order to produce such precondensates, formation and hydrolysis of mono- and dimethylol urea occur simultaneously.

The system of general reaction rate equations can be written:

$$\left.\begin{aligned}
&\frac{dM}{dt} = k \cdot U \cdot F - k' \cdot M - k_1 \cdot M \cdot F + k_2 \cdot D \\
&\frac{dD}{dt} = k_1 \cdot M \cdot F - k_2 \cdot D \\
&U = U_0 - M - D;\ F = F_0 - M - 2\,D \\
&t = 0:\ U = U_0;\ F = F_0;\ M = D = 0 \\
&t \to \infty: \frac{dM}{dt} = \frac{dD}{dt} = 0
\end{aligned}\right\}$$

Concentrations: U = urea; U_0 = urea, initial; F = formaldehyde; F_0 = formaldehyde, initial; M = monomethylol urea; D = dimethylol urea. Reaction rate constants: monomethylol urea: k = formation, k' = hydrolysis; dimethylol urea: k_1 = formation, k_2 = hydrolysis. Reaction time: t.

Since a simple solution to the system of differential equations given above cannot easily be found, numerical solutions were obtained

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[1]) This part is a summary of paper VIII.

by means of an electronic differential analyzer, the EIDA of Chalmers University of Technology, Gothenburg. The rate constants of the different separate reactions, determined as previously described, were introduced into the system of equations.

When the mathematical solutions on the amount of unreacted formaldehyde of the reaction mixtures are compared with the experimentally determined data, a very good agreement is found.

A mathematical solution including all the components of the reaction mixture was compared with experimental figures, and a good agreement was found in this case as well.

Further, a purely empirical expression

$$\log\,\log F_0/F = A \log\log t + \mathrm{B},$$

where A and B are constants, was found to describe the reaction behaviour with a good accuracy. This empirical equation seems to be of value when precondensates are produced industrially.

Considering the equilibrium conditions:

$$t \rightarrow \infty\colon \frac{dM}{\mathrm{d}t} = \frac{dD}{\mathrm{d}t} = 0;$$

the following equilibrium relationships are obtained:

$$\begin{aligned} &U_0 = U\,(1 + K_1\,F + K_2\,F^2)\\ &F_0 = F + U\,(\mathrm{K}_1\,F + 2\,\mathrm{K}_2\,F^2)\\ &U = U_0 - M - D\\ &F = F_0 - M - 2\,D \end{aligned}$$

where $\mathrm{K}_1 = k/k'$; $\mathrm{K}_2 = k\,k_1/k'\,k_2$.

When we introduce the previous rate constants, the equilibrium concentrations of the components can be calculated. Calculated and experimental data are in an acceptable agreement.

In accordance with these findings, it may be concluded that the reaction rate constants determined under specialized conditions are also applicable to the more general cases.

As regards the equilibrium, we may finally conclude that the composition of the reaction mixture is slightly dependent on the buffer which has been used in order to promote the rates of the reactions.

6. The influence of methanol on the rates and equilibria of the urea-formaldehyde reactions[1])

Commercial formaldehyde solutions usually contain methanol, added in order to prevent formaldehyde polymer precipitation. Thus, the influence of the presence of methanol on the reaction rates is of interest for the technical preparation of urea-formaldehyde precondensates.

It has previously[21] been observed that the presence of methanol seems to decrease the urea-formaldehyde reaction rates.

The hemiacetal formation between methanol and formaldehyde is in this study investigated cryoscopically, and the reaction rate and equilibrium constant K were determined. The reaction can be described by a second order relationship, considering the hydrolysis of the reaction product. The reaction rate constants considerably exceed the corresponding figures of the urea-formaldehyde reactions, and this means that the hemiacetal equilibrium is maintained throughout the urea-formaldehyde reaction.

When we accept the assumption[32] that the formation of such a hemiacetal explains the rate decrease, and assume that only the fraction of the formaldehyde which is not combined with methanol takes part in the urea reactions, some calculations can be made.

The rate constants at zero reaction time of the urea or monomethylol urea and formaldehyde reactions would be related as follows:

$$k_0 = k_{C_M} \frac{C_F}{C_F - y}$$

where k_0 = rate constant at zero methanol concentration, k_{C_M} = rate constant at C_M methanol concentration, C_F = initial analytical formaldehyde concentration and y = initial hemiacetal concentration. y can be calculated from the previously mentioned hemiacetal formation rate equation, applied to equilibrium conditions. When experimental k_{C_M} figures, obtained at different methanol concentrations, are converted to k_0 by means the expression given above, the figures are found to be substantially constant. Thus, the experimental results are in agreement with the theoretical treatment.

The initial rates of mono- and dimethylol urea hydrolysis are not, as can be expected, influenced by the presence of methanol.

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[1]) This part is a summary of paper IX.

A reaction rate equation of the urea-formaldehyde reaction when an excess of urea is used, derived under the assumption that the hemiacetal formaldehyde does not react, was applied to experimental data. A good linearity was found, and also an agreement with the corresponding initial rate constant described above.

Finally, the presence of a hemiacetal may also influence the equilibrium conditions of the urea-formaldehyde reactions. The analytically determined »equilibrium» formaldehyde, $C_{F\infty}$, is related to the »free» formaldehyde, $C^{\circ}_{F\infty}$, *i. e.* the amount in actual equilibrium with the ureas, as follows:

$$C_{F\infty} = C^{\circ}_{F\infty} + y$$

This, since the hemiacetal formaldehyde is normally included by the analytical methods. When this expression is combined with the equilibrium equation of the hemiacetal formation, we get the following equation:

$$C_{F\infty} = C^{\circ}_{F\infty} + \frac{C_M}{1 + \frac{1}{\mathrm{K}\, C^{\circ}_{F\infty}}}$$

The influence of methanol on the equilibrium can be calculated by means of this expression, as regards the formaldehyde concentration. (The equilibrium concentrations of the other components can, as shown in another part of this thesis, be calculated when the equilibrium concentration of the formaldehyde is known.) When testing on experimental figures, agreement is found between measured and calculated data.

Thus, we find that both the rates and equilibria of the urea-formaldehyde reactions are influenced by the presence of methanol in the reaction solutions.

7. The activation energy and the heat of reaction of the urea — formaldehyde reactions¹)

The activation energies of the urea-formaldehyde reactions have been investigated previously[19, 22, 24, 27]. The results obtained are somewhat scattered, especially when less accurate methods were used for the formaldehyde analysis.

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¹) This part is a summary of paper X.

In the present study, it is found that the activation energies of mono- and dimethylol urea formation is 15.4 kcal/mole for both of them, and the hydrolysis figures are 20.4 kcal/mole, and the same for both substances in this case as well. These data refer to phosphate and borate buffers. The figures obtained when a carbonate buffer is used are 1—2 kcal/mole above the data of the other two buffers, and this discrepancy may be due to a temperature influence on the pK values of the carbonate.

The heats of reaction when mono- and dimethylol urea is formed were determined by means of a calorimetrical method, and the same figure, 4.9 kcal/mole, was found for both of the reactions.

When we compare the difference between the activation energies of hydrolysis and formation, 5.0 kcal/mole, with the heat of reaction, we find no noticable difference, as can be expected for reactions in solution.

8. Notes on the reaction mechanism[1])

Some of the previous theories connected with the urea-formaldehyde reaction mechanism are:

An anion of urea is the reactive compound in the reactions with formaldehyde[19, 20, 22, 24].

Only dehydrated formaldehyde reacts with the urea or monomethylol urea[19, 20, 22, 23, 33].

The main influence of the temperature on the urea-formaldehyde reactions is due to changes in the equilbrium between hydrated and dehydrated formaldehyde.[20, 24].

In concentrated solutions, a slow depolymerisation of formaldehyde polymers influences the urea-formaldehyde reaction rates[21].

When considering the previous knowledge concerning the state of urea and formaldehyde in solutions, and adding to this some new informations, the following assumptions seems to be of a reasonable probability:

Only formaldehyde in the dehydrated state takes part in the reactions, and the main influence of the temperature on the reaction rates is due to changes in the methylene glycol-formaldehyde equilibrium.

Molecular collisions involving formaldehyde polymers may produce

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[1]) This part is a summary of paper XI.

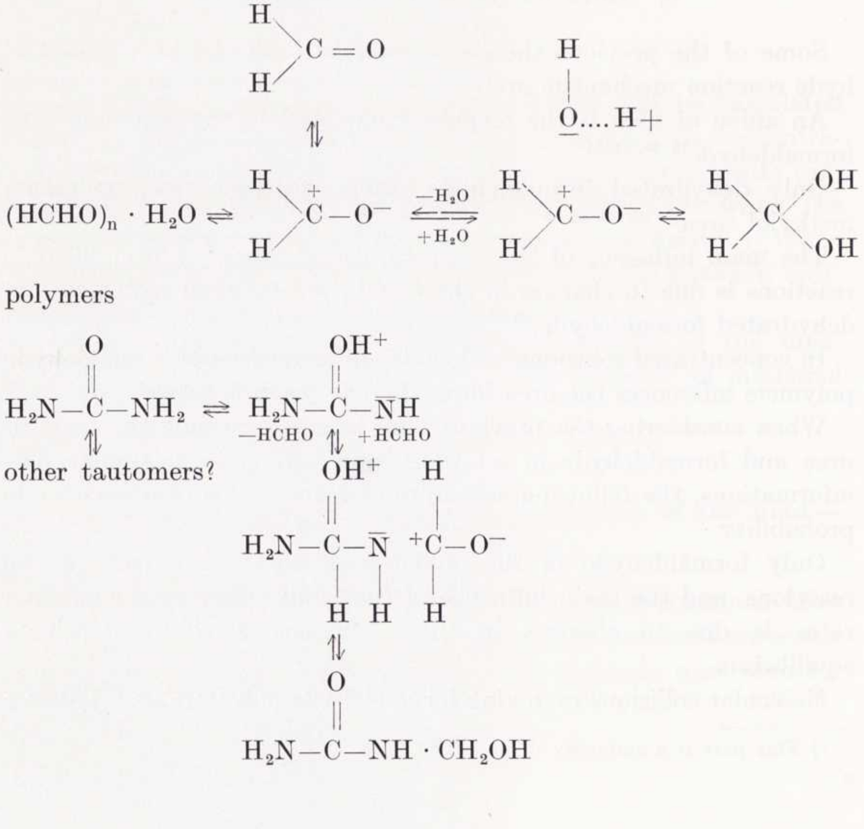
an activated state of formaldehyde, which then immediately reacts with the actual molecule, *i. e.* urea or monometylol urea.

Formaldehyde ions do not play any important role in the reactions in neutral and moderately alkaline solutions.

The reactive urea compound is not an anion present prior to the reaction stage.

It is not probable that the mechanism of the buffer catalysis of the methylene glycol dehydration and that of the urea-formaldehyde reactions are identical, but the catalysis mechanism of these latter reactions may be the same for all of them. (However, the buffer catalysis of the dehydration of methylene glycol has the effect that the equilibrium of the formaldehyde system is maintained during the urea-formaldehyde reactions, keeping the ratio between hydrated and dehydrated formaldehyde constant.)

It is possible that zwitter ions of the urea and formaldehyde represent the activated states of reaction. An example of a reaction mechanism scheme is:



The proton exchange may be catalysed by proton donors and proton acceptors, *i. e.* buffer substances, and may represent the rate determining steps of the reactions.

A similar reaction scheme can also be applied to the monomethylol urea-formaldehyde system.

It will here be stressed that this scheme ought to be regarded as an example of a possible and not of a highly probable reaction mechanism description. Our present knowledge does not allow any conclusive statements.

9. On the preparation of urea — formaldehyde precondensates in the textile finishing plant

The formaldehyde-urea molecular ratios of the precondensates used for the textile crease resisting process are within the range 1.4—2.0. Ratios below 1.4 do not produce resins of a sufficient fastness to washing, and ratios above 2.0 mean an excess of formaldehyde, which substantially remains unreacted.

From the practical point of view it is favourable to prepare stock solutions of urea, eventually containing a buffer substance in accordance with previous parts of this thesis. However, when such stock solutions are prepared, it is important to avoid high dissolution temperatures and to add the buffer after cooling, especially when high pH values are used. The reason is that urea hydrolysis, occuring at high pH and temperatures, may produce ammonia compounds, *e. g.* ammonium carbonates. These substances may then yield ammonia-formaldehyde products, which after neutralization can act as curing catalysts and also give rise to a »fish» odor after the heat treatment of the padded and dried fabric, probably due to a formation of methyl amines. The technical grades of urea are usually of a high purity.

The formaldehyde solutions, however, always contain formic acid and methanol. They are the products of a Cannizzaro reaction, but the latter compound is also added to the formaldehyde solutions in order to prevent formaldehyde polymer precipitation. As known from part *6* of this thesis, the presence of methanol influences both the reaction rates and the equilibrium composition of the urea-formaldehyde reaction mixture. However, when the formaldehyde concentration is known, the methanol concentration can be obtained with a sufficient degree of accuracy from refractivity or density determinations.

When a buffer substance is to be used for the catalysis of the precondensation, it is also necessary to regard its influence on the curing catalysis. If the buffer has a pK value in the range 1—7, it will change the pH decrease in the resin during the heat treatment. However, small amounts of a buffer may improve the stability of the pad solution after the addition of the curing catalyst: pH decreases due to reactions between the catalyst and formaldehyde are retarded.

The selection of reactant concentrations, amount of buffer and also of the reaction temperature is mainly a practical problem: high reaction rates mean, as a rule, a better flexibility of the finishing plant. At high concentrations of the reactants more favourable equilibrium formaldehyde concentrations are obtained. High reaction temperatures increase the amount of unreacted formaldehyde at equilibrium, since the activation energies of the formation and of the hydrolysis are 15 respective 20 kcal/mole. However, the final concentration of formaldehyde is also dependent on the time-temperature relation of the subsequent cooling period.

One of the important problems in connection with the preparation of the precondensates is to find a simple method for the control of the reaction stage. Some physical methods, *e. g.* determinations of the density or refractivity of the reaction mixtures can be used, but the accuracy obtained does not fulfil the practical requirements, especially in the range close to equilibrium.

A determination of the unreacted formaldehyde can be made by means of titrimetric methods, but their accuracy in the range mentioned is moderate, disturbing reactions ought to be controlled *e. g.* by cooling with ice[28].

A good accuracy can be obtained when polarography is applied.

The colorimetric methods which are known to be used for spectrophotometrical determinations of formaldehyde cannot be applied to this problem, since the pH values and reaction times to be used give rise to considerable errors due to continuing reactions and hydrolysis in the urea-formaldehyde system. However, a new spectrophotometrical method will be described in the following.

The method is based on a colour reaction between *Deorlene Dark Blue R* and formaldehyde.

A number of preliminary experiments gave the following results:

a. Water solutions of *Deorlene Dark Blue R* are not very stable, as could be found from their extinction and precipitation behaviour.
b. The rates of reaction between the dyestuff and formaldehyde increase with decreasing pH.
c. At pH < 5 is the yellow colour of the dyestuff solution contamined with a blue component, disturbing the measurements.
d. The rate of the reaction between the dyestuff and formaldehyde is comparatively low at pH $\backsim 7$, and a constant extinction cannot be obtained within 30 minutes at 20° C, and after such a long period continuing reactions and hydrolysis of the urea-formaldehyde compounds will give rise to considerable errors.

When these results are considered, the following procedure was found to be suitable:
Reagent solution: 0.2 g/l *Deorlene Dark Blue R*[1]) in C_2H_5OH, 99.6 %.
Buffer solution: 6.81 g/l KH_2PO_4 + 25 ml/l 1 *M* KOH; pH 6.86.

0.3 parts of a reaction mixture sample (with a formaldehyde concentration ≤ 2 *M*) are added to 10 parts of the buffer solution, immediately followed by 2 ml of the reagent solution. All solutions and also this mixture are kept at 20 ± 0.5° C. The extinction *versus* water at 5650 Å is determined 5 minutes ± 10 seconds after the addition of the reagent.

Extinction curves related to 0 and 2 *M* formaldehyde concentration of the (0.3 parts) sample are given in Fig. 1. In the case of the 2 *M* solution, the curve was not determined before substantially constant readings were obtained, *i. e.* this curve mainly corresponds to an »equilibrium» between the dyestuff and the formaldehyde. Temperature: 20 ± 0.5° C. Cell length: 20 mm. Spectrophotometer: Hilger & Watt's »Uvispec».

The relationship between the concentration of formaldehyde of the sample (0.3 parts) and the extinction at 5650 Å is shown by Fig. 2. Time delay: 5 minutes ± 10 seconds. Other conditions as specified above. Four determinations were made at each formaldehyde concentration, and the average coefficient of variation was 2.0 %.

The influence of the time delay is exemplified by the curves obtained 10 and 15 minutes after the addition of the formaldehyde sample and the reagent to the buffer solution. These curves are also included in Fig. 2.

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[1]) Commercial grade; the concentration is defined by the extinction maximum of Fig. 1.

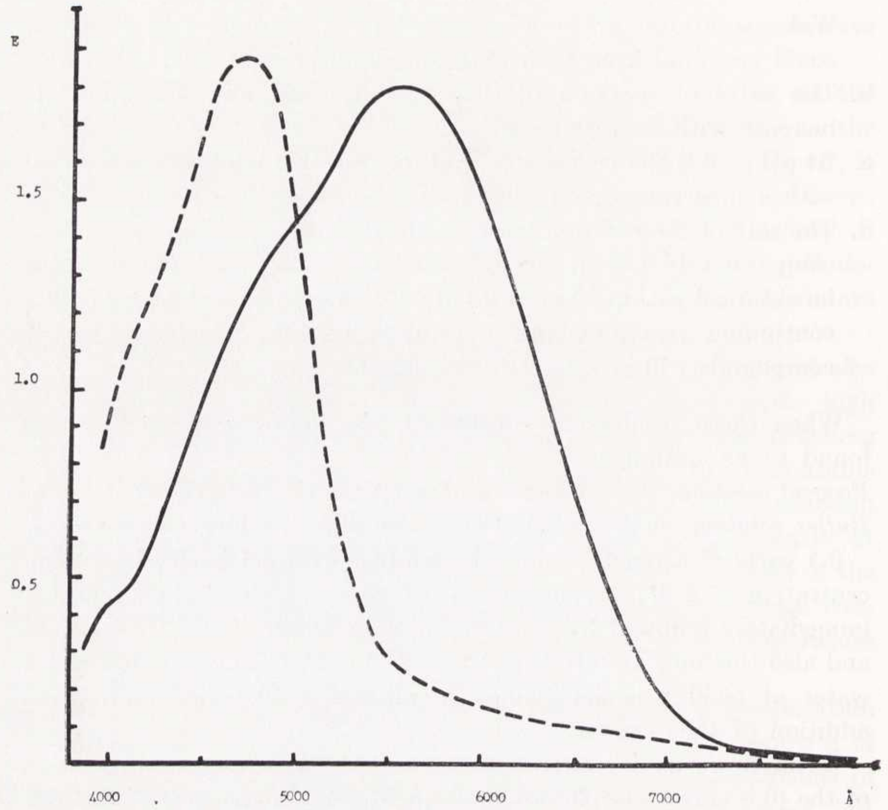

Fig. 1. Extinction curves. Formaldehyde concentration of the samples added to the buffer and reagent: 0 (— — —) and 2 (———) *M*.

The change in the concentration of unreacted formaldehyde during three different reactions between urea and formaldehyde was studied by means of the polarographic method described in part *2* of this thesis, and the corresponding extinction in accordance with the present method was also determined. The extinction figures obtained are plotted in Fig. 2; the formaldehyde concentration refers to the polarographically determined data.

The accuracy obtained may be regarded as being sufficient for practical purposes. Thus, this method can be used as a tool for the control of the precondensate preparation process.

For rough determinations of the state of reaction, this method may be modified to a simple test tube colour test.

The heat of reaction is the same for both the mono- and dimethylol

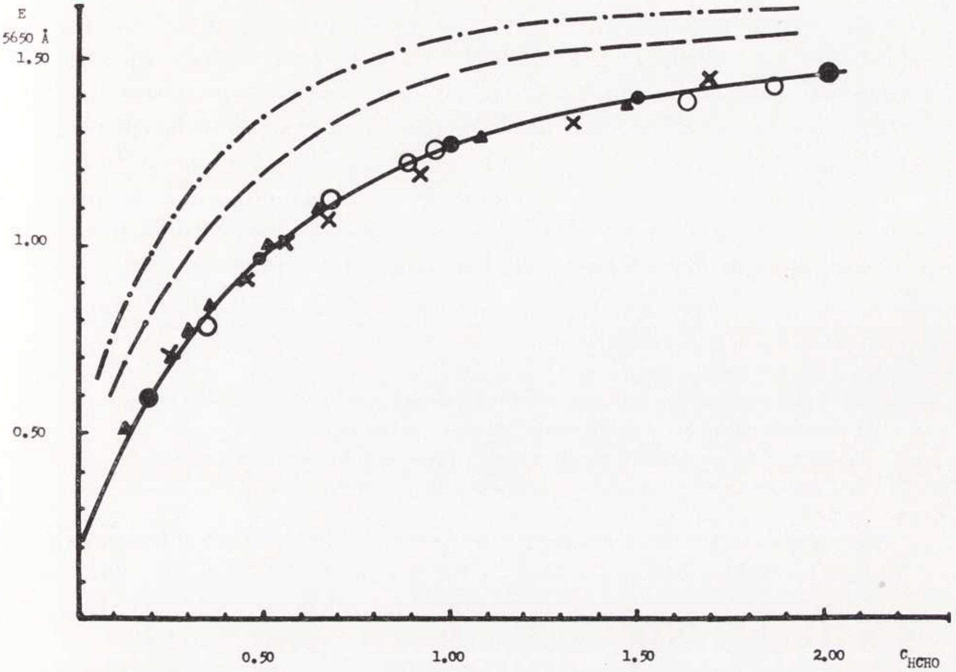

Fig. 2. Relationships between the extinction at 5650 Å and the concentration of formaldehyde of the sample (0.3 parts) added to the buffer and reagent. 20 ± 0.5° C. 5 (———), 10 (— — — —) and 15 (— . — . —) minutes delay between mixing and spectrophotometry. Formaldehyde solutions: ● (all figures of the four determinations at each concentration are within the black area of the corresponding dot). Urea-formaldehyde reaction mixtures: 1 *M* $CO(NH_2)_2$ + 2 *M* HCHO; pH 7.0: ○, 1 *M* $CO(NH_2)_2$ + 2 *M* HCHO + 0.05 *M* Na_2CO_3; pH 10.0: × and 1 *M* $CO(NH_2)_2$ + 1.5 *M* HCHO + 0.05 *M* Na_2CO_3; pH 10.0: ▲.

urea formation, and 5 kcal/mole are liberated. This means that some reaction control data can be obtained from temperature measurements on the reaction mixture, as exemplified by the following procedure:

60 parts of a solution containing 440 g/l urea + 10 g/l sodium carbonate and 55 parts of a solution containing 380 g/l formaldehyde + 80 g/l methanol are mixed in a reaction vessel. The vessel is fitted with a stirring device and coils for heating with steam and cooling with water. The mixture is heated to 55° C, and the steam flow is shut off at this temperature. The temperature then rapidly increases to 70° C, mainly due to the heat of reaction. If any disturbances occur, other final temperatures are obtained. The reaction mixture remains at this temperature for 25 minutes, and is then cooled to 20° C within 10 minutes. After dilution and addition of a curing catalyst is the precondensate solution ready for the padding operation.

The actual temperature increase is, of cource, dependent on the heat transfer through the walls of the reaction vessel, and the temperature-time behaviour has to be compared with predetermined curves. Although this control method is not very accurate, it has proved to be of some practical value at reaction temperatures above 40° C.

Finally, as an example of a more advanced technique for the preparation of urea — formaldehyde precondensates, a short description of the plant in accordance with Fig. 3 will be given.

Instruments. I, IX—XI: impedance bridge recorders, pneumatic controllers. Proportional and integrating responce.

II, VII: Electronic recorders.

III, VIII: Electronic controllers. Proportional and integrating responce.

V: Electronic three — point recorder; thermocouples.

IV: Electronic controller; resistance thermometer. Proportional responce.

VI: Pneumatic level controller. Proportional responce.

Stock solutions of urea (eventually containing buffer substances) and of formaldehyde are stored in the tanks *A* and *B* at 10—25° C. By means of pumps and simple float-controlled switches are these solutions kept at fairly constant levels in the vessels *C* and *D*.

The flow of the urea solution from *C* is controlled by the liquid level in *J*, *via* the controller *VI* and the corresponding valve. The »free» flow is measured with a flow meter, and the »captive» formaldehyde solution flow is controlled by means of the instrument *I* and the valve and flow meter of the pipe from *D*. The formaldehyde-urea molecular ratios are kept constant by means of an adjustable automatic flow ratio controller of *I*.

The solutions are mixed in *F*, holding a few liters of the mixture. The vigorous stirring and mixing action of the pump system used was found to promote a rapid responce of the glass electrode pH measurements in *F*. The glass electrode, the instruments *II* and *III* and their valve control the flow of a sodium hydroxide solution from the vessel *E* so that a preselected, constant pH value of the reaction mixture is maintained.

The mixture is then heated in the heat exchanger *G*, and this vessel holds also only a few liters of the reaction solution. Circulating hot water is used for the heating, and the water temperature is determined by the temperature of the mixture after the heat exchanger; the instrument *IV* and the corresponding valve control the amount of steam blown into the water in the vessel *H*. An oscillatory or slow responce in this part of the system is avoided when a properly

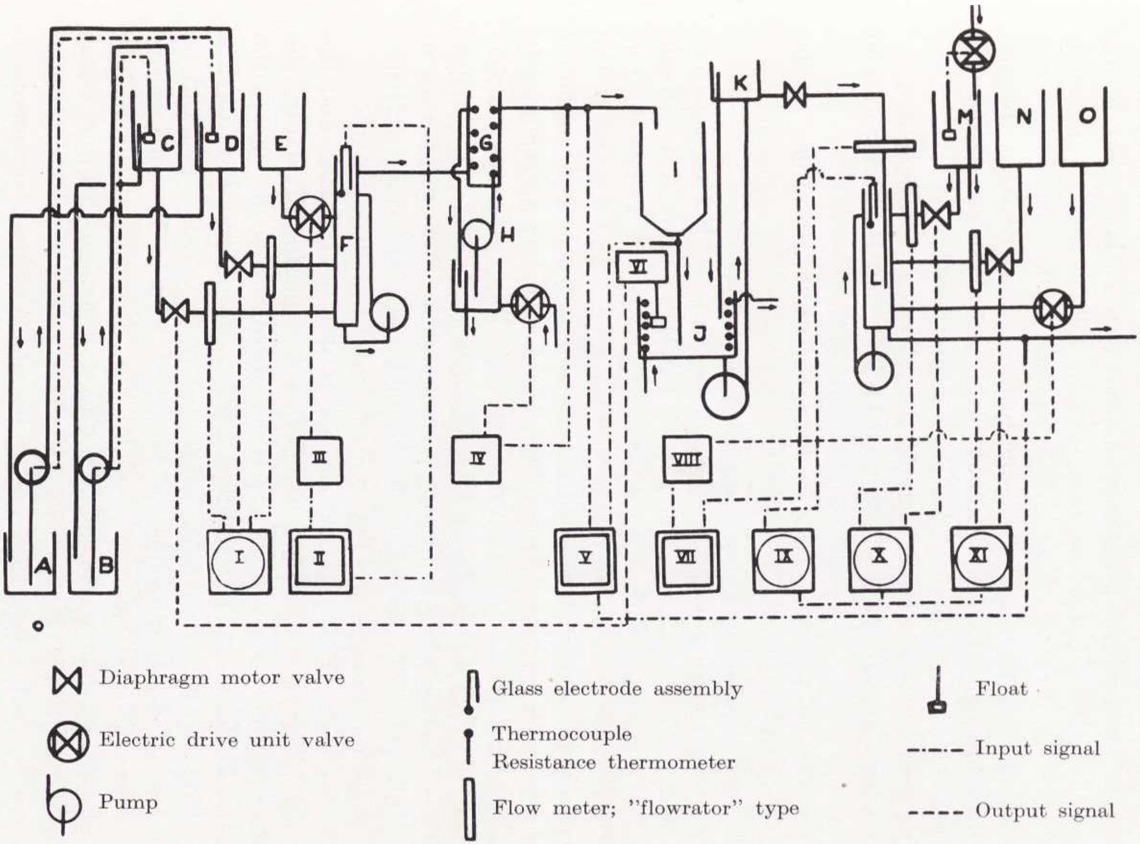

Fig. 3. Schematic diagram of an automatic precondensate preparation plant.

selected quantity of circulating water is used. The volume increase due to steam condensation is drained by means of a simple overflow device. (Steam heating of the heat exchanger was found to introduce considerable stability problems, as the volume-flow ratio is unfavourable.) It is important that a small volume heat exchanger is used; the temperature determination ought to be made before any noticeable temperature increase due to the heat of reaction appears. An interference of this kind would mean that the required reaction temperature is not obtained in the reaction vessel.

The reaction vessel I has to fulfil the following requirements:

The time of reaction shall be adjustable within the range 10—60 minutes.

The time of reaction shall be independent of variations in the rate of flow.

This problem has been solved as shown by Fig. 4.

The vessel has a number of compartments, *a*, having separate outlet holes *b* in the plug *c*, and is revolved by means of a variable speed motor, fitted with a worm gear and connected to the shaft *d*. The heated reaction mixture is fed by the pipe *e*, and remains in the compartment until it is drained when the outlet hole and the hole *f* of the static »plug cock» body *h* coincide, *i. e.* during approximately a full revolution. The mixture flows through the pipe *g* into a cooler.

The reaction time is adjusted by means of the speed of the motor, and the reaction time is not dependent on the flow: differences in flow only mean differences in the liquor level in the compartments, and thus, the time of reaction remains substantially constant.

The cooler *J* (Fig. 3) has a coil for cooling with water, and the required stirring is obtained by means of a pump, circulating the mixture through the vessels *J* and *K*. An overflow pipe keeps the level in *K* constant. The reaction mixture flows from *K* through a pipe, and the rate of flow is controlled by a valve, which can be regarded as the »main valve» of the plant. The valve settings are made manually or are controlled by *e. g.* the level in the padder trough. A flow meter measures the rate of flow, and this flow meter is connected to the instrument *IX*. The output signals determine the flows from the vessels *M* and *N* by means of the instruments *X* and *XI* and their flow meters and valves; constant ratios are maintained as previously described. *M* contains water, and a simple float on-off control keeps the level fairly constant. *N* holds the curing catalyst solution.

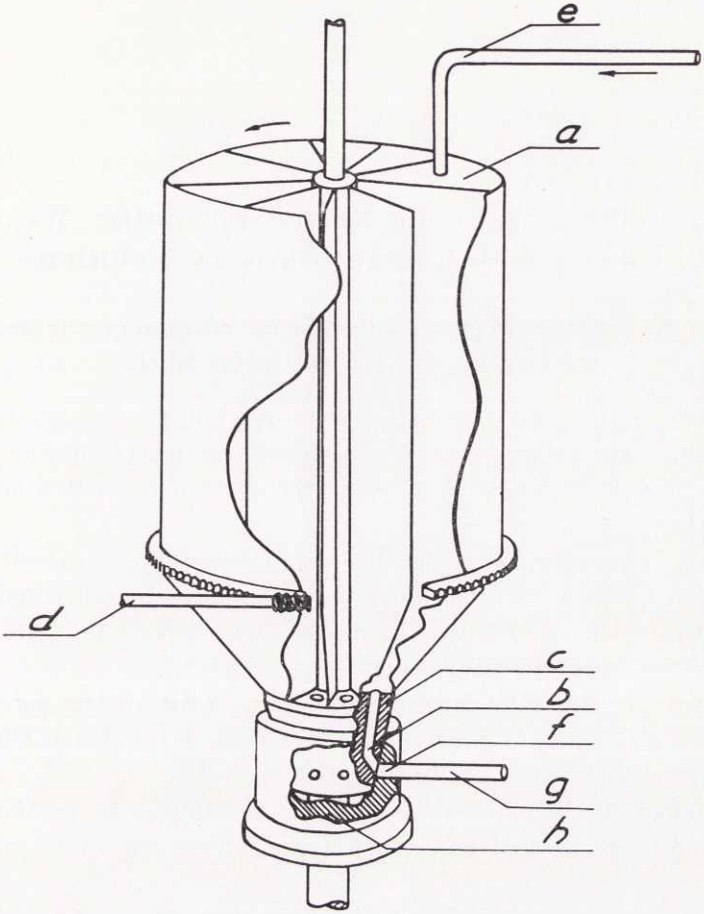

Fig. 4. Reaction vessel.

All these solutions are mixed in *L*, which is in principle designed as *F*, and the pH adjustments (usually to pH < 6.5) are controlled by the glass electrode, the instruments *VII* and *VIII* and the valve, determining the flow of an acid solution from *O*. The precondensate solution flows from *L* to a tank or to the padder trough.

Thermocouples are connected to the instrument *V*. The mixture temperatures before and after the reaction vessel are recorded for a rough control of the process, based on the heat of reaction. The final temperature of the precondensate solution is also measured, since it is essential for the solution stability.

Contributions to the Search for Better Wear Properties — Crease Recovery Relations

10. On the influence of presteaming on the effect of crease resisting treatments of a viscose rayon fabric[1])

As being a part of a search for a better relation between the favourable and undesirable effect of crease resisting treatments of rayon fabrics, the influence of a steaming before the resin treatment is investigated in this study.

It has been reported previously[34] that the swelling power of water on rayon fibers is reduced when the fibers have been treated with saturated steam at 100° C. It is also known [35, 36] that steaming reduces the iodine absorption and the colour yields.

In this investigation three samples were steamed; the maximum pressure and time of treatment were 3 kg/cm^2 and 120 minutes. An untreated sample was also included.

The effect of the steam treatment on the samples before the resin treatment was studied and the following properties were affected significantly:

Water retention, equilibrium moisture content at 100 per cent R. H., $(A_3 + A_4)/A_0$ ratios of the X-ray interferences, dye absorption, iodine adsorption and crease recovery.

Others, however, were not affected significantly:

Dry strength, wet strength, load-elongation curves, number threads per unit length, fabric dry weight per unit area, cuprammonium fluidities and equilibrium moisture content at 65 per cent R. H.

The crease resisting treatments of the samples were made by means of a urea-formaldehyde precondensate, and two different amounts of catalyst were used. Investigations of the crease resisting samples gave the following results:

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[1]) This part is a summary of paper XII.

No significant influence of the steaming and the catalyst concentration on the dry strength, elongation at break and the crease recovery was observed. Significant influence of the catalyst concentration, but not of the steaming conditions, was found on the ratios between the wet strength of the resin treated samples and the samples which have only been subject to steaming.

The water retention of the resin treated samples was significantly influenced by the catalyst concentration, but an influence from the steaming conditions appears only at the low amount of the catalyst.

The wear properties of the fabrics, as they appear from the duty factors[37], are significantly influenced by the catalyst concentrations, and at the high concentration also an influence from the steaming conditions is observed, increased steaming means improved wear properties.

When the different data obtained are analyzed, it seems to be reasonable to assume the following, as regards the internal structure of the fibers and the observed effects:

The steam treatments may affect regions of high degrees of orderliness slightly, and regions of medium degrees to a greater extent.

The wet strength before the crease resisting treatment is not significantly dependent on the distribution of lateral order or water absorption accessibility.

It seems to be probable that the resin only partially interacts with such regions of the fiber, where the water absorption forces are small. In the case of the high catalyst concentration, a more pronounced interaction occurs.

The duty factors and the wet strength ratios may be connected with such interactions.

It is interesting to note that the crease recovery and the duty factors are not found to be simply correlated: the resin composition and the state of the internal fiber structure are both of great importance.

Since it is known from experience that the high of the two catalyst concentrations ought to be used in connection with the fabric used in this study when a good dimensional stability of the fabric and a sufficiently high fastness of the resin to repeated washings are to be obtained, it is obvious that steam treatments before the crease resisting process can be of value as a mean of improving the duty factors, *i. e.* the wear properties of crease resisting fabrics.

11. On glycine as a catalyst of the textile crease resisting process

It is previously known that glycine can be used as a catalyst for the curing of methylol urea resins[38].

The purpose of the present investigation is to study the catalytic properties of this substance in connection with the textile crease resisting treatments by means of methylol ureas.

Experimental

The fabric used for the experiments was a 88 × 68, 30/30, 1.5 denier, 40 mm staple length viscose rayon. The desized and scoured fabric was taken from an industrial run and dried under slack conditions. The crease resisting treatments were carried out by means of a urea-formaldehyde precondensate as follows:

A solution containing 65 g/l urea + 55 g/l paraformaldehyde was heated to 60° C and kept at this temperature until the paraformaldehyde was dissolved. The pH was then adjusted to 7.0, and the mixture was allowed to react during 24 hours without further heating, *i. e.* its temperature decreased slowly and was close to 20° C at the end of the reaction period.

The catalysts; glycine, ammonium chloride and butylamine hydrochloride, were then added in amounts shown by Table 1.

The impregnation and drying (to < 1 per cent H_2O) was made on an overfeed stenter at 70° C drying temperature. The fabric was then given a heat treatment by means of an industrial curing machine of the roller type, fitted with a low-tension device[39]. The different curing conditions appear in Table 1.

After the curing, the different samples were washed at 60° C in a reversing wash wheel of the cylindrical type 5 minutes in 5 g/l soap + 3 g/l sodium carbonate, liquor ratio 30: 1, and then rinsed twice at 40° C for five minutes. Finally, the samples were dried at 40° C under slack conditions. They were then stored at 65 per cent R. H. and 20° C during four weeks before some investigations of the samples.

The properties studied were:

I. The *resin content* was determined by means of stripping at boil with a tartaric acid buffer at pH 3.2 until a constant weight was obtained. The resin content was calculated on the dry weight of the stripped fabric. Number of determinations on each sample: 3.

II. The *water retention* was determined as described by Cameron and Morton[40]. The time of centrifuging was increased to 20 minutes. Number of determinations: 3.

III. The *crease recovery* was determined at 65 per cent R. H. and 20° C. Willow's method, as described by *e. g.* Marsh[41], was

TABLE 1. *Some of the effects of crease resisting treatments carried out with glycine and other catalysts.*

Catalyst	Catalyst concentration, g/1	Curing temperature, °C	Curing time minutes	Resin content1), %	Water retention,2) %	Warp				Weft			
						Crease recovery,3) mm		Duty factor		Crease recovery,4) mm		Duty factor	
							s		s		s		s
Glycine	5	110	6.5	8.0	43	↑ 29	2	↑ 9.7	1.9	↑ 28	2	↑ 9.1	1.3
		130	4.0	8.0	43	29	1	9.4	1.2	28	1	9.1	1.7
		130	6.5	8.6	42	29	1	8.1	1.7	29	1	9.7	1.9
		130	10.0	9.2	39	30	1	9.0	1.7	28	1	8.7	1.4
		150	6.5	9.2	38	↓ 29	1	↓ 8.4	1.1	↓ 28	1	↓ 8.9	1.4
	10	110	6.5	8.2	37	↑ 27	2	↑ 9.0	1.6	↑ 27	2	↑ 9.0	0.8
		130	4.0	8.2	37	28	1	9.6	1.5	28	2	9.4	0.9
		130	6.5	8.7	38	31	2	8.0	1.1	30	2	8.9	0.9
		130	10.0	9.3	36	29	1	8.4	0.8	27	1	8.0	0.6
		150	6.5	9.1	37	↓ 29	1	↓ 8.6	1.1	↓ 28	1	↓ 8.2	0.5
	20	110	6.5	8.8	46	↑ 29	1	↑ 8.0	0.4	↑ 27	1	↑ 8.2	1.1
		130	4.0	8.9	43	31	2	8.2	1.1	27	2	8.5	1.1
		130	6.5	8.9	44	29	1	8.8	1.0	28	1	9.0	1.2
		130	10.0	9.0	40	28	1	9.0	0.9	29	1	8.4	1.1
		150	6.5	8.8	43	↓ 30	1	↓ 9.0	1.1	↓ 29	1	↓ 8.6	1.2
	40	110	6.5	5.7	50	⇑ 27	0	⇑ 4.8	0.4	↑ 28	2	⇑ 5.3	0.7
		130	4.0	6.3	49	28	1	3.4	0.5	26	1	3.8	0.6
		130	6.5	6.3	51	28	1	3.2	0.3	26	1	3.1	0.6
		130	10.0	5.4	55	25	1	3.3	0.4	26	1	3.2	0.3
		150	6.5	5.5	53	⇓ 28	1	⇓ 2.2	0.3	↓ 25	1	⇓ 2.4	0.3
NH_4Cl	10	110	6.5	8.7	31	↑ 29	1	⇑ 5.0	0.4	↑ 29	1	⇑ 4.5	0.6
		130	4.0	8.1	33	30	2	6.2	0.5	29	1	5.6	0.4
		130	6.5	8.8	32	29	2	4.8	0.8	29	2	4.3	0.4
		130	10.0	8.1	31	30	1	3.4	0.5	28	0	3.4	0.5
		150	6.5	8.3	32	↓ 31	1	⇓ 3.7	0.3	↓ 29	1	⇓ 3.7	0.4
$C_4H_9NH_3Cl$ ..	20	110	6.5	8.8	29	↑ 29	1	⇑ 5.5	0.4	↑ 27	2	⇑ 5.3	0.4
		130	4.0	8.5	30	31	1	6.5	0.8	28	1	6.3	0.5
		130	6.5	8.5	31	31	2	5.7	0.5	31	2	5.4	0.6
		130	10.0	8.8	33	31	1	4.5	0.7	28	2	4.4	0.3
		150	6.5	8.6	32	↓ 29	1	⇓ 4.4	0.4	↓ 29	1	⇓ 4.0	0.5

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1) $\bar{s}=0.4$.

2) $\bar{s}=0.6$.

3) Untreated fabric: 17.

4) Untreated fabric: 16; ⟷ No significant differences within the group; ⟺ Significant differences within the group.

used. The recovery figures were determined 10 minutes after the load removal. (No difference in rate of recovery, as this appears from a comparison between figures determined 1 and 10 minutes after unloading the fabric strips, could be detected.) Number of determinations: 5.

IV. The *duty factors* in accordance with Breens and Morton[37] were also determined. The »ball» and »plate» figures to be combined within each series were taken at random. Number of determinations: 5.

The results of I—IV are collected in Table 1.

V. The *dry and wet tensile strength* figures of the series cured at 130° C for 6.5 minutes can be found in Table 3. Number of determinations: 4. SIS[1] 650009.

In order to get some further informations concerning the catalytic behaviour of glycine, the following experiments were made:

VI. A solution of 0.10 *M* glycine and 0.70 *M* formaldehyde at pH 12.0 (adjusted by means of KOH) was allowed to react at 20° C during 48 hours. The solution was then titrated with 2.5 *M* HCl and the titration curve A of Fig. 5 was determined by means of a glass electrode. A back titration was then made by means of KOH (curve B). Further, a titration curve C of 0.6 *M* formaldehyde was determined. The relationship

TABLE 2. *Some of the effects of the crease resisting treatments at the curing condition 130° C and 6.5 minutes.*

Catalyst	glycine				NH_4Cl	$C_4H_9NH_3Cl$	glycine
Catalyst concentration, g/l	5	10	20	40	10	20	10
Crease recovery, warp direction, mm	29	31	29	28	29	31	31
	←			→	←		→
Crease recovery, weft direction, mm	29	30	28	26	29	31	30
	←		→⇐	⇒	←		→
Duty factor, warp direction	8.1	8.0	8.8	3.2	4.8	5.7	8.0
	←		→⇐	⇒	←	→⇐	⇒
Duty factor, weft direction	9.7	8.9	9.0	3.1	4.3	5.4	8.9
	←		→⇐	⇒	←	→⇐	⇒

⟵⟶ No significant differences within the group.

⇐⇒ Significant differences within the group.

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[1] Swedish Standards Association.

TABLE 3. *Tensile strength of crease resisted samples, curing: 130° C and 6.5 minutes*

Catalyst	Catalyst concentration, g/l	Tensile strength, kg/ 5 cm.							
		Dry				Wet			
		Warp		Weft		Warp		Weft	
NH_4Cl	10	↑ 47.8	1.9	↑ 42.7	1.4	↑ 32.4	1.4	↑ 27.9	1.0
$C_4H_9NH_3Cl$.	20	48.5	2.6	42.5	1.7	32.5	1.4	28.6	1.3
glycine	5	48.9	2.3	40.7	1.8	31.3	1.2	26.7	1.2
	10	47.7	1.6	42.8	2.0	↓ 30.2	1.0	↓ 29.6	1.2
	20	46.6	2.0	40.9	1.1	⇕ 27.2	1.3	⇕ 23.6	0.8
	40	↓ 44.2	2.1	↓ 41.0	1.4	⇕ 22.0	0.9	⇕ 21.3	0.8

⟷ No significant differences within the group.
⇔ Significant differences within the group.

between pH and the difference between the abscissae figures of the curves A and C is also given in Fig. 5 (curve D).

In these experiments a large excess of formaldehyde was used, as the titration curves were disturbed by unreacted glycine at low formaldehyde-glycine ratios.

VII. The decrease in pH due to reactions between the catalysts and free formaldehyde of *e. g.* the methylol urea solutions highly influences the stability of these solutions. The pH-time relationships of solutions containing 0.3 *M* catalyst and 0.5 *M* formaldehyde were determined. The initial pH of the catalyst and the formaldehyde solutions was adjusted to 7.0 before mixing. The measurements were made with a glass electrode and the reaction temperature was 20° C. The results can be found in Fig. 6, expressing pH as a function of the logarithm of time (seconds).

The pH values of reaction mixtures, as described above, but also including other glycine and formaldehyde concentrations, extrapolated to infinite reaction time, are given in Table 4.

Methylol urea solutions, prepared as previously described, were made 0.3 *M* with respect to the three different catalysts and then kept at 20° C. The time elapsing until the solutions became apparently opaque were: NH_4Cl — 2 hours, $C_4H_9NH_3Cl$ — 7 hours and H_2NCH_2COOH — 7 hours. Within these time limits, no viscosity changes appeared.

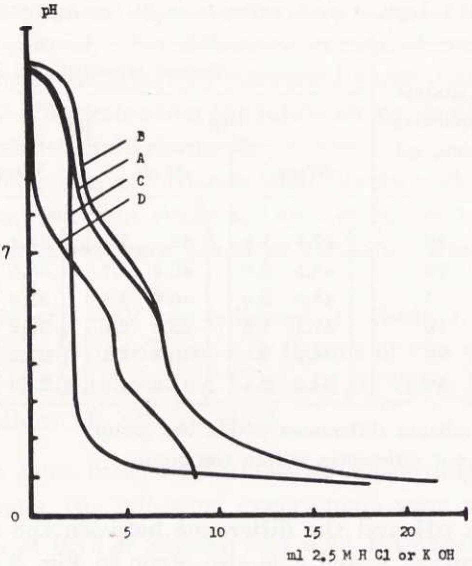

Fig. 5. Titration curves of the glycine-formaldehyde system.

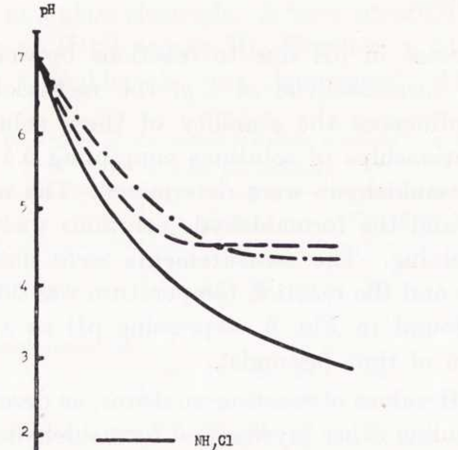

Fig. 6. pH-time relationships of the reactions in solutions containing 0.3 *M* catalyst + 0.5 *M* formaldehyde at 20° C.

TABLE 4. *pH values, extrapolated to infinite reaction time at 20° C of glycine — formaldehyde mixtures.*

Initial glycine concentration, moles/liter	Initial formaldehyde concentration, moles/liter	Infinite pH value
0.05	0.5	4.90
0.10	0.5	4.59
0.30	0.5	4.42
0.05	1.0	4.46
0.10	1.0	4.25
0.30	1.0	4.10
0.05	3.0	4.20
0.10	3.0	4.02
0.30	3.0	3.80

VIII. 3 g of fabric samples, stored for 4 weeks at 65 per cent R. H. and 20° C, representing cases of 10 g/1 catalyst, 6.5 minutes curing time at 130° C and washed as described above, were soaked for 30 minutes in 0.1 *M* HCl at 20° C and then in distilled water 2 × 2 hours. Liquor ratio: 100: 1. The samples were then dried at 20° C. Each dry sample was immersed in 40 ml 0.05 *M* HCl and a titration curve was determined by means of a glass electrode at 20° C. After each addition of a 0.25 M KOH solution, the stirring was continued until a constant pH reading was obtained. Finally, a corresponding curve of 0.05 M HCl was determined. The curves are found in Fig. 7, and the coordinates were adjusted so that the curves coincide at pH 7.0.

Discussion

As seen from Table 1, a series of different amounts of the glycine catalyst was studied, and for comparisons two other substances, ammonium chloride and butylamine hydrochloride at the rates 10 respective 20 g/l, were included. The amounts of these latter catalysts were selected from a number of preliminary experiments and represent the best results of each catalyst, when practical requirements were considered.

When we examine the results, we find from section I that, except for the case of 40 g/l glycine, the resin contents are not fundamentally

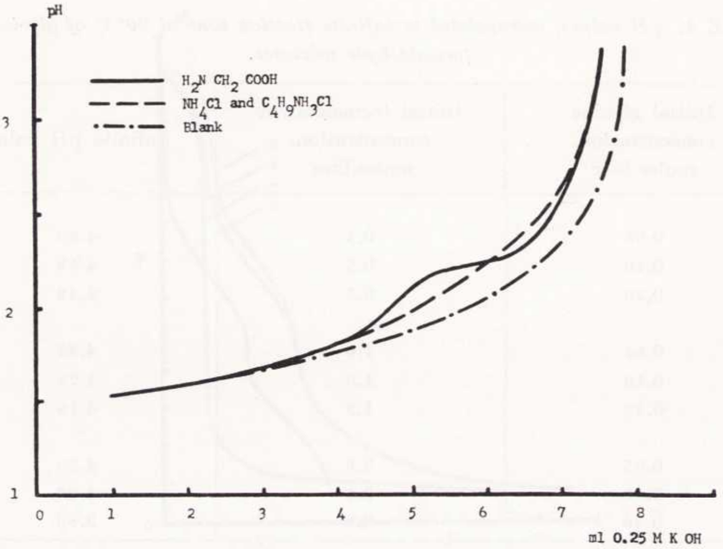

Fig. 7. Titration curves of fabric samples cured by means of different catalysts.

influenced by the catalyst and curing conditions. (Low resin content figures were also found when the two other catalysts were applied at high rates.) It may be reasonable to assume that the effect is connected with an acid hydrolysis of the resin, which runs parallel to the curing. The water retention, section II, seems to be dependent on the catalyst concentration and the curing conditions. Generally, the glycine data are above the figures of NH_4Cl and $C_4H_9NH_3Cl$, and the minimum retention in connection with glycine appears at 10 g/l.

