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 Barrenscheen¹, and was later on applied for spectrophotometrical determination of urea by Watt and Chrisp².

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 Gewing³. 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 (x), 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 in Fig. 1. From a preliminary study it was found that the wavelength at the extinction maximum is constant within the concentration range studied. $\lambda_{\max} = 4270 \text{ Å}$.

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:

$$C_U = 1.16 \times 10^{-2} \times E_{\max} \quad (1)$$

$$C_M = 3.55 \times 10^{-2} \times E_{\max} \quad (2)$$

$$C_D = 23 \times 10^{-2} \times E_{\max} \quad (3)$$

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

$$E_{\max} = 86 C_U + 28 C_M + 4.3 C_D \quad (4)$$

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

For a reaction mixture of urea and formaldehyde, C_U^0 and C_F^0 are the initial urea and formaldehyde concentrations, and we have, provided mono- and dimethylol urea are the reaction products:

$$\begin{aligned} C_U^0 &= C_U + C_M + C_D \\ C_F^0 &= C_F + C_M + 2 C_D \end{aligned}$$

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

$$C_U = 0.0292 E_{\max} - 1.51 C_U^0 + 0.71 C_F^0 - 0.71 C_F \quad (5)$$

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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