The crease recovery and duty factor figures were subject to an analysis of variance, and the significance at 5 per cent has been determined. The two general groups of these calculations have been: within the series of a constant catalyst concentration and within the series of a constant curing condition: 130° C and 6.5 minutes. The results appear from the arrows in the Tables 1 and 2. As regards the glycine, we find that in the concentration range 5—20 g/l the crease recovery and the duty factor are not significantly dependent on the curing conditions at the different catalyst concentrations or on the catalyst concentration at the constant curing condition. At 40 g/l glycine, significant differences appear within the group, except for the weft crease recovery. The 40 g/l figures differ significantly from the 5—20 g/l group at 130° C and 6.5 minutes' curing, except for the warp crease recovery. Within the two groups NH_4Cl and $C_4H_9NH_3Cl$ the crease recoveries are not significantly dependent on the curing conditions, but the duty factors show a dependency.

The figures corresponding to the most favourable concentrations of the three catalysts were also compared, as seen from Table 2. We find that the crease recoveries do not differ significantly. The duty factors of 10 g/l NH_4Cl and 20 g/l $C_4H_9NH_3Cl$ are not significantly different.

However, the duty factors of 10 g/l glycine differ favourably and significantly from the corresponding figures of the two other catalysts.

The tensile strength figures of section V, (Table 3) show no significant difference between the dry state data. The wet tensile strength figures of 20 and 40 g/l glycine are significantly different from the results of 5—10 g/l glycine, 10 g/l NH_4Cl and 20 g/l $C_4H_9NH_3Cl$. The figures of 20 and 40 g/l glycine are below the figures of the other series. This is probably not only dependent on the water-cellulose interaction, *e. g.* shown by the high water retention figures, as found when a comparison with the 5 g/l series of glycine is made.

The reaction between formaldehyde and glycine has been discussed by *e. g.* Baur[42, 43] and Tomiyama[44].

Baur assumes that the reaction product is a weak acid of the following structure: $H_2C = N\ CH_2COOH$.

Tomiyama expects that one molecule of formaldehyde reacts with one molecule of glycine in the alkaline range, yielding the compound $^-OOC\ CH_2\overset{+}{N}H_2\ CH_2O^-$. It may be noticed that this also can be written $^-OOC\ CH_2NH\ CH_2OH$, *i. e.* a methylol glycine. The amount of reaction product was calculated from the pH drop occuring when formaldehyde was added to a buffer system composed of the amino acid and its salt. The calculations include the assumption that the NH_3^+ group gives off an H^+ ion when it reacts with formaldehyde. The equilibrium constants calculated were fairly constant only when the reaction was assumed to be bimolecular.

As shown by the experiments described in sections VI, the reaction between glycine and formaldehyde seems to yield a zwitter ion compound, when carried out in alkaline solutions and with an excess of formaldehyde. The pK values, as they appear from Fig. 5, curve D, are 2.5 and 6.5. The corresponding glycine values are 2.3 and 9.9.

From the back titration experiment, we find that it is rather probable that some kind of a »side reaction» occurs at low pH values, and this reaction changes the dissociation properties of the amino group. That this reaction is not simply a hydrolysis is seen from the fact that no inflexion of the back titration curve, which would correspond to glycine, appears. From the back titration curve it is also seen that the acidic properties of the compound are very little affected by the side reaction.

If not side reaction disturbances occur, the final pH values of a reaction between glycine and formaldehyde would be ≥ 4.5, as seen from the pK values. However, in Table 4 we find figures considerably below this, a behaviour which also indicates the occurance of a side reaction.

Thus, we may conclude that the reactions between glycine and formaldehyde are a little more complicated than assumed by the previously mentioned authors. Further, the requirements on which Tomiyama's calculations were based, seem not be completely fulfilled.

It is, of course, very difficult to make any statements concerning the glycine-formaldehyde reaction product. However, one assumption which seems to be reasonable is that a methylol glycine compound, *e. g.* $\mathrm{HOOC\,CH_2NH\,CH_2OH} \rightleftarrows {}^{-}\mathrm{OOC\,CH_2\overset{+}{N}H_2CH_2OH}$ is formed in alkaline and neutral solutions. Under acid conditions a compound in accordance with Baur may also be formed. This would be a behaviour similar to the urea-formaldehyde reactions.

The precondensate solution stability is highly dependent on the rate and magnitude of the pH decrease when the catalyst is added to the solution. As seen from section VII, the properties of glycine are in this respect to be regarded as favourable.

From section VIII, we may conclude that the glycine incorporates into the resin during the heat treatment, and from the titration curve of Fig. 7 it can be estimated that substantially the whole amount of the glycine is resinified. It may also be noticed that the pK of the polymolecular carboxyl groups, which may be assumed to exist, is not very different from the figures previously given. In accordance with such an existence of acidic groups, a considerable absorption of basic dyes occurs, as compared with the samples of the two other catalysts. This was found when dyeing experiments were carried out.

The difference in shape of the curves in Fig. 7, the water retention figures and the wet strength may indicate that the curing reactions are not entirely the same when the glycine and the two other catalysts are applied.

In summary, we may conclude that the curing properties of glycine are highly favourable, especially when the wear properties of the treated fabrics, as they appear from the duty factors, are considered.

The reactions involved when glycine acts as a catalyst may be a formation of a glycine-formaldehyde reaction product, which then incorporates into the resin.

12. **On the influence of mercerization tension on the properties of a crease resisted cotton fabric**

Crease resisting cotton fabrics are usually given a mercerization prior to the resin treatment. This is made since it is known to reduce the undesirable decreases in the fabric strength, which always appear in connection with crease resisting treatments of cotton.

It is known from industrial experience that the tensile strength decrease of the weft direction is, as a rule, considerably greater than that of the warp direction. This is in itself an interesting problem, and since it is common that the grey goods weft strength is less than the warp strength, due to the fabric construction, it also represents a practical problem of a great importance: Not only the level of the warp and the weft tensile strength but also the ratio between them determines the utility of a fabric.

The influence of the caustic concentration on the effect of a premercerization has been studied recently[48].

However, the effect of different weft tensions applied during the caustic treatment has not been investigated.

Experimental

The fabric used was a 57 × 60, 26/30 cotton print cloth. The fabric was taken from an industrial run in the bleached state (kierboil-hypochlorite bleach). The samples to be mercerized were mounted on a pin-frame so that, without any warp elongation, weft elongations of 0, 5, 10 and 15 per cent were obtained. The fabric-carrying frame was then immersed in 270 g/l NaOH¹), and three samples of each tension were mercerized 1, 5 and 15 minutes, respectively. The specimens were then rinsed in hot water, neutralized with acetic acid, rinsed once more, and finally dried at 40° C. The fabric was still kept under tension on the frame during all these operations. One part of each sample was used for studies of the effect of the merceriza-

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¹) 20° C.

tion, and the other part was primarily subject to a crease resisting treatment. This was made by means of a urea-formaldehyde precondensate as follows:

68 parts of a 440 g/l urea solution were mixed with 76 parts of a solution containing 380 g/l formaldehyde + 80 g/l methanol. The pH was adjusted to 7.0 with NaOH, and the mixture was allowed to react at 70° C during 60 minutes. It was then cooled to 20° C within 10 minutes and then diluted with 236 parts of water. Finally, the catalyst, glycine, was added at a rate of 12.5 g/l.

The fabric samples were then impregnated with this solution on an over-feed stenter, and dried at 100° C to $< 1\ \%$ H_2O. The curing was carried out by means of an industrial curing machine of the roller type, fitted with a low tension device. The curing temperature was 140° C and the time of curing 6 minutes.

The specimens were washed in a rope washing machine of the winch type with five sections. The fabric remained in each section 4 minutes. The treatments were as follows: 2× washing in 1.3 g/l soap + 3 g/l sodium carbonate, 60° C; 2× rinsing, 60° C and finally 1× rinsing at 20° C. They were then hydroextracted and dried on an overfeed stenter at 100° C.

After 4 weeks storage at 65 per cent R. H. and 20° C, the untreated and treated samples were subject to some investigations, described in the following:

I. The *tensile strength* was determined in accordance with SIS¹) 650009, *i. e.* on 5 cm strips at 65 per cent R. H. and 20° C. Five measurements were made on each sample, and the results can be found in Tables 5 and 7. At the same time the *load-elongation curves* were recorded. Between the curves representing each sample group, only minor differences appeared, and the average curves are found in Figures 8—11.²)

II. The *tear strength* was determined as described by SIS¹) 650026 at 65 per cent R. H. and 20° C. The number of determinations on each sample was 3, and the average figure of such a determination was found from the regression line of the breaking loads, as they appear from the load-elongation diagrams recorded during the tear tests. The results are found in Tables 5 and 7.

III. The change in fabric dimension due to the different treatments, as shown by the *number of threads per cm* is given in Table 9.

IV. The *crease recovery* at 65 per cent R. H. and 20° C was determined by means of Willow's method[41]. Five measurements³)

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¹) Swedish Standards Association.

²) All the curves of each »group» are within the black areas.

³) 10 minutes delay between load removal and recovery measurements.

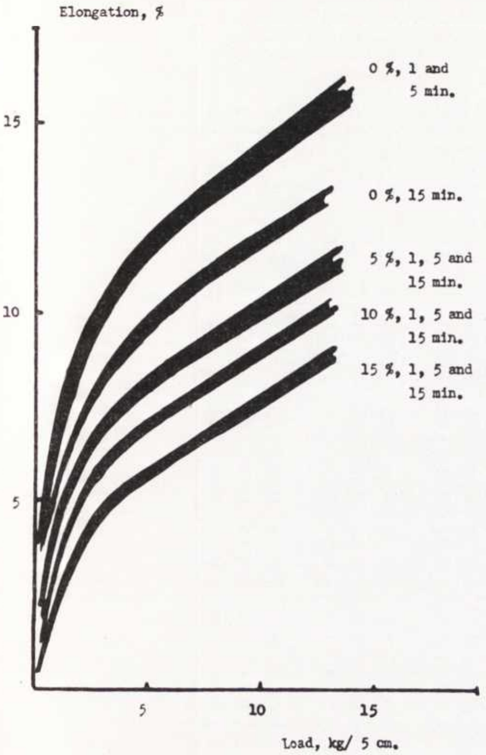


Fig. 8. Load-elongation curves of crease resisted fabric samples, mercerized under different conditions (% weft elongation, minutes of mercerization). Weft direction.

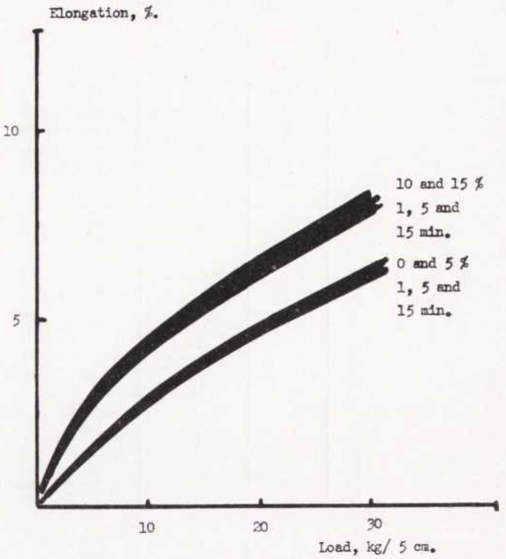


Fig. 9. Load-elongation curves of crease resisted fabric samples, mercerized under different conditions (% weft elongation, minutes of mercerization). Warp direction.

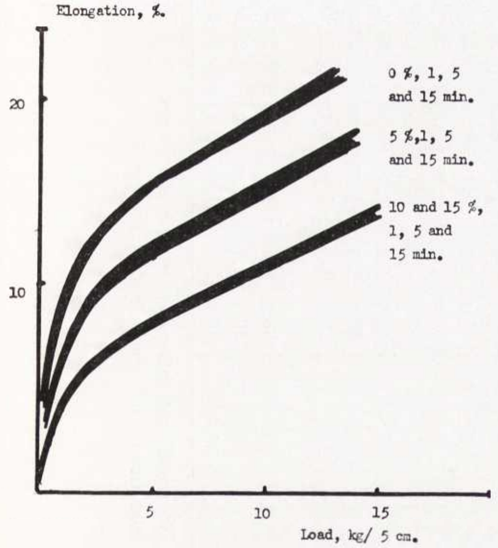


Fig. 10. Load-elongation curves of fabric samples, mercerized under different conditions (% weft elongation, minutes of mercerization). Weft direction.

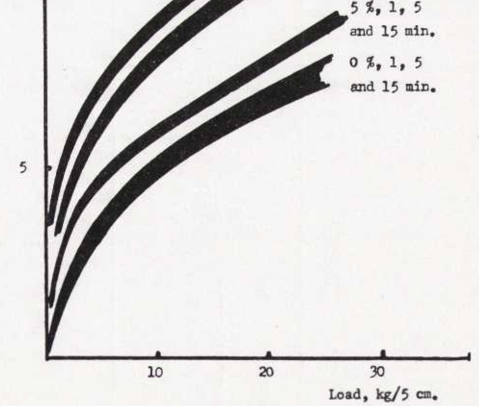


Fig. 11. Load-elongation curves of fabric samples, mercerized under different conditions (% weft elongation, minutes of mercerization). Warp direction.

TABLE 5. *The effect of the mercerization conditions on some of the properties of a crease resisting cotton fabric.*

Mercerization conditions		Σ tensile strength kg/ 5 cm		Tensile strength ratio		Tensile strength kg/ 5 cm				Tear strength kg				Crease recovery mm				Duty factor			
Weft elongation, %	Time of treatment, min.					Warp		Weft		Warp		Weft		Warp		Weft		Warp		Weft	
			s		s		s		s		s		s		s		s		s		s
0	1	↑ 39.2	1.4	⇑ 1.76	0.13	↑ 25.0	1.6	⇑ 14.2	0.5	⇑ 0.35	0.11	↑ 0.77	0.05	↑ 35	1	↑ 34	1	⇑ 1.3	0.3	↑ 1.9	0.2
	5	40.0	2.3	1.88	0.13	26.1	1.8	13.9	0.9	0.37	0.05	0.85	0.05	34	1	34	1	1.4	0.4	1.7	0.2
	15	↓ 41.3	0.7	⇓ 1.52	0.09	↓ 24.9	0.6	⇓ 16.4	0.7	⇓ 0.56	0.05	↓ 0.80	0.00	↓ 36	1	↓ 34	1	⇓ 2.2	0.3	↓ 1.7	0.3
5	1	↑ 40.0	1.8	↑ 1.44	0.12	↑ 23.6	1.6	↑ 16.4	0.8	↑ 0.49	0.05	↑ 0.80	0.08	↑ 36	1	↑ 34	2	↑ 1.5	0.6	↑ 1.6	0.1
	5	41.4	1.6	1.49	0.08	24.8	0.6	16.6	0.9	0.53	0.12	0.77	0.05	35	1	34	2	1.9	0.6	1.5	0.2
	15	↓ 39.8	2.2	↓ 1.55	0.22	↓ 24.7	2.2	↓ 15.9	1.2	↓ 0.53	0.05	↓ 0.91	0.09	↓ 34	1	↓ 33	0	↓ 1.6	0.7	↓ 1.6	0.2
10	1	↑ 40.5	1.6	↑ 1.20	0.11	↑ 22.1	0.6	↑ 18.4	1.5	↑ 0.56	0.10	↑ 0.77	0.05	↑ 35	1	↑ 35	1	↑ 2.4	0.3	↑ 2.0	0.4
	5	39.9	1.3	1.39	0.08	23.2	1.3	16.7	0.8	0.53	0.12	0.72	0.08	35	1	34	2	2.3	0.5	1.9	0.3
	15	↓ 40.6	1.5	↓ 1.36	0.12	↓ 23.4	0.8	↓ 17.2	1.4	↓ 0.59	0.05	↓ 0.80	0.00	↓ 34	1	↓ 34	1	↓ 1.7	0.4	↓ 2.0	0.3
15	1	↑ 38.2	0.6	↑ 1.18	0.19	↑ 20.7	1.0	↑ 17.5	1.7	↑ 0.59	0.05	↑ 0.79	0.05	↑ 35	1	↑ 34	1	↑ 1.5	0.5	↑ 1.5	0.4
	5	36.8	1.2	1.26	0.05	20.5	0.6	16.3	0.8	0.61	0.05	0.75	0.05	35	0	35	0	1.3	0.3	1.3	0.6
	15	↓ 36.2	1.9	↓ 1.29	0.17	↓ 20.4	1.3	↓ 15.8	1.9	↓ 0.58	0.05	↓ 0.77	0.05	↓ 34	1	↓ 34	2	↓ 1.6	0.3	↓ 1.6	0.6

⟷ No significant differences within the group.

⟺ Significant differences within the group.

TABLE 6. *The effect of the mercerization tension on some of the properties of a crease resisting cotton fabric at a mercerization time of 1 minute.*

Weft elongation, %	0	5	10	15
Σ tensile strength, kg/5 cm	39.2	40.0	40.5	38.2
	←			→
Tensile strength ratio	1.76	1.44	1.20	1.18
	⇐	⇒⇐	⇒←	→
Tensile strength, warp direction, kg/5 cm	25.0	23.6	22.1	20.7
	←	→←	→←	→
Tensile strength, weft direction, kg/5 cm	14.2	16.4	18.4	17.5
	⇐	⇒⇐	⇒←	→
Tear strength, warp direction, kg .	0.35	0.49	0.56	0.59
	←	→←		→
Tear strength, weft direction, kg ..	0.77	0.80	0.77	0.79
	←			→
Crease recovery, warp direction, mm	35	36	35	35
	←			→
Crease recovery, weft direction, mm	34	34	35	34
	←			→
Duty factor, warp direction	1.3	1.5	2.4	1.5
	←	→←	→←	→
Duty factor, weft direction	1.9	1.6	2.0	1.5
	←			→

←→ No significant differences within the group.
⇐⇒ Significant differences within the group.

on each sample were made, and the results appear in Tables 5 and 7.

V. The *duty factor* of the resin treated fabric samples were determined, using the method of Breens and Morton[37]. The number of measurements on each sample was 5, and the »ball» and »plate» figures to be combined were taken at random. The testing condition was 65 per cent R. H. and 20° C. The results are shown in Table 5.

VI. The *resin content* of the warp and weft threads of the different samples was determined by means of stripping at boil until a constant weight was obtained. A tartaric acid buffer of pH 3.2 was used. The average resin content was 10 per cent, calculated on the dry weight of the stripped fabric, and no

TABLE 7. *The effect of the mercerization conditions on some of the properties of a mercerized cotton fabric.*

Mercerization condition		Σ tensile strength kg/ 5 cm		Tensile strength ratio		Tensile strength kg/ 5 cm				Tear strength kg				Crease recovery mm			
Weft elongation, %	Time of treatment, min.					Warp		Weft		Warp		Weft		Warp		Weft	
			s		s		s		s		s		s		s		s
0	1	↑ 61.1	1.4	↑ 1.28	0.07	↑ 34.3	1.2	↑ 26.8	0.9	↑ 1.21	0.12	⇑ 1.68	0.14	↑ 24	1	↑ 24	1
	5	60.6	1.6	1.33	0.07	34.6	1.9	26.0	0.8	1.09	0.05	1.28	0.00	24	1	24	1
	15	↓ 59.6	1.7	↓ 1.32	0.05	↓ 33.9	1.6	↓ 25.7	0.8	↓ 1.23	0.20	⇓ 1.29	0.09	↓ 23	1	↓ 23	1
5	1	↑ 61.4	2.4	↑ 1.19	0.18	↑ 33.3	2.0	↑ 28.1	2.5	↑ 1.19	0.15	↑ 1.31	0.09	↑ 23	1	↑ 23	1
	5	58.0	1.0	1.30	0.08	32.8	0.9	25.2	1.1	1.15	0.09	1.36	0.08	22	1	23	1
	15	↓ 58.6	1.2	↓ 1.30	0.09	↓ 33.1	1.9	↓ 25.5	0.4	↓ 1.11	0.12	↓ 1.31	0.17	↓ 24	1	↓ 23	1
10	1	↑ 58.5	2.1	↑ 1.17	0.08	↑ 31.5	1.8	↑ 27.0	2.5	↑ 1.12	0.22	↑ 1.32	0.00	↑ 22	2	↑ 22	1
	5	60.6	1.7	1.16	0.13	32.6	1.9	28.0	1.6	1.09	0.17	1.28	0.08	23	1	23	1
	15	↓ 58.4	2.1	↓ 1.16	0.14	↓ 31.3	2.2	↓ 27.1	2.2	↓ 1.17	0.09	↓ 1.41	0.05	↓ 23	1	↓ 24	1
15	1	↑ 58.9	1.8	↑ 1.09	0.09	↑ 30.7	2.1	↑ 28.2	1.4	↑ 1.25	0.12	↑ 0.96	0.00	↑ 24	1	↑ 22	1
	5	56.2	2.2	1.14	0.06	29.9	2.4	26.3	1.8	1.23	0.12	0.91	0.17	23	1	23	1
	15	↓ 57.9	1.9	↓ 1.11	0.09	↓ 30.4	2.1	↓ 27.5	1.9	↓ 1.33	0.12	↓ 0.93	0.05	↓ 24	1	↓ 23	1

⟷ No significant differences within the group.

⟺ Significant differences within the group.

TABLE 8. *The effect of the mercerization tension on some of the properties of a cotton fabric at a mercerization time of 1 minute.*

Weft elongation, %	0	5	10	15
Σ tensile strength, kg/5 cm	61.1	61.4	58.5	58.9
	←			→
Tensile strength ratio	1.28	1.19	1.17	1.09
	←			→
Tensile strength, warp direction, kg/5 cm	34.3	33.3	31.5	30.7
	←			→
Tensile strength, weft direction, kg/5 cm	26.8	28.1	27.0	28.2
	←			→
Tear strength, warp direction, kg ..	1.21	1.19	1.12	1.25
	←			→
Tear strength, weft direction, kg ..	1.68	1.31	1.32	0.96
	⇐	⇒←	→⇐	⇒
Crease recovery, warp direction, mm	24	23	22	24
	←			→
Crease recovery, weft direction, mm	24	23	22	22
	←			→

←→ No significant differences within the group.
⇐⇒ Significant differences within the group.

TABLE 9. *The influence of the mercerization conditions on the dimensions of crease resisted and untreated samples of a cotton fabric.*

Mercerization conditions		Number of threads per cm			
Weft elongation, %	Time of treatment, min.	Untreated		Treated	
		Warp	Weft	Warp	Weft
0	1	27	23	26	23
	5	27	23	26	22½
	15	27	23	26½	23
5	1	26½	23½	26½	23½
	5	26½	23½	26	23
	15	26½	23	26	23
10	1	24½	24	24	23
	5	25	24	24½	23
	15	25	24	24½	22½
15	1	24½	24	24½.	23½
	5	24	23	24	23½
	15	24	24	24	23

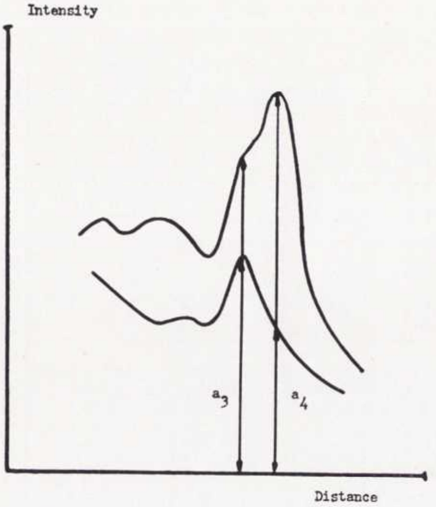


Fig. 12. Photometer curves of X-ray diagrams, parallel with and perpendicular to the fiber direction of the weft. 5 % weft elongation, 5 minutes of mercerization.

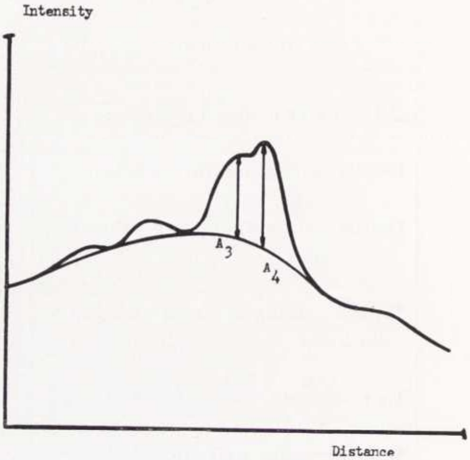


Fig. 13. Photometer curve of the X-ray diagram of a weft fiber powder. 10 % weft elongation, 1 minute of mercerization.

significant differences (at 5 per cent) between the samples, could be detected.

VII. X-ray diffraction patterns of parallelized fiber bundles of the mercerized specimens' warp and weft were determined by means of the method described by *e.g.* Hermans[46], but no corrections for the air scattering were applied. Photometer curves of the intensities parallel with and perpendicular to the fiber direction were recorded and corrections were applied for the hard radiation contribution. An example of the curves is given in Fig. 12. The ratio a_3 between the two A_3 and a_4 between the two A_4 interferences of the curves — as shown in Fig. 12 — were calculated and the results appear in Table 10.

VIII. X-ray diagrams of fiber »powder» of the warp respective the weft of the mercerized samples were determined by substantially the same technique as described above, and an example of the curves is given in Fig. 13. The ratios between the peak intensities of the A_4 and A_3 interferences — as shown by the figure — are found in Table 10.

TABLE 10. *The influence of the mercerization conditions on some X-ray data of a cotton fabric.*

Mercerization condition		Warp		Weft		Warp A_4/A_3	Weft A_4/A_3	$\frac{(A_4/A_3)_{\text{warp}}}{(A_4/A_3)_{\text{welt}}}$
Weft elongation, %	Time of treatment, min.	a_3	a_4	a_3	a_4			
0	1	1.5	3.0	1.6	2.7	1.23	1.10	1.12
	5	1.6	3.2	1.6	2.5	1.26	1.06	1.19
	15	1.6	2.9	1.7	2.5	1.22	1.14	1.07
5	1	1.7	3.4	1.5	2.8	1.17	1.15	1.02
	5	1.7	3.2	1.5	2.6	1.18	1.14	1.04
	15	1.6	3.2	1.6	2.9	1.22	1.11	1.10
10	1	1.6	3.5	1.6	2.8	1.24	1.27	0.98
	5	1.6	3.5	1.6	2.9	1.20	1.20	1.00
	15	1.7	3.3	1.5	2.9	1.24	1.28	0.97
15	1	1.6	3.4	1.6	3.1	1.17	1.22	0.96
	5	1.7	3.2	1.5	2.9	1.19	1.15	1.03
	15	1.6	3.4	1.6	2.7	1.13	1.13	1.00

Discussion

The effects of the treatments on some of the mechanical properties of the fabric are, as previously mentioned, to be found in Tables 5 and 7. The experimental results have been subject to analysis of variance, and in the tables, »significant» refers to significance at 5 per cent. In Tables 5 and 7, the groups investigated represent constant weft elongations during the mercerization, and comparisons between different elongations at 1 minute mercerization time are found in Tables 6 and 8. 1 minute mercerization time was chosen, since this figure is »normal» for modern mercerization machinery.

Tensile strength: The warp tensile strength of the resin treated samples seems to decrease with increasing weft elongation. However, this effect is partially dependent on changes in fabric dimensions, which can be found when the data of Table 9 are considered. Within each group of a constant weft elongation, the time of mercerization is not of any significant importance.

The weft tensile strength of the resin treated samples increases considerably when tension is applied to the weft during the mercerization. In this particular case, 10 per cent weft elongation seems to represent the most favourable condition. Within the groups 5, 10 and 15 per cent elongation, no significant differences due to differences in mercerization time are observed. However, within the group representing 0 per cent elongation, the differences are significant. When the mercerization time is increased up to 15 minutes, a more favourable figure appears, being of the same order as obtained when mercerization tension is applied.

It may be of some interest to compare these results with the corresponding properties of the fabric samples being mercerized, but not given the crease resisting treatment. When neglecting the statistical considerations, a tendency to decreasing warp tensile strength with increasing weft elongation seems to be present. However, when corrections are applied for the changes in the fabric dimensions (Table 9), such a tendency cannot be found. No influence of the time of mercerization on the warp tensile strength is found. The weft figures are not dependent on the mercerization conditions. Thus, the effects on the resin treated fabric are not simply functions of corresponding changes in tensile strength figures of the untreated material due to the mercerization.

The sums of the warp and weft tensile strength figures (combined at random for the statistical calculations) for the samples given a crease resisting treatment are found in Table 5. We find that these sums are substantially constant: only the figures of 15 per cent weft elongation and 5 and 15 minutes mercerization time are slightly below the other. This difference is to a great extent dependent on the differences in number of threads per unit length between the samples.

In the case of samples not given a resin treatment, the corresponding sums are substantially constant, since the warp and weft tensile strength figures are not influenced by the mercerization conditions to any considerable extent.

The ratios between randomly taken warp and weft tensile strength figures of each kind of resin treated samples is the basis of the ratio figures included in Table 5. A pronounced influence from the mercerization tension appears, *e. g.* as seen from the 1 minute mercerization figures of Table 6. Within the groups of 5, 10 and 15 per cent weft elongation, no influence from the time of mercerization appears, but such an influence is found within the 0 per cent group: at 15 minutes of mercerization a decrease appears, as compared with the figures of shorter treatment times.

No significantly different data are found between the different mercerization conditions in the case of samples not given a crease resisting treatment, for the same reason as previously mentioned.

The effect of the mercerization on the tensile strength of the resin treated fabric can be characterized by the sum of the warp and weft tensile strength figures and the ratio between them.

This particular experiment shows that the tensile strength sum of the resin treated fabric is not significantly dependent on the mercerization conditions, but the tensile strength ratio is considerably influenced. This is also known to be valid for everyone of a great number of cotton fabrics, which are within the experience of the present author.

Tear strength: The warp tear strength of the resin treated fabrics does not seem to be dependent on the time of mercerization within the groups of constant weft elongations, except for the 0 per cent group: its 1 and 5 minutes figures are considerably below that of 15 minutes. This latter figure, however, is of the same order as the data obtained when mercerization tension is applied. The figures corresponding to 1 minute mercerization time are not significantly different when the mercerization is carried out with the weft under tension.

The weft tear strength is not significantly influenced by the mercerization conditions.

The warp tear strength figures of samples not given a crease resisting treatment do not differ significantly. The weft tear strength figures, however, are more dependent on the mercerization conditions. When we compare the tear strength data of treated and untreated samples, we find that it does not seem to be probable that any simple correlations exist between their properties in this respect.

Crease recovery: Both the crease resisted samples and the samples not given a crease resisting treatment do not show any influence from the mercerization conditions on the crease recoveries.

Duty factors: The interpretation of duty factor determinations on cotton fabrics is a difficult task. The original work on duty factors was mainly connected with rayon fabrics[37]. With reference to practical experience, it may be assumed that some of the wear properties of crease resisted cotton fabrics are correlated with their duty factors, but tensile and tear strength are probably of a very great importance for the wear behaviour. However, at our present state of knowledge, we may assume that a high duty factor of a crease resisted cotton fabric means better wear properties than a low one, but no statements can be made concerning the practical importance of a given difference in duty factors between two samples.

As regards the present case, the warp direction duty factors are somewhat dependent on the mercerization conditions, and the behaviour is similar to that of the weft tensile strength.

The weft duty factors are not significantly dependent on the mercerization time and tensions.

It may be of some interest to discuss possible mechanisms behind the effects described above. One way to approach the problem is to assume two entirely different possibilities; A: a purely mechanical effect due to changes in the cooperation between the fibers within the yarn and also between the threads when a load is applied, or B: changes in the internal fiber structure, affecting the mechanical effects of a crease resisting treatment.

The following discussion may be applied to assumption A: When a load is applied to the fabric, not all fibers of a yarn cross section are subject to forces of the same magnitude. However, within the yarn there may be a tendency to compensate this by fiber motions, *e. g.* by partial stretching of the coiled fibers or simply by some kind of a slip. Maximum strength will probably appear when the difference in load between single fibers of the yarn cross section is as small as possible, *i. e.* that it does not happen that some fibers break before other fibers carry a considerable load.

A crease resisting treatment may mean that the coiled state of the fibers is made more permanent: the energy difference between the coiled and the straight state is greater than that of untreated fibers. This may also mean that the »compensation» assumed does not occur as easy as for untreated fibers.

A similar discussion may be applied to the yarn as well; in that case the coils of the fibers are compared with the »waves» of the yarn.

When a fabric is mercerized, especially under tension, it would be reasonable that the fibers, and also the yarn, when being in a highly swollen state, change the mechanical positions in such ways that they attain better positions for cooperations of the kind described above. These positions would then remain when the caustic is removed and the fabric is dried. The new state would then be favourable to start from when the crease resisting treatment is carried out.

The role of such a mechanism in the present case seems not to be of any definite importance. The tensile strength figures of the mercerized fabric, Table 7, do not show any influence from an effect of this kind. (An interpretation of *e. g.* the weft tear strength data is very difficult to carry out, since very little is known about what happens within the yarn when a fabric is torn.) A comparison between the load-elongation curves of Figs. 8 and 10 respective 9 and 11 shows that no simple correlations exist between the load-elongation behaviour of the resin treated and the untreated samples. Examples: A separate 0 per cent — 15 minutes curve of Fig. 8 does not appear in Fig. 10, and the coincident 10 and 15 per cent groups of Fig. 10 appear separated in Fig. 8.

The X-ray analysis carried out in the present investigation may form a base for discussions concerning assumption B. The experiments of section VII were made in order to study the influence of the mercerization conditions on the molecular orientation within the fibers. The method applied does not allow any orientation determinations of a high accuracy. It is, *e. g.* very difficult to obtain a bundle of really parallel fibers, However, if any considerable orientation differences are present, they would appear from the figures of Table 10. As seen from this table, such differences do not appear.

The scope of the analysis of the X-ray diffraction patterns of section VIII was to examine the influence of the mercerization conditions on the formation of cellulose II as compared with the remaining cellulose I. This can be made by means of a determination of the ratio between the integrated intensities of the A_4 and A_3 interferences, but such a determination is very difficult to carry out. The A_4 and A_3 intensity distribution curves cover eachother and their zero levels are hidden by other interferences and by contributions from the continous scattering of fiber regions of a low degree of orderliness. The method of analysis used in section VIII and shown by Fig. 13 is purely empirical, but may, with reference to the previous discussion, be as suitable as several other methods for approaching the problem: it seems to be reasonable to assume that some correlation may exist between these A_4/A_3 peak intensity ratios and the ratios between the amounts of cellulose I and cellulose II. The correlation would be of such a kind that decreasing A_4/A_3 ratios mean an increasing fraction of cellulose II.

The general impression of the figures in Table 10 is that the A_4/A_3 ratios of the warp are comparatively little affected by the mercerization conditions, only the figures in connection with 15 per cent weft elongation deviate slightly from the figures of the other groups. The influence on the weft figures is of a greater magnitude, and the maximum figures appear at 10 per cent weft elongation.

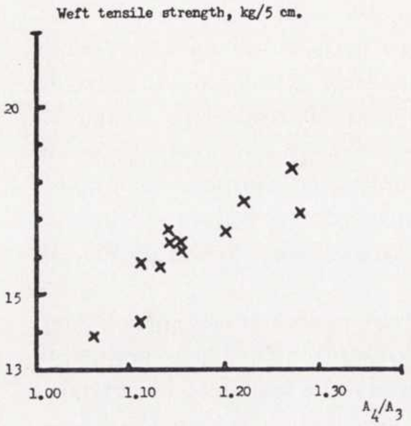


Fig. 14. Relationship between the weft tensile strength and the A_4/A_3 peak intensity ratios of the weft.

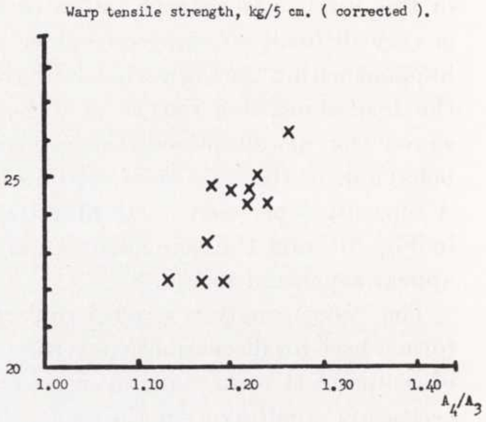


Fig. 15. Relationship between the warp tensile strength and the A_4/A_3 peak intensity ratios of the warp.

The correlation between the A_4/A_3 ratios of the mercerized samples and the corresponding tensile strength of the same samples after the resin treatment is shown by Figs. 14 and 15. Finally, the correlation between the ratios between the warp and weft A_4/A_3 figures of the mercerized samples and their warp and weft tensile strength ratios after the crease resisting treatments appears in Fig. 16. When these diagrams are examined, and the previous discussion is considered, it may be assumed that an increasing fraction of cellulose II of the mercerized samples means decreasing tensile strength figures of the sample after the crease resisting treatment.

The explanation given still remains a hypothesis, since the experimental background does not allow any conclusive statements. However, it is a hypothesis with a fair degree of probability.

It is known that the tensile strength of a cotton fabric increases when the fabric has been subject to a mercerization before the resin treatment. Thus, the unmercerized state, with its high fraction of cellulose I, is not as suitable as the mercerized for crease resisting treatments. If the previously given hypothesis is accepted, this means that there ought to be an optimum cellulose I — cellulose II ratio.

It is also known[45] that the caustic concentration used in this study is within the range producing maximum tensile strength improvements in connection with crease resisting treatments. It may be reasonable that a concentration a little below this range would decrease

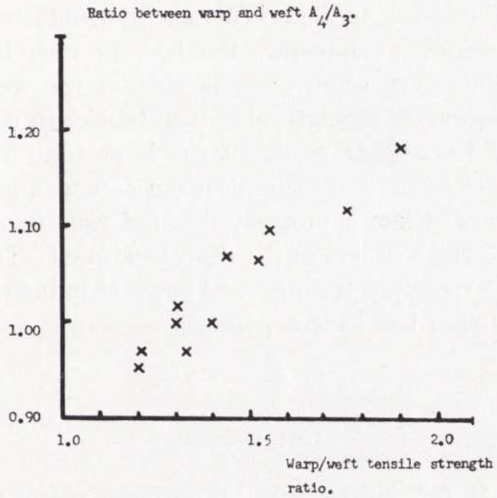


Fig. 16. Relationship between the ratios between the warp and weft A_4/A_3 peak intensity and the corresponding tensile strength ratios.

the fraction of cellulose II, and accordingly give rise to greater improvements, *i. e.* a contrariety to the observed effect. The distribution of cellulose I and II within the fiber may be influenced by the caustic concentration, at higher concentrations also less accessible parts are subject to swelling. However, the restraining action of the mercerization tension is not necessarily of the same kind as the behaviour at a low caustic concentration, in any case when moderate tensions are applied. Since the reaction cellulose I $\rightleftarrows$ swollen cellulose may be partially reversible, the distribution of cellulose I and II within the fiber may not be same if the cellulose I originates from regions which have not been subject to swelling or from regions which have been swollen. It seems to be reasonable to assume that such differences in distribution also may influence the strength properties of the fabric in its final, resin treated state.

However, in the present case the dependence of a change in internal fiber structure on the mercerization conditions is probably one of the more important factors which control the final strength.

Finally, we may discuss the results of the present study from the practical point of view.

When the warp and weft tensile strength figures of the resin treated and untreated samples are compared, it is seen that the tensile strength loss is considerably greater for the weft than for the warp when no mercerization tension is applied. This is, from industrial experience, known to be a common behaviour. Further, the warp tensile strength of the grey goods very often exceeds that of the weft. Thus, the decrease in weft tensile strength of cotton fabrics in connection with crease resisting treatments is one of the important textile finishing problems. However, as seen, this problem can to a great extent be kept under control when a properly selected weft tension is applied during the mercerization before the resin treatment. This is in accordance with the experience from several years of industrial application of the findings described in this paper.

Comments

In the search for better wear properties-crease recovery relations, two different lines may be of the greatest importance: modified resins and modified fibers. Part *11* of this thesis is an example of the former, *10* and *12* of the latter.

A great number of modified precondensates are on the market — methylol melamines, dimethylol cyclic ethylene urea, methyl and ethyl ethers of the methylol compounds etc. — but fundamental differences between them do not exist, as regards the properties discussed here. Also a number of different catalysts are available, but no fundamental improvements have been observed: the results obtained by means of glycine are the best ever observed by the present author. Thus, it may be reasonable to assume that many of the possibilities within the »modified resin line» have been investigated, and that the improvements which can be obtained are limited.

The other line — modified fibers — has not yet been subject to any extensive research. However, the changes in internal fiber properties obtained in accordance with the parts *10* and *12* have a significant and favourable influence on the wear properties-crease recovery relation. Intuitively, it seems to be probable that considerable improvements in this respect can be obtained when more is known about the internal fiber structure and its influence on the effect of crease resisting treatments.

References

1. Landqvist, N. *Swedish Patent* 129833.
2. Dole, M. *J. Am. Chem. Soc.* **53** (1931) 4260.
3. Dole, M. *J. Am. Chem. Soc.* **54** (1932) 3095.
4. Dole, M., Roberts, R. M. and Holley jr., C. E. *J. Am. Chem. Soc.* **63** (1941) 725.
5. Dole, M. and Wiener, B. S. *Trans. Electrochem. Soc.* **72** (1937) 107.
6. Gabbard, J. L. and Dole, M. *Trans. Electrochem. Soc.* **72** (1937) 129.
7. Dole, M. *J. Chem. Physics* **2** (1934) 862.
8. Nicolsky, B. P. *Acta Physicochim. U. R. S. S.* **7** (1936) 597.
9. Gross, P. and Halpern, O. *J. Chem. Physics* **2** (1934) 136.
10. Tendeloo, H. J. C. and Voorspuij, Z. A. J. *Rec. trav. chim.* **62** (1943) 784.
11. Tendeloo, H. J. C. and Voorspuij, Z. A. J. *Rec. trav. chim.* **62** (1943) 793.
12. Fowler, R. and Guggenheim, E. A. *Statistical Thermodynamics*, 2nd Ed., The University Press, Cambridge 1949, p. 429.
13. Winkel, A. and Proske, G. *Ber.* **69** (1936) 693, 1917; **71** (1938) 1785.
14. Vesely, K. and Brdička, R. *Collection Czechoslov. Chem. Communs* **12** (1947) 313.
15. Bieber, R. and Trümpler, G. *Helv. Chim. Acta* **30** (1947) 704.
16. Mejman, N. *Zhur. Fiz. Khim.* **22** (1948) 1454.
17. Weltman, O. and Barrenscheen, H. K. *Klin. Wochschr.* **1922** 1100.
18. Watt, G. W. and Chrisp, J. H. *Anal. Chem.* **25** (1954) 452.
19. Smythe, L. *J. Phys. Colloid Chem.* **51** (1947) 369.
20. Smythe, L. *J. Am. Chem. Soc.* **73** (1951) 2735.
21. Smythe, L. *J. Am. Chem. Soc.* **74** (1952) 2713.
22. Smythe, L. *J. Am. Chem. Soc.* **75** (1953) 574.
23. Crowe, G. and Lynch, C. *J. Am. Chem. Soc.* **70** (1948) 3795.
24. Crowe, G. and Lynch, C. *J. Am. Chem. Soc.* **71** (1949) 3731.
25. Bettelheim, L. and Cedvall, J. *Svensk Kem. Tidskr.* **60** (1948) 208.
26. de Jong, J. *Rec. trav. chim.* **69** (1950) 1566.
27. Květǒn, R. and Králová, M. *Chem. Listy* **46** (1952) 403.
28. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **71** (1952) 643.
29. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **71** (1952) 662.
30. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **71** (1952) 840.
31. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **72** (1953) 88.
32. Takahashi, A. *Chem High Polymers (Japan)* **9** (1952) 48.
33. Ugelstad, J. *The Reaction of Formaldehyde with Amides and the Alkaline Hydrolysis of Alkoxymethyl Ureas* (Diss.) Leiden 1955, p. 54–61.
34. Hubert, E., Matthes, A. and Weisbrod, K. *Kolloid-Z.* **98** (1942) 193.
35. Schwertassek, K. *Faserforschung und Textiltechnik* **3** (1952) 87.
36. Schwertassek, K. *Faserforschung und Textiltechnik* **6** (1955) 351.

37. Breens, L. F. H. and Morton, T. H., *J. Soc. Dyers Colourists* **71** (1955) 513.
38. *Norwegian Patent* 87540.
39. Landqvist, N. *Swedish Patent* 138558.
40. Cameron, W. G. and Morton, T. H. *J. Soc. Dyers Colourists* **64** (1949) 329.
41. Marsh, J. T. *Textile Finishing*, Chapman & Hall Ltd. London 1948, p. 388.
42. Baur, E. *Helv. Chim. Acta* **23** (1940) 233.
43. Baur, E. *Helv. Chim. Acta* **24** (1941) 1018.
44. Tomiyama, T. J. *Imp. Fisheries Inst.* (*Japan*) **33** (1938) 124.
45. Di Masi, A. T. *et al. Am. Dyest. Rep.* **44** (1955) 779.
46. Hermans, P. H. *Physics and Chemistry of Cellulose Fibers.* Elsevier Publishing Company, Inc. Amsterdam 1949, p. 262.

Appendix

The Figs. 14—17 and Table 1 of paper I, p. 607 respective 611, are replaced by the following:

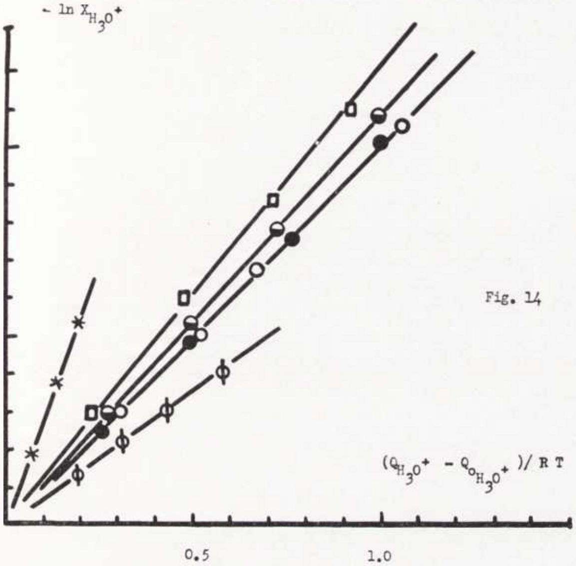


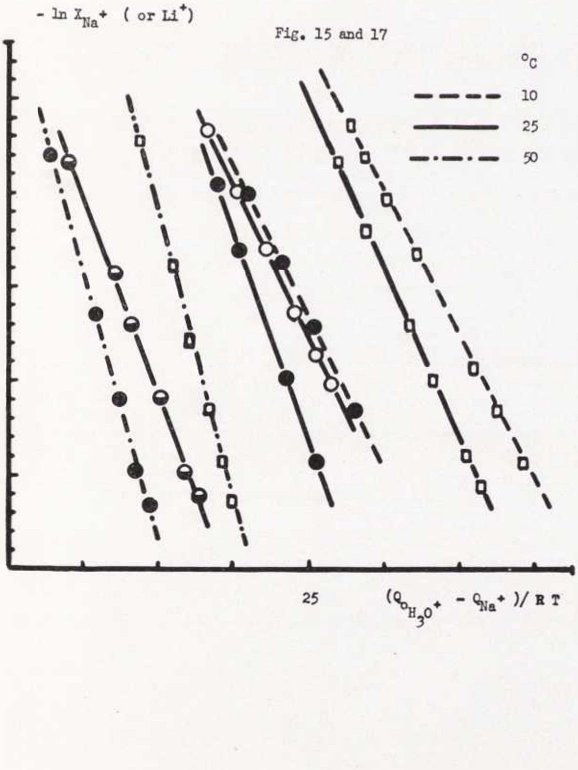
Fig. 14

Table 1.

Electrode and ion.	°C	pK_o	$k_{H_3O^+}$	k_{Na^+}
A Na^+	25	10.4	1.08	1.06
B Na^+	25	11.5	1.00	0.82
C Na^+	10	11.6	1.00	0.80
C Na^+	25	11.1	1.00	1.09
C Na^+	50	10.0	1.00	1.45
C Li^+	10	12.4	1.25	0.76
C Li^+	25	12.1	1.25	0.92
C Li^+	50	10.6	1.25	1.50
D Na^+	25	13.9	0.72	2.22
E Na^+	25	15.0	2.75	0.98

Electrode	A	B	C	C	D	E
Ion	Na^+	Na^+	Na^+	Li^+	Na^+	Na^+
	⊖	○	●	▣	*	ϕ

Fig. 15 and 17



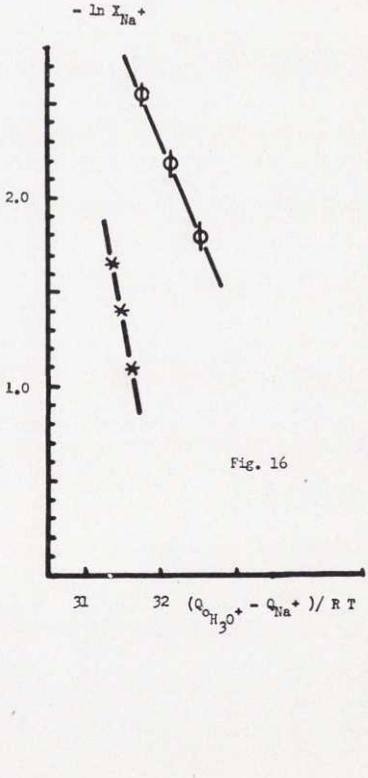


Fig. 16

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ACTA CHEMICA SCANDINAVICA 9 (1955) 595—612

On the Alkaline Error of the Glass Electrode *

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A theoretical treatment is given to the glass electrode alkaline behaviour, considering the influence of the state of adsorption on the adsorption energies. By expanding in series and approximating, the equation deduced has been transformed into earlier known, empirical expressions. Experimental results confirm the theoretical treatment. Finally a differential measuring method has been described, to be applied for correcting the alkaline error in glass electrode measurements when the activity of the sodium ion (or other) is unknown, comprising the use of two glass electrodes of different, but known, alkaline error functions.

Since Hughes[1] discovered the alkaline error of glass electrodes in 1922, several theories have been applied to the quantitative treatment of the difference between hydrogen and glass electrode behaviour. Important contributions in this field have been made by Dole *et al.*[2–7], and also by Nicolsky[8], Gross and Halpern[9] and Tendeloo and Voorspuij[10, 11]. For a more general review of the different theories, reference may be made to Kratz[12].

The theories of Dole and of Nicolsky give the same final equation, which can be written:

$$\log[\exp (F\triangle E/RT) - 1] = \mathrm{pH} + \log \mathrm{C}_{\mathrm{Na}^+} + \mathrm{constant} \qquad (1)$$

($\triangle E$ is the alkaline error, pH and $\mathrm{C}_{\mathrm{Na}^+}$ refer to the solution surrounding the glass electrode.) If $\log [\exp (F\triangle E/RT) - 1]$ is plotted as a function of pH from experimental data, the linear agreement is good, except that the slopes of the lines are not unity, as demanded by eq. (1). Thus, for an electrode made of Corning 015 glass, a slope of 0.57 for 1 M Na^+ at 25° C was found by Dole[13]. (It was also stated in the same paper that no quantitative explanation of the deviation of the slope from unity had been advanced at that time.)

The validity of the Gross and Halpern treatment has been discussed and criticised by Dole[7], who concludes that their final equation is not as good as eq. (1) for explaining glass electrode behaviour in alkaline solutions.

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* This paper is based on a lecture given by the author at the 8:th Congress of Scandinavian Chemists in Oslo, June 14—17, 1953.

The treatment by Tendeloo and Voorspuij gives the equation:

$$\log [\exp (F\triangle E/RT)—1] = \mathrm{pH} + \log [(1 + K_2' \cdot C_{Na+})/K'_1] \qquad (2)$$

($\triangle E$ is the alkaline error, pH and C_{Na+} refer to the surrounding solution, K_1' and K_2' are electrode constants.) The equation is very similar to eq. (1), and for ordinary glass electrodes it fails as does eq. (1) in predicting a slope of unity. However, these authors used an electrode made of Al_2O_3-containing glass with a very high alkaline error. At pH 11 and $C_{Na+} = 0.1$ the error was about 50 times greater than that of an electrode made of Corning 015 glass. In this case eq. (2) is in good agreement with experimental results, but the lack of agreement occurs at low $\triangle E$, which can be expected from the behaviour of said Corning 015 glass. This is also stated by the authors.

The basic ideas of the four different treatments refered to above, have been:

Dole: Ion exchange reactions take place between the glass electrode surface and the surrounding solution, and the equilibrium is treated mathematically by a statistical method used earlier by Gurney [14,15] in studies on other electrode reactions.

Nicolsky: The ion distribution on the glass surface and in the surrounding solution is treated by the law of mass action.

Gross and Halpern: "It is assumed that the electrode glass may be treated as a difficulty soluble salt, which forms with water a saturated solution, so that the water dissolves in the glass until the glass becomes saturated with water. It is also assumed that the mass action law holds for such strong electrolytes as sodium hydroxide and sodium acetate both in water and glass phases, that water, glass, acids, bases *etc.* distribute themselves between the glass and the aqueous phase in accordance with the well-known distribution law, and that the activity coefficients of all ions are the same." (Dole [7]).

Tendeloo and Voorspuij: Dissociation equilibria between the swollen glass surface and the surrounding solution are controlled by real constants of dissociation for the silicic acid in that surface.

In the following discussion a refined treatment of the glass electrode alkaline error will be given, and the influence of the state of adsorption on the adsorption energies will also be considered. This has not been made in the treatments mentioned above.

The *physical model* used for the mathematical treatment is in accordance with the ideas of Tendeloo and Voorspuij [11], the SiO_4-network of the electrode glass being regarded as containing three dimentional interstices, offering room for metal ions such as Na^+ and Ca^{2+}. When the electrode surface is brought in contact with water the network on the surface and to some depth into the glass will pass into a swollen state, the aforesaid metal ions will be dissolved to a great extent and replaced by H^+ or H_3O^+ ions. In this way the *surface layer* is substantially free from other cations, and consists of silicic acid. The silicic acid is then able to take part in ion exchange reactions, so that all states from complete H^+ saturation to a more or less mixed composition of H^+ and other cations are possible. Under these conditions it may be anticipated that the adsorption energies, *i.e.* the forces between adsorbed ions and the adsorption sites, will be dependent on the state of adsorption, so that the energy will not be the same if an adsorbed ion has identical or dissimilar ions as neighbours

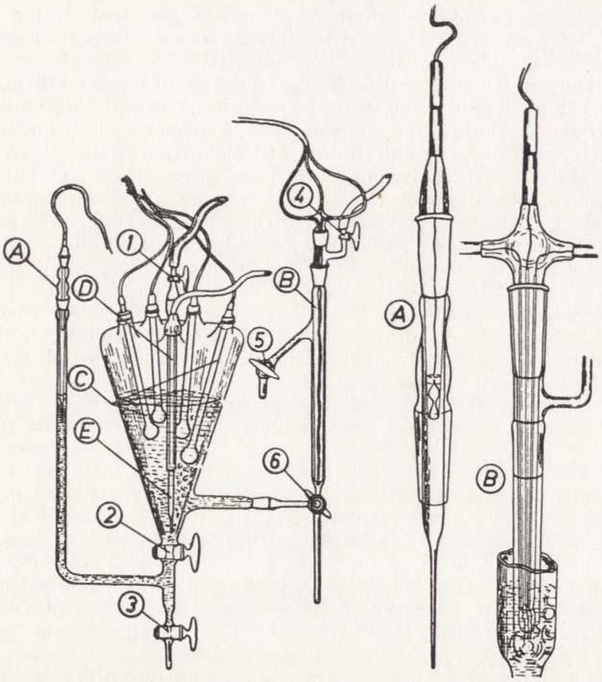


Fig. 1. Apparatus for hydrogen and glass electrode measurements.

on the surrounding adsorption sites. This seems to be reasonable, as the degree of ”energy saturation” of each adsorption site may influence the surrounding sites, with regared to their available adsorption forces. As we are dealing with a network, *i.e.* a kind of a large molecule, the state of the internal resonance energies can to some extent be compared with that of a polybasic acid. However, in the case of glass the effect is more complex, as the glass is a solid acid, where the electrical forces outside the molecule have a large influence on the activity of the adsorbed ions.

EXPERIMENTAL

In the experiments a glass apparatus, Fig. 1, was used, with spaces for four glass electrodes C, a reference electrode A, a hydrogen electrode B and a temperature compensator D, used when measurements were made with instruments having an automatic temperature compensation device. During the measurements the whole system was enclosed in a Faraday cage, and the temperature of the surrounding room, 25° C, controlled by means of a radiant heating device to within 0.1° C, with a temperature change less than 0.1° C per hour. When hydrogen electrodes are used in alkaline solutions, it is of greatest importance that the hydrogen should be of a very high purity. An amount of oxygen exceeding 300 μg per litre can give mixed hydrogen-hydrogen ion and oxygen-hydroxyl ion potentials, disturbing the response of the electrode. The cylinder hydrogen used in this work was purified in the following manner, which gave excellent results. The gas was passed through a tube of stainless steel, with a diameter of 20 millimeters, containing one layer of cut copper wires, and another of platinum deposited on porcelain. The height of each layer was 300 millimeters. The tube was heated by a 1 000 watt heating coil, controlled by an energy regulating device to maintain the temperature of the catalyst at 650 ± 25° C. The gas was in contact with the catalyst for about 5 minutes. It was then passed through a copper pipe for air cooling and bubbled through concentrated sulphuric acid and then through a solution of sodium hydroxide (400 g per litre). Before entering the hydrogen electrode, the gas was passed through a large quantity of thermostated distilled water, in order to avoid temperature changes at the electrode and to attain approximate equilibrium with the vapor pressure of the solution to be investigated. This eliminated changes in concentration, caused by evaporation from the electrode solution. The efficiency of the purification was examined from time to time. The purified hydrogen was bubbled through a small volume of 0.1 *M* KCl, and after one hour of bubbling the oxygen was determined polarographically. The amount of oxygen was always found to be less than a few μg per litre, which was below the limit for side reactions. Anodic polarographic investigations in 0.1 *M* Na_2HPO_4 gave no detectable wave of H_2S, arising from the sulphuric acid and not completely removed by the sodium hydroxide solution. From this it can be concluded that the amount of hydrogen sulphide was less than a few *u*g per litre of solution.

The hydrogen electrode B was designed as a triple electrode with three separate platinum wires for measuring the response of the electrode. In every pH measurement the three electrodes were measured individually several times, and the agreement of the three potentials had to be within the accuracy of the instruments used for the determination, before the measurements were accepted. Experience has shown that oxygen impurities, bad platinum plating and other electrode errors do not give identical potentials. The platinum plating was prepared by electrolysis, using a Pt anode, area 200 mm^2, at a distance from the cathodes of 20—30 mm, in 20% $PtCl_4$ at 4 volts for 15 sec. and at a temperature of 20° C. The cathodes, *i. e.* the three platinum wires of the hydrogen electrode, were each 0.5 mm in diameter and 7 mm in length. The platinum deposit was renewed when necessary, but at least every day. The old deposit was carefully removed and the electrode cleaned by means of sodium chromate in sulphuric acid and rinsed in distilled water before replating. The reference electrode was a 0.1 *M* calomel electrode, this concentration being used as it has a low temperature coefficient and seems, with the electrode design used here to be practically free from variations in diffusion potentials. The electrode was similar to the type introduced by Perley [16].

The apparatus was operated in the following manner: With the cocks 2 and 6 (without grease) and 5 open, the test solution, buffer I or II, was introduced into the apparatus to cover the electrodes. (The reference electrode has a little hole, not shown, to allow the air to escape.) After closing the cocks 2 and 6 and opening 1 and 4, the hydrogen bubbling was started. As the hydrogen electrode space has a small volume, the oxygen in the solution was removed and hydrogen saturation quickly obtained. The minimum time of bubbling was of the order 10—15 minutes. The glass electrode potentials were measured at 5 minute intervals over a period of 30 minutes, thus giving 6 different determinations on each solution. The solution around the glass electrodes was stirred continously by means of the bubbling hydrogen, introduced by means of the pipe E. After 30 minutes the hydrogen electrode potential was determined, and during this measurement, cock 5 was closed, and all the three electrodes tested for coincidence. In order to investigate if any liquid junction potentials arise at the cocks 2 and 6, these cocks were opened and the potential difference determined. To change the pH of the solution, the cocks 1 and 5 were opened and the hydrogen electrode tube and that containing the reference electrode drained by means of cocks 2, 3 and 6. A desired amount of "contrabuffer" II or I was added to the solution around the glass electrodes, which was then stirred violently by means of the hydrogen, and by using the cocks 2, 3 and 6 the hydrogen and reference electrodes were rinsed several times, and finally as much solution removed as was necessary to maintain constant liquid level. The next measurements could then be made. Before and after each series of measurements the apparatus was filled with a control buffer and hydrogen and reference electrodes and asymmetry potential changes checked. As a rule identical values were found, but if this was not the case, the whole series of measurements were rejected and repeated after careful checking of the electrode system. The average accuracy was ± 0.25 mV.

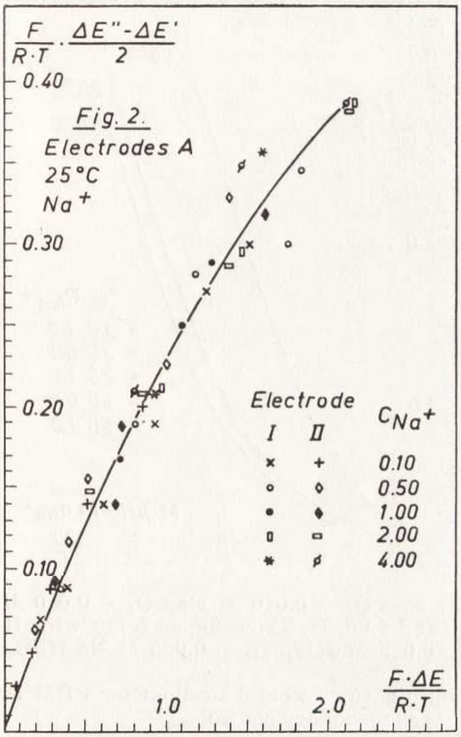


Fig. 2.
Electrodes A
25 °C
Na^+

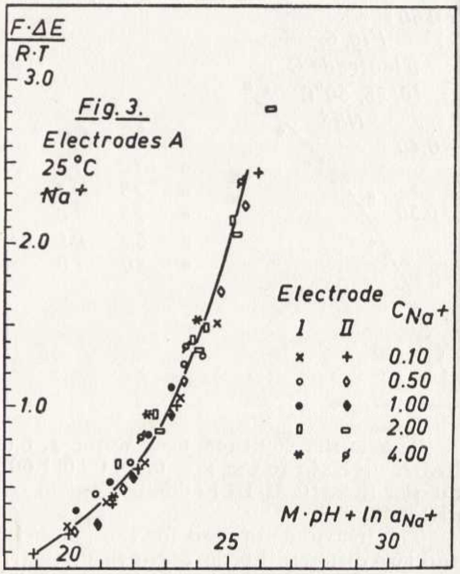


Fig. 3.
Electrodes A
25 °C
Na^+

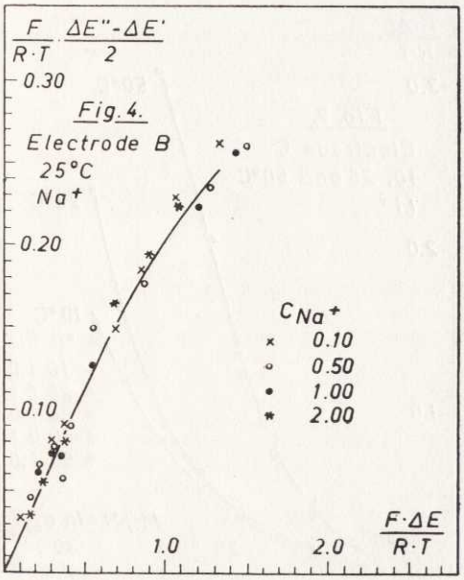


Fig. 4.
Electrode B
25 °C
Na^+

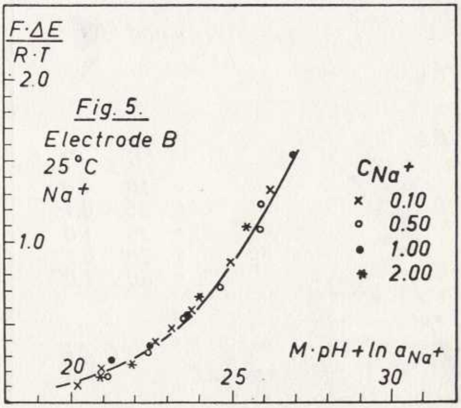
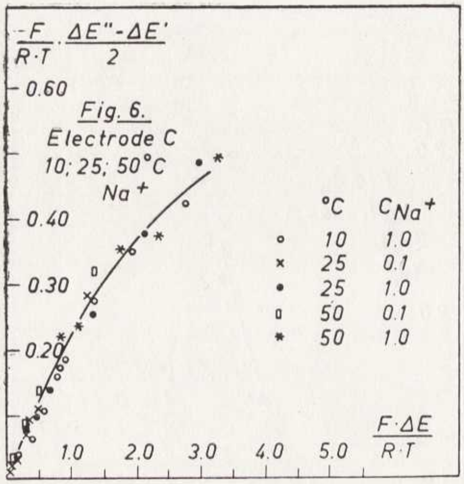
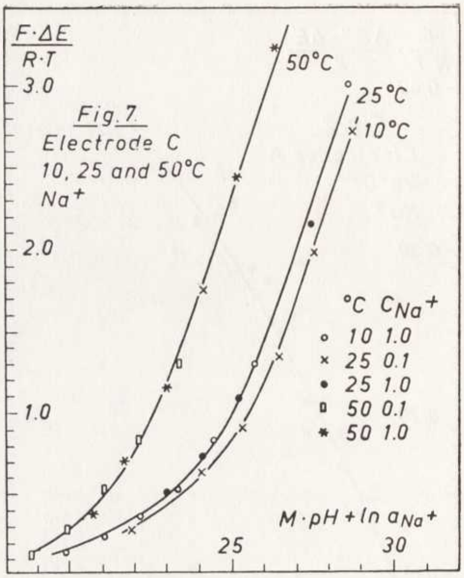


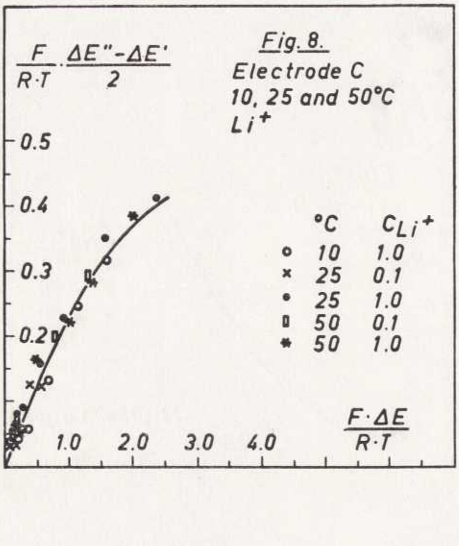
Fig. 5.
Electrode B
25 °C
Na^+

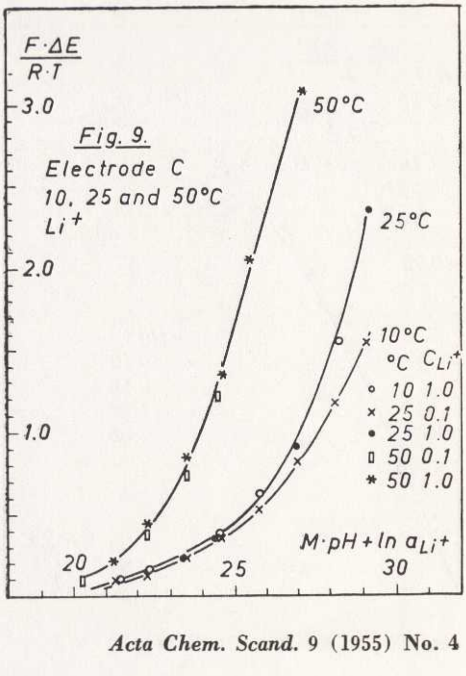


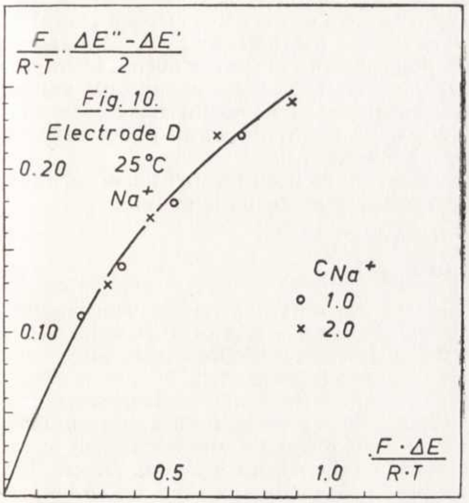


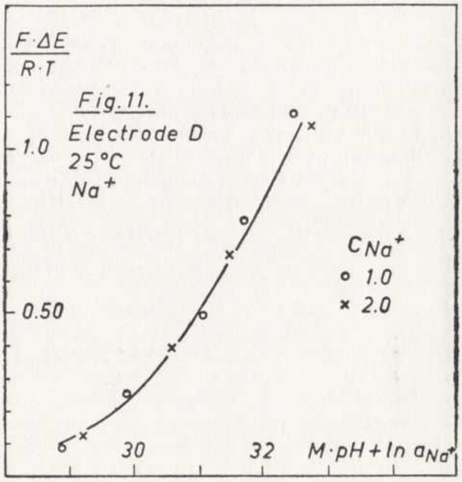
The buffer solutions used were: I. 0.010 *M* Na_3PO_4 + 0.010 *M* Na_2CO_3 + 0.050 *M* NaOH + NaCl to C_{Na+} = 0.10, 0.50, 1.00, 2.00 and 4.00. II. The same as I, but with 10 ml per litre 10 *M* HCl added. Control buffer: 0.025 *M* KH_2PO_4 + 0.025 *M* Na_2HPO_4; pH 6.86.

The instruments used for the potential determinations were a Radiometer PHM 3g and two different Leeds & Northrup instruments as secondary controls.

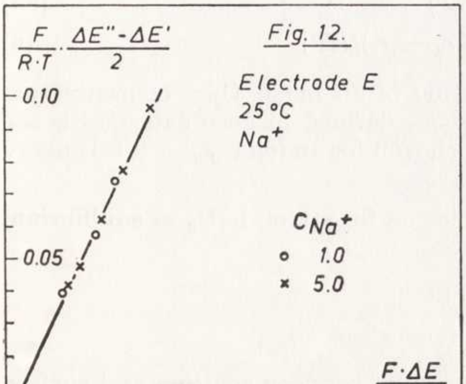


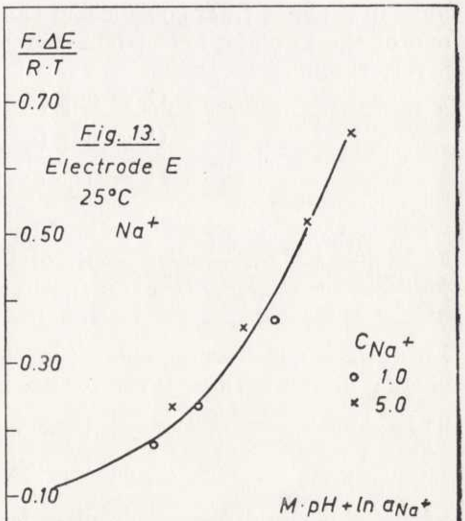






Measurements were made on two commercial glass electrodes, one of type A, and one of another type B, using the method described above. The investigated ranges were: pH 9 − 11.5 and C_{Na^+} 0.10 − 4.00 at a temperature of 25° C. The electrodes A and B have different, but unknown glass composition. For calculations in accordance with the theory presented later in this paper, data obtained by Dole *et al.*[2-7, 12] have also been used. The object of this has been to include still another composition of glass, and also to include the effect of different temperatures, 10, 25 and 50° C, and of different ions, Na^+ and Li^+. (As the other ions investigated by Dole give a very low alkaline error, the accuracy is not sufficient for these calculations. Hence only the Na^+ and Li^+ results have been examined.)





In the present paper, the electrode used by Dole has been denoted by C. Figures for Na^+ at 25° C from the manufacturers' bulletins concerning two different electrodes D and E, having a very low alkaline error, were also used as a basis for mathematical calculations. In this case the data are of doubtful value, as nothing is known of the measuring technique and accuracy, the test solution composition and the activity changes at high pH values. The assumption has been made that NaCl was present in the solution and that the amount of buffer was low. The values have been included since they do give some additional indication of the low alkaline error electrode behaviour.

For the electrodes mentioned above, two functions have been plotted for all of them from experimental data, to be used in the theoretical treatment, namely:

$$F(\triangle E'' - \triangle E')/2\ RT = f(F\triangle E/RT) \tag{3}$$

$$F\triangle E/RT = g(\mathrm{M.pH} + \ln a_{\mathrm{Na}^+}) \tag{4}$$

In these functions $\triangle E$ is the alkaline error at an activity of hydrogen ions corresponding to pH and a sodium activity of a_{Na^+}. $\triangle E''$ is the alkaline error at a pH 0.25 units above the pH value at $\triangle E$, and $\triangle E'$ is that at a pH 0.25 below. M is the logarithm conversion figure. In the case of eq. (4) the sodium ion activity has to be estimated. This is, of cause, a difficult task. In the measurements made by the author, the buffer concentration was kept low and most of the sodium ions are due to NaCl. This gives a simpler solution from the point of view of activity calculations. In all cases the mean activity coefficient of the electrolyte has been applied to Na^+, and has been taken from different papers [17-19]. However, even if the accuracy of the activity figures is moderate, they are to be preferred to the concentration figures used in other treatments. In Figs. 2—13 plots of the functions (3) and (4) are shown, and the mean curve from them will be used later for further calculations.

THEORETICAL

Applied to a system where ions are distributed between different phases, the Boltzmann energy distribution law can be written:

$${}_{\mathrm{i}}\mathrm{C}_{\mathrm{j}} = \exp\left(-{}_{\mathrm{i}}\varepsilon_{\mathrm{j}}/RT\right) \tag{5}$$

where ${}_{\mathrm{i}}\mathrm{C}_{\mathrm{j}}$ = concentration of an ion i in a phase j; ${}_{\mathrm{i}}\varepsilon_{\mathrm{j}}$ = total energy for an ion i in a phase j. If considering the physical model, and eq. (5) is applied to one of the two glass electrode surfaces, *i.e.* to the system solution — surface layer, then:

$${}_{\mathrm{i}}\mathrm{C}_{\mathrm{s}} = \exp\left(-{}_{\mathrm{i}}\varepsilon_{\mathrm{s}}/RT\right) \tag{5a}$$

$${}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}} = \exp\left(-{}_{\mathrm{i}}\varepsilon_{\mathrm{g}}/RT\right) \tag{5b}$$

$${}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}} = {}_{\mathrm{i}}\mathrm{C}_{\mathrm{s}} \cdot \exp[-({}_{\mathrm{i}}\varepsilon_{\mathrm{g}} - {}_{\mathrm{i}}\varepsilon_{\mathrm{s}})/RT] \tag{6}$$

where: ${}_{\mathrm{i}}\mathrm{C}_{\mathrm{s}}$ = concentration in the solution of an ion i, ${}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}}$ = concentration of an ion i in the *surface layer* of the glass, defined in accordance with the *physical model*, ${}_{\mathrm{i}}\varepsilon_{\mathrm{s}}$ = total energy in the solution for an ion i, ${}_{\mathrm{i}}\varepsilon_{\mathrm{g}}$ = total energy in the surface layer for an ion i.

Let: ${}_{\mathrm{i}}U_{\mathrm{s}}$ = equilibrium energy in the solution for an ion i, ${}_{\mathrm{i}}U_{\mathrm{g}}$ = equilibrium energy in the surface layer for an ion i.

Then:

$${}_{\mathrm{i}}\varepsilon_{\mathrm{s}} = {}_{\mathrm{i}}\mathrm{U}_{\mathrm{s}} + \text{constant}$$

$${}_{\mathrm{i}}\varepsilon_{\mathrm{g}} = {}_{\mathrm{i}}U_{\mathrm{g}} + zFE + \text{constant}$$

where E is the difference in electrical potential between solution and surface layer, and z is the valency of i.

From this:

$${}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}} = {}_{\mathrm{i}}\mathrm{C}_{\mathrm{s}} \cdot \exp\left[-\left({}_{\mathrm{i}}U_{\mathrm{g}} + zFE - {}_{\mathrm{i}}U_{\mathrm{s}}\right)/RT\right] \qquad (6b)$$

As the logarithm of the activity coefficient gives the difference between actual and ideal energies in the solution, then if the ideal energy is written ${}_{\mathrm{i}}U_{\mathrm{os}}$:

$${}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}} = {}_{\mathrm{i}}\mathrm{a}_{\mathrm{s}} \cdot \exp\left[-\left({}_{\mathrm{i}}U_{\mathrm{g}} + zFE - {}_{\mathrm{i}}U_{\mathrm{os}}\right)/RT\right] \qquad (7)$$

where ${}_{\mathrm{i}}\mathrm{a}_{\mathrm{s}}$ is the activity of the ion in the solution.

If we define: ${}_{\mathrm{i}}U_{\mathrm{os}} - {}_{\mathrm{i}}U_{\mathrm{g}} = Q_{\mathrm{i}}$
then

$$\Sigma\, {}_{\mathrm{i}}\mathrm{a}_{\mathrm{s}} \cdot \exp\ \left[(Q_{\mathrm{i}} - zFE)/RT\right] = \Sigma\, {}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}} \qquad (8)$$

This can be regarded as the fundamental equation of the glass electrode.

In the following treatment we shall for simplicity select the ions H_3O^+ and Na^+. In this case eq. (8) can be written:

$$E = \frac{RT}{F}\ln\left[\mathrm{a}_{\mathrm{H_3O+}} \cdot \exp\left(Q_{\mathrm{H_3O+}}/RT\right) + \mathrm{a}_{\mathrm{Na+}} \cdot \exp\left(Q_{\mathrm{Na+}}/RT\right)\right] - \frac{RT}{F}\ln \Sigma\, {}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}} \qquad (9)$$

Let $\mathrm{X}_{\mathrm{i}} = {}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}}/\Sigma_{\mathrm{i}}\mathrm{C}_{\mathrm{g}}$, and define $Q_{\mathrm{i}} \rightarrow Q_{\mathrm{oi}}$ ${}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}} \rightarrow {}_{\mathrm{i}}\mathrm{C}_{\mathrm{og}}$ when $\mathrm{X}_{\mathrm{i}} \rightarrow 1$.
If $\mathrm{a}_{\mathrm{Na+}} \cdot \exp\ (Q_{\mathrm{Na+}}/RT) \ll \mathrm{a}_{\mathrm{H_3O+}} \cdot \exp\ (Q_{\mathrm{H_3O+}}/RT)$ eq. (9) can be written:

$$E' = Q_{\mathrm{oH_3O+}}/F - \frac{RT}{F}\ln \Sigma\, {}_{\mathrm{i}}\mathrm{C}_{\mathrm{og}} - \frac{MRT}{F}\,\mathrm{pH} \qquad (10)$$

Let

$$Q_{\mathrm{oH_3O+}}/F - \frac{RT}{F}\ln \Sigma\, {}_{\mathrm{i}}\mathrm{C}_{\mathrm{og}} = e_{\mathrm{o}}$$

then

$$E' = e_{\mathrm{o}} - \frac{MRT}{F}\,\mathrm{pH} \qquad (10a)$$

This is, except e_{o}, the equation for the hydrogen electrode. The differences in e_{o} for the two active surfaces of the glass electrode:

$$e_{\mathrm{o}}'' - e_{\mathrm{o}}' = \varphi \qquad (11)$$

is an expression of the *asymmetry potential*, *i.e.* the deviation in E_{o} in comparison with the hydrogen electrode. If the electrode surfaces change their properties in different ways, this will cause a variation in φ. However, for short periods (of the order 100 hours) φ is a constant.

If it is not possible to neglect the Na^+-term, and if we define:

$$\triangle E = E - E' \qquad (12)$$

then, since

$$\Sigma\, {}_{\mathrm{i}}\mathrm{C}_{\mathrm{g}}/\Sigma\, {}_{\mathrm{i}}\mathrm{C}_{\mathrm{og}} = \mathrm{X}_{\mathrm{H_3O+}} + \mathrm{X}_{\mathrm{Na+}}$$

$$(\mathrm{X}_{\mathrm{H_3O+}} + \mathrm{X}_{\mathrm{Na+}}) \cdot \exp\ \left[(Q_{\mathrm{oH_3O+}} - Q_{\mathrm{H_3O+}})/RT\right] \cdot \exp\ (F \triangle F/RT) =$$

$$\frac{\mathrm{a}_{\mathrm{Na+}}}{\mathrm{a}_{\mathrm{H_3O+}}}\exp\ \left[(Q_{\mathrm{Na+}} - Q_{\mathrm{H_3O+}})/RT\right] + 1 \qquad (13)$$

Applying the distribution law once more:

$$\frac{X_{Na^+}}{X_{H_3O^+}} = \frac{a_{Na^+}}{a_{H_3O^+}} \exp\ [(Q_{Na^+} - Q_{H_3O^+})/RT]$$

and $$\frac{a_{Na^+}}{a_{H_3O^+}} \exp\ [(Q_{Na^+} - Q_{H_3O^+})/RT] + 1 = \frac{X_{Na^+} + X_{H_3O^+}}{X_{H_3O^+}}$$

Combining this with eq. (13) gives:

$$F \cdot \triangle E/RT = (Q_{H_3O^+} - Q_{oH_3O^+})/RT - \ln\ X_{H_3O^+} \tag{14}$$

So far nothing has been assumed concerning the *number* of points for cationic adsorption in the surface layer. Here the assumption will be made that *the number of points is constant.* The reason for this is that only a destruction of the surface layer will change that number, and the possibility of such a destruction seems to be remote. This can be concluded from the fact that the asymmetry potential remains constant, even if the electrode is alternately brought in contact with acid and alkaline solutions, and also from the reproducible alkaline behaviour.

From this assumption we get:

$$\Sigma\ _iC_g = \Sigma\ _iC_{og} = \text{constant} \tag{15}$$

and $$X_{H_3O^+} + X_{Na^+} = 1 \tag{16}$$

It may be pointed out that eq. (16) contains *concentrations, i.e. numbers* of ions. However, the *activity* of the adsorbed ions may change with the state of adsorption, and this will be revealed by variations in U_g and Q_i.
By applying eq. (16), eq. (13) is reduced to:

$$\exp\,[(Q_{oH_3O^+} - Q_{H_3O^+})/RT] \cdot \exp\,(F\triangle E/RT) = \frac{a_{Na^+}}{a_{H_3O^+}} \exp[(Q_{Na^+} - Q_{H_3O^+})/RT] + 1 \tag{17}$$

From the treatment given above it is possible to calculate $X_{H_3O^+}$, X_{Na^+}, $(Q_{H_3O^+} - Q_{oH_3O^+})/RT$ and $(Q_{oH_3O^+} - Q_{Na^+})/RT$ from experimental data on the alkaline error under different conditions. This can be done from two separate values of both $\triangle E$ and $a_{Na^+}/a_{H_3O^+}$ by means of eq. (14) and eq. (17). The first step is to determine $\exp\ [(Q_{oH_3O^+} - Q_{H_3O^+})/RT]$, keeping a_{Na^+} constant.

In practice it is not possible to attain these conditions, as the sodium ion activity changes with the ionic strength when pH is altered. However, errors from this source can be kept low if a suitable solution is used, containing a small amount of buffer with most of the sodium ions present as NaCl. We write:

$$\exp\ [(Q_{oH_3O^+} - Q_{H_3O^+})/RT] = \gamma$$
$$\exp\ [(Q_{Na^+} - Q_{H_3O^+})/RT] = \delta$$

From eq. (17) $$\gamma \cdot \exp\ (F\triangle E/RT) = \delta \frac{a_{Na^+}}{a_{H_3O^+}} + 1$$

and for $\triangle E''$ and $\triangle E'$

$$\gamma \cdot \exp\ (F\triangle E''/RT) = \delta \frac{a_{Na+}}{a''_{H_3O+}} + 1$$

$$\gamma \cdot \exp\ (F\triangle E'/RT) = \delta \frac{a_{Na+}}{a'_{H_3O+}} + 1$$

i.e.

$$\frac{\gamma \cdot \exp\ (F\triangle E'/RT) - 1}{\gamma \cdot \exp\ (F\triangle E''/RT) - 1} = \frac{a''_{H_3O+}}{a'_{H_3O+}}$$

($\triangle E' < \triangle E''$ and correspondingly $a'_{H_3O+} > a''_{H_3O+}$)

With a pH difference of 0.50, which is adequate for over all accuracy in the measurements, we have: $a''_{H_3O+}/a'_{H_3O+} = 1/\sqrt{10}$ and

$$\frac{1}{\gamma} = \exp\,[(Q_{H_3O+} - Q_{oH_3O+})/RT] = \frac{3.16\ \exp(F\triangle E'/RT) - \exp\,(F\triangle E''/RT)}{2.16} \quad (18)$$

Putting as a first approximation $\triangle E = (\triangle E' + \triangle E'')/2$, which is equivalent to assuming that the alkaline error function is a straight line in the small interval between $\triangle E'$ and $\triangle E''$, and combining eq. (14) and eq. (18):

$$X_{H_3O+} = \frac{1.46}{\exp\,(F(\triangle E'' - \triangle E')/2RT]} - 0.462 \cdot \exp\,[F(\triangle E'' - \triangle E')/2RT] \quad (19)$$

From the earlier equation:

$$\frac{X_{Na+}}{X_{H_3O+}} = \frac{a_{Na+}}{a_{H_3O+}} \exp\ [(Q_{Na+} - Q_{H_3O+})/RT]$$

and eq. (14) we get:

$$\ln\ X_{Na+} + (Q_{oH_3O+} - Q_{Na+})/RT = \ln a_{Na+} + M \cdot pH - F\triangle E/RT \quad (20)$$

As $X_{H_3O+} + X_{Na+} = 1$ we can derive X_{Na+} and $(Q_{oH_3O+} - Q_{Na+})/RT$ from eq. (19) and eq. (20). As can be seen from above, it is convenient to plot the functions (3) and (4) from the experimental data, as this considerably reduces the calculation required.

In order to deduce an alkaline error equation, it is necessary to find the dependence of $(Q_i - Q_{oi})/RT$ on X_i. We will here start with the assumption earlier used for localized adsorption layers, *e.g.* by Fowler [20], that the energy of interaction can be expressed as the sum of contributions of pairs of nearest neighbours. If every adsorption point has n neighbours, and an ideal distribution is assumed, every site has a possibility X_i of being occupied by an ion i; the number of pairs will be $\frac{n}{2} \cdot X_i$. As it is assumed that the change in interaction energy, for the whole system given as $X_i \cdot d_i U_g$, is proportional to the change in number of pairs, we get:

$$X_i \cdot d_i U_g = k_2 \cdot \frac{n}{2} dX_i \quad (21)$$

Or, if we write $\frac{2}{n k_2} = k_3$,

$$\frac{dX_i}{X_i} = k_3 \cdot d_i U_g \tag{22}$$

and $$\ln X_i = k_3 \cdot d_i U_g + \text{constant} \tag{23}$$

As we defined ${}_iU_g \rightarrow {}_iU_{og}$ when $X_i \rightarrow 1$, the value of the constant is $-\,{}_iU_{og}$.

and $$\ln X_i = k_3({}_iU_g - {}_iU_{og}) \tag{23a}$$

Regarding the significance of Q_i and Q_{oi} and writing $k_3 \cdot RT = k_4$:

$$\ln X_i = k_4(Q_{oi} - Q_i)/RT \tag{24}$$

From the different experimental figures, plotted in accordance with eq. (3) and eq. (4), and by means of eq. (16), (18), (19) and (20) the functions

$$-\ln X_{H_3O^+} = f\left(\frac{Q_{H_3O^+} - Q_{oH_3O^+}}{RT}\right)$$

$$-\ln X_{Na^+} = f\left(\frac{Q_{oH_3O^+} - Q_{Na^+}}{RT}\right)$$

have been calculated for the different electrodes at different conditions. As can be seen from the diagrams, Figs. 14—17, the requirements of eq. (24) are fullfilled, *i.e.* the experimental results are in agreement with the theoretical equation:

From the distribution law we have:

$$X_i = \frac{a_i}{\Sigma_i C_{og}} \exp\ [(Q_i - EF)/RT]$$

and from this and eq. (24):

$$X_i^{(1 + k_4)/k_4} = \frac{a_i}{\Sigma_i C_{og}} \cdot \frac{\exp\ (Q_{oi}/RT)}{\exp\ (FE/RT)} \tag{25}$$

and $$X_{H_3O^+} = \left(\frac{a_{H_3O^+}}{\Sigma_i C_{og}} \cdot \frac{\exp\ (Q_{oH_3O^+}/RT)}{\exp\ (FE/RT)}\right)^{k_{4H_3O^+}/(1 + k_{4H_3O^+})} \tag{25a}$$

$$X_{Na^+} = \left(\frac{a_{Na^+}}{\Sigma_i C_{og}} \cdot \frac{\exp\ (Q_{oNa^+}/RT)}{\exp\ (FE/RT)}\right)^{k_{4Na^+}/(1 + k_{4Na^+})} \tag{25b}$$

Let $(1 + k_{4H_3O^+})/k_{4H_3O^+} = \vartheta$ and $(1 + k_{4Na^+})/k_{4Na^+} = \tau$; and we get from eq. (25a) and eq. (25b):

$$\frac{X^{\vartheta}_{H_3O^+}}{X^{\tau}_{Na^+}} = \varkappa \cdot \frac{a_{H_3O^+}}{a_{Na^+}} \tag{26}$$

In this treatment eq. [26) is therefore the adsorption isotherm of the glass electrode. As $\Sigma\ X_i = 1$, the general equation for a system containing two different univalent ions can be written:

$$\Sigma\ \left(\frac{\exp\ (Q_{oi}/RT)}{\Sigma_i C_{og}} \cdot \frac{a_i}{\exp\ (FE/RT)}\right)^{k_{4i}/(1 + k_{4i})} = 1 \tag{27}$$

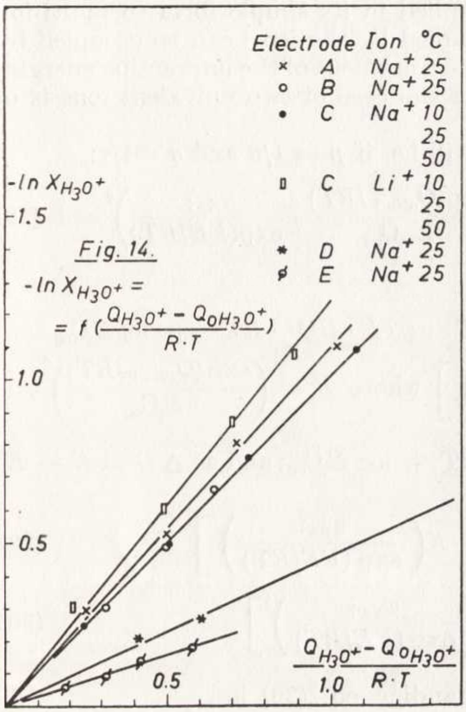


Fig. 14.
$-\ln X_{H_3O^+} = f\left(\frac{Q_{H_3O^+} - Q_{OH_3O^+}}{R \cdot T}\right)$
Electrode Ion °C
× A Na+ 25
○ B Na+ 25
● C Na+ 10, 25, 50
▯ C Li+ 10, 25, 50
✱ D Na+ 25
ø E Na+ 25
$-\ln X_{H_3O^+}$
1.5
1.0
0.5
0.5
1.0
$\frac{Q_{H_3O^+} - Q_{OH_3O^+}}{R \cdot T}$

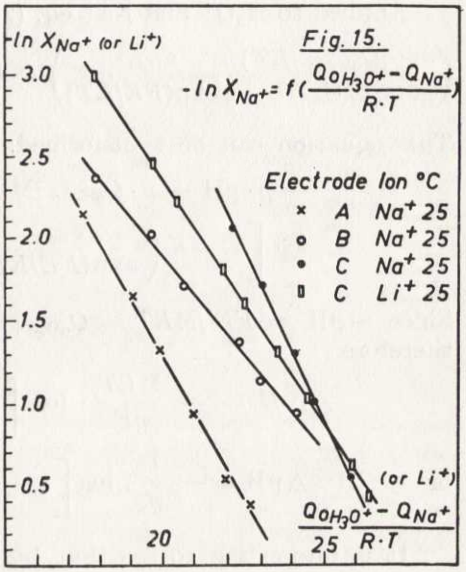


Fig. 15.
$-\ln X_{Na^+} = f\left(\frac{Q_{OH_3O^+} - Q_{Na^+}}{R \cdot T}\right)$
Electrode Ion °C
× A Na+ 25
○ B Na+ 25
● C Na+ 25
▯ C Li+ 25
$\ln X_{Na^+}$ (or Li^+)
3.0
2.5
2.0
1.5
1.0
0.5
20
25
(or Li^+)
$\frac{Q_{OH_3O^+} - Q_{Na^+}}{R \cdot T}$

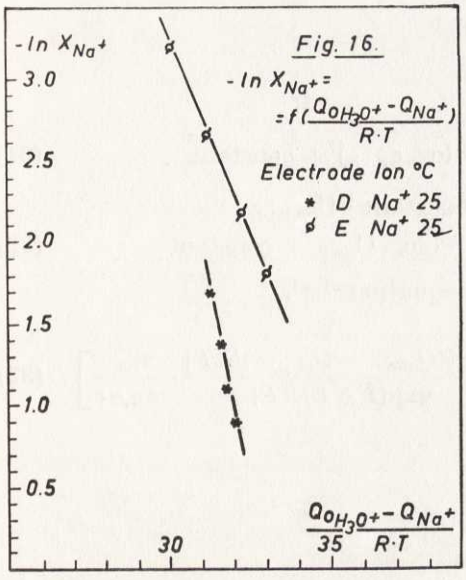


Fig. 16.
$-\ln X_{Na^+} = f\left(\frac{Q_{OH_3O^+} - Q_{Na^+}}{R \cdot T}\right)$
Electrode Ion °C
✱ D Na+ 25
ø E Na+ 25
$-\ln X_{Na^+}$
3.0
2.5
2.0
1.5
1.0
0.5
30
35
$\frac{Q_{OH_3O^+} - Q_{Na^+}}{R \cdot T}$

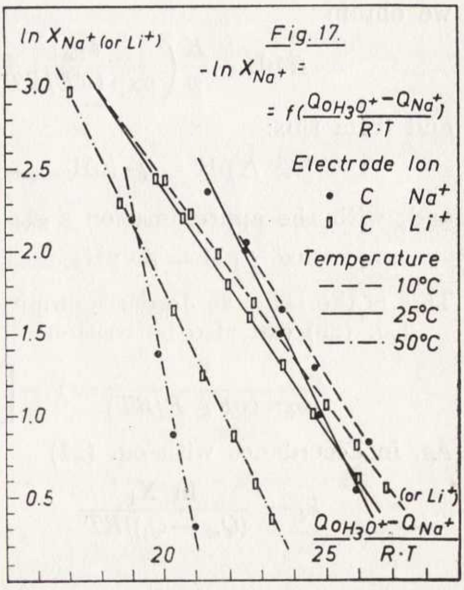


Fig. 17.
$-\ln X_{Na^+} = f\left(\frac{Q_{OH_3O^+} - Q_{Na^+}}{R \cdot T}\right)$
Electrode Ion
● C Na+
▯ C Li+
Temperature
– – – 10°C
—— 25°C
–·–·– 50°C
$\ln X_{Na^+}$ (or Li^+)
3.0
2.5
2.0
1.5
1.0
0.5
20
25
(or Li^+)
$\frac{Q_{OH_3O^+} - Q_{Na^+}}{R \cdot T}$

(This treatment probably cannot be applied in its simple form to multi-ion systems, as the adsorption sites not occupied by the ion i can be occupied by more than one kind of ion. This makes the treatment of the interaction energies more complicated. However, in practice the case of two univalent ions is of most interest.)

Applied to H_3O^+ and Na^+ eq. (27) will be, if $p = 1/\vartheta$ and $q = 1/\tau$:

$$\left(\frac{\exp(Q_{oH_3O+}/RT)}{\Sigma_i C_{og}} \cdot \frac{a_{H_3O+}}{\exp(FE/RT)}\right)^p + \left(\frac{\exp(Q_{oNa+}/RT)}{\Sigma_i C_{og}} \cdot \frac{a_{Na+}}{\exp(FE/RT)}\right)^q = 1 \quad (28)$$

This equation can be transformed:

$$-p \cdot \mathrm{pH} + p \cdot Q_{oH_3O+}/\mathrm{M} \cdot RT - p \cdot F \cdot E/M \cdot RT - p \cdot \log \Sigma_i C_{og} = \log\left[1 - K\left(\frac{a_{Na+}}{\exp(FE/RT)}\right)^q\right] \text{ where } K = \left(\frac{\exp(Q_{oNa+}/RT)}{\Sigma_i C_{og}}\right)^q.$$

Since $-\mathrm{pH} = FE'/\mathrm{M}RT - Q_{oH_3O+}/\mathrm{M}RT + \log \Sigma_i C_{og}$; and as $\triangle E = E - E'$ therefore

$$\triangle E = -\frac{\mathrm{M}RT}{pF} \cdot \log\left[1 - K\left(\frac{a_{Na+}}{\exp(FE/RT)}\right)^q\right] \quad (29)$$

or

$$\triangle \mathrm{pH} = -\frac{1}{p} \cdot \log\left[1 - K\left(\frac{a_{Na+}}{\exp(FE/RT)}\right)^q\right] \quad (30)$$

It is interesting to see that by expanding eq. (30) in

$$\log\,(1 - x) \sim -x \ldots\ldots..$$

we obtain

$$\triangle \mathrm{pH} \sim \frac{K}{p}\left(\frac{a_{Na+}}{\exp(FE/RT)}\right)^q$$

and from this:

$$\log\,\triangle \mathrm{pH} = q \cdot (\mathrm{pH}_{\mathrm{measured}} + \log\,a_{Na+}) + \text{constant} \quad (31)$$

and, with the approximation $a_{Na+} = \text{constant} \cdot C^{a}_{Na+}$:

$$\log\,\triangle\mathrm{pH} = a \cdot \mathrm{pH}_{\mathrm{measured}} + b \cdot \log\,C_{Na+} + \text{constant} \quad (32)$$

This is the same as Jordan's empirical equation [21, 22].

Eq. (29) can also be written:

$$\frac{1}{\exp(pF\triangle E/RT)} = 1 - \left[\frac{\exp[(Q_{oNa+} - Q_{oH_3O+})/RT]}{\exp(F\triangle E/RT)} \cdot \frac{a_{Na+}}{a_{H_3O+}}\right]^q \quad (33)$$

As, in accordance with eq. (24)

$$k_4 = \frac{\ln\,X_i}{(Q_{oi} - Q_i)/RT}$$

is $k_4 = \infty$ if not the interaction is considered. In such a case $p = q = 1$, and from eq. (33):

$$\log\ [\exp(F \triangle E/RT) - 1] = \mathrm{pH} + \log\ a_{\mathrm{Na}^+} \cdot \exp[(Q_{\mathrm{oNa}^+} - Q_{\mathrm{oH_3O}^+})/RT] \qquad (34)$$

This is the same as eq. (1) derived by Dole, neglecting interaction. (Eq. (1) contains C_{Na^+} as Dole starts from what has been defined as ${}_{\mathrm{i}}U_{\mathrm{s}}$ in this paper, instead of the constant value ${}_{\mathrm{i}}U_{\mathrm{os}}$.) As mentioned earlier, the lack of agreement is that the experimental alkaline error figures do not give the slope of unity, as the equation requires.

As, in accordance with the following

$$\exp\ [(Q_{\mathrm{oNa}^+} - Q_{\mathrm{oH_3O}^+})/RT] \cdot \frac{a_{\mathrm{Na}^+}}{a_{\mathrm{H_3O}^+}} = \beta$$

$$F \cdot \triangle E/RT = x$$

eq. (33) can be written:

$$\frac{1}{e^{px}} = 1 - \frac{\beta^q}{e^{qx}} \text{ or } e^{qx} - e^{(q-p)x} = \beta^q$$

and after expanding in series and approximating, we get:

$$e^{qx} - e^{(q-p)x} \sim p \cdot x$$

However, this is also the first member of the expression for $p(e^x - 1)$, and we get:

$$p(e^x - 1) \sim \beta^q$$

And from this

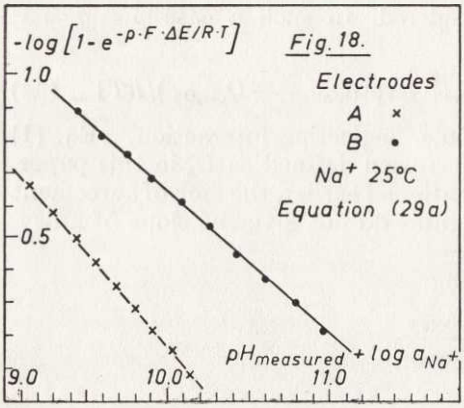
$$\frac{1}{q} \cdot \log[\exp(F \triangle E/RT) - 1] = \mathrm{pH} + \log\ a_{\mathrm{Na}^+} \cdot \exp[(Q_{\mathrm{oNa}^+} - Q_{\mathrm{oH_3O}^+})/RT] + \frac{1}{q} \cdot \log\ p \qquad (35)$$

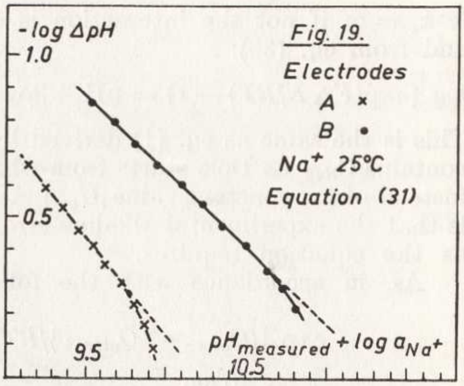
This equation is the same as eq. (1), except that it does not demand a slope of unity, and so can be brought into agreement with the experimental results.

Eq. (29) can also be written:

$$\frac{1}{q} \cdot \log[1 - \exp(-pF\triangle E/RT)] = \mathrm{pH} + \log\ a_{\mathrm{Na}^+} + \log\ K \qquad (29a)$$

From the results obtained for the electrodes A and B, a check on the validity of eq. (29a), (31) and (35) can be obtained from Figs. 18—20. (The values of p are calculated from Fig. 14.) As can be expected from the approximations introduced, the agreement is good for low and moderate alkaline errors, but deviations appear at higher values. Deviations of the same kind can also be found in Dole's investigations, *e.g.* Dole [12], p. 271, Fig. 16.8. In the case of eq. (29a), where no mathematical approximations are introduced, it can be found that the equation is valid also at high alkaline errors, so that it describes the experimental behaviour of the glass electrodes in alkaline solutions.

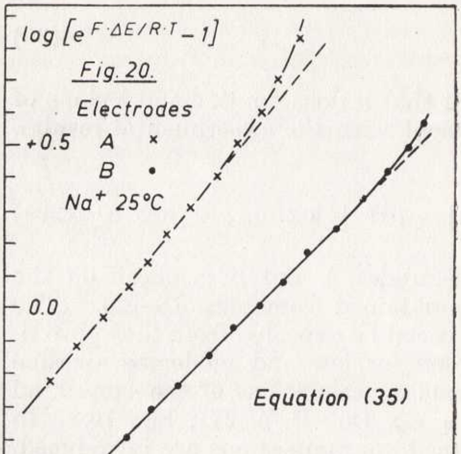


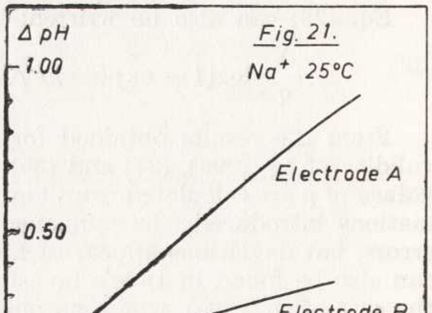


DISCUSSION

In the treatment given above, it has been shown that when the interaction in the surface layer is taken into account, an alkaline error equation can be derived, which is in good agreement with experimental results. The equation can also be approximated to the empirical equation suggested by Jordan, and to an equation of the Dole type, but with a slope in accordance with experimental data. It has also been shown that the interaction can be expressed as the sum of contributions of nearest neighbours. An adsorption isotherm for the glass electrode has been deduced, and the asymmetry potential given thermodynamic significance.

A more exact treatment of the significance of "contributions of nearest neighbours" would of cause be of great interest, but at present there is in-





sufficient theoretical and experimental background. The adsorption isotherm derived is probably of interest for ion exchange resins, where studies on different resins could give an indication of the interaction on a more general basis.

In the case of the glass electrode it would be of interest to determine the absolute amount of adsorbed ions, for example by means of radioactive isotopes. However, this approch is also difficult since it cannot be assumed that *e.g.* tritium is adsorbed to the same extent as protium, and furthermore the determination of tritium is very complicated. Other difficulties arise from the probable isotope equilibrium with water and the fact that the removal of excess solution from the glass will probably disturb the adsorption equilibrium.

However, some interesting figures can be obtained from the potential measurements. If in Figs. 15—17 an extrapolation is made to $-\ln X_{\mathrm{Na^+}} = 0$, *i.e.* $X_{\mathrm{Na^+}} = 1$, it is possible to determine:

$$(Q_{\mathrm{oH_3O^+}} - Q_{\mathrm{oNa^+}})/RT$$

This quantity is essentially the energy involved in the dissociation, so that a kind of dissociation constant, K_{o}, can be found from the formula:

$$(Q_{\mathrm{oH_3O^+}} - Q_{\mathrm{oNa^+}})/RT = -\ln\ K_{\mathrm{o}}$$

or

$$pK_{\mathrm{o}} = (Q_{\mathrm{oH_3O^+}} - Q_{\mathrm{oNa^+}})/\mathrm{M} \cdot RT \tag{36}$$

It may be expected that pK_{o} will be of the same order as the pH at which the alkaline error appears. pK_{o} can be considered as a characteristic of the glass electrode. Other characteristics are the interaction constants $k_{4\mathrm{H_3O^+}}$ and $k_{4\mathrm{Na^+}}$ in eq. (24) and these and pK_{o} will completely define the alkaline behaviour of the electrode. In Table 1 the values in question can be found for the electrodes studied. It would be of a great interest to determine these characteristics as functions of the electrode glass composition, and so facilitate the search for suitable glass electrode glasses.

A DIFFERENTIAL MEASURING METHOD

In the Swedish Patent 129833 a method is described for correcting the alkaline error in pH measurements when the activity of the sodium ion (or other) is unknown. The principle is that the measurements are made with two glass electrodes of different, but known, alkaline error functions. From the

Table 1. Characteristic constants of some glass electrodes.

Electrode and ion.	Temperature C°	pK_0	$k_{4\mathrm{H_3O^+}}$	$k_{4\mathrm{Na^+}}$
A Na+	25	10.4	1.08	0.36
B Na+	25	11.3	1.00	0.24
C Na+	10	11.6	1.00	0.32
C Na+	25	11.3	1.00	0.44
C Na+	50	10.1	1.00	2.00
C Li+	10	12.6	1.25	0.27
C Li+	25	12.2	1.25	0.32
C Li+	50	10.5	1.25	0.42
D Na+	25	14.3	0.41	1.00
E Na+	25	15.5	0.32	0.48

difference in measured pH for the two electrodes, $pH_1—pH_2$, the alkaline error for each can be found from a predetermined diagram. If curves similar to Fig. 2 are plotted from experimental data for the electrodes, each value of $M \cdot pH + \ln a_{Na^+}$ corresponds to the alkaline errors $\triangle pH_1$ and $\triangle pH_2$, and as $pH_1—pH_2 = \triangle pH_2 - \triangle pH_1$ the required functions

$$pH_1 - pH_2 = f(\triangle pH_1) = g(\triangle pH_2)$$

can be determined. Such functions for the electrodes A and B are shown in Fig. 21.

The method seems to be valuable as highly stable low alkaline error electrodes seems to be rare, and for high temperature measurements, where even low alkaline error electrodes show a considerable deviation from ideal behaviour, and also when such electrodes are used for pH determinations in a range of high alkalinity. The method is also of interest when measuring at low temperatures, where the electrical resistance of some of said electrodes is rather high.

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REFERENCES

1. Hughes, W. S. *J. Am. Chem. Soc.* **44** (1922) 2860.
2. Dole, M. *J. Am. Chem. Soc.* **53** (1931) 4260.
3. Dole, M. *J. Am. Chem. Soc.* **54** (1932) 3095.
4. Dole, M., Roberts, R. M. and Holley jr., C. E. *J. Am. Chem. Soc.* **63** (1941) 725.
5. Dole, M. and Wiener, B. S. *Trans. Electrochem. Soc.* **72** (1937) 107.
6. Gabbard, J. L. and Dole, M. *Trans. Electrochem. Soc.* **72** (1937) 129.
7. Dole, M. *J. Chem. Physics* **2** (1934) 862.
8. Nicolsky, B. P. *Acta Physicochim. U. R. S. S.* **7** (1936) 597.
9. Gross, P. and Halpern, O. *J. Chem. Physics* **2** (1934) 136.
10. Tendeloo, H. J. C. and Voorspuij, Z. A. J. *Rec. trav. chim.* **62** (1943) 784.
11. Tendeloo, H. J. C. and Voorspuij, Z. A. J. *Rec. trav. chim.* **62** (1943) 793.
12. Kratz, L. *Die Glaselektrode und ihre Anwendungen*, Steinkopff, Frankfurt/Main 1950, p. 244.
13. Dole, M. *The Glass Electrode*, John Wiley & Sons, Inc., New York 1941, p. 270.
14. Gurney, R. W. *Proc. Roy. Soc.* **A134** (1931) 137.
15. Gurney, R. W. *Proc. Roy. Soc.* **A136** (1932) 378.
16. Perley, G. A. *Trans. Electrochem. Soc.* **92** (1948) 497.
17. Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, 5th Ed., Berlin 1923—1936.
18. Conway, B. E. *Electrochemical Data*, Elsevier Publishing Company, London 1951.
19. Harned, H. S. and Nims, L. F. *J. Am. Chem. Soc.* **54** (1932) 423.
20. Fowler, R. and Guggenheim, E. A. *Statistical Thermodynamics*, 2nd Ed., The University Press, Cambridge 1949, p. 429.
21. Jordan, D. O. *Trans. Faraday Soc.* **34** (1938) 1305.
22. Jordan, D. O. and Powney, J. *J. Soc. Chem. Ind.* **56** (1937) 133T.

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difference in measured pH for the two electrodes, $\mathrm{pH}_1 - \mathrm{pH}_2$, the alkaline error for each can be found from a predetermined diagram. If curves similar to Fig. 2 are plotted from experimental data for the electrodes, each value of $M \cdot pM + \ln a_{\mathrm{Me}^+}$ corresponds to the alkaline errors $\Delta\,\mathrm{pH}_1$ and $\Delta\,\mathrm{pH}_2$, and as $\mathrm{pH}_1 - \mathrm{pH}_2 = \Delta\,\mathrm{pH}_2 - \Delta\,\mathrm{pH}_1$ the required functions

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REFERENCES

1. Hughes, W. S. *J. Am. Chem. Soc.* 44 (1922) 2860.
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5. Dole, M. and Wiener, B. Z. *Trans. Electrochem. Soc.* 72 (1937) 107.
6. Gabbard, J. L. and Dole, M. *Trans. Electrochem. Soc.* 72 (1937) 129.
7. Dole, M. *J. Chem. Physics* 2 (1934) 862.
8. Nicolsky, B. P. *Acta Physicochim. U. R. S. S.* 7 (1937) 597.
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11. Tendeloo, H. J. C. and Voorspuij, Z. A. J. *Rec. trav. chim.* 62 (1943) 793.
12. Kratz, L. *Die Glaselektrode und ihre Anwendungen.* Steinkopff, Frankfurt/Main 1950, p. 244.
13. Dole, M. *The Glass Electrode,* John Wiley & Sons, Inc., New York 1941, p. 250.
14. Gurney, R. W. *Proc. Roy. Soc.* A134 (1931) 137.
15. Gurney, R. W. *Proc. Roy. Soc.* A136 (1932) 378.
16. Perley, G. A. *Trans. Electrochem. Soc.* 92 (1945) 497.
17. Landolt-Börnstein, *Physikalisch-Chemische Tabellen,* 5th Ed., Berlin 1923—1936.
18. Conway, B. E. *Electrochemical Data,* Elsevier Publishing Company, London 1951.
19. Harned, H. S. and [illegible]
20. Fowler, R. and Guggenheim, E. A. *Statistical Thermodynamics,* 2nd Ed., The Cam[illegible]
21. [illegible]
22. [illegible]

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On the Polarography of Formaldehyde *

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In the paper a mathematical treatment is given for the polarographic behaviour of formaldehyde in neutral and alkaline solutions. This treatment is co-ordinated with earlier, simplified solutions, which are valid at high rates of methylene glycol dehydration. The derivations are extended to give a method for determination of the equilibrium and dehydration rate constants when the limiting current is controlled both by catalysis and by diffusion. The effect of the hydroxyl ions produced at the electrode surface has been considered for the case of unbuffered or slightly buffered solutions. The theoretical conclusions are verified experimentally. The spectrophotometric equilibrium constant of methylene glycol—formaldehyde is checked experimentally and found to be in agreement with earlier published results.

Despite the fact that the polarographic determination of formaldehyde is a well-established analytical process, only simplified mathematical treatments are given for the formaldehyde polarographic current. The purpose of the following paper is to give a more rigorous treatment, in order to make it possible to find equilibrium and dehydration rate constants for the system formaldehyde—methylene glycol from experimental data. The rate of dehydration is of a considerable interest in discussions on the mechanism of several formaldehyde reactions, *e. g.* in the methylol urea synthesis.

WATER SOLUTIONS OF FORMALDEHYDE

According to *e. g.* Auerbach and Barschall [1], in concentrated water solutions formaldehyde is present as trioxymethylene glycol, $HO \cdot (CH_2O)_3 \cdot OH$. When diluted, this compound depolymerises to methylene glycol, $HO \cdot CH_2 \cdot OH$. The rate of the depolymerisation,

$$HO \cdot (CH_2O)_3 \cdot OH + 2\ H_2O = 3\ HO \cdot CH_2\ OH \qquad (A)$$

has been studied by Wadano *et al.*[2], and it has been shown that it is dependent on pH, having a minimum at $pH \sim 3.5$.

In the electrolytic dissociation of methylene glycol the following reactions probably occur:

$$HO \cdot CH_2 \cdot OH = H_2C^+ \cdot OH \quad + OH^- \qquad (B)$$

$$HO \cdot CH_2 \cdot OH = H_2C^+ \cdot O^- \quad + H^+ + OH^- \qquad (C)$$

$$HO \cdot CH_2 \cdot OH = HO \cdot CH_2 \cdot O^- + H^+ \qquad (D)$$

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* This investigation forms a part of a thesis presented in the partial fullfillment for the degree of "tekn. lic.". Chalmers University of Technology, Gothenburg, September 1954.

Wadano [2] states that reaction (B) is of interest at $pH < 2.6$, (C) at $2.6 < pH < 4.6$ and (D) at $pH > 4.6$. The dissociation constant of reaction (D) has been determined by *e. g.* Euler and Lövgren [3] and Lévy [4]. A large temperature effect has been observed, at 0° C $pK = 14.0$, at 20° C $pK = 13.4$ and at 50° C $pK = 12.5$.

A spectrophotometric study of the equilibrium between methylene glycol and formaldehyde

$$HO \cdot CH_2 \cdot OH = HCHO + H_2O \tag{E}$$

has been made by Schou [5] in a 13 *M* solution and by Bieber [6] in a 0.86 *M* solution. Schou estimates the equilibrium constant to be $< 1/1250$, and by means of extrapolation from measurements in a temperature range close to 60° C Bieber gets a probable constant value at 20° C of the order 10^{-4}.

THE POLAROGRAPHIC BEHAVIOUR OF FORMALDEHYDE

The polarographic reduction of formaldehyde at low temperatures (25° C) gives a limiting current which is less than that deduced from the concentration polarisation, *i. e.* from the Ilkovič [7] equation:

$$\bar{i}_d = 607\, n\, C \sqrt{D}\, m^{2/3}\, t_1^{1/6} \tag{1}$$

where $\bar{i}_d$ = diffusion current in μA, n = number of Faradays of electricity required per mole of electrode reaction, C = concentration of the solution of the electroreducible substance in millimoles/l, D = diffusion constant of the same substance in cm^2/sec, m = weight of mercury flowing from the capillary in mg/sec and t_1 = drop time in seconds.

From comparisons between Mn^{2+} and formaldehyde at a high temperature (80° C), where the formaldehyde reduction also follows eq. (1), Jahoda [8] found the following electrode reaction:

$$HCHO + 2\ H_2O + 2\ e = CH_3OH + 2\ OH^- \tag{F}$$

i. e. $n = 2$. In the same paper Jahoda reports that the temperature coefficient of the limiting current at low temperatures is too large to be explained solely as a function of the change of the diffusion constant of formaldehyde. It was also assumed that the behaviour mentioned could be explained if the rate of the electrode reaction was controlled by the depolymerisation of formaldehyde polymers, *e. g.* in accordance with reaction (A). However, Jahoda's assumption is not in agreement with the findings of Auerbach and Barschall [1] and Wadano *et al.*[2] Later Winkel and Proske [9] introduced the idea that only the dehydrated formaldehyde was able to take part in the electrochemical reaction at the electrode surface, and that the equilibrium corresponding to reaction (E) controlls the limiting current. This approch has subsequently been applied by Veselý and Brdička [10] and Bieber and Trümpler [11]. Their work has demonstrated that no real concentration polarisation occurs at the electrode surface; the limiting current is determined by the rate of dehydration of methylene glycol when the formaldehyde concentration at the electrode surface decreases in consequence of the electrode reaction. According to Bieber and Trümpler [11], the limiting current is highly dependent on pH and temperature. In buffered solutions the relationship between limiting current and formaldehyde concentration was found to be linear; in unbuffered solutions this was not the case. Vesely and Brdička [10] found that reaction (E) is subject to acid — base catalysis as defined by Brönsted, *i. e.* the current is not only dependent on pH but also on the activities of the acids and bases present.

Briefly, we have the following picture of the electrode reaction: When the equilibrium between formaldehyde and methylene glycol is disturbed by the reduction at the electrode surface, the aldehyde deficiency is compensated by dehydration of the glycol. If the rate of dehydration is small in comparison with the diffusion of formaldehyde, the latter rate determines the limiting current. If the rate of dehydration is high, the current is still determined by a rate of diffusion, but in this case the diffusion is that of methylene glycol. However, if the rates of dehydration and diffusion are of the same order, both are of importance.

In a simplified mathematical treatment on the polarography of formaldehyde, Vesely and Brdička [10] applied a method introduced by Wiesner [12] for similar electrode processes. This treatment is based on the statistical "half mean path" which can be traversed by a molecule between dehydration and hydration. In accordance with this, the limiting current can be expressed as follows:

$$\bar{i}_{\mathrm{k}} = \frac{0.573\sqrt{t_1 k_2 k_{\mathrm{h}}}}{1 + 0.573\sqrt{t_1 k_2 k_{\mathrm{h}}}} \cdot \bar{i}_{\mathrm{d}}^* \tag{2}$$

where $\bar{i}_{\mathrm{k}}$ = limiting current, "catalytic current", t_1 = drop time, k_2 = the rate constant of the dehydration of the methylene glycol under the conditions occurring and k_{h} = the equilibrium constant of reaction (E). $\bar{i}_{\mathrm{d}}^*$ is the theoretical diffusion current, calculated from eq. (1), assuming that concentration polarisation of the analytical amount of formaldehyde is the current-determining step.

When considering the decrease in methylene glycol concentration at high pH due to a dissociation reaction in accordance with (D), the following equation was given:

$$\bar{i}_{\mathrm{k}} = \frac{\mathrm{b}\sqrt{a_{\mathrm{H_3O^+}}}}{a_{\mathrm{H_3O^+}} + K_{\mathrm{a}} + \mathrm{b}\sqrt{a_{\mathrm{H_3O^+}}} + \mathrm{b}\,K_{\mathrm{a}}/\sqrt{a_{\mathrm{H_3O^+}}}}\,\bar{i}_{\mathrm{d}}^* \tag{3}$$

where $b = 0.573\sqrt{t_1 k_2 k_{\mathrm{h}}}$, K_{a} = dissociation constant of reaction (D).

Vesely and Brdička used eq. (3) to calculate K_{a} from experimental data, and found a good agreement with earlier mentioned values.

However, the mathematical treatment reviewed above involves several approximations: a) The non-linearity of the concentration gradient and b) the change of this gradient due to the growth of the mercury drop are neglected. c) The assumption on "half the mean path" is not significant from the theoretical point of view.

In an investigation concerning the catalytic currents in the polarography of some organic acids, *e. g.* pyruvic acid, Koutecký and Brdička [13] have given a mathematical treatment not involving the approximations a) and c). If we apply this method of treatment to the polarography of formaldehyde we get:

$$\bar{i}_{\mathrm{k}} = \frac{0.81\sqrt{t_1 k_2 k_{\mathrm{h}}}}{1 + 0.81\sqrt{t_1 k_2 k_{\mathrm{h}}}}\,\bar{i}_{\mathrm{d}}^* \tag{4}$$

This is valid if the electrode is regarded as a steady sphere with the same area as the mean area of the dropping electrode. The very small correction for the curved surface of the electrode is, as usual, neglected in this case as well. When the theories are tested on experimental data, eq. (2) and (4) are identical, as the difference in the constants 0.57 and 0.81 only changes the numerical value of the parameter $k_2 \cdot k_h$.

During 1953 rigorous mathematical solutions, valid for several kinds of catalytic currents were given by Koutecký [14-17]. A mathematical technique was used that originated from Mejman [18]. However, in the case of formaldehyde only a simplified solution was given (Koutecký [17]), valid under the same conditions as needed for eq. (2) and (4), *i. e.* when the gradient layer is very close to the electrode surface. The equation derived is

$$\bar{i}_k = \frac{0.87 \sqrt{t_1 k_2 k_h}}{1 + 0.87 \sqrt{t_1 k_2 k_h}} \, \bar{i}_d{}^* \tag{5}$$

In the following a rigorous treatment will be given, avoiding the approximations a), b) and c). The mathematical technique is based on the Mejman-Koutecký method.

THEORETICAL

When considering the influence of the growth of an electrode drop on the concentration gradient in the solution surrounding the drop, we get, in accordance with Ilkovič [7], the following equation:

$$\left(\frac{\partial C_{HCHO}}{\partial t}\right)_{diffusion} = D \frac{\partial^2 C_{HCHO}}{\partial x^2} + \frac{2\,x}{3\,t} \frac{\partial C_{HCHO}}{\partial x} \tag{6a}$$

where x is the distance from the electrode surface.
Since

$$\left(\frac{\partial C_{HCHO}}{\partial t}\right)_{catalysis} = k_2 \, C_{HO \cdot CH_2 \cdot OH} - k_1 \, C_{HCHO} \tag{6b}$$

we obtain

$$\frac{\partial C_{HCHO}}{\partial t} = D \frac{\partial^2 C_{HCHO}}{\partial x^2} + \frac{2\,x}{3t} \frac{\partial C_{HCHO}}{\partial x} + k_2 \, C_{HO \cdot CH_2 \cdot OH} - k_1 \, C_{HCHO} \tag{7a}$$

and correspondingly:

$$\frac{\partial C_{HO \cdot CH_2 \cdot OH}}{\partial t} = D \frac{\partial^2 C_{HO \cdot CH_2 \cdot OH}}{\partial x^2} + \frac{2\,x}{3\,t} \frac{\partial C_{HO \cdot CH_2 \cdot OH}}{\partial x} - \tag{7b}$$

$$-k_2 \, C_{HO \cdot CH_2 \cdot OH} + k_1 \, C_{HCHO}$$

where k_2 is the dehydration and k_1 the hydration rate constant of reaction (E) and $D \sim D_{HCHO} \sim D_{HO \cdot CH_2 \cdot OH}$ (this will be discussed later).

Initial conditions: $t = 0$, $x > 0$: $C_{HO \cdot CH_2 \cdot OH} = C^*_{HO \cdot CH_2 \cdot OH}$, $C_{HCHO} = C^*_{HCHO}$.
Boundary conditions: $t > 0, x = 0$: $C_{HCHO} = 0$, $(\partial \, C_{HO \cdot CH_2 \cdot OH} / \partial \, s) = 0$. (No flux of $HO \cdot CH_2 \cdot OH$ at the electrode surface.)

Introducing:

$$\psi = C_{\mathrm{HO \cdot CH_2 \cdot OH}} + C \qquad , \varphi = C_{\mathrm{HO \cdot CH_2 \cdot OH}} - \sigma \cdot C_{\mathrm{HCHO}},\ k_2 = \varrho,\ k_1/k_2 = 1/k_{\mathrm{h}} = \sigma \tag{8}$$

and adding eq. (7a) and (7b), then multiplying eq. (7a) by σ and subtracting from eq. (7b) will give the respective equations:

$$\frac{\partial \psi}{\partial t} = D \frac{\partial^2 \psi}{\partial x^2} + \frac{2x}{3t} \frac{\partial \psi}{\partial x} \tag{9a}$$

$$\frac{\partial \varphi}{\partial t} = D \frac{\partial^2 \varphi}{\partial x^2} + \frac{2x}{3t} \frac{\partial \varphi}{\partial x} - \varrho\,(1+\sigma) \cdot \varphi \tag{9b}$$

Substituting: $l = \varrho \cdot (1+\sigma),\ s = x \Big/ \sqrt{\dfrac{12}{7} D t}$ and $\chi = l$ (10)

we have from eq. (9a) and (9b):

$$\frac{\partial^2 \psi}{\partial s^2} + 2s \frac{\partial \psi}{\partial s} - \frac{12}{7} \cdot \chi \frac{\partial \psi}{\partial \chi} = 0 \tag{11a}$$

$$\frac{\partial^2 \varphi}{\partial s^2} + 2s \frac{\partial \varphi}{\partial s} - \frac{12}{7} \chi \frac{\partial \varphi}{\partial \chi} = \frac{12}{7} \chi\, \varphi \tag{11b}$$

Initial conditions: $s \to \infty$, $\varphi = 0$, $\psi = \psi^* = C^*_{\mathrm{HO \cdot CH_2 \cdot OH}} + C^*_{\mathrm{HCHO}}$, *i. e.* the analytical formaldehyde concentration of the solution.

Boundary conditions: $s = 0$, $\varphi = \psi$, $(\partial \varphi / \partial s) = -\sigma\,(\partial \psi / \partial s)$;
Eq. (11b) can be transformed into an equation of the (11a) type by means of the substitution $\varphi = \Phi \cdot \exp(-\chi)$. It is assumed that the (11a) type has a solution in the form of a power series:

$$\psi = \sum_{\mathrm{i}} \psi_{\mathrm{i}}(s)\, \chi^{\mathrm{i}}, \text{ and } \varphi = \mathrm{e}^{-\chi} \sum_{\mathrm{i}} \Phi_{\mathrm{i}}(s)\, \chi^{\mathrm{i}} \tag{12}$$

where ψ_{i} (and Φ_{i}) is determined by the equation:

$$\frac{\mathrm{d}^2 \psi_{\mathrm{i}}}{\mathrm{d}s^2} + 2s \frac{\mathrm{d}\psi_{\mathrm{i}}}{\mathrm{d}s} - 2\,a_{\mathrm{i}} \cdot \psi_{\mathrm{i}} = 0 \tag{13}$$

If we assume that

$$K_{\alpha} = \sum_{\mathrm{j}=0}^{\infty} a^{\alpha}_{\mathrm{j}} \cdot s_{\mathrm{j}},\ L_{\alpha} = \sum_{\mathrm{j}=0}^{\infty} c^{\alpha}_{\mathrm{j}} \cdot s^{\mathrm{j}+1} \tag{14}$$

are linear, independent solutions of eq. (13), and $a^{\alpha}_{0} = c^{\alpha}_{0} = 1$.

$a^{\alpha}_{\mathrm{j}+2} / a^{\alpha}_{\mathrm{j}} = 2\,(\alpha - \mathrm{j}) / (\mathrm{j}+1)(\mathrm{j}+2)$, $c^{\alpha}_{\mathrm{j}+2} / c^{\alpha}_{\mathrm{j}} = 2\,(\alpha - \mathrm{j} - 1) / (\mathrm{j}+2)(\mathrm{j}+3)$, and from this: $\lim\limits_{s \to 0} K_{\alpha} = 1$, $\lim\limits_{s \to 0} L_{\alpha} = 0$, $\lim\limits_{s \to 0} K'_{\alpha} = 0$ and $\lim\limits_{s \to 0} L'_{\alpha} = 1$.

For this the following recurrence equation is obtained:

$$p_{\alpha}\, p_{\alpha+1} = 2\,(\alpha + 1);\ p_{\alpha} = \lim_{s \to \infty} K_{\alpha}(s) \,/\, L_{\alpha}(s) \tag{15}$$

(p_{α} can also be expressed as a Γ-function, *e. g.* for $\alpha = 6/7$ we have

$$p_{6\,\mathrm{i}/7} = 2\,\Gamma(6\,\mathrm{i}/14 + 1) \,/\, \Gamma(6\,\mathrm{i}/14 + 1/2)).$$

From this, and with regard to the initial conditions, we get the solutions of eqs. (11a) and (11b):

$$\psi = \sum_{\mathrm{i}=0}^{\infty} a_{\mathrm{i}}\,(K_{\alpha\mathrm{i}} - p_{\alpha\mathrm{i}} \cdot L_{\alpha\mathrm{i}}) \cdot \chi^{\mathrm{i}} + \psi^* p_0\, L_0 \tag{16a}$$

$$\varphi = \mathrm{e}^{-\chi} \sum_{\mathrm{i}=0}^{\infty} b_{\mathrm{i}}\,(K_{\alpha\mathrm{i}} - p_{\alpha\mathrm{i}} \cdot L_{\alpha\mathrm{i}}) \cdot \chi^{\mathrm{i}} \tag{16b}$$

(The initial conditions are fullfilled since $\lim\limits_{s \to \infty} (K_{\alpha i} - p_{\alpha i} \cdot L_{\alpha i}) = 0$ and $\lim\limits_{s \to \infty} p_0 \cdot L_0 = 1$, as found when solving eq. (13) for L_0.)

Remembering that $L_{\alpha i}(0) = 0$ and $K_{\alpha i}(0) = 1$, we get from the boundary conditions:

$$\varphi_{s=0} = e^{-\chi} \sum_{i=0}^{\infty} b_i \cdot \chi^i, \quad \psi_{s=0} = \sum_{i=0}^{\infty} a_i \cdot \chi^i \tag{17}$$

i. e. $\varphi = \psi$ when $s = 0$ gives:

$$\sum_{i=0}^{\infty} b_i \cdot \chi^i = e^{\chi} \sum_{i=0}^{\infty} a_i \cdot \chi^i = \sum_{i=0}^{\infty} \sum_{j=0}^{i} \frac{a_j}{(i-j)!} \chi^i \tag{18}$$

The boundary condition $(\partial \varphi / \partial s) = - \sigma (\partial \psi / \partial s)$ when $s = 0$, and

$$\begin{aligned} \frac{\partial \psi}{\partial s} &= \sum_{i=0}^{\infty} a_i (K'_{\alpha i} - p_{\alpha i} L'_{\alpha i}) \chi^i + \psi^* p_0 L_0' \\ \frac{\partial \varphi}{\partial s} &= e^{-\chi} \sum_{i=0}^{\infty} b_i (K'_{\alpha i} - p_{\alpha i} L'_{\alpha i}) \chi^i \end{aligned} \tag{19}$$

since $K'_{\alpha i}(0) = 0$ and $L'_{\alpha i}(0) = 1$:

$$\begin{aligned} \left(\frac{\partial \psi}{\partial s}\right)_{s=0} &= - \sum_{i=0}^{\infty} a_i p_{\alpha i} \chi^i + \psi^* p_0 \\ \left(\frac{\partial \varphi}{\partial s}\right)_{s=0} &= - e^{-\chi} \sum_{i=0}^{\infty} b_i p_{\alpha i} \chi^i \end{aligned} \tag{20}$$

Then we have:

$$\frac{1}{\sigma} \sum_{i=0}^{\infty} b_i p_{\alpha i} \chi^i = \psi^* p_0 \sum_{i=0}^{\infty} \frac{\chi^i}{i!} - \sum_{i=0}^{\infty} \sum_{j=0}^{i} \frac{a_j p_{\alpha j}}{(i-j)!} \chi^i$$

and for the i:th term:

$$\frac{1}{\sigma} b_i p_{\alpha i} = \psi^* \frac{p_0}{i!} - \sum_{j=0}^{i-1} \frac{a_j p_{\alpha j}}{(i-j)!} - a_i p_{\alpha i} \tag{21}$$

Similarly we have:

$$b_i = \sum_{j=0}^{i-1} \frac{a_j}{(i-j)!} + a_i \tag{22}$$

From eqs. (21) and (22) we have:

$$a_i p_{\alpha i} = \frac{\psi^* p_0 \sigma}{(1 + \sigma) i!} - \sum_{j=0}^{i-1} \frac{a_j p_{\alpha j}}{(i-j)!} \left(1 + \frac{p_{\alpha i} / p_{\alpha j} - 1}{1 + \sigma}\right) \tag{23}$$

Or, when $\sigma \gg 1$:

$$a_i p_{\alpha i} = \frac{\psi^* p_0}{i!} - \sum_{j=0}^{i-1} \frac{a_j p_{\alpha j}}{(i-j)!} \left(1 + \frac{p_{\alpha i} / p_{\alpha j} - 1}{\sigma}\right) \tag{24}$$

The equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + \frac{2x}{3t}\frac{\partial c}{\partial x}$$

and the initial and boundary conditions $x > 0,\ t = 0{:}\ C = C^*,\ x = 0,\ t > 0{:}\ C = 0$ correspond to the conditions of concentration polarisation. As has been shown by Koutecký *et al.*[19] we obtain from this:

$$i_d = -\,C^*\, p_0\, n\, F\, q\, D \left(\frac{\partial s}{\partial x}\right)_{x=0}$$

(q = the average area of the mercury drop.) Since in accordance with Ilkovič[7]

$$i_k = -\,n\, F\, q\, D \left(\frac{\partial C_{HCHO}}{\partial x}\right)_{x=0} \quad \text{we have:}$$

$$i_k \,/\, i_d = \Omega = (\partial C_{HCHO} \,/\, \partial s)_{s=0} \,/\, p_0 \cdot C^* \tag{25}$$

In accordance with earlier parts of the paper:

$$\psi = C_{HO\cdot CH_2\cdot OH} + C_{HCHO},\ (\partial C_{HO\cdot CH_2\cdot OH} \,/\, \partial s)_{s=0} = 0$$

and we have: $$\Omega = (\partial \psi \,/\, \partial s)_{s=0} \,/\, p_0 \cdot C^*_{HCHO} \tag{26}$$

Since $\psi^* = C^*_{HO\cdot CH_2\cdot OH} + C^*_{HCHO}$ and $C^*_{HO\cdot CH_2\cdot OH} = \sigma \cdot C^*_{HCHO}$

(chemical equilibrium) we obtain:

$$\Omega = 1 + \sigma - \sum_{i=0}^{\infty} \frac{a_i\, p_{ai}}{p_0\, C^*_{HCHO}}\, \chi^i \tag{27}$$

Or, on introducing the symbol

$$\varepsilon_i = a_i\, p_{ai} \,/\, p_0\, C^*_{HCHO} \tag{28}$$

$$\Omega = 1 + \sigma - \sum_{i=0}^{\infty} \varepsilon_i\, \chi^i \tag{29}$$

From this, by means of eq. (23):

$$\varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!}\left(1 + \frac{p_{ai} / p_{aj} - 1}{1 + \sigma}\right) \tag{30}$$

Or, when $\sigma \gg 1$:

$$\varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!}\left(1 + \frac{p_{ai} / p_{aj} - 1}{\sigma}\right) \tag{31}$$

(Since $\Omega = 1$ when $\chi = 0$ we find $\varepsilon_0 = \sigma$.)

However, if we start from the φ-function, we obtain:

$$\Omega = -\,(\partial \varphi \,/\, \partial s)_{s=0} \,/\, \sigma\, p_0\, C^*_{HCHO} \tag{32}$$

and if we write $\nu_i = b_i\, p_{ai} \,/\, p_0\, C^*_{HCHO}$ we obtain for $\sigma \gg 1$:

$$\nu_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!}\,(1 - p_{ai} \,/\, p_{aj}) \qquad 33)$$

where ε_j is defined in accordance with eq. (31),

i. e.
$$\Omega = \frac{1}{\sigma}\, e^{-\chi} \sum_{i=0}^{\infty} \nu_i \chi^i \tag{34}$$

For small values of ϱ and large values of σ a solution can be obtained as follows: If these conditions are valid, $C_{HO \cdot CH_2 \cdot OH}$ can be regarded as being constant, *i. e.* $C^*_{HO \cdot CH_2 \cdot OH}$, and we get:

$$\frac{\partial C_{HCHO}}{\partial t} = D\,\frac{\partial^2 C_{HCHO}}{\partial x^2} + \frac{2\,x}{3\,t}\,\frac{\partial C_{HCHO}}{\partial x} + \varrho\,\sigma\left(\frac{C^*_{HO \cdot CH_2 \cdot OH}}{\sigma} - C_{HCHO}\right) \tag{35}$$

Initial and boundary conditions: $t = 0, x > 0$: $C_{HCHO} = C^*_{HCHO}$; $t > 0, x = 0$: $C_{HCHO} = 0$.

Introducing $C^*_{HO \cdot CH_2 \cdot OH} / \sigma - C_{HCHO} = \tau$, $\varrho\,\sigma = l$, $(l = \varrho\,(1 + \sigma) \sim \varrho\,\sigma,\ \sigma \gg 1.)$
and $s = x \Big/ \sqrt{\frac{12}{7} D\,t}$, $\chi = l\ t$:

$$\frac{\partial^2 \tau}{\partial s^2} + 2\,s\,\frac{\partial \tau}{\partial s} - \frac{12}{7}\,\chi\,\frac{\partial \tau}{\partial \chi} = \frac{12}{7}\,\chi\,\tau \tag{36}$$

Initial and boundary conditions: $\chi = 0,\ s \to \infty : \tau = 0$; $\chi > 0,\ s = 0,\ \tau = \tau^* = C^*_{HO \cdot CH_2 \cdot OH} / \sigma$.

In accordance with earlier parts of the paper:

$$\tau = e^{-\chi} \sum_{i=0}^{\infty} a_i\, (K_{\alpha i} - p_{\alpha i}\, L_{\alpha i})\, \chi^i \tag{37}$$

Here a_i has to be chosen so that the following boundary condition is satisfied:

$$\tau_{s=0} = e^{-\chi} \sum_{i=0}^{\infty} a_i\, \chi^i = \tau^*$$

Since $K_{\alpha i}(0) = 1$, $L_{\alpha i}(0) = 0$:

$$a_i\, \chi^i = e^{\chi}\, \tau^* = \tau^* \sum_{i=0}^{\infty} \frac{\chi^i}{i!}$$

and

$$a_i = \tau^*\, \frac{1}{i!} \tag{38}$$

$K'_{\alpha i}(0) = 0$ and $L'_{\alpha i}(0) = 1$ gives:

$$\left(\frac{\partial \tau}{\partial s}\right)_{s=0} = -\ \tau^*\, e^{-\chi} \sum_{i=0}^{\infty} p_{\alpha i}\, \frac{\chi^i}{i!}$$

and

$$\Omega = e^{-\chi} \sum_{i=0}^{\infty} \frac{p_{\alpha i}}{p_0}\, \frac{\chi^i}{i!} \tag{39}$$

Recapitulating, the results of the three different treatments given above are:

I. $\Omega = 1 + \sigma - \sum\limits_{i=0}^{\infty} \varepsilon_i \chi^i$

$$\text{a)}\ \varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!}\left(1 + \frac{p_{\alpha i}/p_{\alpha j} - 1}{1+\sigma}\right);\ \text{general solution.}$$

$$\text{b)}\ \varepsilon_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!}\left(1 + \frac{p_{\alpha i}/p_{\alpha j} - 1}{\sigma}\right);\ \sigma \gg 1.$$

II. $\Omega = \frac{1}{\sigma} e^{-\chi} \sum\limits_{i=0}^{\infty} \nu_i \chi^i$

$$\nu_i = \frac{\sigma}{i!} - \sum_{j=0}^{i-1} \frac{\varepsilon_j}{(i-j)!}(1 - p_{\alpha i}/p_{\alpha j});\ \sigma \gg 1$$

III. $\Omega = e^{-\chi} \sum\limits_{i=0}^{\infty} \frac{p_{\alpha i}}{p_0} \frac{\chi^i}{i!}$; ϱ comparatively small, $\sigma \gg 1$.

For numerical calculations we need $p_{\alpha i}$ and $p_{\alpha i}/p_{\alpha j}$. If we compare eqs. (11a) and (13) we find $\alpha = 6/7$. By means of the earlier mentioned Γ-function and eq. (15) such calculations can be made. For ε_i, $\sigma \gg 1$, we obtain the following results: $\varepsilon_0 = \sigma$, $\varepsilon_1 = -0.500$, $\varepsilon_2 = 0.0585$, $\varepsilon_3 = -0.0112$, $\varepsilon_4 = 0.00320$, $\varepsilon_5 = -0.00101$, $\varepsilon_6 = 0.000226$ and $\varepsilon_7 = -0.0000491$. Since $\varepsilon_0 = \sigma$ and $\varepsilon_{i \neq 0} \ll \sigma$ we find that $\nu_i \sim \sigma\, p_{\alpha i}/p_0\, i!$; we here have the same factor as in solution III.

$p_{\alpha i}/p_0\, i!$ has, for other purposes, been calculated by Koutecký[16]. In that paper Koutecký has treated electrode reactions of the type $A \overset{el}{\rightleftharpoons} B$, *i. e.* the reduced compound B is reoxidized to A by an oxidizing agent, which is present in such an excess in the solution that its concentration can be regarded as constant even at the electrode surface. The solution obtained is the same as III, and it can easily be found that this problem and the reduction of formaldehyde under the conditions of III can be regarded as identical processes, even though Koutecký's mathematical treatment was somewhat different. When assuming $\sigma \gg 1$ ($\sigma \sim 10^4$, as will be discussed later), calculations on Ω as a function of χ from I—III give the same results for the χ-values in the range of practical interest; however, the slow convergence of the series makes them less suitable at high χ-values. Calculations under this condition will be discussed later.

Since the function i_k/i_d relates to the change in current during the life of the mercury drop, and in polarography the average current is measured, we have to find

$$\overline{\Omega} = \overline{i_k} / \overline{i_d}$$

where $\overline{i_k}$ and $\overline{i_d}$ are the average currents. The average current is defined by the equation

$$\overline{i} = \frac{1}{t_1} \int_0^{t_1} i \ \mathrm{d}t$$

where t_1 is the drop time. (Ilkovič [7]). It is also found from Ilkovič that i_d = constant. $t^{1/6}$, and then we have:

$$\overline{\Omega} = \frac{\overline{i}_\mathrm{k}}{\overline{i}_\mathrm{d}} = \frac{\int\limits_0^{t_1} \frac{i_\mathrm{k}}{i_\mathrm{d}}\, t^{1/6}\,\mathrm{d}t}{\int\limits_0^{t_1} t^{1/6}\,\mathrm{d}t} \tag{40}$$

and

$$\overline{\Omega} = \frac{\overline{i}_\mathrm{k}}{\overline{i}_\mathrm{d}} = \frac{7}{6}\,\chi_1^{-\frac{7}{6}} \int\limits_0^{\chi_1} \Omega\, \chi^{1/6}\,\mathrm{d}\chi \tag{41}$$

$(\chi_1 = l \cdot t_1)$

The $\overline{\Omega}$ value related to III and the Ω function too, can be found in Koutecký [16], where they were calculated for the electrode reaction mentioned previously. In the same paper it was also shown that when $\chi_1 > 10$ the following empirical equation approximates a solution of the $\overline{\Omega}$ function:

$$\overline{\Omega} = 0.812\,\chi_1^{1/2} + 1.92\,\chi_1^{-7/6} \tag{42}$$

Then, when $\chi_1 \gg 1$, we get the asymptotic solution:

$$\overline{\Omega} = 0.81\sqrt{\chi_1} \tag{43}$$

For moderate and large χ_1, three different equations have earlier been derived — (2), (4) and (5) — suitable for calculations. Eq. (5) is an approximation of the expression:

$$\overline{i}_\mathrm{k} / \overline{i}_{\mathrm{d\,HO\cdot CH_2\cdot OH}} = \sum_{\mathrm{i}=0}^{\infty} \omega_\mathrm{i}\,\eta^\mathrm{i},\ \omega_\mathrm{i} = \delta_\mathrm{i} / (1 - 3\ i/7),$$

$$\eta = \sigma \Big/ \sqrt{\frac{12}{7}\, l\, t_1},\ \delta_0 = 1 \text{ and } \delta_{\mathrm{i}+1} / \delta_\mathrm{i} = -p_{-3\,(\mathrm{i}+1)/7}.$$

or, for moderate values of $l\ t_1$:

$$\overline{i}_\mathrm{k} / \overline{i}_{\mathrm{d\,HO\cdot CH_2\cdot OH}} = \sum_{\mathrm{i}=1}^{\infty} \beta_\mathrm{i}\,\eta^{-\mathrm{i}},\ \beta_\mathrm{i} = \sqrt{\pi}\,\gamma_\mathrm{i} / 2\,(1 + 3\,i/7),$$

$$\gamma_1 = 1 \text{ and } \gamma_{\mathrm{i}+1} / \gamma_\mathrm{i} = -p_{3\,\mathrm{i}/7}\ (\varrho\,\sigma \gg 1, \sigma \gg 1.\ \text{Koutecký}^{17})$$

From this we obtain $\beta_1 = 0.62$ and since $\eta^{-1} = \sqrt{\frac{12}{7}\, t_1\, k_2\, k_\mathrm{h} \cdot \frac{1}{\sigma}}$:

$$\overline{i}_\mathrm{k} / \overline{i}_{\mathrm{d\,HO\cdot CH_2\cdot OH}} = 0.81\sqrt{t_1\, k_2\, k_\mathrm{h}} \tag{44}$$

for moderate values of $k_2\ k_\mathrm{h}$. The same result can be obtained from eq. (4) under the same conditions. Since $\chi_1 = k_2\, t_1 / k_\mathrm{h}$ and $k_\mathrm{h}\, \overline{i}_{\mathrm{d\,HO\cdot CH_2\cdot OH}} = \overline{i}_{\mathrm{d\,HCHO}}$ when $\sigma \gg 1$, eq. (43) can be written as eq. (44).

When dealing with formaldehyde we have, as will be shown later in this paper, $\sigma \gg 1$. That is, the functions deduced above, which are valid for small and moderate values of χ_1, coincide asymptotically at $0.81 \sqrt{t_1 k_2 k_h}$ with the solutions for large values. From this we find that the two functions cover a large range of dehydration rates. For small and moderate values of $t_1 k_2 k_h$ eq. (44) is found to be a better approximation than the function $0.87 \sqrt{t_1 k_2 k_h}$, which is obtained from eq. (5), and when considering the whole range of validity, eq. (4) is probably better than eq. (5), as regards the accuracy. However, it has to be remembered that these equations involve the approximation $D_{HCHO} \sim D_{HO \cdot CH_2 \cdot OH}$; this is not the case with the functions for small values of χ_1. (The diffusion of $HO \cdot CH_2 \cdot OH$ is negligible, as may be seen from comparisons between eqs. (6a), (6b) and (35) and the solutions corresponding to these equations.) Since the gradient layer at the electrode surface is thin (which can be found from the experimental results given later), the error introduced when neglecting the curvature of the electrode surface seems to be infinitesimal.

As was shown by *e. g.* Veselý and Brdička [10], a pure catalytic current is independent of the height of the mercury column between the level of the mercury in the reservoir and the tip of the capillary. A diffusion current, however, is proportional to the square root ot this height. This is the case since:

$$\bar{i}_d = \text{constant} \cdot m^{2/3}\, t_1^{1/6} \quad \text{and} \quad \bar{i}_k = \text{constant} \cdot m^{2/3}\, t_1^{2/3}$$

which easily can be derived from eq. (1) and (44).

An analysis of the dependence of the current upon the drop time can be used in order to investigate the electrode reaction; and in the case of formaldehyde we have:

A. $\bar{i} \cong \bar{i}_{d\,HCHO}$ $\bar{i}$ dependent of the drop time.

B. $\bar{i}_{d\,HCHO} \ll \bar{i} \ll \bar{i}_{d\,HO \cdot CH_2 \cdot OH}$ $\bar{i}$ independent of the drop time.

C. $\bar{i} \cong \bar{i}_{d\,HO \cdot CH_2 \cdot OH}$ $\bar{i}$ dependent of the drop time.

In the case A the limiting current is a function of ϱ, σ and t_1 as predicted by eqs. (39) and (41). Since

$$\lim_{\chi_1 \to 0} \bar{i}_k / \bar{i}_{d\,HCHO} = 1 \tag{45}$$

it is possible to determine σ from the effect of t_1 on the limiting current. For this purpose we can from experimental data plot the function:

$$\bar{i} / m^{2/3}\, t_1^{1/6} = f(t_1) \tag{46}$$

On extrapolating to $t_1 = 0$, *i. e.* $\chi_1 = 0$, we get, by means of eq. (1), $C_{o\,HCHO}$, and when the analytical concentration of formaldehyde is known, σ can be calculated. A better accuracy than that of the extrapolation can be obtained by the following method:

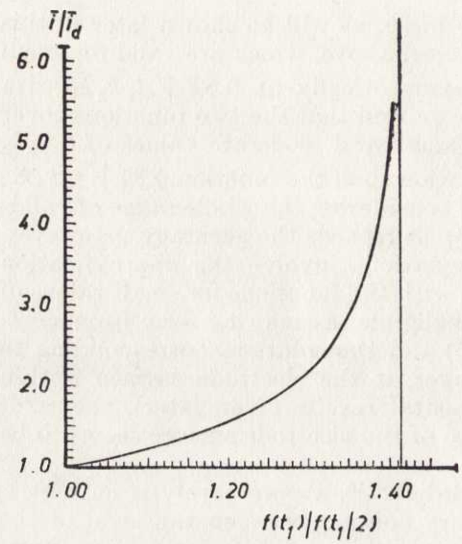

Fig. 1. $\bar{i}/\bar{i}_d$ *as a function of* $f(t_1)/f(t_1/2)$.

We have:

$$\mathrm{f}(t_1)/\mathrm{f}(t_1/2) = (\bar{i}_k/\bar{i}_d)_{t_1}/(\bar{i}_k/\bar{i}_d)_{t_1/2} = \bar{\Omega}(\chi_1)/\bar{\Omega}(\chi_1/2) = \mathrm{g}(\chi_1)$$

$\mathrm{g}(\chi_1)$ as being a function of χ_1 can be calculated from eqs. (39) and (41). Then $\bar{\Omega}(\chi_1) = (\bar{i}_k/\bar{i}_{d\,\mathrm{HCHO}})_{t_1}$ is obtained from the equations mentioned above, *i. e.* a function $\bar{i}_k/\bar{i}_{d\,\mathrm{HCHO}} = \mathrm{h}(\mathrm{f}(t_1)/\mathrm{f}(t_1/2))$ can be deduced. This function is given in Fig. 1.

And from this $\bar{i}_{d\,\mathrm{HCHO}}$, *i. e.* both ϱ and σ can be found. In case B the limiting current follows eq. (43), in the case C eq. (4) or at very high pH values eq. (3)*. *I. e.* $\sigma = 1/k_h$ and $\varrho = k_2$ can be calculated for the whole range A—C. From this discussion we find that both the equilibrium constant and the dehydration rate constants for the system methylene glycol-formaldehyde can be studied by means of polarography.

In accordance with reaction (F) hydroxyl ions are produced at the electrode surface during the polarographic reduction of formaldehyde. Since reaction (E) is acid-base catalysed, we can assume that in an unbuffered or slightly buffered solution no linear limiting current-formaldehyde concentration curve can be found. That this is the case in unbuffered solutions was shown by Bieber and Trümpler [11]. Since the hydroxyl ions change the composition and the catalytic properties of the solution surrounding the electrode drop, the change of cource depends on the degree of buffering, *i. e.* the more buffered the solution, the more linear the current-concentration curve. The mathematical analysis of a case involving a moderate degree of buffering seems to be very difficult; for unbuffered solutions a simple, approximate treatment can be given: From eqs. (1) and (43) we have:

$$\bar{i}/C_{\mathrm{HO\cdot CH_2\cdot OH}}\ m^{2/3}t_1^{1/6} = \mathrm{constant}\cdot\sqrt{t_1 k_2 k_h} \qquad (47)$$

---

* as found from the previous treatment $b = 0.81\sqrt{t_1 k_2 k_h}$ is to be preferred.

The dehydration rate constant represents the sum of the products of the activity of the catalyst and the catalysing power constant:

$$k_2 = \sum_{i} k_i\, a_i \tag{48}$$

(Veselý and Brdička [10]). For unbuffered solutions we obtain a simplified solution to the problem if we only consider the OH^- concentration. And in such a case:

$$(\bar{i} \,/\, C_{HO \cdot CH_2 \cdot OH}\, m^{2/3}\, t_1^{1/6})^2 = \text{constant} \cdot t_1\, C_{o\,OH^-} \tag{49}$$

If the reaction layer is supposed to be very thin, $C_{o\,OH^-}$, the average concentration of hydroxyl ions in this layer, can be found from eq. (1), and

$$\bar{i} = \text{constant} \cdot (1 \,/\, m^{2/3}\, t_1^{7/6})\ (\bar{i} \,/\, C_{HO \cdot CH_2 \cdot OH})^2$$

or, when the capillary characteristics are constant:

$$\bar{i} = \text{constant} \cdot (\bar{i} \,/\, C_{HO \cdot CH_2 \cdot OH})^2 \tag{50}$$

This simplified solution is applicable in the range of validity of eq. (43) to solutions which are unbuffered or have a very low degree of buffering. (In the latter case, however, a slight contribution from the buffer substance catalysis can be expected.) As has been shown by Bieber and Trümpler [11] the half wave potential of formaldehyde increases with increasing pH. In the case mentioned above more or less skew polarograms can be expected, since the increase in current means an increase in pH.

EXPERIMENTAL

The investigations have been carried out in the following apparatus: In a large beaker, containing 0.1 M KCl, a "polarographic cell" is immersed. The solution to be investigated is brought into this cell in such a quantity that the level is above that of the KCl solution. This is done in order to prevent any back flow into the cell through the glass filter disc which separates the cell solution from that of the beaker. The capillary enters the cell by means of a cork stopper, and nitrogen can be bubbled through the solution in the cell, in order to remove dissolved oxygen. The gases can escape through a water trap; the use of this device prevents air from entering the cell. The flow of mercury at the electrode is determined by means of a funnel-fitted capillary, which enters the cell through the stopper. The funnel can be turned into the line of the dropping mercury, and after the required time has elapsed, the funnel is swung clear of the drops. The mercury in the funnel is then sucked up into a flask connected to the capillary outside the cell. The flask is then removed and the mercury washed with distilled water, after which it is dried and weighed. The mercury of the electrode is delivered from a reservoir, connected to the capillary by means of a thick—walled rubber tubing, which has been boiled in NaOH and rigorously rinsed and dried. The reference electrode is a saturated calomel electrode, immersed in the KCl solution. The electrode device is thermostated by means of an infrared lamp outside the beaker, and a contact thermometer and a relay give an on-off regulation of the lamp. The beaker solution is kept in motion by a stirrer. One of the advantages of this thermostating device is that the flow of heat is cut off practically at the same time as the current. By adjusting the distance between the lamp and the beaker the on-off periods can be given a suitable length. The temperature can easily be controlled within 0.03° C. Since the purity of the mercury used is of greatest importance, the mercury was distilled in a vacuum apparatus.

All chemicals in the investigation were of A. R. quality, except the formaldehyde, which was a Merck product of high purity, only containing traces of methanol and formic acid. ($<10^{-4}$ M in a solution containing $\sim$380 g/l formaldehyde).

Table 1. Results of the polarographic measurements on formaldehyde.

Supporting electrolyte	$C_{(HCHO)a}$ mmole/l	u cm	$\bar{i}$ μ A	t sec	m mg/sec	$\frac{\bar{i}}{m^{2/3}\, t^{1/6}\, C}$	$\frac{\bar{i}}{m^{2/3}\, t^{2/3}\, C}$
0.0025 M KH_2PO_4 + 0.0025 M Na_2HPO_4 pH 6.86, 20° C	12.7	11.1					
		11.1					
		11.1					
		11.1	0.333	2.07	4.55	0.00846	0.00587
		11.0					
		10.9					
		11.0					
		11.0	0.330	3.00	3.05	0.0103	0.00594
		10.8					
		10.9					
		10.9					
		10.9	0.327	4.01	2.34	0.0116	0.00582
		10.8					
		10.7					
		10.8					
		10.8	0.324	4.93	1.89	0.0128	0.00577
pH 6.86	25.4	11.1					
		11.2					
		11.1					
		11.1	0.666	2.07	4.47	0.00852	0.00592
		11.0					
		11.1					
		11.0					
		11.0	0.660	3.04	3.09	0.0102	0.00585
		10.9					
		10.9					
		10.9					
		10.9	0.654	4.04	2.30	0.0117	0.00581
		10.8					
		10.8					
		10.7					
		10.8	0.648	5.02	1.86	0.0129	0.00575

Supporting electrolyte	$C_{(HCHO)_a}$ mmole/l	u cm	$\bar{i}$ μ A	t sec	m mg/sec	$\frac{\bar{i}}{m^{2/3}\,t^{1/6}\,C}$	$\frac{\bar{i}}{m^{2/3}\,t^{2/3}\,C}$
0.0050 M KH_2PO_4 + 0.0050 M Na_2HPO_4 pH 6.86, 20° C	12.7	12.0 11.9 12.0					
		12.0	0.360	2.10	4.55	0.0099	0.00683
		11.8 11.7 11.8					
		11.8	0.354	2.94	3.06	0.0112	0.00656
		11.7 11.7 11.7					
		11.7	0.351	4.25	2.36	0.0136	0.00658
		11.6 11.6 11.5					
		11.6	0.354	5.88	1.74	0.0158	0.00652
pH 6.86	25.4	17.8 17.8 17.8					
		17.8	0.712	2.48	3.44	0.0106	0.00671
		17.7 17.7 17.7					
		17.7	0.710	2.82	3.07	0.0111	0.00662
		17.6 17.6 17.5					
		17.6	0.705	4.21	2.10	0.0135	0.00658
		17.4 17.4 17.4					
		17.4	0.695	5.82	1.45	0.0156	0.00646

Supporting electrolyte	$C_{(\mathrm{HCHO})_a}$ mmole/l	u cm	$\bar{i}$ μ A	t sec	m mg/sec	$\frac{\bar{i}}{m^{2/3}\,t^{1/6}\,C}$	$\frac{\bar{i}}{m^{2/3}\,t^{2/3}\,C}$
0.010 M Na_2CO_3 pH 9.54, 20° C	6.35	12.2 12.2 12.2					
		12.2	0.448	2.75	2.82	0.0326	0.0197
		12.0 12.0 12.0					
		12.0	0.480	3.41	2.04	0.0382	0.0208
		11.9 11.9 11.9					
		11.9	0.437	4.80	1.45	0.0444	0.0202
pH 9.54	12.7	12.3 12.2 12.3					
		12.3	0.985	2.08	3.36	0.0305	0.0210
		12.1 12.1 12.0					
		12.1	0.968	3.11	2.27	0.0366	0.0208
		11.9 11.9 11.9					
		11.9	0.953	4.88	1.43	0.0455	0.0206
0.010 M Na_2CO_3 pH 10.44, 20° C	2.03	13.1 13.1 13.1					
		13.1	0.394	3.39	2.28	0.0920	0.0495
		13.0 13.1 13.1					
		13.1	0.394	3.82	2.04	0.0966	0.0494
		13.0 13.0 13.1					
		13.0	0.390	5.12	1.52	0.108	0.0490

Supporting electrolyte	$C_{(HCHO)_a}$ mmole/l	u cm	$\bar{i}$ μ A	t sec	m mg/sec	$\frac{\bar{i}}{m^{2/3} t^{1/6} C}$	$\frac{\bar{i}}{m^{2/3} t^{2/3} C}$
pH 10.46	4.07	19.7					
		19.6					
		19.7					
		19.7	0.789	2.78	2.82	0.0824	0.0494
		19.6					
		19.6					
		19.6					
		19.6	0.785	3.76	2.08	0.0945	0.0489
		19.6					
		19.5					
		19.5					
		19.5	0.780	5.11	1.52	0.109	0.0486
0.010 *M* Na_2CO_3 pH 10.83, 20° C	0.635	13.3					
		13.3					
		13.3					
		13.3	0.160	2.01	3.85	0.0915	0.0645
		13.4					
		13.4					
		13.4					
		13.4	0.161	4.10	1.95	0.129	0.0640
		13.3					
		13.4					
		13.3					
		13.3	0.160	5.26	1.48	0.147	0.0642
pH 10.81	1.27	10.7					
		10.6					
		10.7					
		10.7	0.321	2.06	3.87	0.0915	0.0648
		10.7					
		10.8					
		10.8					
		10.8	0.324	4.12	1.94	0.131	0.0645
		10.7					
		10.7					
		10.7					
		10.7	0.321	5.30	1.48	0.147	0.0642

Supporting electrolyte	$C_{(HCHO)_a}$ mmole/l	u cm	$\bar{i}$ μA	t sec	m mg/sec	$\frac{\bar{i}}{m^{2/3}t^{1/6}C}$	$\frac{\bar{i}}{m^{2/3}t^{2/3}C}$
0.10 . *M* NaOH pH ~ 12.7, 20° C	0.127	10.1 10.1 10.0					
		10.1	0.202	2.81	2.72	0.690	0.410
		9.6 9.7 9.6					
		9.6	0.185	4.22	1.69	0.810	0.395
		8.8 8.8 8.7					
		8.8	0.177	5.85	1.32	0.880	0.380
pH ~ 12.7	0.353	13.5 13.4 13.5					
		13.5	0.540	2.78	2.60	0.689	0.412
		12.6 12.7 12.6					
		12.6	0.509	4.20	1.65	0.810	0.394
		12.0 12.0 12.0					
		12.0	0.481	5.88	1.26	0.870	0.358

The technique and chemicals described above were subsequently used in order to investigate the relationship between limiting current, flow of mercury and drop time at 20 ± 0.03° C for the solution compositions shown in Table 1. The formaldehyde concentration was determined on the stock solution by the method of Blank and Finkenheimer, and a result of 380 ± 2 g/l was obtained. The buffer substances of the supporting electrolytes were dissolved in a measuring flask, the required amount of formaldehyde added, and the solution diluted to a volume close to the final. By means of HCl or NaOH pH was adjusted. For the pH determinations the glass electrode differential technique described in the Swedish Patent 129833 was applied, and an accuracy of ± 0.01 pH obtained. The solutions prepared were kept at 20° C for 24 hours, in order to prevent any influence from reaction (A). Then the pH was rechecked (no changes found), the solutions made up to the final volume with water and poured into the cell. Since the second wave of dissolved oxygen interferes with the formaldehyde wave at low concentrations of the aldehyde, a removal of dissolved oxygen is necessary, especially when a high degree of accuracy is needed. This was achieved by bubbling nitrogen slowly through the solution in the cell; this also provides valuable stirring during the period of temperature stabili-

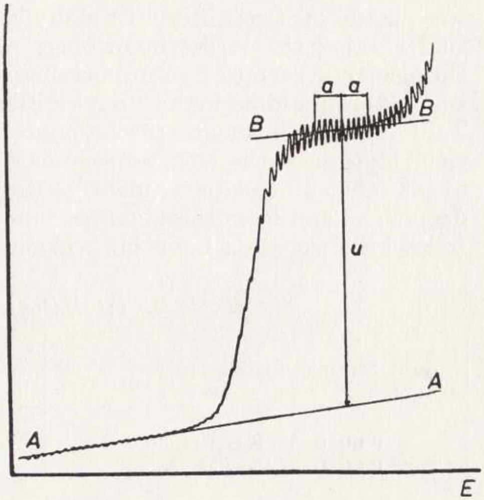

Fig. 2. Polarogram of formaldehyde, $C_{(\mathrm{HCHO})_a} = 1.27 \times 10^{-3}$, *20° C, supporting electrolyte:* 0.010 M Na_2CO_3, *pH 10.81.*

sation. Here, of course, we encounter the question of whether the formaldehyde concentration is disturbed during the process, *i. e.* whether any formaldehyde is removed by the nitrogen. However, it was found that during the time of bubbling used in this case, 30 minutes, no change could be found in any of the solutions investigated. It might be assumed that a rapid flow of nitrogen and very long bubbling times have to be avoided, especially at high pH values, since the rate of dehydration is then high. The capillary tubes were carefully cleaned, in order to make the drop cycle completely reproducible. A suitable method for cleaning is to suck concentrated nitric acid through the capillary tube for 10 minutes, then distilled water for 10 minutes, and finally methanol. The suction has to be maintained until the capillary is completely dry.

When evaluating the polarograms the method shown in Fig. 2 has been applied. With the small currents occurring in this case it is necessary to make a correction for the condenser current. The usual method for such a correction has been applied, *i. e.* the line A—A along the average current curve is drawn. The limiting current is then determined by the vertical distance u between the line A—A and the point of inflexion between formaldehyde and supporting electrolyte on the current-voltage curve. (This method has often been used, *e. g.* by Brdička [20].) The point of inflexion is found by drawing the mean current curve and the line B—B, and bisecting the part of the line that lies on the curve. The drop times and the flows of mercury were determined at the potential corresponding to the point of inflexion. The polarograms were recorded by means of a LKB type 3 266 polarograph and a Leeds & Northrup Speedomax G recorder. The rate of voltage increase was 0.1 V/min. As a secondary control a Radiometer type PO3g polarograph was used.

RESULTS

The results of the measurements are given in Table 1. The u values of three measurements for each composition of the solution are to be found in the table, the average of these values was used in the further treatments. The treatments involve the calculation of the numerical value of the function

$$\bar{i} \, / \, C_{(\mathrm{HCHO})_a} \cdot m^{2/3} \; t_1^{1/6} \qquad (51)$$

i. e. the function (46), but including the analytical amount of formaldehyde ($\sigma \gg 1$). For each composition of the supporting electrolyte measurements were made on two different aldehyde concentrations; this was done in order to find whether the earlier mentioned influence of the hydroxyl ions produced at the electrode surface is of importance. If this is the case, differences in the functions (51) should be found. Such differences did not occur, as can be seen from Table 1. The influence of the concentration of the buffer in the supporting electrolyte, *i. e.* the acid — base catalysis, is exemplified by the experiments at pH 6.86. In the diagrams 3—5 the expression (51) has been plotted against drop time, and from these curves functions in accordance with eq. (46) and the following discussion have been calculated. The results are given in Table 2,

Table 2. $f(t)/f(t/2)$ from experimental data.

Supporting electrolyte	pH	$C_{(HCHO)_a} \times 10^3$	f(5)/f(2.5)
0.0050 *M* KH_2PO_4 + 0.0050 *M* Na_2HPO_4	6.86	12.7 25.4	1.41
0.0025 *M* KH_2PO_4 + 0.0025 *M* Na_2HPO_4	6.86	12.7 25.4	1.41
0.010 *M* Na_2CO_3	9.54	6.35 12.7	1.42
0.010 *M* Na_2CO_3	10.44 10.46	2.03 4.07	1.41
0.010 *M* Na_2CO_3	10.83 10.81	0.635 1.27	1.43
0.10 *M* NaOH	~12.7	0.127 0.353	1.30

and are in agreement with the postulates in Fig. 1: at pH 9.5, 10.4 and 10.8 the limit 1.4 is obtained. This is not the case at pH 12.7, as might be expected from eq. (3). The results at pH 6.86 are not obviously different from the values at pH 9.5—10.8, *i. e.* the equilibrium constant cannot be determined with a high degree of accuracy. In order to find whether the difference is statistically significant, the following expression has been included in the tables; since this is very suitable for tests on eq. (44):

$$\bar{i} \,/\, C_{(HCHO)_a} \cdot m^{2/3} \; t_1^{2/3}$$

Regression analysis applied to the group pH 9.5, 10.4 and 10.8 and the group pH 6.86 reveals a significant difference. (I. Sandelius, private communication.)

From a diffusion constant of 16 × 10^{-6} cm^2/sec and the fact that $\bar{i} / \bar{i}_d > 3.5$ (Fig. 1) it can be postulated that $k_h < 3 \times 10^{-4}$, and the value 10^{-4} seems to be very probable when regarding the significant difference mentioned above.

From measurements on the temperature dependence of the formaldehyde limiting current, Bieber and Trümpler [11] found an "activation energy" for this

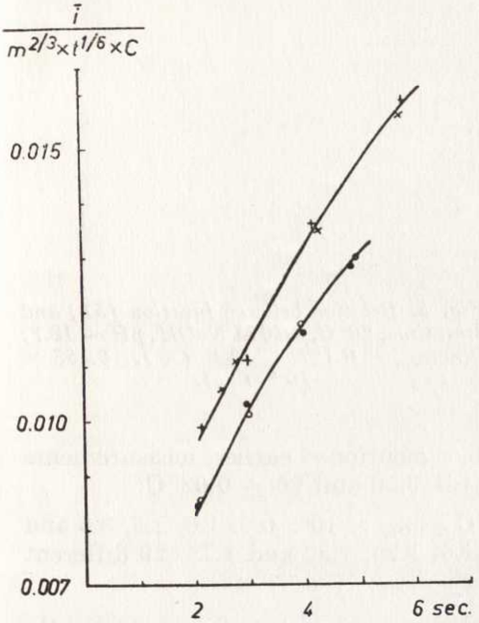

Fig. 3. Relation between function (51) and drop time, 20° C, pH 6.86; $C_{(\mathrm{HCHO})_a}$ = 12.7 × 10^{-3} (●), 25.4 × 10^{-3} (○), supporting electrolyte: 0.0025 M KH_2PO_4 + 0.0025 M Na_2HPO_4; $C_{(\mathrm{HCHO})_a}$ = 12.7 × 10^{-3} (+), 25.4 × 10^{-3} (×), supporting electrolyte: 0.0050 M KH_2PO_4 + 0.0050 M Na_2HPO_4.

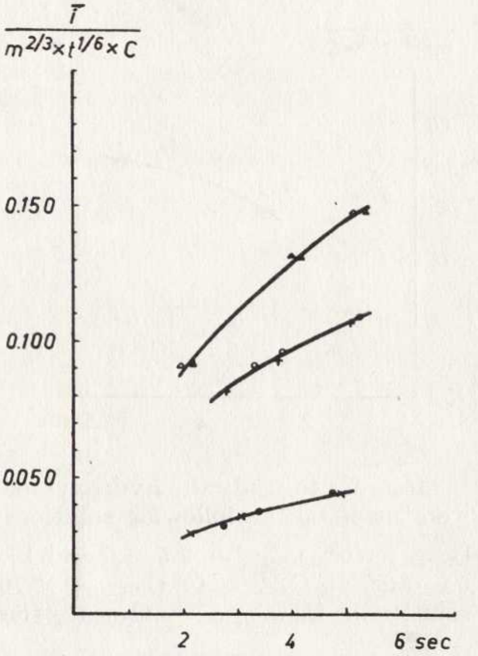

Fig. 4. Relation between function (51) and drop time, 20° C, 0.010 M Na_2CO_3; $C_{(\mathrm{HCHO})_a}$ = 6.35 × 10^{-3} (●), 12.7 × 10^{-3} (×), pH 9.54; $C_{(\mathrm{HCHO})_a}$ = 2.03 × 10^{-3} (+), pH 10.44; $C_{(\mathrm{HCHO})_a}$ = 4.07 × 10^{-3} (○), pH 10.46; $C_{(\mathrm{HCHO})_a}$ = 0.635 × 10^{-3} (△), pH 10.83; $C_{(\mathrm{HCHO})_a}$ = 1.27 × 10^{-3} (▲), pH 10.81.

current of the order 14 kcal. From spectrophotometrical data Bieber [6] deduced an activation energy of the dehydration of methylene glycol of 14.6 kcal. Since $k_1/k_2 = 1/k_h$ eq. (44) can be written:

$$\overline{i} \,/\, \overline{i}_{\mathrm{d\ HO\cdot CH_2\cdot OH}} = 0.81\ k_h \sqrt{t_1 k_1} \qquad (52)$$

From this we find that the hydration rate constant is only slightly dependent on the temperature. This means that measurements at other temperatures would not be more favourable when determining the equilibrium constant, since the change in this constant is chiefly dependent on the change in the dehydration rate. Measurements at 0° C and 50° C have confirmed this. Measurements at low pH values are also of no help, as can be found when examining the results from Bieber and Trümpler [21]; mixtures of methanol and water were also investigated in the present study, but no results of interest were obtained.

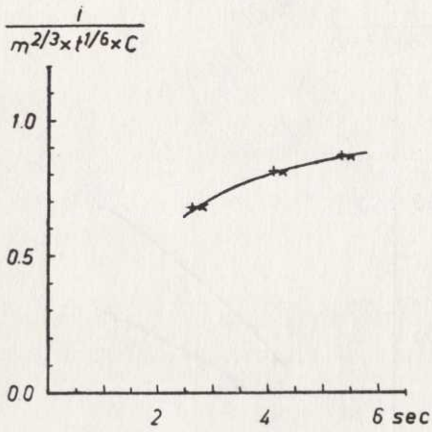

Fig. 5. Relation between function (51) and drop time, 20° C, 0.10 M *NaOH, pH* ~ *12.7; $C_{(HCHO)_a}$ = 0.127 × 10^{-3} (+), 0.353 × 10^{-3} (×).*

In order to study the hydroxyl ion effect mentioned earlier, measurements were made on the following solutions at pH 9.20 and 20 ± 0.03° C:

$C_{borax} \times 10^3$: 0.5, 1.0, 2.5, 5.0 and 15.0: $C_{(HCHO)_a} \times 10^2$: 0.5, 1.0, 2.5, 3.5 and 5.0, and at $C_{borax} = 0$: $C_{(HCHO)_a} \times 10^2$: 1.0, 1.25, 1.50 and 1.75 (29 different solutions). $C_{HO \cdot CH_2 \cdot OH} = C_{(HCHO)_a}$ since $\sigma \gg 1$.

The experimental results are given in Fig. 6, and in unbuffered or slightly buffered solutions the linear relationship required by eq. (50) is found. The

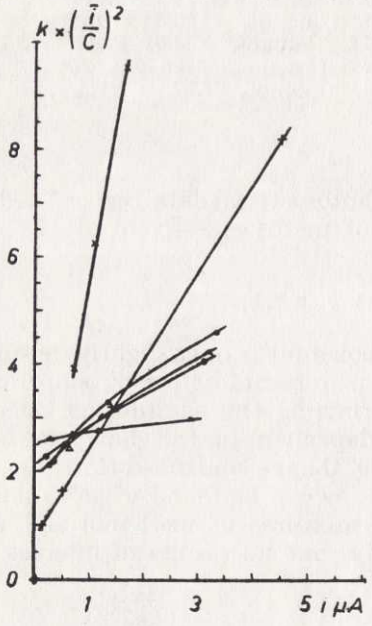

Fig. 6. Hydroxyl ion effect in unbuffered and slightly buffered solutions. $C_{borax} \times 10^3$ = 0 (×), 0.5 (+), 1.0 (●), 2.5 (△), 5.0 (○) and 15.0 (▲).

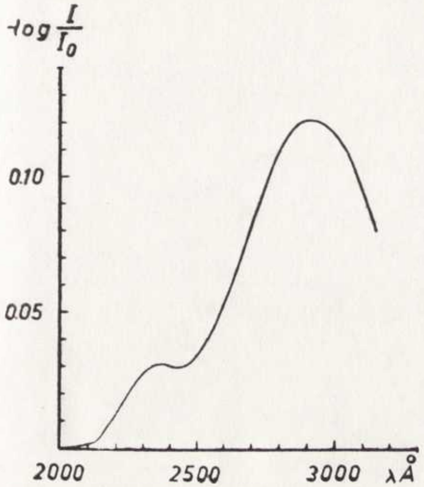

Fig. 7. Ultraviolet absorption curve of 4.75 M *HCHO in 0.05* M *KH_2PO_3 + KOH, pH 6.70, 50° C.*

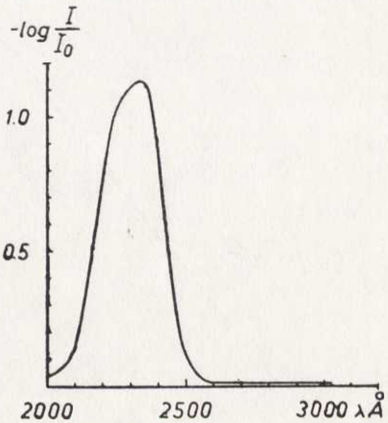

Fig. 8. An ultraviolet absorption curve of formic acid.

polarograms were also skew, in accordance with the earlier discussion. In the slightly buffered solutions the contribution of the buffer substance to the catalysis is shown by $(\bar{i} / C_{(HCHO)_a})^2 \neq 0$ when $\bar{i} = 0$.

SPECTROPHOTOMETRICAL INVESTIGATIONS

Measurements in the ultraviolet range were made on formaldehyde in order to check Bieber's [6] result, and to find whether trioxymethylene glycol is of any importance at a temperature of 50° C. If such is the case, the extrapolation made by Bieber would be open to criticism.

The instrument used was a Hilger & Watt "Uvispec" spectrophotometer. The lid of the transmission cell housing was removed and replaced by another, with three holes. Through one of these connections hot air (~ 60° C) from a simple hair-drying device was blown into the housing, through another the air was allowed to escape through a long, curved rubber tubing, preventing any light leakage into the cell housing. Through the third hole a contact thermometer on-off regulates the air flow. The temperature of the cell solutions was measured by a thermo-couple, and the contact thermometer was adjusted so that the cell temperature was maintained at 50 ± 0.5° C. The cells, protected by air—tight rubber caps, were kept in the housing during 20 minutes, which time was found to be enough to give a constant temperature in the cell solutions.

By means of this device the wavelength interval 2 000—3 200 Å was investigated; cell length 2 cm, temperature 50° C, $C_{(HCHO)_a}$: 1.27, 3.18, 3.81, 5.08 and 6.35. The solvent was 0.05 M KH_2PO_4 + KOH, pH 6.70. Fig. 7 is an example of the absorption curves obtained. The curves have absorption bands at 2 300 and 2 800 Å. As postulated by *e. g.* Bieber [6] the latter is the

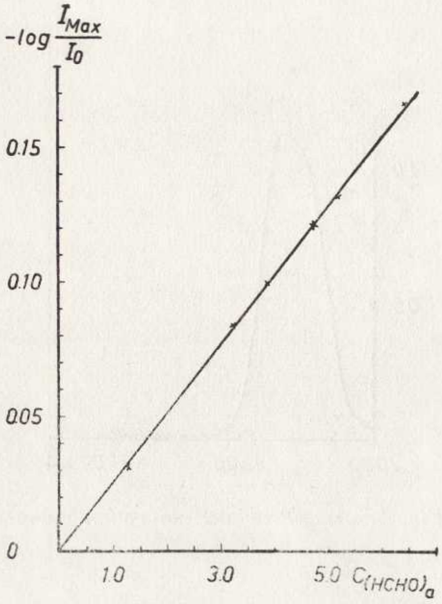

Fig. 9. Relation between maximum extinction and formaldehyde concentration, 0.05 M *KH_2PO_4 + KOH, pH 6.70, 50° C.*

formaldehyde band. The absorbtion in the 2 300 Å range is probably due to traces of formic acid present in the formaldehyde solution, the results of an investigation on a formic acid solution at the same pH and temperature makes this assumption very probable, as can be found from Fig. 8. Fig. 9 shows the relation between the maximum extinction in the 2 860 band and the formaldehyde concentration. If we use the extinction coefficient estimated by Bieber[6] (13.5), and calculate the equilibrium constant at 50° C, we get the value 0.96×10^{-3}. This is in good agreement with the result obtained if Bieber's results are extrapolated to the same temperature: 1.15×10^{-3}. As a linear relationship is found for maximum extinction and formaldehyde concentration, the trioxymethylene glycol from reaction (A) seems to be of no importance. In accordance with Auerbach and Barschall[1], the trioxymethylene glycol fraction increases with increasing concentration, *i. e.* the methylene glycol fraction decreases. Of course, this may be compensated by a change in the extinction coefficient, since at high concentrations there is a solvent mixture of water, methylene glycol and trioxymethylene glycol. However, the probability of such compensation seems to be very low. At 20° C the case mentioned above can not be neglected, *i. e.* the influence of trioxymethylene glycol. From measurements at 20° C, $C_{(HCHO)_a} = 6.35$, and from the equilibrium constant 10^{-4} we find $C_{HO \cdot CH_2 \cdot OH} / \Sigma C_{HCHO} = 0.6$. This result is in agreement with the figure expected from Walker[22]. However, the result cannot be assigned too much value, in view of the influence of the solution composition on the extinction coefficient and the low accuracy at the low absorption in question. Finally, solutions with $C_{(HCHO)_a} = 6.35$ have been studied at 50° C and pH 4.6, 6.7, 9.2 and 10.8. No pH dependence could be detected.

Table 3. Dehydration rate constants of methylene glycol.

Electrolyte	k_2 20° C
0.0050 M KH_2PO_4 + 0.0050 M Na_2HPO_4 pH 6.86	$\sim 1.9 \times 10^{-2}$
0.0025 M KH_2PO_4 + 0.0025 M Na_2HPO_4 pH 6.86	$\sim 1.7 \times 10^{-2}$
0.010 M Na_2CO_3	
pH 9.54	~ 0.3
pH 10.44	~ 1.8
pH 10.88	~ 2.8

From the above we see that nothing is in disagreement with Bieber's results. It has been shown that the extrapolation to 20° C is possible, since at 50° C no trioxymethylene glycol of practical importance seems to be present, even at high concentrations; Bieber's measurements have been made at a temperature above 50° C and a concentration below that used here. This means that the extrapolated values refer to dilute solutions. And we find that we have several reasons to accept Bieber's result:

$$k_h \simeq 10^{-4}$$

A comparison with the polarographic result, $k_h < 3 \times 10^{-4}$, and the result of the spectrophotometrical measurement at 20° C, makes the value given above very probable.

THE RATE OF DEHYDRATION OP METHYLENE GLYCOL

Since $\bar{i} \,/\, \bar{i}_d > 3.5$ even at pH 6.9, eq. (44) can be applied to the pH range 7—11 without appreciable error, and the order of the rates of dehydration of methylene glycol can be calculated.

From eq. (44) and $k_h \sim 10^{-4}$ we get:

$$k_{2\,20^\circ C} = 0.7 \times 10^{-3} \cdot \bar{i}^2 \,/\, C^2_{(HCHO)_a} \cdot m^{4/3}\ t_1^{4/3} \qquad (53)$$

The reaction rate constants calculated from eq. (53) and based on the measurements presented in Table 1, can be found in Table 3.

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REFERENCES

1. Auerbach, F. and Barschall, H. *Arb. kaiserl. Gesundh.* **22** (1905) 594.
2. Wadano, M., Trogus, C. and Hess, K. *Ber.* **67** (1934) 174.
3. Euler, H. and Lövgren, T. *Z. anorg. Chem.* **147** (1925) 123.
4. Lévy, M. *J. Biol. Chem.* **105** (1934) 157.
5. Schou, S. A. *J. chim. phys.* **26** (1929) 69.
6. Bieber, R. *Über das polarografische Verhalten der niederen, gesättigten alifatischen Aldehyde, besonders des Formaldehyds* (Diss.) Zürich 1948, p. 98–100.
7. Ilkovič, D. *Collection Czechoslov. Chem. Communs* **6** (1934) 498; *J. chim. phys.* **35** (1938) 129.
8. Jahoda, F. G. *Collection Czechoslov. Chem. Communs* **7** (1935) 415.
9. Winkel, A. and Proske, G. *Ber.* **69** (1936) 693, 1917; **71** (1938) 1785.
10. Veselý, K. and Brdička, R. *Collection Czechoslov. Chem. Communs* **12** (1947) 313.
11. Bieber, R. and Trümpler, G. *Helv. Chim. Acta* **30** (1947) 704.
12. Wiesner, K. *Chem. Listy* **41** (1947) 6.
13. Koutecký, J. and Brdička, R. *Collection Czechoslov. Chem. Communs* **12** (1947) 337.
14. Koutecký, J. *Chem. Listy* **47** (1953) 9.
15. Koutecký, J. *Chem. Listy* **47** (1953) 323.
16. Koutecký, J. *Collection Czechoslov. Chem. Communs* **18** (1953) 311.
17. Koutecký, J. *Collection Czechoslov. Chem. Communs* **18** (1953) 597.
18. Mejman, N. *Zhur. Fiz. Khim.* **22** (1948) 1454.
19. Koutecký, J., Brdička, R. and Hanuš, V. *Collection Czechoslov. Chem. Communs* **18** (1953) 611.
20. Bieber, R. and Trümpler, G. *Helv. Chim. Acta* **30** (1947) 1286.
21. Walker, J. F. *Formaldehyde,* Reinhold Publishing Co., New York, 1944, p. 33.

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

VII. A Spectrophotometrical Method for Quantitative Determination of Urea and Methylol Ureas of the Reaction Mixture

NILS LANDQVIST

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

VII. A Spectrophotometrical Method for Quantitative Determination of Urea and Methylol Ureas of the Reaction Mixture

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A spectrophotometrical method for quantitative determination of urea, mono- and dimethylol urea in reaction mixtures of urea and formaldehyde is described. The method is based on a colour reaction between the ureas and *p*-dimethylaminobenzaldehyde in the presence of hydrochloric acid. The influence of side reactions is sufficiently reduced when the reaction mixture sample is added to an excess of a methanolic solution of the reagent.

A comparatively selective colour reaction between urea and *p*-dimethylaminobenzaldehyde in acid solutions was described by Weltman and Barrenscheen [1], and was later on applied for spectrophotometrical determination of urea by Watt and Chrisp [2].

This kind of reaction has been found to be suitable for a quantitative determination of urea, mono- and dimethylol urea of urea-formaldehyde reaction mixtures, when combined with a determination of unreacted formaldehyde.

However, it is necessary to reduce the rates of reaction of the components of the reaction mixture in the presence of a strong acid, in order to obtain consistent results. This condition is realized when the reaction mixture sample is added to a large excess of a methanolic solution of the reagent.

In the following some experiments are described, on which the analytical method is based.

Reagent solution: 10 g/l *p*-dimethylaminobenzaldehyde, dissolved in methanol after addition of 10 ml/l concentrated hydrochloric acid. For one of the experiments a series of different concentrations was used. All chemicals of A. R. quality.

Other chemicals: Urea of A. R. quality; mono- and dimethylol urea prepared in accordance with Walter and Gewing [3]. Cryoscopic molecular weights: 90 ± 1 and 120 ± 1, respectively. Formaldehyde, containing only traces of methanol and formic acid.

Spectrophotometer: Hilger & Watt's "Uvispec". Cell length 20 mm.

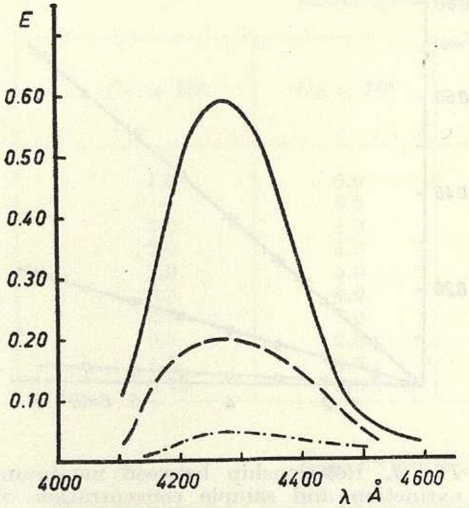

Fig. 1. Extinction curves of 0.0070 M urea (———), 0.0070 M monomethylol urea (— — —) and 0.0120 M dimethylol urea (—·—·). 2 ml sample + 10 ml reagent solution.

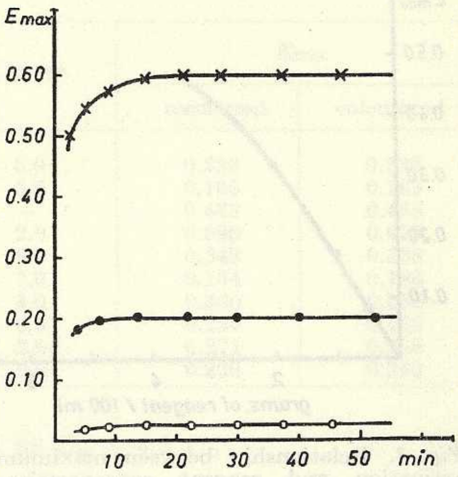

Fig. 2. Relationship between maximum extinction and time delay between preparation and spectrophotometry. 0.0070 M solutions of urea (×), mono- (●) and dimethylol urea (○). 2 ml sample + 10 ml reagent solution.

All experiments were carried out at 20 °C. The samples of the mono- and dimethylol urea solutions were added to the reagent solutions immediately after the dissolution of the ureas in distilled water. This was made in order to avoid disturbances from hydrolysis reactions.

A. To 2 ml of 0.0070 M urea, 0.0070 M mono- and 0.0120 M dimethylol urea, 10 ml of the reagent solution were added. When a constant extinction was attained (after ~20 min), the extinction curves were determined. The results are given i Fig. 1. From a preliminary study it was found that the wavelength at the extinction maximum is constant within the concentration range studied. $\lambda_{\max} = 4\,270$ Å.

B. The dependence of the maximum extinction on the time elapsed between reagent addition and spectrophotometry is described by Fig. 2. The curves are related to 0.0070 M solutions, 2 ml sample and 10 ml reagent solution. At lower concentrations the asymptotic values were attained with less delay of time. As found from these measurements, 20—30 min interval between preparation and measurement is sufficient; the value attained is then constant during 1—2 h.

C. The relation between *p*-dimethylaminobenzaldehyde concentration of the reagent solution and maximum extinction is elucidated by Fig. 3, related to 0.0020 M urea, 2 ml sample + 10 ml reagent solution. The same behaviour was also observed for the methylol ureas. Below a reagent concentration of 20 g/l the curves are linear. From these results it might be concluded that the

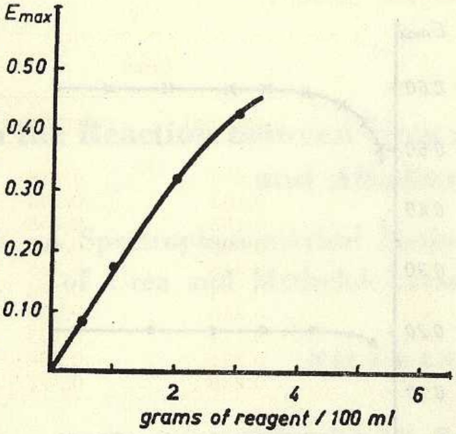

Fig. 3. Relationship between maximum extinction and reagent concentration. 0.0020 M urea. 2 ml sample + 10 ml reagent solution.

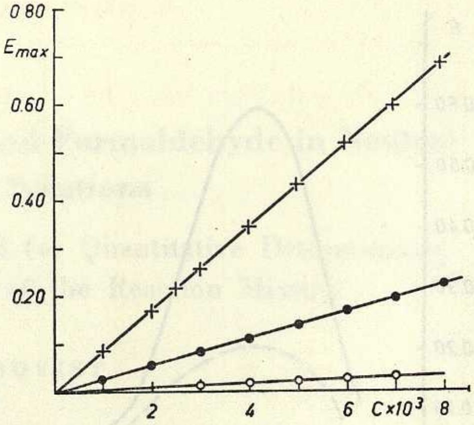

Fig. 4. Relationship between maximum extinction and sample concentration of urea (+), mono- (●) and dimethylol urea (○).

concentration of the coloured compound is determined by an equilibrium between the reagent and the ureas.

D. In Fig. 4 the relation between the concentration of urea, mono- and dimethylol urea of the reaction samples and the maximum extinction is shown. 2 ml sample added to 10 ml reagent solution; 30 min time delay between preparation and measurement.

A good linearity is present over the concentration range studied, $0 < C < 7 \times 10^{-3}$. The curves are described by the expressions:

$$C_{\mathrm{U}} = 1.16 \times 10^{-2} \times E_{\max} \tag{1}$$

$$C_{\mathrm{M}} = 3.55 \times 10^{-2} \times E_{\max} \tag{2}$$

$$C_{\mathrm{D}} = 23 \times 10^{-2} \times E_{\max} \tag{3}$$

where C_{U} = sample concentration of urea, C_{M} = sample concentration of monomethylol urea, C_{D} = sample concentration of dimethylol urea, $E_{\max}$ = maximum extinction.

E. To several of the solutions mentioned above formaldehyde was added in amounts corresponding to 0.1 M just before the addition of the reagent solution. No immediate or time dependent influence on the extinction was observed. The same behaviour was also found for mixtures of urea and methylol ureas.

F. In order to investigate whether the expressions (1)—(3) are valid also for solutions containing mixtures of urea and the methylol ureas, such mixtures were studied. The compositions and the results are given in Table 1. As can be seen, there is a good correlation between actual and calculated data. Thus, we can, for the concentration range investigated, accept the expression:

Table 1. Experimental and calculated maximum extinction data of urea, mono- and dimethylol urea solution mixtures.

$C_U \times 10^3$	$C_M \times 10^3$	$C_D \times 10^3$	E_{max}	
			measured	calculated
1.0	5.0	3.0	0.239	0.238
—	5.0	5.0	0.165	0.163
5.0	1.0	—	0.463	0.458
7.0	3.0	2.0	0.690	0.695
2.0	5.0	6.0	0.342	0.338
0.5	4.0	7.0	0.184	0.186
3.0	3.0	3.0	0.350	0.355
0.5	2.0	6.0	0.124	0.125
1.5	4.5	3.0	0.271	0.268
0.75	6.0	2.0	0.238	0.242

$$E_{max} = 86\ C_U + 28\ C_M + 4.3\ C_D \tag{4}$$

This expression is easily derived from (1)—(3).

For a reaction mixture of urea and formaldehyde, C_U° and C_F° are the initial urea and formaldehyde concentrations, and we have, provided mono- and dimethylol urea are the reaction products:

$$C_U^\circ = C_U + C_M + C_D$$
$$C_F^\circ = C_F + C_M + 2\ C_D$$

By means of this and eqn. (4) we obtain:

$$C_U = 0.0292\ E_{max} - 1.51\ C_U^\circ + 0.71\ C_F^\circ - 0.71\ C_F \tag{5}$$

Thus, from a determination of the concentration of unreacted formaldehyde, C_F, and the spectrophotometrical measurement, the actual composition of a reaction mixture might be determined with, from the technical point of view, good accuracy.

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REFERENCES

1. Weltman, O. and Barrenscheen, H. K. *Klin. Wochschr.* **1922** 1100.
2. Watt, G. W. and Chrisp, J. H. *Anal. Chem.* **25** (1954) 452.
3. Walter, G. and Gewing, M. *Kolloid-Beih.* **34** (1934) 163.

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

I. Experimental Studies of the Rates of the Equimolecular Reaction

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Some methods for formaldehyde determinations in urea-formaldehyde reaction solutions are examined. A number of effects which have to be considered when applying polarography to this subject are analysed and a suitable supporting electrolyte composition given.

The results of reaction rate studies at 20° C of the equimolecular reaction between urea and formaldehyde at comparatively high concentrations of the reactants are given. From these studies it is found that at a urea-formaldehyde ratio of 1:1 no theoretically significant reaction order is present. The previously reported rapid initial reaction was not observed. In buffered solutions, as in unbuffered, the reaction order was approximately 1.6. In buffered solutions a reaction of second order is present if an excess of urea is used. From such reaction studies rate constants can be calculated. The reaction was found to be subject to acid-base catalysis, and different catalysts show different catalysing power. A linear relationship was found between the rate constants and the amounts of catalyst present. The hydroxyl ion catalysis is not found to be a simple function of the hydroxyl ion activity.

The rates of the reaction

$$H_2N—CO—NH_2 + HCHO = H_2N—CO—NH—CH_2OH \qquad (A)$$

were previously studied by Smythe, Crowe and Lynch, Bettelheim and Cedvall and De'Jong.

By means of a hydroxylamine titration method Smythe [1] investigated the rate of the equimolecular urea-formaldehyde reaction in concentrated, unbuffered solutions at a pH of about 7 and at different temperatures. The reaction product was found to be monomethylol urea, and no dimethylol urea was present in sufficient quantity to be detected. The reaction was of the bimolecular type, except for a rapid initial stage. An activation energy of 14.6 kcal/mole was obtained. Later on, Smythe [2] took a special interest in the initial rapid reaction. It was found that influence of urea hydrolysis products could not explain this reaction, and repeated experiments, also here made by means of the hydroxylamine method, were in agreement with his earlier observations. In the temperature range 20—40° C the initial reaction during the first 300 seconds included 36—46 % of the complete condensation reaction. The mechanism of the rapid reaction was also discussed by Smythe [3], and in the same work the effect of small amounts of some compounds present in the reaction solution was also studied. (Na_2HPO_4, $H_3C-COONa$, $H_2N-CH_2-COONa$, $Na_2B_4O_7$, CH_3OH and hydroquinone.) Smythe found that the highest rate was obtained in 1:300 Na_2HPO_4. In this investigation, as in the previous, a change in pH during the initial reaction was observed. Finally, Smythe [4] studied the urea-formaldehyde reaction in dilute solutions by means of polarography. In this case no rapid initial reaction could be found. Similar studies of dilute solutions, also made by means of polarography, are due to Crowe and Lynch [5,6], and the experiments included buffered, alkaline solutions. (0.1 M $NaHCO_3$, pH 8.7; 0.05 M H_3BO_3 + 0.05 M LiCl + 0.045 M LiOH, pH 10.1; 0.1 M Na_2CO_3, pH 11.2; 0.05 M LiOH, pH 12.7.) The reaction was found to be of second order, and the rate was increasing with pH and temperature. An activation energy of 15.9 kcal/mole was calculated.

Bettelheim and Cedvall [7] investigated the urea-formaldehyde reaction in unbuffered, concentrated solutions at 40° C in the neutral and alkaline range. The change in formaldehyde concentration of the reaction mixture was determined by means of a sodium sulfite titration method (Lemme-Doby). Also in this case a bimolecular reaction was found, but the initial reaction was more moderate, only including about 15 % of the complete reaction.

Finally, De'Jong [8] checked the initial rapid reaction in solutions prepared from repeatedly crystallised urea, and in this investigation no reaction of such a kind could be found. However, in the experiments an excess of urea was used. The previously observed initial reaction was assumed to be due to ammonia impurities, and these impurities would react with the formaldehyde rapidly. De'Jong did not mention what formaldehyde analysing method he used.

The purpose of the following paper is to examine the methods for formaldehyde determination in urea-formaldehyde reaction mixtures and to describe experimental studies at 20° C with special regard to the reaction order and the influence of pH and buffer substances.

DETERMINATION OF FORMALDEHYDE IN UREA—FORMALDEHYDE REACTION SOLUTIONS

The use of *polarography* for determination of formaldehyde in urea-formaldehyde reaction solutions was primarily introduced by Crowe and Lynch [5,6]. From formaldehyde limiting current measurements in solutions containing the same amount of buffer substances and of the same pH as the reaction mixtures, the formaldehyde was determined directly in these mixtures. Smythe [4] used a somewhat different method: Samples from the reaction solutions were analysed on formaldehyde polarographically at 25° C; the supporting electrolyte was 0.095 M Na_2HPO_4 + 0.022 M KH_2PO_4, pH 7.15. Calibration curves gave a linear relationship between limiting current and formaldehyde concentration, except for small deviations at low formaldehyde concentrations. These deviations are probably due to difficulties when evaluating the polarograms; this seems to be probable since Na^+ and K^+ are the cations of the supporting electrolyte and the waves of these ions interfere with the formaldehyde wave. The evalution difficulties are also increased because the formaldehyde current-voltage curve shows a maximum at high concentrations (Smythe [4], p. 575, Fig. 2). Smythe mentions that methylol urea acts as a maximum suppressor,

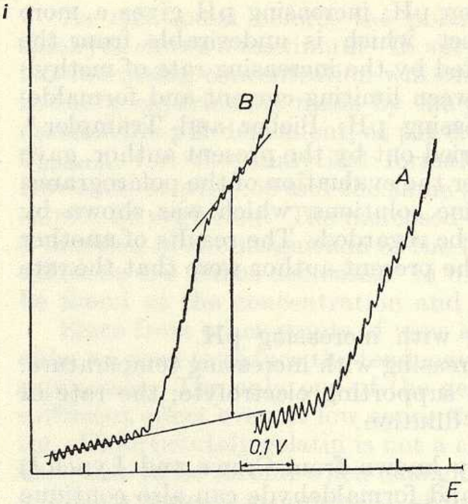

Fig. 1. Formaldehyde polarograms of a urea — formaldehyde reaction solution, $C_{Na^+} =$ *0.2; obtained by means of Smythe's method (A) and the method described in this paper (B).*

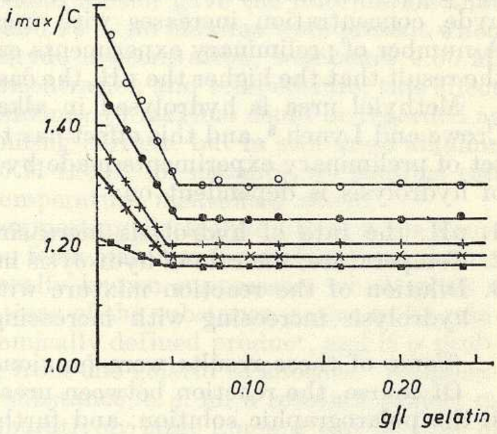

Fig. 2. The maximum suppression effect of gelatin at different formaldehyde concentrations: 0.150 (○), 0.100 (●), 0.060 (+), 0.025 (×) and 0.010 (■) at 25° C. Supporting electrolyte: 0.10 M Li_2CO_3*, pH 9.50.*

but this effect is of course not present at the beginning of the urea-formaldehyde reaction. Within the limits of the experimental conditions used by Smythe, the method seems to be applicable. However, the determination becomes more complicated if the reaction mixtures contain a considerable amount of Na^+ due to buffer substances present. When the sodium and formaldehyde waves interfere, the accuracy is often low. An example is given in Fig. 1, polarogram A, representing a 15 % urea-formaldehyde reaction mixture, the molar ratio of urea to formaldehyde is 1:1.5 and 6 % formaldehyde is still unreacted. The Na^+ concentration is 0.2 M, and the polarogram was recorded at 25° C with a supporting electrolyte according to Smythe and by means of a LKB type 3 266 polarograph. The dilution ratio was 1:20. Air oxygen was present and no maximum suppressor used. The drop time of the mercury electrode was 3.5 sec. From the diagram it is found that we have reasons to look for a supporting electrolyte which is more generally applicable.

Since the cation of the supporting electrolyte ought to have as negative half wave potential as possible, in order to reduce the interference, $(CH_3)_4N^+$ would be suitable. However, this ion might cause some uncontrolled reactions in solutions containing methylol urea and formaldehyde, and therefore it might be better to use Li^+. The half wave potential of Li^+ is more negative than that of Na^+, the difference being 0.16 V, and this would decrease the difficulties mentioned above, especially if a suitable pH of the supporting electrolyte is chosen. As shown by Bieber and Trümpler [9], the half wave potential of formaldehyde is dependent on pH; increasing pH gives a more negative half wave potential. This effect, which is undesirable from the point of view of interference, is compensated by the increasing rate of methylene glycol dehydration, *i. e.* the ratio between limiting current and formaldehyde concentration increases with increasing pH; Bieber and Trümpler [9]. A number of preliminary experiments carried out by the present author, gave the result that the higher the pH, the easier the evaluation of the polarograms.

Methylol urea is hydrolysed in alkaline solutions, which was shown by Crowe and Lynch [5], and this effect has to be regarded. The results of another set of preliminary experiments made by the present author were that the rate of hydrolysis is dependent on:

1. pH; the rate of hydrolysis increasing with increasing pH.
2. Temperature; the rate of hydrolysis increasing with increasing temperature.
3. Dilution of the reaction mixture with supporting electrolyte; the rate of hydrolysis increasing with increasing dilution.

(Some of these results were previously known from Crowe and Lynch [5])

Of course, the reaction between urea and formaldehyde can also continue in the polarographic solution, and further preliminary experiments gave the results that the rate of this reaction is dependent on 1 and 2 in the same way as the hydrolysis. The opposite effect is present in the case 3, decreasing reaction rates were found when the dilution was increased.

The influence of the buffer concentration of the supporting electrolyte on the reactions mentioned above was not studied, because the concentration is limited by the solubility of the Li^+ salts, and because a concentration close to this limit has to be used. This is necessary since otherwise the hydroxyl ions produced at the electrode surface during the reduction of formaldehyde

$$HCHO + 2\ H_2O = CH_3OH + 2\ OH^- \qquad (B)$$

will change the acid-base catalysis of the electrode reaction, *i. e.* will reduce the linear interval of the current concentration curve, as can be concluded from Landqvist [10]. (For further informations concerning the theory of formaldehyde polarography, reference is given to that paper.)

When considering the interference, the hydrolysis and the continuing reaction mentioned above, 0.1 M Li_2CO_3, pH 9.5 might be a suitable supporting electrolyte. The solubility of Li_2CO_3 does not permit a higher concentration than 0.1 M, and no other suitable buffer substance for the pH range in question could be found. The pK'' of the carbonate at the ionic strength here present is of the order 9.8, and this means that a slight influence of of hydroxyl ions at moderate and high limiting currents may be expected.

As regards the temperature of the polarographic solutions, an increased temperature is likely to cause an increased limiting current-formaldehyde concentration ratio, *i. e.* gives a favourable effect. However, at the same time the increased rate of the reactions previously mentioned is unfavourable. Because the temperature coefficient of the limiting current is high (Crowe and Lynch [6], Fig. 1), it is necessary to maintain a good temperature constancy. From the point of view of thermostating a temperature a little above the room temperature is useful, *i. e.* 25° C is in most cases to be preferred.

As mentioned before, the polarographic current-voltage curve of formaldehyde shows a maximum. In very dilute solutions this effect is not present, but increasing concentration will cause more pronounced maxima. Some preliminary experiments made by the present author gave the information that maxima are pH-dependent, at pH 6.9 and 25° C no maxima were present when $C_{(HCHO)a}$, *i. e.* the analytical formaldehyde concentration, was below 0.05 M. However, at pH 9.50 and the same concentration and temperature, this effect cannot be neglected. The increased tendency to maxima could be regarded as a function of the magnitude of the limiting current, but in still more alkaline solutions the effect decreases. In 0.05 M LiOH, for instance, no maxima can be found at the concentration and temperature mentioned above.

Since from other points of view a supporting electrolyte pH of 9.5 is desirable, we need to reduce the tendency to form maxima, *i. e.* to find a maximum suppressor. The only one of the generally known suppressors which gives a sufficient effect even at low concentrations of the substance, seems to be gelatin. Unfortunately gelatin is not a chemically defined product, and it is probably wise to be careful when changing from one gelatin to another. When expecting a large "consumption" of the substance, *e. g.* for a research project or for industrial control purposes, a comparatively large amount can be kept in stock, so that the same product is available for the whole investigation. The gelatin is preferably dried and grinded dry. After grinding the gelatin is thoroughly mixed. Before using a batch it might be tested to find the appropriate concentration at the highest amounts of formaldehyde expected.

In the following an investigation is described the purpose of which was to study the relationship between maximum suppression and formaldehyde and gelatin concentrations. The experiments were made in an open cell, *i. e.* dissolved oxygen was present, and at 25° C. The drop time of the mercury electrode was 3.4 sec. and the mercury flow 1.57 mg/sec. The supporting electrolyte was 0.10 M Li_2CO_3, pH 9.50. The investigation included 5 formaldehyde concentrations, covering the range 0.00—0.15 M. All chemicals were of A. R. quality, except for formaldehyde, which was a Merck product of high purity, only containing traces of methyl alcohol and formic acid.* The reference electrode was of the saturated calomel type.

In Fig. 2 the function $I_{max}/C_{(HCHO)a}$, where I_{max} = maximum current and $C_{(HCHO)a}$ = analytical formaldehyde concentration, is plotted as a function of the gelatin concentration in g/l. From this study we find the following:

1. Maxima are dependent on the formaldehyde concentration; increasing concentrations give rise to increased maxima.
2. A limiting gelatin concentration is present, *i. e.* at a concentration above this limit no maxima occur.
3. The limiting concentration is dependent on the amount of formaldehyde present, but to a comparatively low degree.

The findings 2 and 3 are in accordance with the idea that one kind of polarographic maximum suppression mechanism includes the adsorption of the maximum suppressor at the electrode surface (Heyrovsky [11]).

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* $< 2 \cdot 10^{-4}$ M at 380 g/l formaldehyde.

When gelatin is used in solutions containing formaldehyde, the possibility of reactions between these two components cannot be neglected. In order to find if a reaction occur when applying the conditions mentioned above, $I_{\max}/C_{(\mathrm{HCHO})\mathrm{a}}$ was measured in the supporting electrolyte in question and at a gelatin concentration of 0.20 g/l and a formaldehyde concentration of 0.15 M. The temperature was 25° C as before. During the 60 minutes studied no time dependence could be observed, *i. e.* no gelatin-formaldehyde reaction was found. It is probably necessary to apply the same test to every new batch of gelatin, since it cannot *a priori* be postulated that the results here obtained are valid for any type of gelatin.

From Fig. 2 it is seen that the limiting concentration of gelatin is of such an order that 0.12 g/l is sufficient in the here actual concentration range.

Smythe [4] reports that methylol urea acts as a maximum suppressor, however, preliminary experiments made by the present author gave the result that the limiting concentration of this suppressor was comparatively high: 2—3 g/l. Such a high concentration will decrease the accuracy at low formaldehyde concentration determinations too much, since the equilibrium formaldehyde concentration of methylol urea in such a case can exceed the amount to be determined. Thus, the use of monomethylol urea as a maximum suppressor cannot be recommended.

In Fig. 1, polarogram B is obtained by means of a supporting electrolyte comprising 0.10 M Li_2CO_3, pH 9.50, 0.12 g/l gelatin; the temperature was 25° C. The reaction mixture investigated was the same as that of curve A of the same figure. The result will clearly explain that the method is suitable also in more difficult cases.

Fig. 3 shows a calibration curve, *i. e.* the limiting current — formaldehyde concentration relationship; supporting electrolyte as above, drop time 3.4 sec. and flow of mercury 1.62 mg/sec. At high aldehyde concentrations the hydroxyl ion effect is present and the linearity lost. However, the linearity is good up to 0.06 M formaldehyde, but attention must be drawn to the fact that this concentration is not of a general significance, as it relates to the conditions of the capillary here used. This since the "diffusion layer" of hydroxyl ion neutralisation by the supporting electrolyte buffer substances and the corresponding layer of methylene glycol dehydration and formaldehyde reduction are entirely different. Thus, for each capillary the corresponding calibration curve has to be obtained experimentally. Theoretical calculations in this field seem to be very complicated.

For some of the formaldehyde concentrations in Fig. 3, four polarograms were recorded, 3, 6, 12 and 18 minutes from the moment when a 1.0 M formaldehyde stock solution and the supporting electrolyte were mixed. No influence of time could be found, *i. e.* the rate of depolymerisation of any formaldehyde polymers present was in this case sufficiently high to prevent any disturbances.

In order to investigate the role of continuing reaction and hydrolysis in the polarographic solution when the here studied supporting electrolyte is used, the following reactions were investigated by means of polarography: 4.0 M urea + 4.0 M formaldehyde, and 4.0 M urea + 8.0 M formaldehyde. The solutions were 0.1 M with respect to Na_2CO_3 and had a pH of 9.80. The

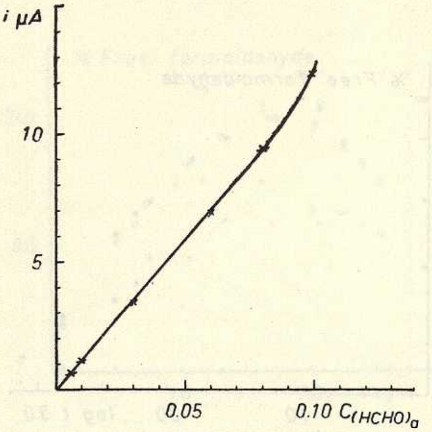

Fig. 3. A limiting current — formaldehyde concentration curve at 25° C. Supporting electrolyte: 0.10 M Li_2CO_3 + 0.12 g/l gelatin, pH 9.50.

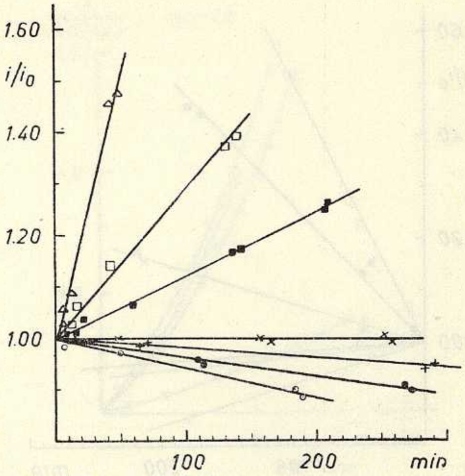

Fig. 4. Continuing reaction and hydrolysis effects in 0.10 M Li_2CO_3 + 0.12 g/l gelatin, pH 9.50. The temperature was 25° C and the dilution 1:100. Reaction solution: 4.0 M $CO(NH_2)_2$ + 4.0 M HCHO in 0.10 M Na_2CO_3, pH 9.80 and at 20° C. The curves are related to the following degree of reaction: 1 % (△), 26 % (□), 33 % (■), 52 % (×), 78 % (+), 86 % (●) and 94 % (○).

reaction temperature was 20° C. The polarography was carried out at 25° C and the dilution ratio was 1:100. These conditions seem to be "unfavourable" as regards the effects to be studied. The results obtained can be found in Figs. 4 and 5, where the ratio between the actual limiting current and the current extrapolated to zero time is plotted against the time from mixing the sample and the supporting electrolyte. For both reactions we find that in the beginning of the urea-formaldehyde reaction this reaction continues in the polarographic solution. However, during the later parts of the reaction, hydrolysis is the most important effect. The curves of the functions are approximately straight lines, and for accurate determinations the zero time extrapolation mentioned above can easily be applied. If the accuracy need is moderate — of the order 3 % — it is sufficient to record the polarograms within 5 minutes from mixing. It was further observed that within the limits of the linear part of the current-concentration curve, no influence of the dilution ratio (1:5—1:100) on the polarographic result was found. However, it must always be regarded that the dilution does not change the buffer concentration of the polarographic solution so much that the calibration curve becomes invalid. The effects here mentioned were also found when a supporting electrolyte in accordance with Smythe was used.

From this it is seen that the use of polarography in studies of the urea-formaldehyde reaction rates requires the consideration of a number of effects.

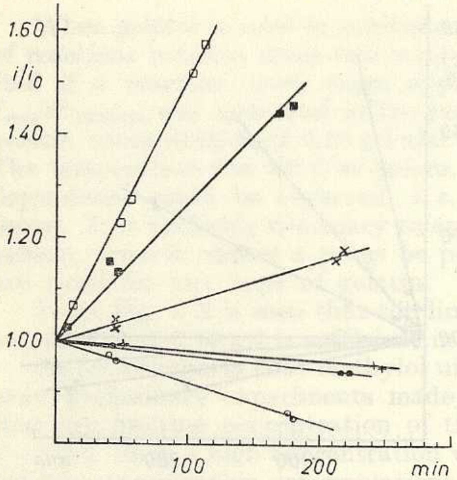

Fig. 5. Continuing reaction and hydrolysis effects in 0.10 M Li_2CO_3 *+ 0.12 g/l gelatin, pH 9.50. The temperature was 25° C and the dilution 1:100. Reaction solution: 4.0 M* $CO(NH_2)_2$ *+ 8.0 M HCHO in 0.10 M* Na_2CO_3*, pH 9.80 and at 20° C. The curves are related to the following degree of reaction: 10 % (□), 39 % (■), 70 % (×), 82 % (+) and 86 % (○).*

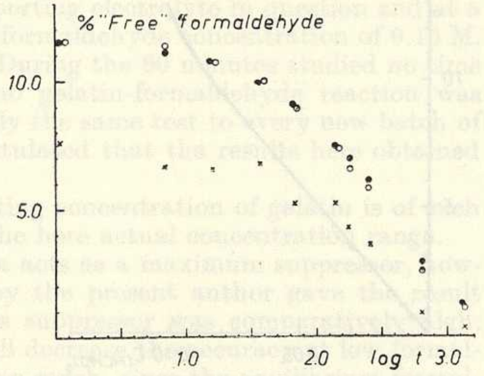

Fig. 6. Reaction between 3.92 M $CO(NH_2)_2$ *+ 3.92 M HCHO at 20° C in an unbuffered solution with the initial pH 8.0. Per cent "free" formaldehyde of the reaction solution was determined by means of: polarography (●), the sulfite method (○) and the hydroxylamine method (×).*

However, when such a consideration is given, the polarographic method offers several advantages, *e. g.* reliability, speed and accuracy.

In order to examine *the titration methods* previously applied (Smythe, Bettelheim and Cedvall) two experiments were carried out, involving the reaction between 3.92 M $CO(NH_2)_2$ + 3.92 M HCHO and 1.96 M $CO(NH_2)_2$ + 3.92 M HCHO at 20° C in unbuffered solutions with an initial pH of 8.0. These reactions were studied by means of: a) the polarographic method described in this paper, b) the hydroxylamine titration method, and c) the sulfite titration method.

The hydroxylamine titration method was applied as follows:

2 ml of the reaction mixture were measured by a pipet into a 100 ml Erlenmeyer flask, 10 ml distilled water added, 10 drops of bromophenol blue indicator, followed by 20 ml 10 % by weight hydroxylamine hydrochloride solution. (This represents 79 % hydroxylamine hydrochloride excess at the highest formaldehyde concentration.) Exactly 30 seconds from the midpoint of the time taken for the pipet to deliver 20 ml solution, the titration of the liberated hydrochloric acid with 0.5 M NaOH begun and was completed within 1 – 2 minutes. The endpoint was matched against a standard. (Smythe [1].)

The sulfite method was handled in accordance with the following description:

2 ml of the reaction mixture were measured by a pipet into a 100 ml Erlenmeyer flask, 10 ml distilled water and 5 drops of thymolphthalein indicator added, followed by 25 ml 15 % by weight (anhydrous) sodium sulfite solution. (This amount of sodium sulfite

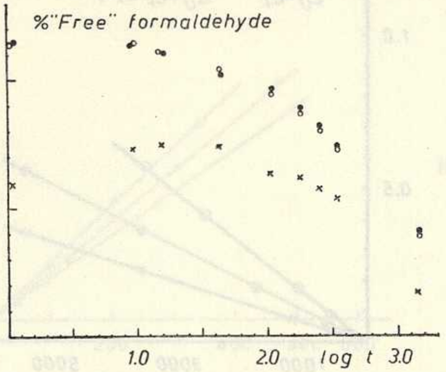

Fig. 7. *Reaction between 1.96 M* $CO(NH_2)_2$ *+ 3.92 M HCHO at 20° C in an unbuffered solution with the initial pH 8.0. Per cent "free" formaldehyde of the reaction solution was determined by means of: polarography (●), the sulfite method (○) and the hydroxylamine method (×).*

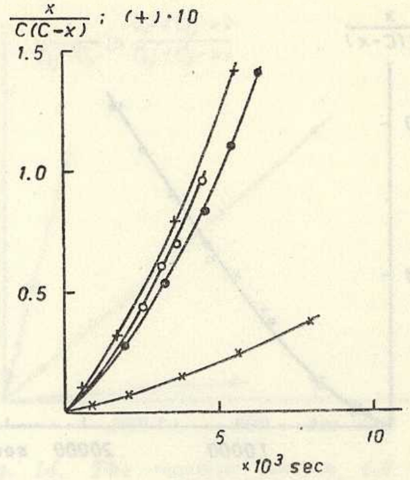

Fig. 8. The reaction between 4.0 M $CO(NH_2)_2$ *+ 4.0 M HCHO at 20° C in: an unbuffered solution, initial pH 6.70 (×); 0.10 M* KH_2PO_4*, pH 6.70 (●); 0.10 M borax, pH 9.20 (×) and 0.10 M* Na_2CO_3*, pH 9.80 (○).*

represents 87 % excess at the highest formaldehyde concentration.) The sulfite solution was neutralised against an indicator standard (pale blue), which also was used for the titration with 0.5 M HCl. The titration begun exactly 1 minute from the midpoint of the sulfite delivery.

The results of these comparative investigations are given in Figs. 6 and 7, where the amount of "free" formaldehyde of the reaction solution is plotted against the logarithm of the reaction time in minutes, as determined by means of the different analytical methods. From the results it is found that the agreement between the polarographic and the sulfite method is good. The hydroxylamine method, however, gives different results. The values obtained were generally too low; in the beginning of the reaction a figure about 35 % below the theoretical value was obtained. The influence of the time used for completing the titration, *i. e.* the time from the start of a titration 30 seconds after mixing and to a completed titration, is eludicated by the following experiment. A reaction sample containing 4.20 % "free" formaldehyde (polarography and sulfite method) was analysed by means of the hydroxylamine method as described above, 10 ml sample used, and the titration was completed at different time delays. The results were:

Titration time min.	% »free» formaldehyde obtained
0.5	3.49
1.0	4.12
1.5	4.50
2.0	4.74

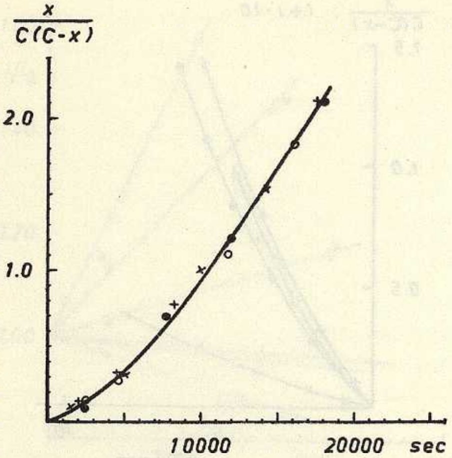

Fig. 9. The reaction in 0.05 M Li_2CO_3, pH 9.50 at 20° C between: 4.0 M $CO(NH_2)_2$ + 4.0 M HCHO (○), 2.0 M $CO(NH_2)_2$ + 2.0 M HCHO (●), 1.0 M $CO(NH_2)_2$ + 1.0 M HCHO (×) and 0.5 M $CO(NH_2)_2$ + 0.5 M HCHO (+).

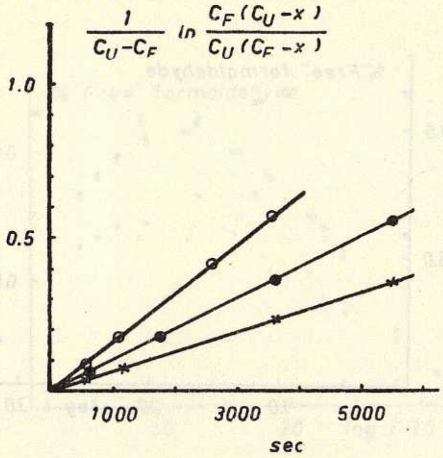

Fig. 10. The reaction between 4.0 M $CO(NH_2)_2$ + 0.4 M HCHO at 20° C, pH 6.70 and $C_{KH_2PO_4}$: 0.1 (○), 0.05 (●) and 0.025 (×).

From this it might be concluded that the time interval "1—2 minutes" is not defined sufficiently sharply when a high accuracy is needed.

The influence of the amount of reaction mixture sample used for the titrations can be found from the following data, obtained by analysing a reaction

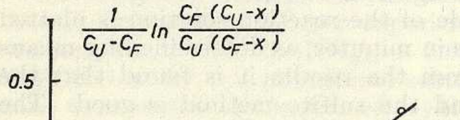

Fig. 11. The reaction between 4.0 M $CO(NH_2)_2$ + 0.4 M HCHO at 20° C, pH 9.20 and C_{borax}: 0.1 (○), 0.05 (●) and 0.025 (×).

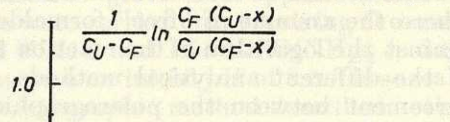

Fig. 12. The reaction between 4.0 M $CO(NH_2)_2$ + 0.4 M HCHO at 20° C, pH 10.00 and $C_{Na_2CO_3}$: 0.2 (○), 0.1 (●), 0.05 (×) and 0.025 (+).

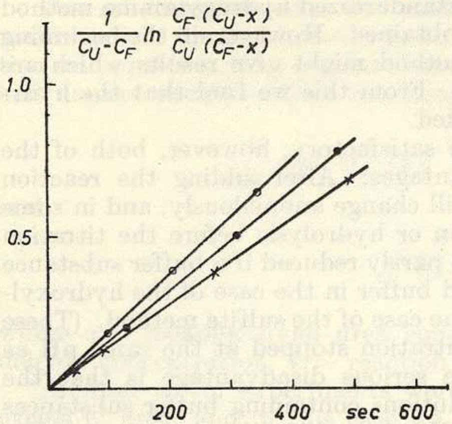

Fig. 13. The reaction between 4.0 M $CO(NH_2)_2$ *+ 0.4 M HCHO at 20° C, pH 11.5 and* $C_{Na_2CO_3}$: *0.2 (○), 0.1 (●) and 0.05 (×).*

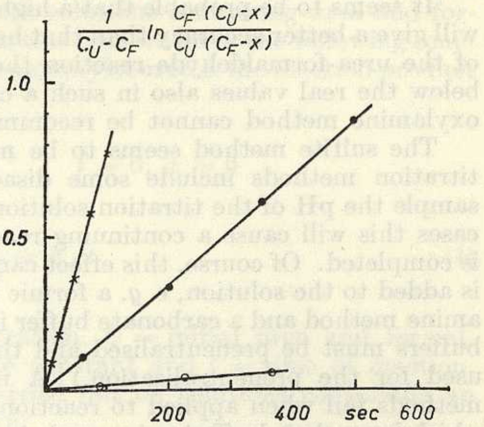

Fig. 14. The reaction between 4.0 M $CO(NH_2)_2$ *+ 0.4 M HCHO at 20° C and: 0.1 M* $Na_4P_2O_7$*, pH 8.50 (○); 0.1 M* Na_3PO_4*, pH 11.50 (●) and 0.1 M* Na_3PO_4*, pH 12.40 (×).*

solution containing 4.30 % "free" formaldehyde by means of the hydroxylamine method, titration time 1.5 minutes: 2 ml sample: 1.65 %, 5 ml sample: 2.97 % and 10 ml sample: 4.27 % "free" formaldehyde.

A similar experiment made by means of the sulfite method gave the results: 2 ml sample: 4.27 % and 5 ml sample: 4.33 % "free" formaldehyde. Within the practical limits of titration times no influence similar to that described for the hydroxylamine method could be found in this case.

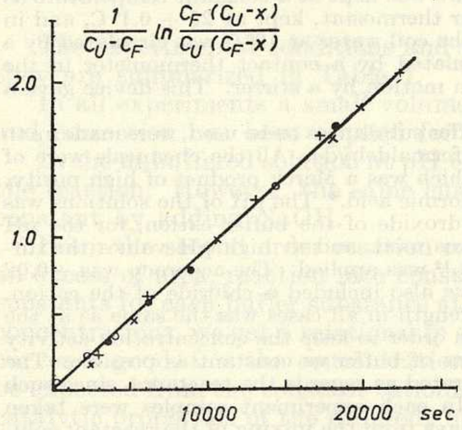

Fig. 15. The reaction in 0.05 M Li_2CO_3*, pH 9.50 at 20° C.* $C_{HCHO} = 0.10$ *and* $C_{CO(NH_2)_2}$: *4.0 (○), 2.0 (●), 1.0 (×) and 0.5 (+).*

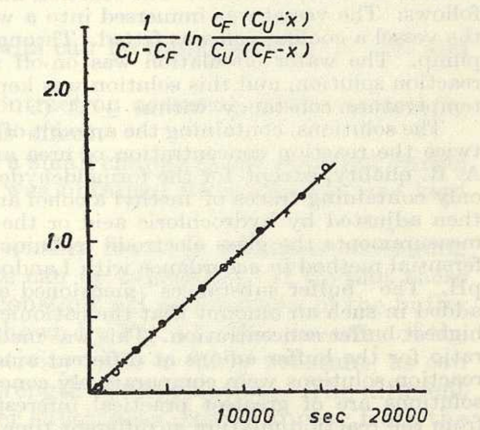

Fig. 16. The reaction in 0.05 M Li_2CO_3*, pH 9.50 at 20° C.* $C_{CO(NH_2)_2} = 4.0$ *and* C_{HCHO}: *0.50 (○), 0.25 (●), 0.10 (×) and 0.05 (+).*

It seems to be probable that a highly standardized hydroxylamine method will give a better accuracy than that here obtained. However, in the beginning of the urea-formaldehyde reaction the method might give results which are below the real values also in such a case. From this we find that the hydroxylamine method cannot be recommended.

The sulfite method seems to be more satisfactory; however, both of the titration methods include some disadvantages: After adding the reaction sample the pH of the titration solution will change anomalously, and in some cases this will cause a continuing reaction or hydrolysis before the titration is completed. Of course, this effect can be partly reduced if a buffer substance is added to the solution, *e. g.* a formic acid buffer in the case of the hydroxylamine method and a carbonate buffer in the case of the sulfite method. (These buffers must be preneutralised and the titration stopped at the same pH as used for the preneutralisation.) A more serious disadvantage is that the methods fail when applied to reaction solutions containing buffer substances which have their buffering intervals in a pH range where the titration must be completed. A simple oxidation method, applicable to the sulfite titration method, cannot easily be found, otherwise such a method would solve the problems in question. Another possibility would be the use of ion exchange resins for removing the buffer substances; such a method, however, seems to be comparatively slow.

Thus, when considering a general applicability, the polarographic method might be preferred.

EXPERIMENTAL STUDIES OF THE EQUIMOLECULAR UREA-FORMALDEHYDE REACTION IN NEUTRAL AND ALKALINE SOLUTIONS

The experiments were carried out in a closed flask or an open beaker at 20° C. At this temperature no difference could be found between the results obtained by means of a closed or an open vessel. The reaction mixture was kept at a constant temperature as follows: The vessel was immersed into a water thermostat, kept at 25 ± 0.1° C, and in the vessel a cooling coil was fitted. Through the coil water at 10° C was circulated by a pump. The water circulation was on-off regulated by a contact thermometer in the reaction solution, and this solution was kept in motion by a stirrer. This device gave a temperature constancy within ±0.1° C.

The solutions, containing the amount of buffer substances to be used, were made up to twice the reaction concentration of urea and formaldehyde. All the chemicals were of A. R. quality, except for the formaldehyde, which was a Merck product of high purity, only containing traces of methyl alcohol and formic acid.* The pH of the solutions was then adjusted by hydrochloric acid or the hydroxide of the buffer cation; for the pH measurements the glass electrode technique was used, and at high pH values the differential method in accordance with Landqvist [12] was applied. The accuracy was ±0.02 pH. The "buffer substances" mentioned above also included a chloride of the cation, added in such an amount that the cationic strength in all cases was the same as at the highest buffer concentration. This was made in order to keep the concentration-activity ratio for the buffer anions at different amounts of buffer as constant as possible. The reaction solutions were comparatively concentrated as regards the reactants, since such solutions are of greatest practical interest. In each experiment samples were taken from the reaction mixture at different time delays from the mixing of the reactant solutions, the pH constancy checked (no differences found) and the "free" formaldehyde content determined polarographically by means of the method previously described.

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* $< 2.10^{-4}$ M at 350 g/l formaldehyde.

One set of experiments was made with solutions containing urea and formaldehyde in the molecular ratio 1:1. In this case we have the following reaction rate equation, if we assume that monomethylol urea is the reaction product and neglect the hydrolysis reaction:

$$\frac{\mathrm{d}t}{\mathrm{d}x} = k\ (C - x)^2 \qquad\qquad t = 0,\ x = 0$$

and

$$\frac{x}{C\ (C - x)} = k \cdot t \tag{1}$$

where x = monomethylol urea concentration, C = initial urea and formaldehyde concentration, k = reaction rate constant and t = time of reaction.

Another set of experiments were carried out on solutions containing an excess of urea, and in this case we have:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\ (C_{\mathrm{U}} - x) \cdot (C_{\mathrm{F}} - x)$$

where C_{U} = initial urea concentration and C_{F} = initial formaldehyde concentration.

From this we obtain:

$$\frac{1}{C_{\mathrm{U}} - C_{\mathrm{F}}} \cdot \ln \frac{C_{\mathrm{F}}\ (C_{\mathrm{U}} - x)}{C_{\mathrm{U}}\ (C_{\mathrm{F}} - x)} = k \cdot t \tag{2}$$

or, when $C_{\mathrm{F}} \ll C_{\mathrm{U}}$:

$$\frac{1}{C_{\mathrm{U}}} \cdot \ln \frac{C_{\mathrm{F}}}{C_{\mathrm{F}} - x} = k \cdot t \tag{2a}$$

The experimental conditions and results can be found in Figs. 8—16, and they are summarized in Table 1.

In all experiments a small volume contraction occurred, of the order 1 %, and correction has been applied for this effect.

In the unbuffered solution at pH 6.70 a small change in pH occurred during the reaction. However, the same curve was obtained when the pH was kept constant by adding NaOH.

From the second order reaction relationship found in solutions containing an excess of urea, reaction rate constants can be calculated. If we plot these constants for each buffer substance at a constant pH as functions of the buffer concentrations, we get a relationship as shown by Fig. 17. The linearity of the curves is good, *i. e.* the concentration-activity ratio is fairly constant, as can be expected from the constant cationic strength of the solutions. The different catalytic properties of the different buffer substances clearly appear from the diagram. If the curves of Fig. 17 are extrapolated to zero buffer concentration, the sum of the "zero reaction rate" and the hydroxyl ion catalytic contribution, k_0, can be calculated. The relation between the logarithm of k_0 and pH is shown in Fig. 18.

Table 1. Experimental data of the equimolecular urea-formaldehyde reaction in neutral and alkaline solutions at 20° C.

Fig.	$C_{CO(NH_2)_2}$	C_{HCHO}	Buffer substance	C_{buffer}	pH	Reaction order	$k \cdot 10^3$
8	4.00	4.00	—	—	6.70 *	—	—
8	4.00	4.00	KH_2PO_4	0.100	6.70	—	—
8	4.00	4.00	borax	0.100	9.20	—	—
8	4.00	4.00	Na_2CO_3	0.100	9.80	—	—
9	4.00	4.00	Li_2CO_3	0.050	9.50	—	—
9	2.00	2.00	Li_2CO_3	0.050	9.50	—	—
9	1.00	1.00	Li_2CO_3	0.050	9.50	—	—
9	0.50	0.50	Li_2CO_3	0.050	9.50	—	—
10	4.00	0.40	KH_2PO_4	0.100	6.70	2	0.16
10	4.00	0.40	KH_2PO_4	0.050	6.70	2	0.10
10	4.00	0.40	KH_2PO_4	0.025	6.70	2	0.065
11	4.00	0.40	borax	0.100	9.20	2	0.080
11	4.00	0.40	borax	0.050	9.20	2	0.060
11	4.00	0.40	borax	0.025	9.20	2	0.052
12	4.00	0.40	Na_2CO_3	0.200	10.00	2	0.34
12	4.00	0.40	Na_2CO_3	0.100	10.00	2	0.20
12	4.00	0.40	Na_2CO_3	0.050	10.00	2	0.12
12	4.00	0.40	Na_2CO_3	0.025	10.00	2	0.10
13	4.00	0.40	Na_2CO_3	0.200	11.50	2	1.9
13	4.00	0.40	Na_2CO_3	0.100	11.50	2	1.6
13	4.00	0.40	Na_2CO_3	0.050	11.50	2	1.4
14	4.00	0.40	$Na_4P_2O_7$	0.100	8.50	2	0.13
14	4.00	0.40	Na_3PO_4	0.100	11.50	2	1.6
14	4.00	0.40	Na_3PO_4	0.100	12.40	2	7.5
15	4.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
15	2.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
15	1.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
15	0.50	0.10	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.50	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.25	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.10	Li_2CO_3	0.050	9.50	2	0.091
16	4.00	0.05	Li_2CO_3	0.050	9.50	2	0.091

* initial pH; final pH was 6.50.

From these experiments the following conclusions might be drawn:

1. The polarographic and the sulfite method for formaldehyde determinations in urea-formaldehyde reaction solutions give similar results (Figs. 6 and 7).
2. The hydroxylamine method gives, especially in the beginning of the urea-formaldehyde reaction, too low formaldehyde concentration values (Figs. 6 and 7).
3. The accuracy of the hydroxylamine method seems to be moderate (Figs. 6 and 7).

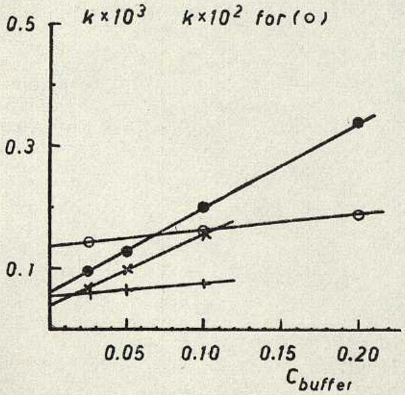

Fig. 17. Relationsship between the reaction rate constant of 4.0 M $CO(NH_2)_2$ *+ 0.4 M HCHO at 20° C and the buffer substance concentrations:* Na_2CO_3, *pH 11.5 (○),* Na_2CO_3, *pH 10.0 (●), borax, pH 9.2 (+) and* KH_2PO_4, *pH 6.7 (×).*

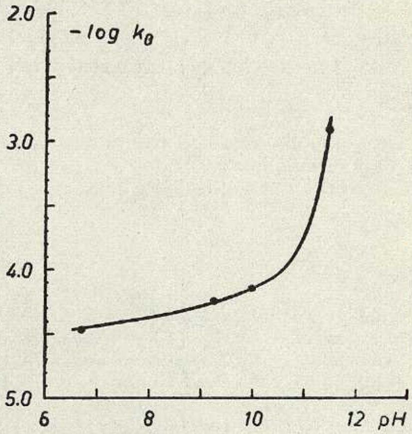

Fig. 18. Relationship between the logarithm of the reaction rate constant at zero buffer concentration and pH for the reaction 4.0 M $CO(NH_2)_2$ *+ 0.4 M HCHO at 20° C.*

4. When applying the polarographic method, continuing reaction and hydrolysis effects in the polarographic solution must be considered (Figs. 4 and 5).

5. In an unbuffered solution, 4.0 M $CO(NH_2)_2$ + 4.0 M HCHO, initial pH 6.70 and at 20° C, no rapid initial reaction can be found. No theoretically significant reaction order is present; the order is approximately 1.6. (A number of repeated experiments of this kind, at different concentrations of the reactants and different initial pH, and also such carried out with the pH of the reaction solution kept constant, gave the same result.) (Fig. 8).

6. In buffered solutions and a urea-formaldehyde ratio of 1:1 at 20° C no theoretically significant reaction order is present and no initial reaction observed. The reaction order is approximately 1.6 (Fig. 8).

7. At the urea-formaldehyde ratio 1:1, in buffered solutions at 20° C, no obvious concentration dependence of the reaction rate can be seen (Fig. 9).

8. In buffered solutions containing 4.0 M $CO(NH_2)_2$ + 0.4 M HCHO a second order reaction occurs (Figs. 10—14).

9. The rate of the second order reaction in solutions containing an excess of urea is not obviously dependent on this excess or the concentration of the reactants. (At a low urea-formaldehyde ratio, 5:1, small deviations from linearity are present, showing a tendency to a non-linear relationship.) (Figs. 15 and 16).

10. The urea-formaldehyde reaction at 20° C in solutions containing an excess of urea is subject to an *acid-base catalysis*. Different acid and base ions show different catalysing power. An extremely small effect is present in the

case of borate ions (Fig. 17). The same effects were observed at a urea-formaldehyde ratio of 1:1.

11. The hydroxyl ion catalytic effect is not a simple function of the activity of this ion (Fig. 18).

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REFERENCES

1. Smythe, L. *J. Phys. Colloid Chem.* **51** (1947) 369.
2. Smythe, L. *J. Am. Chem. Soc.* **73** (1951) 2735.
3. Smythe, L. *J. Am. Chem. Soc.* **74** (1952) 2713.
4. Smythe, L. *J. Am. Chem. Soc.* **75** (1953) 574.
5. Crowe, G. and Lynch, C. *J. Am. Chem. Soc.* **70** (1948) 3795.
6. Crowe, G. and Lynch, C. *J. Am. Chem. Soc.* **71** (1949) 3731.
7. Bettelheim, L. and Cedvall, J. *Svensk Kem. Tidskr.* **60** (1948) 208.
8. De'Jong, J. *Rec. trav. chim.* **69** (1950) 1566.
9. Bieber, R. and Trümpler, G. *Helv. Chim. Acta* **30** (1947) 704.
10. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 595.
11. Heyrovský, J. *Polarographie*, Springer, Berlin 1941, p. 171.
12. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 867.

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

II. Experimental Studies of the Rates of the Equimolecular Reaction between Monomethylol Urea and Formaldehyde

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The paper includes the results of experimental studies at 20° C of the reaction between monomethylol urea and formaldehyde in comparatively concentrated solutions. The relationship between the amount of dimethylol urea produced by the reaction and the reaction time cannot be described by a simple second order reaction rate equation. However, an equation deduced with regard to the influence of dimethylol urea hydrolysis is in agreement with experimental results. The reaction is found to be subject to an acid-base catalysis, but the hydroxyl ion contribution to this catalysis is not a simple function of the hydroxyl ion activity. The influence of the concentration of the reactants on the reaction rate constants was found to be small.

A study of the rates of the reaction between monomethylol urea and formaldehyde,

$$H_2N \cdot CO \cdot NH \cdot CH_2OH + HCHO = HOCH_2 \cdot NH \cdot CO \cdot NH \cdot CH_2OH$$

is due to Květoň and Králová [1]. In their investigations they used the hydroxylamine method for determining the amount of "free" formaldehyde of the reaction solutions. Since they found that this method, as it was described by Smythe [2], gives too low formaldehyde concentration data, the method was somewhat modified and highly standardized. The authors report an accuracy of ± 5% when the hydroxylamine method is used as they recommend. (However, the results obtained by Landqvist [3] in a critical analysis of some of the methods suitable for formaldehyde determinations in urea-formaldehyde reaction solutions, and the appearence of an initial rapid reaction in the experiments, as carried out by Květoň and Králová, gives the impression that ± 5 % might be a too optimistic figure when the modified method is more generally applied.)

According to Květoň and Králová, the accuracy is moderate if the later part of a reaction between urea and formaldehyde at a molar ratio of 1:2 is used for an investigation of the reaction between monomethylol urea and formaldehyde. Thus, these authors also studied the reaction rates when starting from these latter compounds in 1 M solutions. In order to examine the influence of pH on the reaction rates, experiments were made at different pH in citric and boric acid buffers. (Corrections applied for the influence of the buffer substances on the results of the hydroxylamine titrations?) A minimum reaction rate was found at pH 6.5. All reaction rates were calculated by means of an equation corresponding to a second order reaction, and no regard was given to the influence of hydrolysis effects. Except for a rapid initial stage, the reactions were found to be of second order. However, only the middle part of the reaction was used for calculations, and when examining the rate constant data at long reaction times, deviations are found to be present. (Table 2 in the paper by Květoň and Králová.) Finally, an activation energy of 12.2 kcal was determined.

In the following the results of some experiments on the equimolecular reaction between monomethylol urea and formaldehyde are given. The purpose of these experiments has been to investigate the influence of pH and buffer substances on the reaction rates and the effect of the concentration of the reactants. A reaction rate equation will be deduced, with regard to the dimethylol urea hydrolysis.

The experimental technique was the same as previously described by Landqvist [3]. Monomethylol urea was prepared in accordance with Walter and Gewing [4]. The cryoscopic molecular weight of this monomethylol urea was 90 ± 2. The monomethylol urea was dissolved in cold water and the cryoscopic measurements made immediately in order to prevent hydrolysis effects. All experiments were carried out at 20 ± 0.1 ° C and all chemicals were of A. R. quality, except for the formaldehyde, which was a Merck product of high purity, only containing traces* of formic acid and methyl alcohol.

The dry methylol urea was added to a solution containing formaldehyde and the buffer substances at the pH wanted. (The pH was then re-checked during the reaction, and no changes found, except for an experiment on an unbuffered solution, initial pH 6.70.) The addition of solid monomethylol urea was made in order to prevent any undesirable hydrolysis effects. The substance was brought into the solution and dissolved within 30—60 seconds; the reaction time was calculated from the midpoint of the time needed for complete dissolution. The maximum concentration used was 1 M, since the solubility of dimethylol urea is moderate.

When neglecting the hydrolysis of methylol ureas, we obtain the following reaction rate equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1 \cdot (C - x)^2 \qquad t = 0,\ x = 0 \tag{1}$$

i. e.

$$\frac{x}{C \cdot (C - x)} = k_1 \cdot t \tag{2}$$

---

* $< 2 \times 10^{-4}$ M at 380 g/l formaldehyde.

where x = concentration of dimethylol urea, C = initial concentration of the reactants, t = time of reaction and k_1 = reaction rate constant.

However, when regarding the hydrolysis of dimethylol urea, but still neglecting that of monomethylol urea, we find:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1 \cdot (C - x)^2 - k_2 \cdot x \qquad t = 0,\ x = 0 \tag{3}$$

where k_2 = the rate constant of the dimethylol urea hydrolysis.
We write

$$k_2/k_1 = \sigma, \text{ i. e. the equilibrium constant.}$$

Since at equilibrium $\mathrm{d}\,x/\mathrm{d}\,t = 0$, we have:

$$\sigma = \frac{k_2}{k_1} = \lim_{t \to \infty} \frac{(C - x)^2}{x} \tag{4}$$

Under these conditions we obtain the following solution to eqn. (3)

$$k_1 \cdot t = \varphi = \frac{1}{\sqrt{4 \cdot C \cdot \sigma + \sigma^2}} \ln \frac{1 - 2 \cdot x/(2 \cdot C + \sigma + \sqrt{4 \cdot C \cdot \sigma + \sigma^2})}{1 - 2 \cdot x/(2 \cdot C + \sigma - \sqrt{4 \cdot C \cdot \sigma + \sigma^2})} \tag{5}$$

In each experiment the equilibrium constant was determined by extrapolation of the amount of "free" formaldehyde of the reaction solution to infinity reaction time.

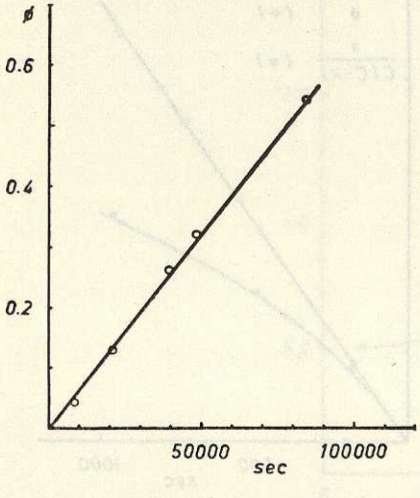

Fig. 1. Reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C in an unbuffered solution, initial pH 6.70.

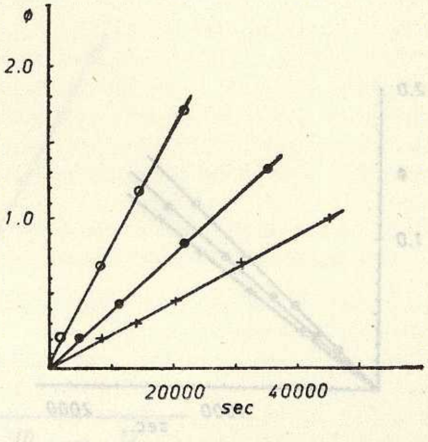

Fig. 2. Reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C and pH 6.70 at $C_{KH_2PO_4}$: 0.1 (○), 0.05 (●) and 0.025 (+).

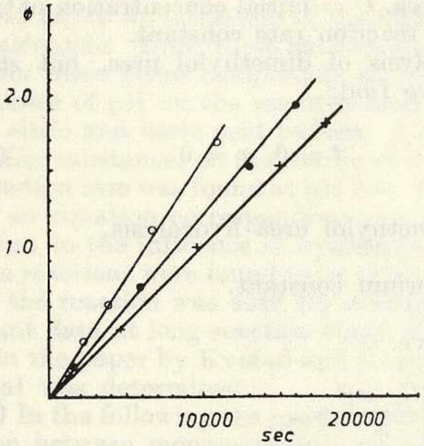

Fig. 3. Reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C and pH 9.20 at C_{borax} : 0.1 (○), 0.05 (●) and 0.025 (+).

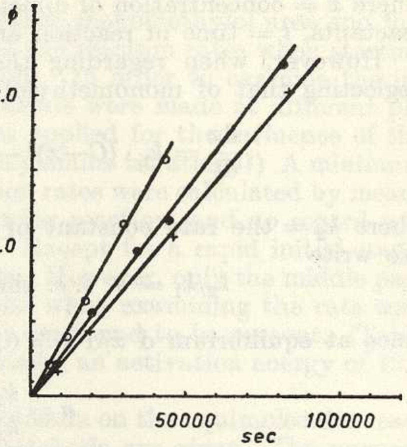

Fig. 4. Reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C and pH 10.00 at $C_{Na_2CO_3}$: 0.1 (○), 0.05 (●) and 0.025 (+).

In Figs. 1—7 the function (5) is plotted from experimental data, and in the case of Fig. 6 a comparison is also made to eqn. (2). In this investigation the reactions were continued much longer than was made by Květoň and Králová, since the later part of the reaction is of great practical interest. The composi-

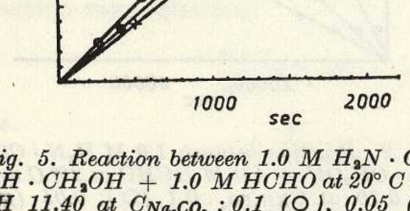

Fig. 5. Reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C and pH 11.40 at $C_{Na_2CO_3}$: 0.1 (○), 0.05 (●) and 0.025 (+).

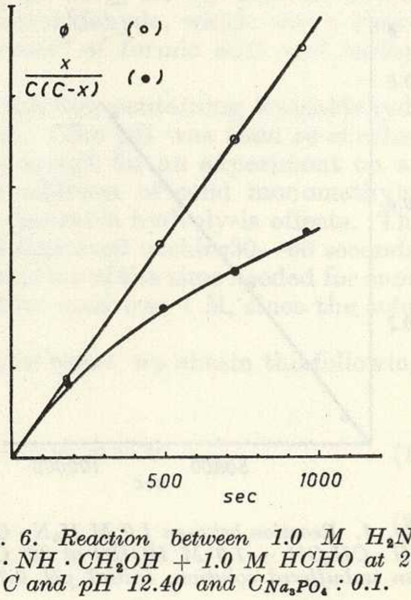

Fig. 6. Reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C and pH 12.40 and $C_{Na_3PO_4}$: 0.1.

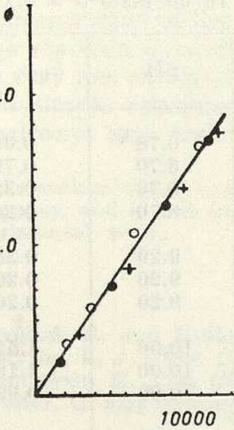

Fig. 7. *Reaction at 20° C, pH 10.00 and $C_{Na_2CO_3}$ 0.1 between $H_2N \cdot CO \cdot NH \cdot CH_2OH$ and HCHO at the concentrations: 1.0 (○), 0.5 (●) and 0.25 (+).*

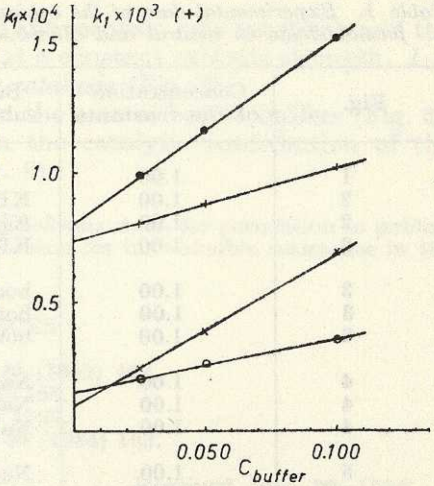

Fig. 8. *Relationship between the reaction rate constant of 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C and the buffer substance concentrations: KH_2PO_4, pH 6.70 (×); borax, pH 9.20 (○); Na_2CO_3, pH 10.00 (●); Na_2CO_3, pH 11.50 (+).*

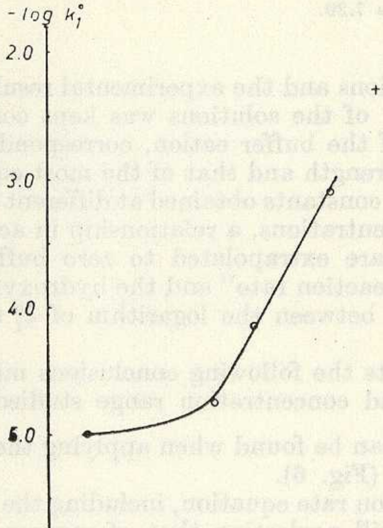

Fig. 9. *Relationship between the logarithm of the reaction rate constant extrapolated to zero buffer concentration and pH for the reaction between 1.0 M $H_2N \cdot CO \cdot NH \cdot CH_2OH$ + 1.0 M HCHO at 20° C. (+) refers to 0.1 M Na_3PO_4 pH 12.40.*

Table 1. Experimental data of the equimolecular reaction between monomethylol urea and formaldehyde in neutral and alkaline solutions at 20° C. In all cases $\sigma = 0.11$.

Fig.	Concentration of the reactants	Buffer substance	C_{buffer}	pH	$k_1 \times 10^4$
1	1.00	—	—	6.70 *	0.064
2	1.00	KH_2PO_4	0.100	6.70	0.79
2	1.00	KH_2PO_4	0.050	6.70	0.38
2	1.00	KH_2PO_4	0.025	6.70	0.24
3	1.00	borax	0.100	9.20	0.35
3	1.00	borax	0.050	9.20	0.26
3	1.00	borax	0.025	9.20	0.20
4	1.00	Na_2CO_3	0.100	10.00	1.52
4	1.00	Na_2CO_3	0.050	10.00	1.16
4	1.00	Na_2CO_3	0.025	10.00	0.99
5	1.00	Na_2CO_3	0.100	11.50	10.2
5	1.00	Na_2CO_3	0.050	11.50	8.7
5	1.00	Na_2CO_3	0.025	11.50	8.0
6	1.00	Na_3PO_4	0.100	12.40	48
7	1.00	Na_2CO_3	0.100	10.00	1.5
7	0.50	Na_2CO_3	0.100	10.00	
7	0.25	Na_2CO_3	0.100	10.00	

* Initial pH; final pH was 7.20.

tions of the reaction solutions and the experimental results are given in Table 1. (The cationic strength of the solutions was kept constant by adding an amount of the chloride of the buffer cation, corresponding to the difference between actual cationic strength and that of the most concentrated solution.)

When plotting the rate constants obtained at different buffer concentrations as functions of these concentrations, a relationship in accordance with Fig. 8 is found. If the curves are extrapolated to zero buffer concentration we get the sum of the "zero reaction rate" and the hydroxyl ion catalytic contribution: k_1^0. The relation between the logarithm of k_1^0 and pH is shown by Fig. 9.

From these experiments the following conclusions might be drawn, as regards the temperature and concentration range studied:

1. No linear relationship can be found when applying the simple second order reaction rate equation (Fig. 6).
2. When applying a reaction rate equation, including the regard of dimethylol urea hydrolysis, but still neglecting that of monomethylol urea, a good linearity is obtained (Figs. 1—7).
3. No rapid initial reaction can be found (Figs. 1—7).
4. The concentration of the reactants do not affect the reaction rate constants to any considerable extent (Fig. 7).

5. A linear relationship is present between the reaction rate constants and the concentration of the buffer substances at a constant cationic strength. *I. e.* the reaction is subject to an *acid-base catalysis* (Fig. 8).
6. A very low catalytic effect is present in the case of borate buffers (Fig. 3).
7. No simple relationship exists between the catalytic contribution of the hydroxyl ions and their activity (Fig. 9).

The author wishes to thank the board of *Rydboholms A. B.* for permission to publish this paper, and is also indebted to Mr. G. Johanson for his valuable assistance in the experimental work.

REFERENCES

1. Květoň, R. and Králová, M. *Chem. Listy* **46** (1952) 403.
2. Smythe, L. *J. Phys. Colloid Chem.* **51** (1947) 369.
3. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1127.
4. Walter, G. and Gewing, M. *Kolloid-Beihefte* **34** (1934) 163.

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

III. Experimental Studies of the Rates of Hydrolysis of Monomethylol Urea

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

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III. Experimental Studies of the Rates of Hydrolysis of Monomethylol Urea

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

The rates of monomethylol urea hydrolysis at 20° C are investigated. The reaction cannot be described by a simple first order reaction rate equation, and the rate constants were determined by means of an extrapolation method applied to the first order equation relationship.

The hydrolysis is found to be subject to an acid-base catalysis, but the hydroxyl ion contribution is no simple function of the hydroxyl ion activity. The influence of the concentration of the reactants on the reaction rate constants is found to be small.

The rate of the hydrolysis of monomethylol urea:

$$H_2N-CO-NH-CH_2OH = H_2N-CO-NH_2 + HCHO$$

was studied by Crowe and Lynch [1]. The amount of liberated formaldehyde was determined by means of polarography directly in the reaction solutions. The experiment only included the hydrolysis of 0.00344 M monomethylol urea in 0.05 M LiOH; the reaction was studied by adding a monomethylol urea stock solution to an equal amount of 0.10 M LiOH. The time elapsed between the preparation of the stock solution and the addition to LiOH is not mentioned; thus it is not known if the hydrolysis occurring in the stock solution was controlled. No linear relationship was found when applying a first order reaction rate equation, but from the slope of the curve at zero reaction time, the constant was calculated.

From comparisons made between the hydrolysis rate constant obtained by this experiment and the corresponding constant of the equimolecular reaction between urea and formaldehyde an equilibrium constant of 20.5 was calculated by these authors. The equilibrium constant found from the latter of the reactions, extrapolated to infinite reaction time, was of the order 26. All data refer to 0.05 M LiOH.

The purpose of the following study is to investigate the rate of hydrolysis of monomethylol urea in comparatively concentrated solutions at 20° C with regard to the influence of pH, buffer and monomethylol urea concentration.

The experimental technique was the same as previously described (Landqvist[2]). The monomethylol urea was prepared in accordance with Walter and Gewing[3]. The cryoscopic molecular weight was found to be 90 ± 2. All hydrolysis experiments were carried out at $20 \pm 0.1°$ C, and all chemicals used were of A. R. quality. Dry monomethylol urea was added to a solution containing the buffer substances at the pH wanted and, if occurring, the very small change in pH was quickly adjusted. (The pH was re-checked during the reaction, and no changes observed, except for a reaction in an unbuffered solution with an initial pH of 6.70.) Solid monomethylol urea was added in order to prevent any influence of hydrolysis before mixing, *i. e.* in order to obtain a real zero reaction time. This time was calculated from the midpoint of the time needed for dissolving the monomethylol urea, which was of the order 30—60 seconds, since the maximum concentration of monomethylol urea was ≤ 1.0 M.

When neglecting the reaction between the hydrolysis products and a reaction between monomethylol urea and liberated formaldehyde producing dimethylol urea, we find the following reaction rate equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k' (C_0 - x) \qquad t = 0,\ x = 0 \tag{1}$$

and

$$\ln \frac{C_0}{C_0 - x} = k'\ t \tag{2}$$

where x = the concentration of urea or formaldehyde, C_0 = initial concentration of monomethylol urea, t = time of reaction and k' = the rate constant of monomethylol urea hydrolysis.

If $x \ll C_0$ we obtain:

$$\frac{x}{C_0} = k'\ \mathrm{t} \tag{3}$$

A complete reaction rate equation requires the consideration of all the factors mentioned above. Since the rates of dimethylol urea hydrolysis are unknown, the general case cannot easily be treated. However, the rate constants can, as previously mentioned, be determined from the slope of the function (2) at zero reaction time. This method does not permit a high degree of accuracy. If the slopes of the function (2), when plotted from experimental data, were determined graphically and then plotted as functions of reaction time logarithmically, it was found that

$$\sqrt{\frac{1}{\mathrm{d}\ \ln\ [C_0/(C_0 - x)]/\mathrm{d}t}} = f(t) \tag{4}$$

is a suitable function for linear extrapolations to zero reaction time in the present case. By applying this method, a better accuracy could be obtained.

Table 1. Experimental data of the hydrolysis of monomethylol urea in neutral and alkaline solutions at 20° C.

$C_{\mathrm{H_2N.CO.NH.CH_2OH}}$	Buffer substance [1]	C_{buffer}	pH	$k' \times 10^5$	$\frac{k'}{k}$ from reaction rate data
1.00	—	—	6.70 [2]	0.057	—
1.00	KH_2PO_4	0.100	6.70	0.60	0.037
1.00	KH_2PO_4	0.050	6.70	0.35	0.035
1.00	KH_2PO_4	0.025	6.70	0.22	0.034
1.00	borax	0.100	9.20	0.30	0.037
1.00	borax	0.050	9.20	0.23	0.038
1.00	borax	0.025	9.20	0.19	0.037
1.00	Na_2CO_3	0.100	10.00	0.76	0.040
1.00	Na_2CO_3	0.050	10.00	0.46	0.041
1.00	Na_2CO_3	0.025	10.00	0.35	0.035
0.50	Na_2CO_3	0.100	10.00	0.77	—
0.25	Na_2CO_3	0.100	10.00	0.77	—
1.00	Na_2CO_3	0.100	11.50	6.6	0.036
1.00	Na_2CO_3	0.050	11.50	5.8	0.036
1.00	Na_2CO_3	0.025	11.50	5.2	0.037
					Av. 0.037

[1] In all cases such amounts of a chloride of the buffer cation were added that a cationic strength corresponding to that of the most concentrated solution was obtained.

[2] Initial pH; the final pH was 7.05.

The compositions of the reaction solutions and the experimental results are given in Table 1. In this table the equilibrium constants, as calculated from the figures here obtained and the corresponding constants of the equimolecular reaction between urea and formaldehyde (Landqvist [2]), can also be found. (These data are the inverse of the figures given by Crowe and Lynch [1].) No influence of pH and the catalytic properties of the reaction solution on the equilibrium constants can be observed.

No experimental equilibrium constants have been determined, since they cannot be assumed to be similar to the constants calculated from the reaction rates. All the reactions previously mentioned might be included in the experimental equilibrium. When regarding the hydrolysis of monomethylol urea and the reaction between the liberated urea and formaldehyde, we have:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = k' \ (C_0 — F) — k \ F^2 \tag{5}$$

where F = the concentration of liberated formaldehyde, k = the urea-formaldehyde reaction rate constant when the reaction product is monomethylol urea. Thus, at equilibrium we obtain:

$$k'/k = F_{\infty}^2/(C_0 — F_{\infty}) \tag{6}$$

where F_{∞} = the amount of free formaldehyde at equilibrium.

During the hydrolysis the amount of free formaldehyde reaches a maximum and then decreases asymptotically; the change is very small and is probably

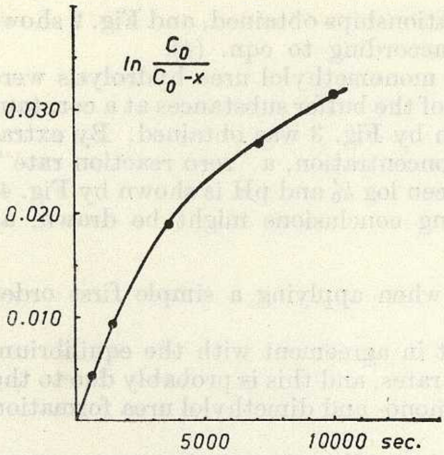

Fig. 1. The eqn. (2) relationship of the hydrolysis of 1.0 M monomethylol urea in 0.100 M Na_2CO_3*, pH 10.00, 20° C.*

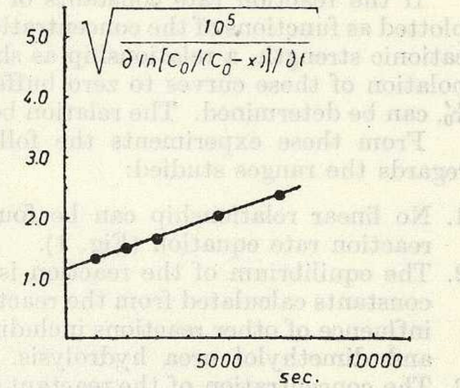

Fig. 2. The extrapolation method applied to the curve of Fig. 1.

due to dimethylol urea and urea-formaldehyde reactions. However, the amount of free formaldehyde at maximum was only about 1/4 of the amount calculated from eqn. (6) and no linear relationship was found when applying the solution to eqn. (5) to experimental data. Such results are to be expected from the previous discussion.

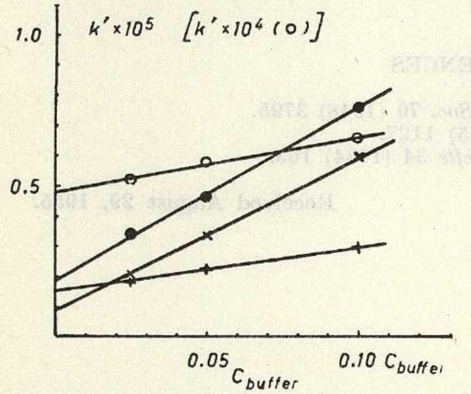

Fig. 3. Relationship between the reaction rate constants of the hydrolysis of 1.0 M monomethylol urea and the concentrations of the buffer substances at 20° C. KH_2PO_4*, pH 6.70 (×); borax, pH 9.20 (+);* Na_2CO_3*, pH 10.00 (●) and* Na_2CO_3*, pH 11.50 (○).*

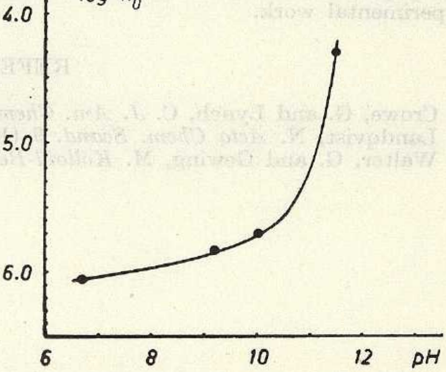

Fig. 4. Relationship between the logarithm of the reaction rate constant, extrapolated to zero buffer concentration, and pH for the hydrolysis of 1.0 M monomethylol urea at 20° C.

Fig. 1 is an example of the eqn. (2) relationships obtained, and Fig. 2 shows the corresponding extrapolation curve according to eqn. (4).

If the reaction rate constants of the monomethylol urea hydrolysis were plotted as functions of the concentrations of the buffer substances at a constant cationic strength, a relationship as shown by Fig. 3 was obtained. By extrapolation of these curves to zero buffer concentration, a "zero reaction rate", k_0', can be determined. The relation between log k_0' and pH is shown by Fig. 4.

From these experiments the following conclusions might be drawn, as regards the ranges studied:

1. No linear relationship can be found when applying a simple first order reaction rate equation (Fig. 1).
2. The equilibrium of the reaction is not in agreement with the equilibrium constants calculated from the reaction rates, and this is probably due to the influence of other reactions including mono- and dimethylol urea formation and dimethylol urea hydrolysis.
3. The concentration of the reactant does not affect the reaction rate constant to any considerable extent (Table 1).
4. A linear relationship is present between the reaction rate constants and the concentration of the buffer substances at a constant cationic strength, *i. e.* the reaction is subject to an *acid-base catalysis* (Fig. 3).
5. A very low catalytic effect is present in the case of borate buffers (Table 1).
6. The equilibrium constant, as calculated from the reaction rates, of the reaction between urea and formaldehyde producing monomethylol urea, is 0.037 (Table 1).
7. No pH dependence of the equilibrium constant seems to be present.

The author wishes to thank the board of *Rydboholms A.B.* for permission to publish this paper, and is also indebted to Mr. G. Johansson for his valuable assistance in the experimental work.

REFERENCES

1. Crowe, G. and Lynch, C. *J. Am. Chem. Soc.* **70** (1948) 3795.
2. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1127.
3. Walter, G. and Gewing, M. *Kolloid-Beihefte* **34** (1934) 163.

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

IV. Experimental Studies of the Rates of Hydrolysis of Dimethylol Urea

NILS LANDQVIST

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The rate of hydrolysis of dimethylol urea at 20° C was studied. The reaction cannot be described by a simple first order reaction rate equation, but an equation deduced with regard to the reaction between monomethylol urea and formaldehyde is in agreement with experimental data.

The reaction is found to be subject to an acid-base catalysis, but the hydroxyl ion contribution to the catalysis is not a simple function of the hydroxyl ion activity. The influence of the concentration of the reactants on the reaction rate constants is found to be small. The equilibrium constant of the reaction between monomethylol urea and formaldehyde at 20° C is 0.11.

The rates of the hydrolysis of dimethylol urea,

$$HOCH_2 \cdot NH \cdot CO \cdot NH \cdot CH_2OH = HOCH_2 \cdot NH \cdot CO \cdot NH_2 + HCHO$$

were studied by Květŏn and Králová [1] in 0.32 M unbuffered solutions, pH 7.0, at different temperatures. The hydroxylamine titration method used by these authors for determining the amount of "free" formaldehyde of the reaction solutions was previously discussed by Landqvist [2,3], and the accuracy obtained seems to be moderate. No linear relationship was found when applying a first order reaction rate equation, but from the slopes of the curves at zero reaction time, rate constants were calculated. The activation energy was found to be 16.9 kcal.

In the following paper the results of some experimental studies of the rates of dimethylol urea hydrolysis are given. The purpose of these experiments has been to investigate the influence of pH and buffer substances on the reaction rates and the effect of the concentration of dimethylol urea. A reaction rate equation will be deduced, including the regard of the reaction between the compounds liberated during the hydrolysis.

The experimental technique was the same as previously described by Landqvist [2]. The dimethylol urea was prepared in accordance with Walter and Gewing [4]. The cryoscopic molecular weight of the product was found to be 120 ± 2. All experiments were carried out at 20 ± 0.1° C, and all chemicals used were of A. R. quality.

Dry dimethylol urea was added to a solution containing the buffer substances at the pH wanted. (The pH was then re-checked during the reaction and no changes found, except for a reaction in unbuffered solution at an initial pH of 6.70.) The addition of solid dimethylol urea was made in order to get a real zero reaction time, and this time was calculated from the midpoint of the time needed for dissolving the substance, and this latter time was of the order 30—60 seconds. The moderate solubility of dimethylol urea and the need of a short dissolving time gave a maximum concentration of 0.5 M, and this figure was also the upper limit used in this investigation.

When neglecting the reaction between the hydrolysis products, we obtain the following reaction rate equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_2 \cdot (C - x) \qquad t = 0,\ x = 0 \tag{1}$$

i. e.

$$\ln \frac{x}{C - x} = k_2 \cdot t \tag{2}$$

where x = concentration of monomethylol urea or formaldehyde, C = initial concentration of dimethylol urea, t = time of reaction and k_2 = hydrolysis reaction rate constant.

When regarding the reaction between the hydrolysis products, *i. e.* the condensation reaction between monomethylol urea and formaldehyde, but still neglecting the monomethylol urea hydrolysis, we obtain:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_2 \cdot (C - x) - k_1 \cdot x^2 \qquad t = 0,\ x = 0 \tag{3}$$

We write $k_1/k_2 = \tau$; $\tau = 1/\sigma$, where σ is the equilibrium constant, as previously used by Landqvist [3].

Since at equilibrium $\mathrm{d}\,x/\mathrm{d}\,t = 0$, we find:

$$\tau = \lim_{t \to \infty} \frac{C - x}{x^2} \tag{4}$$

Under these conditions we get the following solution to eqn. (3)

$$k_2 \cdot t = \psi = \frac{1}{\sqrt{1 + 4 \cdot \tau \cdot C}} \ln \frac{1 + 2 \cdot \tau \cdot x/(1 + \sqrt{1 + 4 \cdot \tau \cdot C})}{1 + 2 \cdot \tau \cdot x/(1 - \sqrt{1 + 4 \cdot \tau \cdot C})} \tag{5}$$

In each experiment the equilibrium constant was determined by extrapolation to infinity reaction time.

In Figs. 1—7 the function (5) is plotted from experimental data, and Fig. 6 also includes a comparison made to eqn. (2). The compositions of the reaction

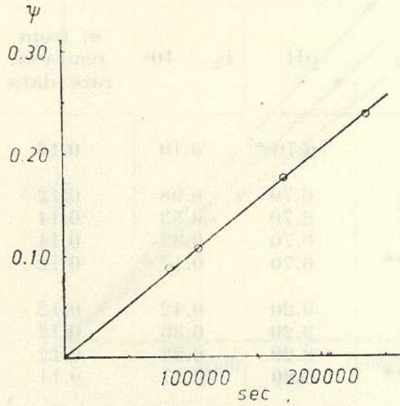

Fig. 1. Hydrolysis of 0.5 M dimethylol urea at 20° C in an unbuffered solution, initial pH 6.70.

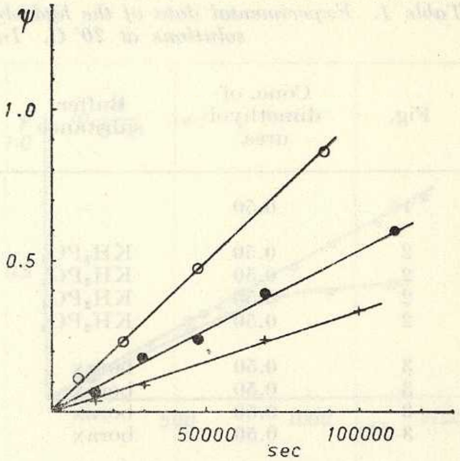

Fig. 2. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 6.70; $C_{KH_2PO_4}$: 0.1 (○), 0.05 (●) and 0.025 (+).

solutions and the experimental results are also given in Table 1. In this table the equilibrium constants, which can be calculated from the reaction rates here obtained and previously given data of the rates of the reaction between monomethylol urea and formaldehyde (Landqvist [3]), *i. e.* k_2/k_1, can also be found.

In Fig. 8 the relationship between the reaction rate constants and the buffer concentrations for each buffer substance is given. This represents the results

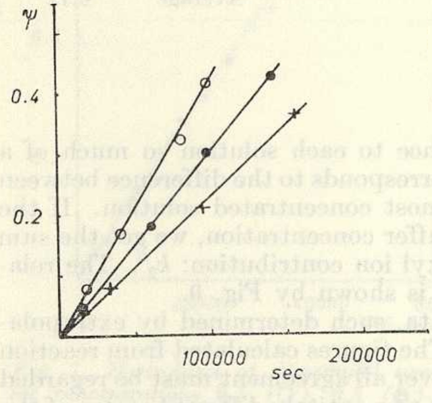

Fig. 3. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 9.20; C_{borax}: 0.1 (○), 0.05 (●) and 0.025 (+).

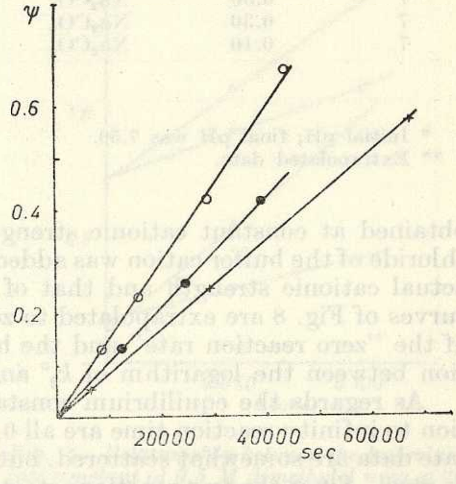

Fig. 4. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 10.00; $C_{Na_2CO_3}$: 0.1 (○), 0.05 (●) and 0.025 (+).

Table 1. Experimental data of the hydrolysis of dimethylol urea in neutral and alkaline solutions at 20° C. In all cases $\sigma = 1/\tau = 0.11$.

Fig.	Conc. of dimethyol urea	Buffer substance	C_{buffer}	pH	$k_2 \times 10^5$	σ; from reaction rate data
1	0.50	—	—	6.70 *	0.10	0.16
2	0.50	KH_2PO_4	0.100	6.70	0.98	0.12
2	0.50	KH_2PO_4	0.050	6.70	0.53	0.14
2	0.50	KH_2PO_4	0.025	6.70	0.33	0.14
2	0.50	KH_2PO_4	0.00 **	6.70	0.12	0.12
3	0.50	borax	0.100	9.20	0.42	0.12
3	0.50	borax	0.050	9.20	0.30	0.12
3	0.50	borax	0.025	9.20	0.23	0.12
3	0.50	borax	0.00 **	9.20	0.17	0.11
4	0.50	Na_2CO_3	0.100	10.00	1.45	0.11
4	0.50	Na_2CO_3	0.050	10.00	1.10	0.11
4	0.50	Na_2CO_3	0.025	10.00	0.90	0.11
4	0.50	Na_2CO_3	0.00 **	10.00	0.74	0.09
5	0.50	Na_2CO_3	0.100	11.50	11.0	0.11
5	0.50	Na_2CO_3	0.050	11.50	9.3	0.11
5	0.50	Na_2CO_3	0.025	11.50	8.3	0.10
5	0.50	Na_2CO_3	0.00 **	11.50	7.4	0.10
6	0.50	Na_3PO_4	0.100	12.40	54	0.11
6	0.50	Na_3PO_4	0.050	12.40	54	—
6	0.50	Na_3PO_4	0.025	12.40	54	—
7	0.50	Na_2CO_3	0.100	10.00	1.5	
7	0.30	Na_2CO_3	0.100	10.00		
7	0.10	Na_2CO_3	0.100	10.00		
					Average	0.12

* Initial pH; final pH was 7.50.
** Extrapolated data.

obtained at constant cationic strength, since to each solution so much of a chloride of the buffer cation was added as corresponds to the difference between actual cationic strength and that of the most concentrated solution. If the curves of Fig. 8 are extrapolated to zero buffer concentration, we get the sum of the "zero reaction rate" and the hydroxyl ion contribution: k_2°. The relation between the logarithm of k_2° and pH is shown by Fig. 9.

As regards the equilibrium constant data, such determined by extrapolation to infinity reaction time are all 0.11. The figures calculated from reaction rate data are somewhat scattered, but the over all agreement must be regarded as good. Since the two reactions starts from two entirely different states of the reaction solutions, differences in the activity of both the reactants and the catalysts may be present.

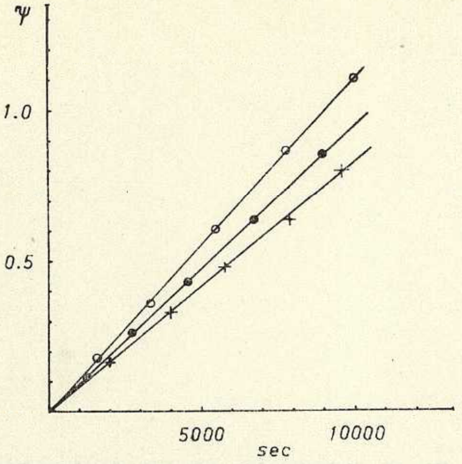

Fig. 5. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 11.50; $C_{Na_2CO_3}$: 0.1 (○), 0.05 (●) and 0.025 (+).

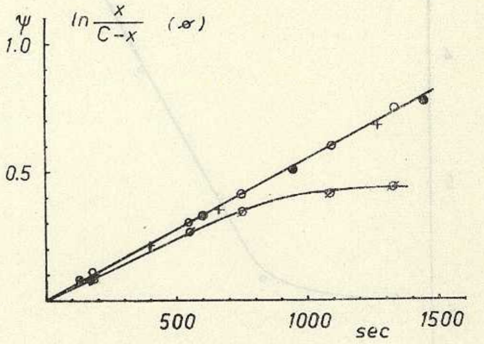

Fig. 6. Hydrolysis of 0.5 M dimethylol urea at 20° C and pH 12.40; $C_{Na_3PO_4}$: 0.1 (○), 0.05 (●) and 0.025 (+). (Φ) $C_{Na_3PO_4}$: 0.1.

From these experiments the following conclusions might be drawn, as regards the temperature and concentration range studied:

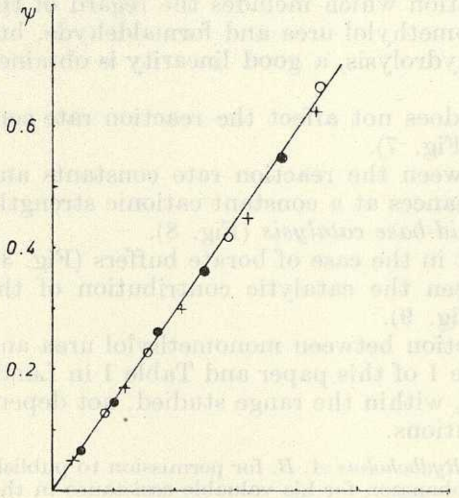

Fig. 7. Hydrolysis of dimethylol urea at the concentrations 0.5 (○), 0.3 (●) and 0.1 (+). At 20° C, pH 10.00 and $C_{Na_2CO_3}$: 0.1.

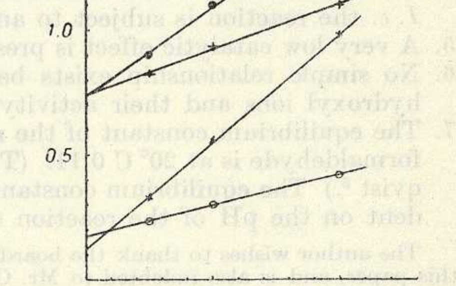

Fig. 8. Relationship between the hydrolysis rate constant of 0.5 M dimethylol urea at 20° C and the buffer substance concentrations; KH_2PO_4, pH 6.70 (×); borax, pH 9.20 (○); Na_2CO_3, pH 10.00 (●); Na_2CO_3, pH 11.50 (+).

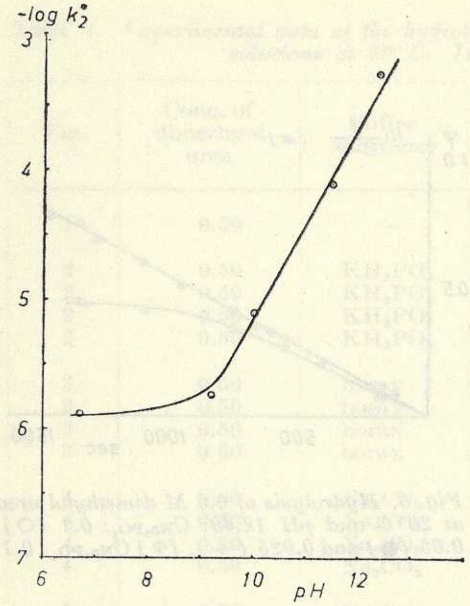

Fig. 9. Relationship between the logarithm of the reaction rate constant, extrapolated to zero buffer concentration, and pH for the hydrolysis of dimethylol urea at 20° C.

1. No linear relationship can be found when applying a simple first order reaction rate equation (Fig. 6).
2. When applying a reaction rate equation which includes the regard of the condensation reaction between monomethylol urea and formaldehyde, but still neglecting monomethylol urea hydrolysis, a good linearity is obtained (Figs. 1—7).
3. The concentration of the reactants does not affect the reaction rate constants to any considerable extent (Fig. 7).
4. A linear relationship is present between the reaction rate constants and the concentration of the buffer substances at a constant cationic strength. *I. e.* the reaction is subject to an *acid-base catalysis* (Fig. 8).
5. A very low catalytic effect is present in the case of borate buffers (Fig. 3).
6. No simple relationship exists between the catalytic contribution of the hydroxyl ions and their activity (Fig. 9).
7. The equilibrium constant of the reaction between monomethylol urea and formaldehyde is at 20° C 0.11. (Table 1 of this paper and Table 1 in Landqvist [3].) The equilibrium constant is, within the range studied, not dependent on the pH of the reaction solutions.

The author wishes to thank the board of *Rydboholms A. B.* for permission to publish this paper, and is also indebted to Mr. G. Johansson for his valuable assistance in the experimental work.

REFERENCES

1. Květoň, R. and Králová, M. *Chem. Listy* **46** (1952) 403.
2. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1127.
3. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1459.
4. Walter, G. and Gewing, M. *Kolloid-Beihefte* **34** (1934) 163.

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8

On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

VIII. Studies of the Reactions and Equilibria at Formaldehyde-Urea Molecular Ratios in the Range 1.4—2.0

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

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Reactions and equilibria at formaldehyde-urea ratios in the range 1.4—2.0 were investigated experimentally at 20 °C.

The general reaction rate equation was solved by means of an electronic differential analyser, using rate constants previously determined for the different reactions involved. The equilibrium concentrations were calculated, and both the course of reaction and equilibrium show a good agreement between experimental and theoretically determined data.

An empirical relationship between free formaldehyde and reaction time is also given.

For several practical purposes, *e. g.* the use of methylol ureas for textile finishing purposes, the reaction between formaldehyde and urea at molecular ratios within the range 1.4—2.0 is of a great interest. The purpose of the following paper is to describe studies of the kinetics of such reactions at 20 °C and to give the results of investigations on the equilibrium state of said reactions.

The experiments were carried out by means of the chemicals and the technique previously described [1,9].

We introduce the following symbols:

Concentrations: U = urea; U_0 = urea, initial; F = formaldehyde; F_0 = formaldehyde, initial; M = monomethylol urea; D = dimethylol urea.

Reaction rate constants: monomethylol urea: k = formation, k' = hydrolysis; dimethylol urea: k_1 = formation, k_2 = hydrolysis.

Reaction time: t.

If mono- and dimethylol urea are assumed to be the reaction products, see *e. g.* de Jong and de Jonge [2-4], the general reaction rate equations can be written:

$$\left.\begin{aligned}
&\frac{\mathrm{d}M}{\mathrm{d}t} = k \cdot U \cdot F - k' \cdot M - k_1 \cdot M \cdot F + k_2 \cdot D \\
&\frac{\mathrm{d}D}{\mathrm{d}t} = k_1 \cdot M \cdot F - k_2 \cdot D \\
&U = U_0 - M - D;\ F = F_0 - M - 2\ D \\
&t = 0:\ \ U = U_0;\ F = F_0;\ M = D = 0 \\
&t \rightarrow \infty\ \frac{\mathrm{d}M}{\mathrm{d}t} = \frac{\mathrm{d}D}{\mathrm{d}t} = 0
\end{aligned}\right\} \quad (1)$$

If we write: $\tau = k \cdot t$; $k'/k = \alpha$; $k_1/k = \beta$; $k_2/k = \gamma$; we have:

$$\left.\begin{aligned}
&\frac{\mathrm{d}M}{\mathrm{d}\tau} = U_0 \cdot F_0 - [U_0 + (1+\beta) \cdot F_0 + \alpha] \cdot M + (1+\beta) \cdot M^2 + \\
&\qquad (3 + 2\ \beta) \cdot M \cdot D - (2\ U_0 + F_0 - \gamma) \cdot D + 2\ D^2 \\
&\frac{\mathrm{d}D}{\mathrm{d}\tau} = \beta \cdot F_0 \cdot M - \beta \cdot M^2 - 2\ \beta \cdot M \cdot D - \gamma \cdot D \\
&\tau = 0:\ \ M = D = 0;\ \tau \rightarrow \infty\ \ :\ \ \frac{\mathrm{d}M}{\mathrm{d}\tau} = \frac{\mathrm{d}D}{\mathrm{d}\tau} = 0
\end{aligned}\right\} \quad (2)$$

Since a simple solution to the system of differential equations given above cannot easily be found, numerical solutions were obtained by means of an electronic differential analyser, the EIDA of Chalmers University of Technology, Gothenburg.

The accuracy of the solutions are, as calculated on the initial formaldehyde concentrations, of the order 3 %. Thus, the figures related to high τ values, $\tau > 4$, are moderately accurate. However, the equilibrium concentrations can be calculated exactly, as will be shown later on.

Numerical solutions given as $F = f(\tau)$ curves in Figs. 1—3 refer to 1 M urea and formaldehyde-urea ratios 1.4, 1.6 and 2.0. The buffer concentration was 0.050 M and the temperature 20 °C. The buffers were KH_2PO_4, pH = 6.70; borax, pH = 9.20; Na_2CO_3, pH = 10.00 at cationic strengths as in previous studies [1,5–7]. The reaction rate constants were taken from these studies. As can be seen, experimental data agree closely with the calculated curves. From this is might be concluded that the reaction rate constants, as previously determined under specialized conditions, are applicable to the more general case.

An example of the concentration-reaction time relationships of the reactants and the reaction products is given in Fig. 4, as calculated by means of the electronic differential analyser for 1.0 M urea + 1.7 M formaldehyde, 0.050 M Na_2CO_3, pH 10.00, 20 °C. The concentrations of urea, mono- and dimethylol urea were determined in accordance with Landqvist [9]. As seen from Fig. 4, experimental data and calculated curves are in a close agreement.

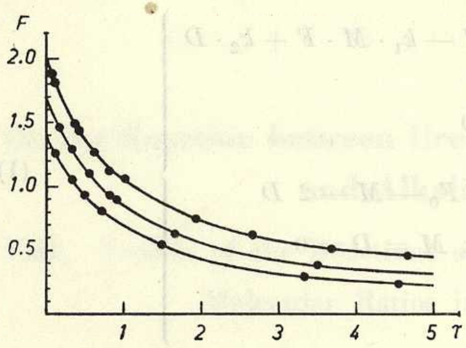

Fig. 1. Relationship between unreacted formaldehyde and the τ-value for the reactions between formaldehyde and 1 M urea at the molecular ratios 1.4, 1.7, 2.0; 0.050 M KH_2PO_4, pH 6.70. Temperature: 20 °C. The curve: theoretical solution, (●): experimental data.

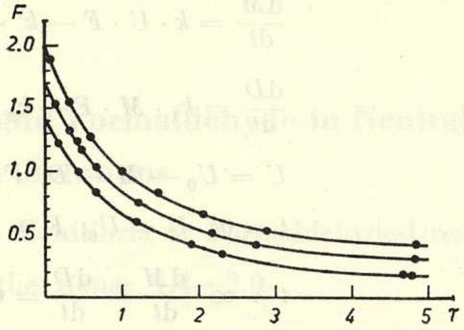

Fig. 2. Relationship between unreacted formaldehyde and the τ-value for the reactions between formaldehyde and 1 M urea at the molecular ratios 1.4, 1.7, 2.0; 0.050 M borax, pH 9.20. Temperature: 20 °C. The curve: theoretical solution, (●): experimental data.

In a previous paper [8], an empirical equation for the relationship between free formaldehyde and the reaction time was given:

$$\log \log \frac{F_0}{F} = A \cdot \log \log t + B \tag{3}$$

This equation was found to be approximately valid in the case of equal con-

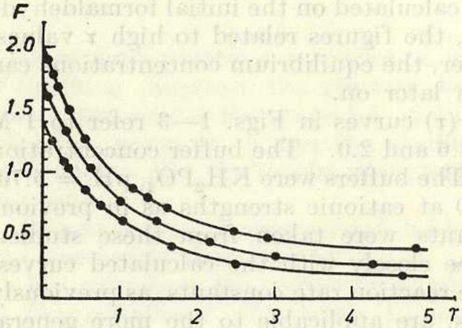

Fig. 3. Relationship between unreacted formaldehyde and the τ-value for the reactions between formaldehyde and 1 M urea at the molecular ratios 1.4, 1.7, 2.0; 0.050 M Na_2CO_3, pH 10.00. Temperature: 20 °C. The curve: theoretical solution, (●): experimental data.

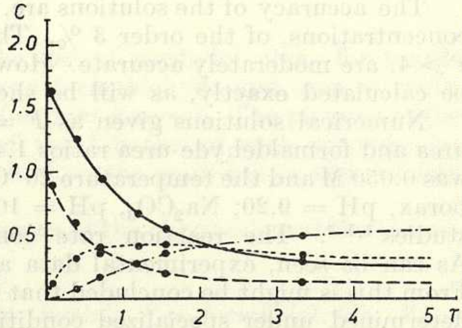

Fig. 4. Relationship between the reaction solution composition and the τ-value; 1.0 M urea and 1.7 M formaldehyde. 0.050 Na_2CO_3, pH 10.00, 20°C. (——) formaldehyde, (— — —) urea, (. . . .) monomethylol urea and (—.—.—) dimethylol urea. The curves: theoretical solutions, (●): experimental data.

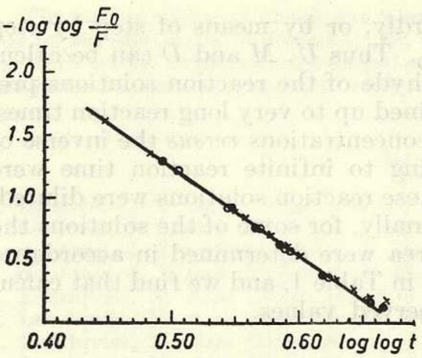

Fig. 5. The expression (3) applied to the reaction between formaldehyde and 1 M urea at the molecular ratios 1.4 (●), 1.7 (○) and 2.0 (×). 0.050 M KH_2PO_4, pH 6.70, 20 °C.

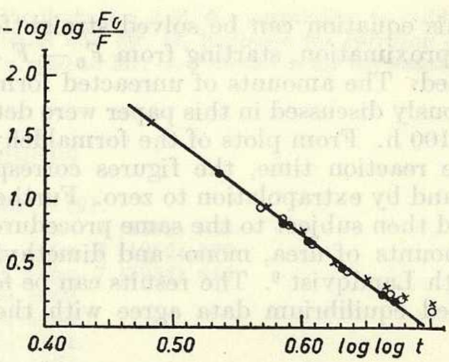

Fig. 6. The expression (3) applied to the reaction between formaldehyde and 1 M urea at the molecular ratios 1.4 (●), 1.7 (○) and 2.0 (×). 0.050 M borax, pH 9.20, 20 °C.

centrations of the reactants. The same equation applied to the solutions mentioned above is shown by the plots of Figs. 5—7. Curves of this kind may be of value when applied to practical work.

From the previous equations we find the equilibrium conditions:

$$t \rightarrow \infty : \frac{\mathrm{d}M}{\mathrm{d}t} = \frac{\mathrm{d}D}{\mathrm{d}t} = 0$$

$$M = \frac{k}{k'} \cdot U \cdot F = K_1 \cdot U \cdot F; \; D = \frac{k_1}{k_2} \cdot M \cdot F = \frac{k \cdot k_1}{k' \cdot k_2} \cdot U \cdot F^2 = K_2 \cdot U \cdot F^2$$

$$U_0 = U \; (1 + K_1 \cdot F + K_2 \cdot F^2); \; F_0 = F + U \; (K_1 \cdot F + 2 \cdot K_2 \cdot F^2)$$

and

$$\frac{F_0 - F}{U_0} = \frac{K_1 \cdot F + 2 \; K_2 \cdot F^2}{1 + K_1 \cdot F + K_2 \cdot F^2} \tag{4}$$

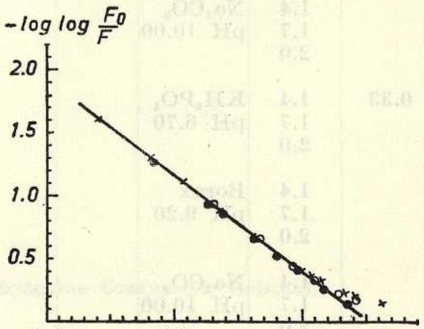

Fig. 7. The expression (3) applied to the reaction between formaldehyde and 1 M urea at the molecular ratios 1.4 (●), 1.7 (○) and 2.0 (×). 0.050 M Na_2CO_3, pH 10.00, 20 °C.

This equation can be solved straightforwardly, or by means of step by step approximation, starting from $F_0 - F \sim F_0$. Thus U, M and D can be calculated. The amounts of unreacted formaldehyde of the reaction solutions previously discussed in this paper were determined up to very long reaction times, ~100 h. From plots of the formaldehyde concentrations *versus* the inverse of the reaction time, the figures corresponding to infinite reaction time were found by extrapolation to zero. Further, these reaction solutions were diluted, and then subject to the same procedure. Finally, for some of the solutions the amounts of urea, mono- and dimethylol urea were determined in accordance with Landqvist [9]. The results can be found in Table 1, and we find that calculated equilibrium data agree with the observed values.

Table 1. Equilibrium data of reactions between formaldehyde and urea at the molecular ratios 1.4, 1.7 and 2.0. Temperature 20 °C. Buffer concentrations: 0.050 M.

Urea concentration U_0	Molecular ratio	Buffer	Calculated data				Observed data			
			U	M	D	F	U	M	D	F
1.0	1.4	KH_2PO_4	0.13	0.47	0.41	0.13	0.13	0.46	0.41	0.12
	1.7	pH 6.70	0.06	0.38	0.56	0.21	0.07	0.36	0.57	0.21
	2.0		0.03	0.28	0.69	0.34	0.03	0.27	0.70	0.33
	1.4	Borax	0.14	0.43	0.43	0.11	0.15	0.43	0.42	0.11
	1.7	pH 9.20	0.07	0.36	0.57	0.19	0.07	0.34	0.59	0.18
	2.0		0.03	0.26	0.71	0.32	0.02	0.28	0.70	0.32
	1.4	Na_2CO_3	0.15	0.40	0.45	0.10	0.16	0.43	0.41	0.10
	1.7	pH 10.00	0.07	0.33	0.60	0.17	0.08	0.32	0.60	0.18
	2.0		0.03	0.23	0.74	0.30	0.03	0.24	0.73	0.29
0.50	1.4	KH_2PO_4				0.10				0.10
	1.7	pH 6.70				0.16				0.16
	2.0					0.23				0.22
	1.4	Borax				0.09				0.09
	1.7	pH 9.20				0.15				0.15
	2.0					0.20				0.20
	1.4	Na_2CO_3				0.10				0.09
	1.7	pH 10.00				0.13				0.13
	2.0					0.20				0.20
0.33	1.4	KH_2PO_4				0.09				0.09
	1.7	pH 6.70				0.13				0.14
	2.0					0.18				0.18
	1.4	Borax				0.08				0.07
	1.7	pH 9.20				0.12				0.12
	2.0					0.16				0.16
	1.4	Na_2CO_3				0.09				0.08
	1.7	pH 10.00				0.11				0.11
	2.0					0.16				0.15

The author wishes to thank the board of Rydboholms A.B. for permission to publish this paper, and is also indebted to Dr. V. Wenzel and Mr. Ö. Karlsson for carrying out the work on the electronic differential analyser, and to Mr. G. Johansson for his valuable assistance in the experimental work.

REFERENCES

1. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1121.
2. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **7** (1952) 643.
3. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **7** (1952) 662.
4. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **7** (1952) 840.
5. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1459.
6. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1466.
7. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1471.
8. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1477.
9. Landqvist, N. *Acta Chem. Scand.* **11** (1957) 776.

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9

I

On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

IX. The Influence of Methanol on the Rates of Reaction

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

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IX. The Influence of Methanol on the Rates of Reaction

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The effects of methanol on the rates of the urea-formaldehyde reactions were studied. Decreased rates were observed at increasing amounts of methanol in the case of urea or monomethylol urea and formaldehyde reactions. No influence on the hydrolysis reactions was found.

The formation of a hemiacetal between methanol and formaldehyde was studied cryoscopically as regards the rate constants and the equilibrium. On the basis of the theory that the hemiacetal does not take part in the reactions mentioned above some rate and equilibrium relationships were derived and found to be in agreement with experimental data.

It has been observed by, *e. g.*, Smythe [1] that the presence of methanol in urea-formaldehyde reaction mixtures decreases the rate of reaction. Since commercially available formaldehyde solutions very often contain methanol, added in order to prevent polymer precipitation, the effect mentioned is of some technical importance. The scope of the following paper is to describe some investigations carried out in order to study the influence of methanol on the rates of the different urea-formaldehyde reactions.

It is known that methanol and formaldehyde form a hemiacetal as follows:

$$HCHO + CH_3OH = CH_3 \cdot O \cdot CH_2OH \qquad (A)$$

The role of such a compound in water-methanol solutions containing different amounts of formaldehyde was investigated cryoscopically.

Chemicals: Formaldehyde stock solutions prepared by means of distillation of A. R. paraformaldehyde solutions.

Procedure: All experiments refer to 20 °C. Formaldehyde solutions were prepared by dilution of stock solutions at least 24 h before the addition of the methanol; this was made in order to allow any depolymerisation reactions to be completed. The alcohol was then stirred into these solutions and samples were taken and investigated cryoscopically until a constant value was obtained. This means that from time to time samples at 20°C were cooled quickly and the freezing temperature determined; the total change in this temperature was calculated as the difference between the temperatures at extrapolated zero and infinite reaction time. The figure corresponding to zero reaction time was always in good agreement with calculated data.

The equilibrium constants of reaction (A) were calculated from:

$$\frac{C_{\mathrm{CH_3OCH_2OH}}}{C_{\mathrm{HCHO}} \cdot C_{\mathrm{CH_3OH}}} = K \tag{1}$$

The reaction solution composition and the results obtained can be found in Table 1.

Table 1. Equilibrium constants of the hemiacetal formation between methyl alcohol and formaldehyde. 20 °C.

$C_{\mathrm{CH_3OH}}$	C_{HCHO}	K liter / moles
0.100	0.100	0.67
0.100	0.274	0.63
0.250	0.264	0.63
0.500	0.264	0.64
1.018	0.274	0.66
0.250	0.537	0.63
1.018	0.537	0.68
0.500	1.048	0.64
		Av. 0.65

As seen from this table, the K values are acceptably constant, thus reaction (A) may be the most important one under the conditions here studied.

The reaction rate equation can be written:

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k_1\ (C_{\mathrm{M}} - y) \cdot (C_{\mathrm{F}} - y) - k_2 \cdot y \tag{2}$$

where

y = concentration of the hemiacetal.
C_{M} = initial concentration of methanol.
C_{F} = initial concentration of formaldehyde.
k_1 = formation rate constant.
k_2 = dissociation rate constant.
t = time of reaction.

Initial conditions: $t = 0,\ y = 0.$

The solution to eqn. (2) can be written:

$$\varphi = k_1 \cdot t = \frac{1}{\sqrt{b^2 - 4\,a}} \cdot \ln \frac{(2\ y + b - \sqrt{b^2 - 4\,a}) \cdot (b + \sqrt{b^2 - 4\,a})}{(2\ y + b + \sqrt{b^2 - 4\,a}) \cdot (b - \sqrt{b^2 - 4\,a})} \tag{3}$$

where $a = C_{\mathrm{M}} \cdot C_{\mathrm{F}};\ b = -\,(C_{\mathrm{M}} + C_{\mathrm{F}} + \frac{1}{K});\ K = \frac{k_1}{k_2}.$

Applied to the reactions studied, eqn. (3) gives relationships as exemplified by Fig. 1, when the equilibrium constant mentioned previously is introduced into the equation. Since the rate of reaction is high as compared with the experimental technique — *i. e.* the cryoscopic measurements — figures corresponding to the initial part of the reaction could not be obtained. Despite of this lack of accuracy, we may accept

$$k_1 = 0.65 \times 10^{-3} \text{ liter/moles} \cdot \text{sec.}$$
$$k_2 = 1.0 \times 10^{-3} \text{ sec}^{-1}.$$

These figures are related to unbuffered solutions. Since addition of buffer substances considerably increases the reaction rates, no accurate measurements could be made on solutions containing such substances.

The reaction between urea or monomethylol urea and formaldehyde and the hydrolysis of mono- and dimethylol urea were investigated as previously described [2–5]. The solutions were the same as the 0.050 M KH_2PO_4, pH 6.70, series of the previous papers, but they also contained methanol.

The experimental results can be found in Table 2.

Table 2. Reaction rate constants of the reactions between urea or monomethylol urea and formaldehyde and of the hydrolysis of mono- and dimethylol urea in the presence of methanol; 0.050 M KH_2PO_4, pH 6.70, 20 °C.

C_{methanol}	C_{urea}	$C_{\text{monomethylol urea}}$	$C_{\text{dimethylol urea}}$	$C_{\text{formaldehyde}}$	$k \cdot 10^5$ *	$k_0 \cdot 10^5$ * calculated
0.000	4.0			0.40	10	10
0.094	4.0			0.40	10	11
0.72	4.0			0.40	8.3	10
1.34	4.0			0.40	6.4	10
0.000	2.0			0.20	10	10
0.063	2.0			0.20	10	11
0.69	2.0			0.20	8.2	11
1.31	2.0			0.20	6.2	10
0.72	2.0			0.80	8.0	11
0.00		1.0		1.0	3.8	3.8
0.22		1.0		1.0	3.5	3.8
0.85		1.0		1.0	2.6	3.6
1.47		1.0		1.0	2.1	3.6
0.00		1.0			0.35	
0.63		1.0			0.35	
1.25		1.0			0.34	
0.00			1.0		0.53	
0.63			1.0		0.52	
1.25			1.0		0.53	

* The rate constants of the formation reactions: liter / moles · sec.; the hydrolysis reactions: sec^{-1}.

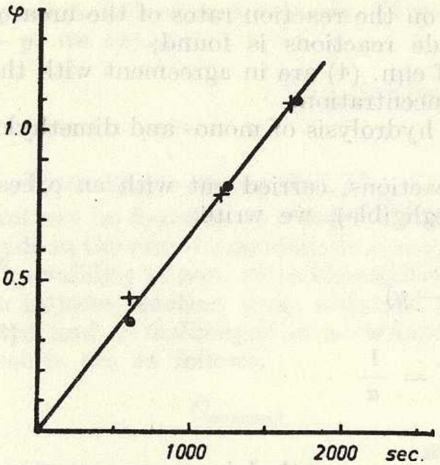

Fig. 1. Relationship in accordance with eqn. (3) of 0.500 M CH_3OH + 0.264 M HCHO (+) and 0.500 M CH_3OH + 1.048 M HCHO (●). 20 °C.

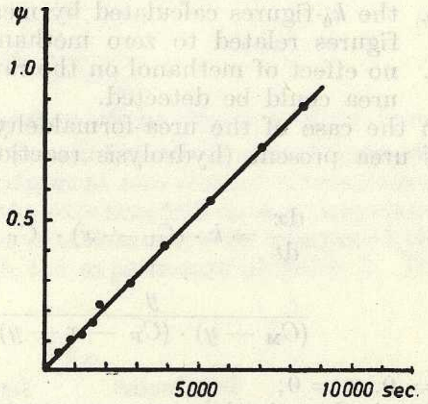

Fig. 2. Relationship in accordance with eqn. (6) for 4.0 M urea + 0.4 M formaldehyde; 0.050 M KH_2PO_4, pH 6.70, 20 °C; 1.34 M methanol.

If we compare the rate constant of hemiacetal hydrolysis and the rate constants of the urea — formaldehyde reaction systems, and remember that the hemiacetal hydrolysis appears to be catalysed by buffer substances, we may assume that the equilibrium in accordance with eqn. (1) is maintained throughout the urea or monomethylol urea and formaldehyde reactions. Assuming that the change in rates of the last mentioned reactions is dependent on the formation of a hemiacetal between methanol and formaldehyde [6], and further that this hemiacetal does not take part in the reactions with urea or monomethylol urea, we find that the rate constants *at zero reaction time* of the urea or monomethylol urea and formaldehyde reactions would be related as follows:

$$\frac{k_0}{k_{C_M}} = \frac{C_F}{C_F - y} \tag{4}$$

where

k_0 = reaction rate constant at zero methanol concentration.
k_{C_M} = reaction rate constant at C_M methanol concentration.
C_{C_F} = initial formaldehyde concentration.
y = initial hemiacetal concentration.

y as calculated from eqn. (2): $y^2 - (C_M + C_F + \frac{1}{K}) \cdot y + C_M \cdot C_F = 0$; symbols defined as previously.

The results, as found in Table 2, can be summarized: Within the range studied, 0—1.3 M methanol,

A. a considerable influence of methanol on the reaction rates of the urea or monomethylol urea and formaldehyde reactions is found;
B. the k_0-figures calculated by means of eqn. (4) are in agreement with the figures related to zero methanol concentration;
C. no effect of methanol on the rates of hydrolysis of mono- and dimethylol urea could be detected.

In the case of the urea-formaldehyde reactions, carried out with an excess of urea present (hydrolysis reactions negligible), we write:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k \cdot (C_{\mathrm{U}} - x) \cdot (C_{\mathrm{F}} - x - y)$$

$$\frac{y}{(C_{\mathrm{M}} - y) \cdot (C_{\mathrm{F}} - x - y)} = K = \frac{1}{\alpha} \tag{5}$$

$t = 0,\ x = 0;$

Here is C_{U} = initial urea concentration; x = monomethylol urea concentration; k = rate constant and t = time of reaction. Other symbols as previously defined. If $y \ll C_{\mathrm{M}} + C_{\mathrm{F}} + \alpha - x$, we obtain the following solution to eqn. (5):

$$\psi = k \cdot t = \frac{\alpha + C_{\mathrm{M}} + C_{\mathrm{F}} - C_{\mathrm{U}}}{(C_{\mathrm{U}} - C_{\mathrm{F}}) \cdot (C_{\mathrm{U}} - C_{\mathrm{F}} - \alpha)} \cdot \ln \frac{C_{\mathrm{U}}}{C_{\mathrm{U}} - x} + \frac{\alpha + C_{\mathrm{M}}}{\alpha \cdot (C_{\mathrm{U}} - C_{\mathrm{F}})} \cdot$$

$$\cdot \ln \frac{C_{\mathrm{F}}}{C_{\mathrm{F}} - x} - \frac{C_{\mathrm{M}}}{\alpha \cdot (C_{\mathrm{U}} - C_{\mathrm{F}} - \alpha)} \cdot \ln \frac{C_{\mathrm{F}} + \alpha}{C_{\mathrm{F}} + \alpha - x} \tag{6}$$

An example of the relationships according to this equation, plotted from experimental data, $C_{\mathrm{M}} = 1.34$, $C_{\mathrm{U}} = 4.0$, $C_{\mathrm{F}} = 0.40$, in shown by Fig. 2. As seen a good linearity and agreement with the corresponding rate constant from Table 2 is present.

As a result of the fact that only the forward reaction rates are influenced by the presence of methanol, the equilibrium formaldehyde concentration, as determined analytically, may also be dependent on the amount of alcohol in the reaction mixtures.

Under the conditions used for the polarographic analysis of the amount of equilibrium formaldehyde of the reaction mixtures, all hemiacetal is completely hydrolysed. (The figures obtained on formaldehyde solutions with and without methanol present are the same, when samples of the solutions are added to the supporting electrolyte in accordance with the previous paper [2].) Thus, the analytically determined "equilibrium" formaldehyde concentration $C_{\mathrm{F}\infty}$ is related to the concentration of "free" formaldehyde $C^{\circ}_{\mathrm{F}\infty}$, *i. e.* the amount in actual equilibrium with urea, mono- and dimethylol urea, as follows: $C_{\mathrm{F}\infty} = C^{\circ}_{\mathrm{F}\infty} + y$; y is the concentration of the hemiacetal.

Eqn. (1) can be written

$$\frac{y}{(C_{\mathrm{M}} - y) \cdot C^{\circ}_{\mathrm{F}\infty}} = K \tag{7}$$

Symbols defined as previously. If we combine this expression with $C_{F_\infty} = C^\circ_{F_\infty} + y$, we obtain:

$$C_{F_\infty} = C^\circ_{F_\infty} + \frac{C_M}{1 + \frac{1}{K \cdot C^\circ_{F_\infty}}} \tag{8}$$

From above we see that $C^\circ_{F_\infty}$ is independent of the presence of methanol and can be found from a determination of the analytical amount of formaldehyde in the urea-formaldehyde reaction mixtures at zero alcohol concentration. The validity of eqn. (8) is exemplified by the experimental data, extrapolated to infinite reaction time, obtained for the reactions between monomethylol urea and formaldehyde in accordance with the experiments of Table 2. The results are as follows:

C_{methanol}	C_{F_∞}	
	measured	calculated
0.00	0.22 *	—
0.22	0.25	0.25
0.85	0.33	0.33
1.47	0.40	0.39

* Thus, $C^\circ_{F_\infty} = 0.22$.

The principle introduced is, of course, generally applicable to these problems.

The influence of methanol on the reaction rates may also be attributed to influences on the ion activities of the catalysts. However, the behaviour of the mono- and dimethylol urea hydrolysis reactions, as seen from Table 2, shows that such effects may be negligible.

The conclusions to be drawn from the investigations described in this paper may be: The reduction in reaction rates of the urea or monomethylol urea and formaldehyde reactions caused by methanol depends mainly on the formation of a hemiacetal between methanol and formaldehyde. The hemiacetal does not take part in the reactions, and the equilibrium conditions of the hemiacetal are maintained throughout the reactions between the ureas and the formaldehyde.

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REFERENCES

1. Smythe, L. *J. Am. Chem. Soc.* **74** (1952) 2713.
2. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1127.
3. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1459.
4. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1466.
5. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1471.
6. Takahashi, A. *Chem. High Polymers (Japan)* **9** (1952) 48.

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Symbols defined as previously. If we combine this expression with $C_{F_\infty} = C^0_{F_\infty} + y$ we obtain

$$\frac{C_M}{1 + \frac{1}{K \cdot C^0_{F_\infty}}} + C_{F_\infty} = C^0_{F_\infty} \qquad (8)$$

From above we see that C_{F_∞} is independent of the presence of methanol and can be found from a determination of the analytical amount of formaldehyde in the urea-formaldehyde reaction mixtures at zero alcohol concentration. The validity of eqn. (8) is exemplified by the experimental data, extrapolated to infinite reaction time, obtained for the reactions between monomethylol urea and formaldehyde in accordance with the experiments of Table 2. The results are as follows:

C_{methanol}	C_{F_∞} measured	C_{F_∞} calculated
0.00	0.22 *	
0.36	0.25	0.26
0.85	0.33	0.33
1.47	0.40	0.39

* Thus, $C^0_{F_\infty} = 0.22$.

The principle introduced is, of course, generally applicable to these problems.

The influence of methanol on the reaction rates may also be attributed to influences on the ion activities of the catalysts. However, the behaviour of the mono- and dimethylol urea hydrolysis reactions, as seen from Table 2, shows that such effects may be negligible.

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REFERENCES

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

VI. Experimental Studies of the Activation Energy and the Heat of Reaction

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

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VI. Experimental Studies of the Activation Energy and the Heat of Reaction

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

The activation energies of the formation and hydrolysis of mono- and dimethylol urea were determined. The activation energies of the reactions between urea — formaldehyde and monomethylol urea — formaldehyde were found to be 15.4 kcal/mole, and the activation energies of the corresponding hydrolysis reactions 20.4 kcal/mole. The heat of reaction of the formation reactions was found to be the same in both cases: 4.9 kcal/mole.

The activation energy of the reaction between urea and formaldehyde at equal concentrations was determined by *e.g.*: (1) Smythe [1]; the amount of unreacted formaldehyde of the 4 M unbuffered reaction solutions was determined by means of the hydroxylamine titration method. The activation energy obtained was 14.7 kcal/mole; (2) Smythe [2]; the reactions in dilute, unbuffered solutions (0.1 M) were studied by means of polarography. Activation energy obtained: 15.3 kcal/mole; (3) Crowe and Lynch [3]; polarographic determinations in 0.05 M LiOH at low concentrations of the reactants. Activation energy: 15.9 kcal/mole.

The activation energy of the reaction between monomethylol urea and formaldehyde was determined by Květon and Králová [4]. ~2 M reaction solutions and the amount of unreacted formaldehyde determined by means of the hydroxylamine method. Activation energy: 12.2 kcal/mole.

The activation energy of dimethylol urea hydrolysis was also studied by Květoň and Králová [4]. Hydroxylamine method used, activation energy: 16.9 kcal/mole.

As regards the moderate accuracy of the hydroxylamine titration method, reference is given to Landqvist [5].

The purpose of the following paper is to describe experimental studies of the activation energies of mono- and dimethylol urea formation and hydrolysis. The heat of reaction of the forward reactions is given.

Table 1. The activation energy of mono- and dimethylol formation and hydrolysis reactions.

Reaction solution	Buffer	C_{buffer}	pH	Temperature °C	Rate constant $\times 10^5$	E kcal/mole
4.0 M urea + 0.4 M formaldehyde	KH_2PO_4	0.025	6.70	20	6.5	16.0
				30	16.1	14.9
				40	35	
		0.050		20	10.2	14.8
				30	23.1	16.2
				40	54	
		0.100		20	16.0	15.4
				30	38	15.1
				40	84	
	borax	0.050	9.20	20	6.0	15.1
				30	14.0	15.7
				40	32	
						Av. 15.4
	Na_2CO_3	0.050	10.00	20	12.2	16.2
				30	30.0	16.8
				40	73	
1.0 M monomethylol urea + 1.0 M formaldehyde	KH_2PO_4	0.025	6.70	20	2.40	15.6
				30	5.8	15.3
				40	13.1	
		0.050		20	3.8	15.1
				30	8.9	15.4
				40	20.2	
		0.100		20	6.9	14.9
				30	16.0	15.9
				40	37	
	borax	0.050	9.20	20	2.60	14.9
				30	6.0	16.1
				40	13.9	
						Av. 15.4
	Na_2CO_3	0.050	10.00	20	12.2	16.8
				30	30.2	16.4
				40	71	
1.0 M monomethylol urea	KH_2PO_4	0.025	6.70	20	0.221	20.5
				30	0.70	19.9
				40	2.01	
		0.050		20	0.35	20.3
				30	1.10	20.3
				40	3.20	
		0.100		20	0.60	20.4
				30	1.88	20.8
				40	5.7	
	borax	0.050	9.20	20	0.233	20.7
				30	0.74	20.4
				40	2.23	
						Av. 20.4
	Na_2CO_3	0.050	10.00	20	0.46	21.0
				30	1.52	21.3
				40	4.6	

0.5 M dimethylol urea	KH_2PO_4	0.025	6.70	20	0.33	19.7
				30	1.03	20.8
				40	2.99	
		0.050		20	0.53	20.7
				30	1.70	20.4
				40	5.02	
		0.100		20	0.98	20.4
				30	3.11	20.1
				40	9.0	
	borax	0.050	9.20	20	0.302	20.8
				30	0.97	20.1
				40	2.79	
						Av. 20.4
	Na_2CO_3	0.050	10.00	20	1.08	21.6
				30	3.7	22.3
				40	11.9	

* In all cases such an amount of a chloride of the buffer cation was added that a cationic strength corresponding to 0.200 M solutions was maintained.

THE ACTIVATION ENERGIES

The activation energy investigations were carried out as previous studies at 20° C; Landqvist [5]. The temperature interval was 20—40° C. The pH values of the reaction solutions refer to 20° C.

Since the pK of the buffers are dependent on the temperature, and the OH^- catalysis of the reactions is comparatively small, it seems to be most important to keep the concentration of the buffer acid and base as constant as possible (Landqvist [5-8]).

The compositions of the reaction solutions and the reaction rate constants obtained can be found in Table 1. The activation energy, E, from experimental data are included in the table. Examples of the Arrhenius equation relationship are given in Fig. 1.

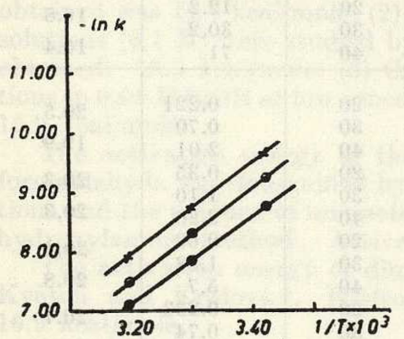

Fig. 1. The relationship between the logarithm of the reaction rate constant and the inverse of the temperature. 4.0 M $CO(NH_2)_2$ + 0.40 M HCHO; $C_{KH_2PO_4} = 0.025$ (×), 0.050 (○) and 0.100 (●). pH 6.70.

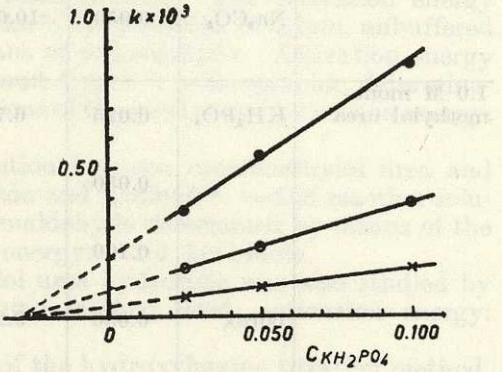

Fig. 2. The relationship between the reaction rate constant and the concentration of the KH_2PO_4 buffer at pH 6.70. The temperatures were: 20° C (×), 30° C (○) and 40° C (●).

At all temperatures and reactions acid — base catalysis as previously reported (Landqvist[5-8]) occurred. An example of the reaction rate constant-buffer concentration (constant cationic strength) relationship is given in Fig. 2. If the curves corresponding to the different temperatures are extrapolated to a reaction rate constant equal to zero, the same (negative) abscissa value was found. These observations support the assumption that the changes in pH due to the change in temperature can be neglected, as regards their influence on the catalysis. The change in the buffer activity is unknown. The activation energies of KH_2PO_4 and borax buffered solutions support an assumption that the influence from this is moderate. In the case of Na_2CO_3 buffers slightly different figures are obtained. The differences between the formation and hydrolysis activation energies are all of the same order, why the carbonate behaviour is probably due to changes in the catalytic properties.

From Table 1 we find reasons to accept the activation energy value 15.4 kcal/mole of the formation reactions; the corresponding hydrolysis figure is 20.4 kcal/mole.

HEAT OF REACTION

The heats of reaction of mono- and dimethylol urea formation were determined calorimetrically. In order to reduce the influence from side reactions; *i. e.* formation of dimethylol urea from urea and formaldehyde and mono- and dimethylol urea hydrolysis, and in order to obtain as complete reactions as possible, the study was made on solutions containing an excess of urea or formaldehyde respectively. In the latter case no formation of tri- and tetramethylol urea is likely to occur, as could be concluded from the consumption of formaldehyde. The catalytic properties were selected to give proper reaction rates. The experiments were carried out as follows.

Monomethylol urea formation. An amount of 500 ml of a 4.0 M urea solution, 0.025 M with respect to Na_2CO_3, pH 11.50, was poured into a Dewar vessel. Through holes in the cork stopper of the vessel a stirrer and a Beckman thermometer were immersed in the urea solution. Through another hole in the stopper a "test tube" was immersed. The tube was made of a polyethylene sheet, and contained 50 ml of a 4 M formaldehyde solution, pH 11.50. When a constant temperature was obtained, 20° C, the tube was torn and the two reactants quickly mixed. Heat transfer through the vessel was corrected for by extrapolation of the time — temperature curve. Corrections for the heats of dilution of the reactants were obtained by replacing the formaldehyde respective urea by distilled water with the same buffers dissolved. The specific heat of the reaction solution was determined by immersing a polyethylene "test tube" containing a known amount of ice. The heat absorption by the calorimeter was determined by the same technique and with distilled water in the vessel.

Dimethylol urea formation. The same technique was used in this case as well. The solution was 500 ml 1.0 M formaldehyde, 0.050 M Na_2CO_3, pH 11.50. The tube contained 4.5 g dry monomethylol urea. Solid monomethylol urea was used in order to prevent influence from hydrolysis reactions. The substance was brought into solution rapidly, and disturbances from this step of the experiment were negligible.

The chemicals used were of A. R. quality, except for the formaldehyde, which was a Merck product containing only traces of methyl alcohol and formic acid ($<4.10^{-4}$ M in solutions containing 380 g/l). The monomethylol urea was prepared in accordance with Walter and Gewing [9]; cryoscopic molecular weight: 90 ± 2.

The heat of reaction was found to be the same for both mono- and dimethylol urea formation, namely 4.9 kcal/mole.

It may be of some interest to compare the activation energy differences ΔE, and the heat of reaction, Q. For processes in solutions we have: $\Delta E \cong Q$. The average difference between the formation and hydrolysis activation energies are 5.0 kcal/mole (Table 1). This figure, as compared with the heat of reaction 4.9 kcal/mole, shows that a good agreement is present.

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REFERENCES

1. Smythe, L. *J. Phys. & Colloid Chem.* **51** (1947) 369.
2. Smythe, L. *J. Am. Chem. Soc.* **75** (1953) 574.
3. Crowe, G. and Lynch, C. *J. Am. Chem. Soc.* **71** (1949) 3731.
4. Květŏn, R. and Kràlovà, M. *Chem. Listy* **46** (1952) 403.
5. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1121.
6. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1459.
7. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1466.
8. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1477.
9. Walter, G. and Gewing, M. *Kolloid-Beih.* **34** (1934) 163.

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REFERENCES

1. Smythe, L. J. *Phys. & Colloid Chem.* 51 (1947) 369.
2. Smythe, L. J. *Am. Chem. Soc.* 75 (1953) 574.
3. Crowe, G. and Lynch, C. J. *Am. Chem. Soc.* 71 (1949) 3731.
4. Kvĕton, R. and Kratová, M. *Chem. Listy* 46 (1952) 493.
5. Landqvist, N. *Acta Chem. Scand.* 9 (1955) 1127.
6. Landqvist, N. *Acta Chem. Scand.* 9 (1955) 1459.
7. Landqvist, N. *Acta Chem. Scand.* 9 (1955) 1466.
8. Landqvist, N. *Acta Chem. Scand.* 9 (1955) 1477.
9. Walter, G. and Gewing, M. *Kolloid-Beih.* 34 (1931) 163.

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11

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

X. Notes on the Reaction Mechanism

NILS LANDQVIST

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On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

X. Notes on the Reaction Mechanism

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The rates of the reactions of the urea-formaldehyde system are compared with other experimental data connected with urea and formaldehyde. The conclusions drawn from such comparisons are partly in favour of previous assumptions, partly not.

Some of the conclusions are: It is probable that a tautomer of urea may be the activated state for reactions with formaldehyde, and the tautomer may be of a zwitter ion structure. If the reactive compound would be an anion, the anion is not present in any considerable quantities prior to the reaction collisions. Only dehydrated formaldehyde or a resonance structure of dehydrated formaldehyde may react with urea or monomethylol urea. The rates of the depolymerisation, dehydration or hydration reactions of formaldehyde are of such a magnitude that they do not influence the rates of the reactions of the urea-formaldehyde system. The buffer catalysis of the urea-formaldehyde reactions is probably not simply connected with a formation of a buffer-formaldehyde complex prior to the reactions with urea or monomethylol urea.

Some of the previous theories connected with the urea-formaldehyde reaction mechanism are:

A. An anion of urea is the reactive compound in reactions with formaldehyde[1–5].

B. Only dehydrated formaldehyde reacts with urea or monomethylol urea [1,2,4–6].

C. In concentrated solutions the slow depolymerisation of formaldehyde polymers influences the urea-formaldehyde reaction rates [7].

D. The main influence of the temperature on the urea-formaldehyde reactions is due to changes in the equilibrium between hydrated and dehydrated formaldehyde [4,5].

E. The hydrolysis of methylol ureas catalysed by hydroxyl ions is connected with a dissociation of the OH group of the compound: $—OH + OH^- = —O^- + H_2O$. The rate of hydrolysis is proportional to the concentration of the $—O^-$ compound [6].

THE STATE OF UREA SOLUTIONS

I. There are several reasons to assume that urea tautomers exist. In favour of this assumption is:

X-Ray analysis shows a decrease in the bond length between carbon and nitrogen atoms. This is a typical effect of resonance hybrids [8].

Raman- och infrared spectra of solid urea show that the force constants of the C — N and C = O bonds are 35 % above, respective 39 % below the expected figures. The occurrence of hydrogen bonds is not found to be probable [9]. The presense of such bonds was assumed by another author [10], and the occurrence of tautomers representing any considerable fraction of the total amount of urea was not found to be probable. However, in this latter investigation no force constant calculations were made. The differences in opinion are also connected with differences in the interpretation of the absorbtion bands.

II. A urea tautomer may be of a zwitter ion structure, and the reasons for this assumption are:

The dielectric constant decreases considerably when urea is added to water, and the same effect is produced by amino acids [8].

The melting point of urea is considerably above the figure to be expected. Amino acids show the same behaviour [8].

III. No alkaline dissociation of urea could be detected when titrations were made with a hydrogen electrode for the pH measurements [11].

As mentioned in a previous paper [12], pH measurements in highly alkaline solutions by means of hydrogen electrodes require a high degree of hydrogen purity. In order to examine the investigation referred to above, the titration curves of 1.0 M urea and of distilled water at 20 °C after addition of HCl have been determined by means of the glass electrode differential method [12]. Accuracy: ± 0.02 pH. The results are shown by Fig. 1. From this diagram it might be concluded that if any alkaline dissociation of urea occurs, p$K > 13$. Thus, the previous result is confirmed.

THE STATE OF FORMALDEHYDE SOLUTIONS

IV. In concentrated solutions is the formaldehyde partly present as linear polymers [13].

V. The rate of depolymerisation of the polymers is highly dependent on pH and temperature. A rate minimum exists in the pH range 3—4. From studies below and above this range the specific catalytic constants of hydrogen and hydroxyl ions were found to be 3.7 and 3.7×10^7 liter/moles × sec, respectively, at 20 °C. The activation energy is 17.4 kcal. The reaction is mainly monomolecular, and is assumed to include the formation of a polymer zwitter ion. Correspondingly, the polymerisation reaction would involve a monomer zwitter ion [14].

VI. From diamagnetic measurements it was found that the equilibrium between polymeric and monomeric aldehyde is dependent on pH; also at pH 10 the dependency is of a considerable magnitude [15].

In order to investigate this result further, cryoscopic measurements have

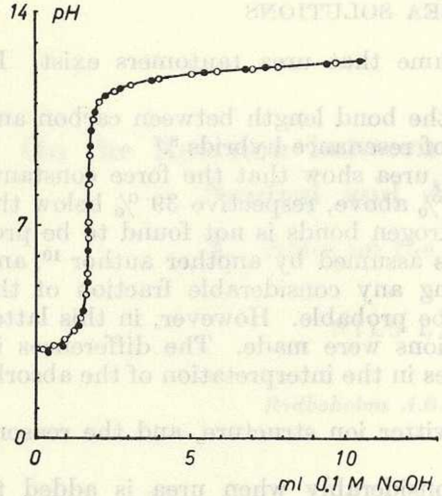


Fig. 1. Titration curve of 1.0 M urea (○) and of water (●) after addition of HCl to pH∼3. 20 °C.

been made on pure formaldehyde solutions, pH 5.5, and after addition of NaOH to pH 10. A stock solution of formaldehyde, 12.6 M, was prepared by distillation of a paraformaldehyde-water mixture, and allowed to attain equilibrium before it was used for the experiments. The stock solution was then, with and without addition of NaOH, diluted to concentrations in the range 0—6 M. Temperature 20 °C. The cryoscopic measurements were made immediately after the dilution and after 24 h storage. The results obtained are shown by Table 1. As seen, there is a considerable deviation from unity in the $(t_C—t_0)_{\mathrm{pH}\,10}$ / $(t_C—t_0)_{\mathrm{pH}\,5.5}$ ratios * when the measurements were made immediately after the dilution. However, after the storage such a devia-

Table 1. The ratios between the differences in freezing temperatures at the formaldehyde concentrations C and zero at pH 10.0 and 5.5 when the measurements are made immediately after dilution from a 12.6 M stock solution and after 24 h storage. Temperature 20 °C.

$\sum_{n=1}^{\infty} n\mathrm{C}_{(\mathrm{HCHO})_n}$	$(t_C-t_0)_{\mathrm{pH}\,10.0}$ / $(t_C-t_0)_{\mathrm{pH}\,5.5}$	
	Immediate measurements	After 24 h storage
1.0	1.67	1.00
2.0	1.43	1.00
3.0	1.35	1.00
4.0	1.31	1.00
6.0	1.28	1.00

---

* t_C and t_0 are the freezing temperatures at the formaldehyde concentrations C and zero, respectively.

tion does not exist. This effect may be a function of differences in rate of depolymerisation: after 24 h storage the equilibrium is probably attained at both pH values. Thus, it might be concluded that the pH influence referred to above is not found when the solutions are allowed to attain equilibrium conditions.

VII. The state of monomeric formaldehyde is described as an equilibrium between methylene glycol and dehydrated formaldehyde, and this equilibrium is highly in favour of the glycol [13]. The equilibrium constant [16,17] is $\sim 10^{-4}$. ($K = C_{\mathrm{HCHO}} / C_{\mathrm{HOCH_2OH}}$)

VIII. Both an acid and alkaline dissociation of formaldehyde is present [14,18,19]. At 20 °C the dissociation constants are: $\mathrm{p}K = 5.8$ and 13.4, respectively.

IX. The methylene glycol dehydration is catalysed by buffer substances [17,20]. The activation energy of the dehydration reaction is 14 kcal [16]; the figure corresponding to the hydration reaction is close to zero [17]. The catalysis by buffer substances as studied in a previous paper [17], is further exemplified by Table 2.

X. The composition of formaldehyde solutions can be summarized as follows [21]; the data refer to 20 °C.

$\Sigma\, C_{\mathrm{HCHO}}$	% polymers	% monomer
0.67	1	99
1.67	11	89
5.00	36	64
9.33	59	41

The temperature influence on the composition of the solutions was exemplified by the fact that the amount of polymers is below 1 % in 0.7 M solutions at 45 °C and in 7.3 M solutions at 100 °C.

Table 2. Polarographically determined dehydration rate constants of methylene glycol. Temperature 20 °C.

Analytical C_{HCHO}	Buffer *	pH	C_{buffer}	$k \times 10^2$ sec^{-1}
0.0157	$\mathrm{KH_2PO_4}$	6.70	0.100	5.9
			0.050	3.4
			0.025	1.7
0.00392	borax	9.20	0.100	57
			0.050	40
			0.025	30
0.00785	$\mathrm{Na_2CO_3}$	10.00	0.100	60
			0.050	49
			0.025	46

* To all solutions such amounts of the chloride of the buffer cation was added that a cationic strength corresponding to the most concentrated solution was obtained.

THE UREA OR MONOMETHYLOL UREA AND FORMALDEHYDE REACTIONS

When the collision theory of reaction will be used here for discussions, this does not mean that the theory is generally accepted. However, the frequency factors calculated can be used as a base for probability discussions: from a distribution curve, made from a great number of experimental data [22], it can be seen that 8 % of the frequency factors exceed 10^{13}, and only 4 % exceed 10^{14}.

In the following the calculations refer to data given in a series of previous papers [23–26]. The activation energy to be used is 15.4 kcal [27], equal for both the reactions.

The rate constants of the reactions between urea or monomethylol urea and formaldehyde are, within the range studied, 2×10^{-5}—2×10^{-3} liter/moles × sec. 20 °C, pH 6.70—11.50. Not only the formation reaction, but also the hydrolysis is catalysed by buffer substances [1,5,23–26]. The rate constants mentioned correspond to the frequency factors 5×10^{6}—5×10^{8}, *i.e.* the values are considerably below the figure to be expected from the collision theory, $\sim 3 \times 10^{11}$.

However, if we apply the assumption (B, see above) that only dehydrated formaldehyde reacts, and use the equilibrium constant 10^{-4} for the methylene glycol—fomaldehyde equilibrium (VII), the "corrected" rate constants corresponding to this would be 0.2—20 liter/moles. sec., and the frequency factors 5×10^{10}—5×10^{12}. When we compare these figures with the probability of different frequency factors as mentioned above, we find that if the dehydrated aldehyde is the formaldehyde reactant, the reactive structure of urea probably ought to be at least 1 % of the total amount. As previously mentioned (A,B), several reaction mechanism theories include the assumption that an anion of urea reacts with dehydrated formaldehyde. Since $pK > 13$ (III) for the formation of such an anion, it is not very probable that a reaction mechanism of this kind would be of any considerable importance in neutral and moderately alkaline solutions, if the anion is assumed to exist prior to the reaction stage. The complex relationships between pH and the logarithm of the reaction rate constants extrapolated to zero buffer concentration [23,24], show that the reaction mechanism is not solely including the presence of an anion of urea, as regards the effect of pH on the rates. Further, the catalytic effect of buffers cannot simply be explained by assumptions on the formation of the anion prior to the reaction stage.

The order of the dissociation constants of formaldehyde (VIII) shows that it is not very probable that formaldehyde ions would be of importance for the reactions in neutral and moderately alkaline solutions.

At this stage of the discussion some of the previous experimental results ought to be examined. From one of the papers [23] (Fig. 9 of Ref.[23]) it is seen that the rate relationship curves of the equimolecular urea—formaldehyde reactions are practically independent of the reactant concentrations in the interval studied, 0.5—4 M, 20 °C. As regards the monomethylol urea—formaldehyde reactions, the same behaviour was observed [24] in the studied range, 0.25—1 M, 20 °C. From above (X) it is known that at the upper concentrations of the ranges mentioned, the fraction of formaldehyde polymers is not negligible. This would mean that the monomer fraction decreases when the concentration increases, and the fraction of the dehydrated formaldehyde too. A consequence of this would be a decrease in the rate constants.

This decrease in the concentration of the dehydrated aldehyde is exemplified by some data previously given [28]. When repeating the experiments on which these data are based, a fairly good agreement with the 60 °C figures was obtained. At 30 °C the very low absorption did not permit any accurate calculations.

An explanation to the non—influence of |the presence of a considerable fraction of polymeric formaldehyde may be that collisions involving polymers also are active for producing a state of the aldehyde which is able to react with urea. The number of collisions is, from the theoretical point of view, more dependent on the number of HCHO groups than on their state: polymers or monomers.

This is seen from the well-known expression

$$Z = \sigma_{1;2}^{2} n_1 n_2 \sqrt{8\pi RT\left(\frac{1}{\mathrm{M}_1} + \frac{1}{\mathrm{M}_2}\right)}$$

Z = number of collisions pr ml and sec between the molecules 1 and 2. $\sigma_{1;2}$ = sum of molecular radii, n_1 and n_2 = number of molecules pr ml. M_1 and M_2 = molecular weights. When the number, n, of one of the molecules decreases by polymer formation, σ increases since polymerisation means an increase in molecular dimensions.

Another explanation could be that a concentration effect connected with the formaldehyde is compensated by an opposite effect connected with the urea. When examining the results of the previous paper [23] (Table 1 and Figs. 15 and 16 of Ref.[23]), we find that such an assumption is improbable.

As mentioned previously, (V), the specific catalytic constant of hydroxyl ions for the formaldehyde polymer depolymerisation is 3.7×10^7 liter/moles × sec at 20 °C. If we compare this figure with the data of Table 2, we find that the rates of depolymerisation considerably exceed the rates of methylene glycol dehydration. Thus, when dehydrated formaldehyde is liberated in solutions containing polymers, the rate of methylene glycol dehydration might be the rate determining step.

It may also be of some interest to compare the catalytic effect of some buffer substances at a constant cationic strength on the dehydration rate constants of methylene glycol, as given in Table 2, with the catalytic effect of the same buffers on the reactions of the urea—formaldehyde system [23–26]. Such a comparison is given in Table 3, where the constants of the equation describing the rate constant — buffer concentration relationship

$$k = k_0 + a \cdot C_{\text{buffer}} \tag{1}$$

can be found. k = rate constant at the buffer concentration C_{buffer}, k_0 = rate constant at the extrapolated zero buffer concentration.

If we examine the data of Table 3, we find that the rates of methylene glycol dehydration is considerably greater than the figures related to the urea—formaldehyde system. Thus, the dehydration rates have no influence on the rates of the urea—formaldehyde forward reactions. Since the hydration

Table 3. The constants of eqn. (1) of the methylene glycol dehydration and of the urea-formaldehyde reactions. Temperature 20 °C. Dehydration and hydrolysis reactions: k_0 sec^{-1}; a liter/moles · sec, Formation reactions: k_0 liter/moles · sec. a liter^2/moles^2 · sec.

Reactioo	Buffers						$a_{KH_2PO_4}$: a_{borax} : $a_{Na_2CO_3}$
	KH_2PO_4, pH 6.70		borax, pH 9.20		Na_2CO_3, pH 10.00		
	$k_0 \times 10^5$	$a \times 10^5$	$k_0 \times 10^5$	$a \times 10^5$	$k_0 \times 10^5$	$a \times 10^5$	
Methylene glycol dehydration	1 200	45 000	23 000	34 0000	41 000	18 0000	1 : 7.6 : 4.0
$H_2N \cdot CO \cdot NH_2$ + HCHO	3.4	126	4.3	37	6.7	133	1 : 0.29 : 1.1
$H_2N \cdot CO \cdot NH \cdot CH_2OH$ + HCHO	0.9	60	1.5	20	8.1	71	1 : 0.33 : 1.2
$H_2N \cdot CO \cdot NH \cdot CH_2OH$ hydrolysis	0.09	5.1	0.15	1.5	0.21	5.5	1 : 0.29 : 1.1
$HOCH_2 \cdot NH \cdot CO \cdot NH \cdot CHOH_2$ hydrolysis	0.11	8.7	0.18	2.4	0.72	7.3	1 : 0.28 : 0.8

reaction rates are 10^4 times greater than the dehydration rates, the same conclusion can be drawn regarding the hydrolysis reactions of the methylol ureas.

Another conclusion which might be drawn from Table 3 is that the mechanisms of methylene glycol dehydration and of the urea—formaldehyde reactions are probably not identical. This since the catalytic effect of the different buffers on the different reactions deviates considerably, as seen from the $a_{KH_2PO_4}$: a_{borax}: $a_{Na_2CO_3}$ ratios. The ratios connected with the urea—formaldehyde reactions are practically identical for all of these latter reactions. Thus, the catalysis of the rate determining step of the urea—formaldehyde reactions is probably not simply connected with the formation of an activated buffer—formaldehyde complex during the dehydration reaction, a complex which would represent an activated state for reactions with urea or monomethylol urea. However, the catalysts, *i.e.* buffers, H_2O and OH^-, increase the prior formaldehyde depolymerisation and dehydration reactions to such an extent that these reactions do not influence the rates of the urea—formaldehyde reactions.

Since polarographic investigation on formaldehyde in connection with the urea-formaldehyde reactions have previously [4] been used for discussions (A, B, D) regarding these reactions, some of the interpretations given will be examined.

The extent of formaldehyde dehydration was estimated from the ratios between actual "formaldehyde wave height" and the "total dehydrated wave height". The "total dehydrated wave height" was assumed to refer to a less steep slope appearing at increased temperatures when a log $i = f(1/T)$ curve is plotted from experimental data obtained on formaldehyde solutions containing buffer substances; (i = polarographic limiting current, T = temperature in °K). As easily seen from a previous paper [21], the change in slope mentioned does not mean that the formaldehyde is completely dehydrated; the less steep slope appears when the rate of methylene glycol dehydration exceeds the rate of diffusion of this substance to such an extent that the latter rate controls the polarographic electrode process.

It was further found that the following expression, derived from the Arrhenius equation:

$$\log \frac{k_2}{k_1} = \frac{\Delta E_a}{\Delta E_{aa}} \cdot \log \frac{i_2}{i_1} \tag{2}$$

is in a good agreement with experimental data. k_2 and k_1 = rate constants of the urea-formaldehyde reactions at two different temperatures but at the same buffer composition. i_2 and i_1 = the corresponding polarographic limiting currents of formaldehyde under the same conditions. ΔE_a and ΔE_{aa} = the "activation energies" of the urea-formaldehyde reaction, respectively the polarographic limiting current of formaldehyde. It is easily seen that eqn. (2) is self-consistent:

$$\log \frac{k_2}{k_1} = \log Z_k - \log Z_k - \frac{\Delta E_a}{\mathrm{M} \cdot R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{i_2}{i_1} = \log Z_i - \log Z_i - \frac{\Delta E_{aa}}{\mathrm{M} \cdot R} \cdot \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$(\mathrm{M} = \ln 10)$

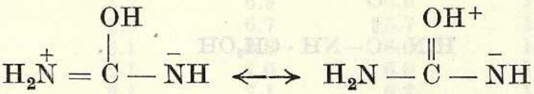
and thus eqn. (2) is obtained from these expressions. Any pair of reactions will give the coincidence observed, provided they obey the Arrhenius equation.

Finally, a relationship between urea-formaldehyde reaction rate constants and the polarographic limiting currents of formaldehyde at different pH values was given. However, this relationship is purely empirical [29].

It has previously been stated that the influence of the temperature on the urea—formaldehyde forward reaction rates is mainly due to changes in the equilibrium between hydrated and dehydrated formaldehyde (D); this assumption is also verified by comparisons between the activation energies referred to in this paper. Thus, the formation of an active state of urea would not be connected with any considerable change in energy.

Since our present knowledge of the state of urea in water solutions is highly limited, it is difficult to give any statement regarding the activated form of urea. However, it seems to be probable that urea tautomers exist, and that they may represent a considerable fraction of the total amount (I). Further, a zwitter ion structure of a tautomer is not improbable (II).

It has previously been assumed [3] that the urea structures

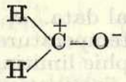


$$H_2\overset{+}{N}=\overset{OH}{\overset{|}{C}}-\overset{-}{N}H \longleftrightarrow H_2N-\overset{OH^+}{\overset{\|}{C}}-\overset{-}{N}H$$

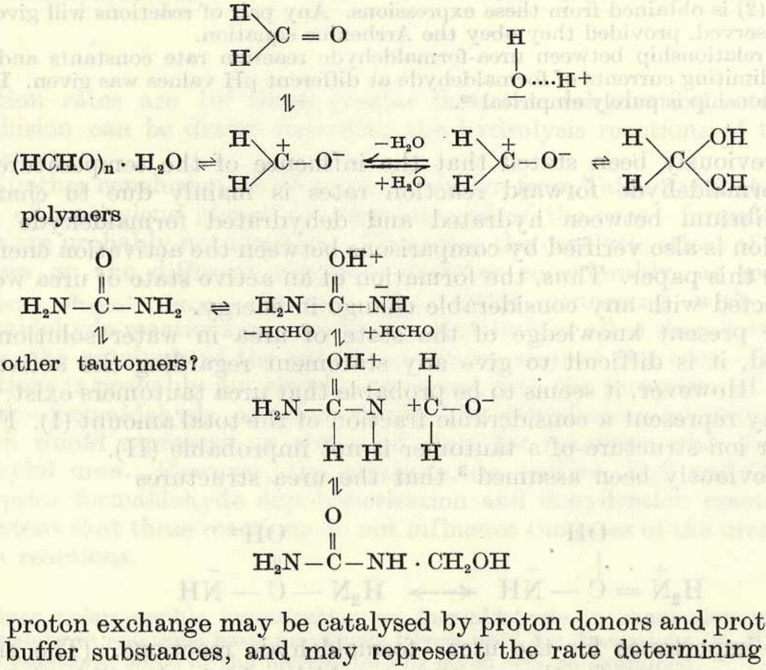
would be of importance for the urea—formaldehyde reactions. (The anion assumed to be necessary for the reactions would be obtained mainly through ionization to $HN=\overset{OH}{\overset{|}{C}}-\overset{-}{N}H$. The low probability of the formation of such an ion prior to the reaction with formaldehyde as a part of the reaction mechanism has been discussed above.)

The structures shown above may be in agreement with the requirements which follow from the experimental results regarding the state of urea previously mentioned in this paper. Further, a nitrogen atom is activated as a nucleophilic center.

In the polymerisation reactions of formaldehyde, a zwitter ion was assumed to be of importance (V), and the structure of the zwitter ion would be:



This structure may simply be regarded as a symbol for a resonance state of the dehydrated formaldehyde molecule, where the carbon atom is activated as an electrophilic center. With reference to the previous discussions regarding the formaldehyde polymers, and if we assume that the formaldehyde zwitter ion is in an activated state for both the hydration—dehydration reaction and for the reactions with urea or monomethylol urea, we get, *e.g.*, the following example of a possible reaction mechanism:



The proton exchange may be catalysed by proton donors and proton acceptors, *i.e.* buffer substances, and may represent the rate determining steps of the reactions.

A similar reaction scheme can also be applied to the monomethylol urea—formaldehyde system.

It will here be stressed that this scheme ought to be regarded as an example of a *possible* and not of a highly probable reaction mechanism description. Our present knowledge does not allow any conclusive statements.

THE HYDROLYSIS REACTIONS

A hydrolysis reaction mechanism previously assumed (E) may be within the scope of the scheme given above.

The shape of the rate constant—C_{OH^-} curve was shown to be in favour of the assumption that the anion of the methylol compound can be regarded as the activated complex for the hydrolysis reaction [6].

However, it is interesting to note that an assumption that the ionic form does *not* react, *i.e.* solely the -OH compound would be reactive and subject to a hydroxyl ion catalysis, is "verified" by the same experimental results.

This is found from the following:

$$\mathrm{R \cdot CH_2OH + OH^- = R \cdot CH_2O^- + H_2O}$$

$$\frac{C_{\mathrm{R \cdot CH_2O^-}}}{C_{\mathrm{R \cdot CH_2OH}} \cdot C_{\mathrm{OH}^-}} = K$$

$$C_{\mathrm{R \cdot CH_2OH}} + C_{\mathrm{R \cdot CH_2O^-}} = C_{\mathrm{total}}$$

and

$$\frac{C_{\mathrm{total}}}{C_{\mathrm{R \cdot CH_2OH}}} - 1 = K \cdot C_{\mathrm{OH}^-}$$

If only $\mathrm{R \cdot CH_2OH}$ reacts and under the influence of hydroxyl ion catalysis, this means that the actual hydrolysis rate constant k is related to a rate constant k_0 at the same hydroxyl ion concentration and extrapolated from the slope of the $k = f(C_{\mathrm{OH}^-})$ curve at $C_{\mathrm{OH}^-} = 0$ as follows:

$$\frac{k_0}{k} = \frac{C_{\mathrm{total}}}{C_{\mathrm{R \cdot CH_2OH}}}$$

($C_{\mathrm{total}} \ll C_{\mathrm{NaOH}}$ in the experiments, thus $C_{\mathrm{OH}^-} \sim C_{\mathrm{NaOH}}$)
and thus:

$$K = \frac{1}{C_{\mathrm{OH}^-}} \cdot \left(\frac{k_0}{k} - 1\right)$$

If we apply this expression to the figures taken from the experimental curves [6] related to monomethylol urea, MU, and also include the data for methylol benzamine, MB, methylol propioamide, MP and methylol chloroacetamide, MCh, we get the following K values:

C_{OH}	K_{MU}	K_{MB}	K_{MP}	K_{MCh}
0.2	1.7	6.9	5.6	16.0
0.3	2.0	6.7	5.7	15.3
0.4	2.1	6.8	6.0	15.1
0.6	2.1	7.0	6.0	14.6
1.0	2.1	7.1	6.2	14.7

When regarding the experimental accuracy to be expected, these results mean that no distinction between the two opposite reaction mechanism theories can be made.

However, the assumption (E) seems not to be unreasonable, even when there is a lack of significance in the experiments referred above. The initial stage of the hydrolysis reaction would, *e.g.*, be an ionization of the -OH group, followed by a proton transfer in accordance with the scheme above.

Table 4. The k_0 and a ratio between formation and hydrolysis reactions of the urea-formaldehyde system. k_0 and a formation, k_0' and a' hydrolysis. Temperature 20°C.

Buffer	pH	Monomethylol urea		Dimethylol urea	
		k_0/k_0'	a/a'	k_0/k_0'	a/a'
KH_2PO_4	6.70	38	25	8.2	6.9
Borax	9.20	29	25	8.3	8.3
Na_2CO_3	10.00	32	24	11.3	9.7

It may be of some interest to compare the formation—hydrolysis k_0 and a ratios, respectively, at different buffer solution compositions calculated from the figures of Table 3. These ratios can be found in Table 4. As seen, the ratios of the urea or monomethylol urea and formaldehyde reaction systems are of the same order, and as regards the urea—formaldehyde reaction the a ratios are practically constant. This may be in favour of an assumption that the buffer catalysis mechanism of both the formation and the hydrolysis are identical. However, the variations in the other ratios do not exclude such an identity even in these cases; the ionization state of the reactants may influence the activites of the different buffer ions in different ways when these ions are approaching in order to promote a proton transfer.

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REFERENCES

1. Smythe, L. *J. Phys. Colloid Chem.* **51** (1947) 369.
2. Smythe, L. *J. Am. Chem. Soc.* **73** (1951) 2735.
3. Smythe, L. *J. Am. Chem. Soc.* **75** (1953) 574.
4. Crowe, G. and Lynch, C. *J. Am. Chem. Soc.* **71** (1949) 3731.
5. de Jong, J. I. and de Jonge, J. *Rec. trav. chim.* **7** (1952) 643.
6. Ugelstad, J. *The Reaction of Formaldehyde with Amides and the Alkaline Hydrolysis of Alkoxymethyl Ureas* (Diss.) Leiden 1955, p. 54–61.
7. Smythe, L. *J. Am. Chem. Soc.* **74** (1952) 2713.
8. Sidgwick, N. V. *The Organic Chemistry of Nitrogen*, Clarendon Press, Oxford, 1937, p. 285.
9. Kellner, L. *Proc. Roy. Soc. London* **A 177** (1941) 456.
10. Sundara Rao, A. L. *J. Indian Chem. Soc.* **18** (1941) 337.
11. Bell, J., Gillespie, W. A. and Taylor, D. B. *Trans. Faraday Soc.* **39** (1943) 137.
12. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 595.
13. Auerbach, F. and Barschall, H. *Arb. kaiserl. Gesundh.* **22** (1905) 594.
14. Wadano, M., Trogus, C. and Hess, K. *Ber.* **67** (1934) 174.
15. Sauterey, R. *Ann. chim. Paris* (*12*) **7** (1952) 1.
16. Bieber, R. *Über das polarografische Verhalten der niederen, gesättigten alifatische Aldehyde, besonders des Formaldehyds* (Diss.) Zürich 1948, p. 98–100.
17. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 867.
18. Euler, H. and Lövgren, T. *Z. anorg. Chem.* **147** (1925) 123.
19. Lévy, M. *J. Biol. Chem.* **105** (1934) 157.
20. Veselý, K. and Brdička, R. *Collection Czechoslov. Chem. Communs.* **12** (1947) 313.

21. Walker, F. *Formaldehyde*, Reinhold Publishing Company, New York 1953, p. 53.
22. Moelwyn — Hughes, E. A. *The Kinetics of Reactions in Solution*, Clarendon Press, Oxford, 1933.
23. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1127.
24. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1459.
25. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1466.
26. Landqvist, N. *Acta Chem. Scand.* **9** (1955) 1471.
27. Landqvist, N. *Acta Chem. Scand.* **10** (1956) 244.
28. Walker, F. *Formaldehyde*, Reinhold Publishing Company, New York 1953, p. 51.
29. Crowe, G. *Private communication.*

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