[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, CANISIUS COLLEGE]

The Critical Increment of Ionic Reactions. II. The Influence of Dielectric Constant and Ionic Strength

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On the assumption that the rates of ionic reactions are functions only of the temperature, dielectric constant and ionic strength, equations were derived[3] recently which predicted the influence of dielectric constant and ionic strength upon critical increments. The calculated results were shown to be in satisfactory agreement with the observed critical increments in the reaction between ammonium and cyanate ions over the temperature range of 30 to 70°. The reaction was studied in water whose dielectric constant varied with temperature, and in mixtures of water with methanol at the fixed dielectric constants of 63.5 and 55. In the present investigation, the reaction between ammonium and cyanate ions was studied over the same temperature range in mixtures of water with methanol at fixed dielectric constants of 50, 45, 40 and 35, and also in a constant alcohol composition mixture of 28.3%, whose dielectric constant varied with temperature. The experimental critical increments were then compared with the predicted values obtained by means of the theoretical equations.[3]

Experimental

All materials were prepared or purified as described in previous papers,[4] which also describe the procedure used in this investigation. All temperatures were checked against a thermometer recently calibrated by the Bureau of Standards. Thermostat temperatures were maintained constant within ±0.01°. Dielectric constants for water and for water–methanol mixtures were taken from the work of Åkerlöf.[5]

Using Scatchard's[6] treatment for the rate of reaction in a changing environment, Warner and Warrick[4b] developed the equation

$$k_0t = \left\{\frac{1 + 4A\ \sqrt{C}}{C}\right\} - \left\{\frac{1 + 4A\ \sqrt{C^0}}{C^0}\right\} \quad (1)$$

where A is the Debye-Hückel constant in $\ln \gamma_i = -Az_i^2\sqrt{\mu}$. Average values of the limiting velocity constant obtained by this method are listed in Table I.[7]

Deviations (δ) of the experimental value of $C/(1 + 4A\sqrt{C})$ from the value calculated from the average k_0 are plotted against the experimental value of this function in Fig. 1[4b]. The filled circles represent values of $C^0/(1 + 4A\sqrt{C^0})$. Limiting velocity constants can also be calculated from bimolecular constants determined by the method of slopes[4] by means of the equation[8]

$$\log k_1 = \log k_0 + \frac{\epsilon^2 Z_A Z_B K}{DkT(1 + Kb)} \quad (2)$$

which applied to our reaction becomes

$$\log k_0 = \log k_1 + \frac{3.63 \times 10^6\sqrt{\mu}}{(TD)^{3/2} + 100.6DT\sqrt{\mu}} \quad (3)$$

Equation (3) yields[3,4b] somewhat higher values for k_0 than equation (1). However, plotting the corresponding $\log k_0$ values against $1/T$ in water, and in methanol–water mixtures of D = 63.5–55 gives[3] parallel lines. While the average k_0 values listed in Table I have been obtained by means of equation (1), it must be emphasized that there is no real reason for believing that equation (1) yields better results in this case than equation (3). In Table II, we give velocity constants (k_1) at $\sqrt{\mu}$ = 0.194 obtained from k_0 by the relation[4b]

$$k_1 = k_0/(1 + 2A\ \sqrt{\mu}) \quad (4)$$

The lines obtained by plotting $\log k_0$ and $\log k_1$, respectively, against $1/T$ for water, and for methanol–water mixtures of 28.3% constant composition, and for methanol–water mixtures of D = 63.5, 55, 50, 45, 40 and 35 can be expressed by the general equation

$$\log k = \log K - (E/4.58T) \quad (5)$$

In Fig. 3, $\log k_0$ is plotted against $1/T$ for the various media. Values of $\log K_0$ and E_0 and of $\log K_1$ and E_1 obtained by means of equation (5) are listed in Tables I and II, respectively. The tables also contain values of k_0 and k_1 calculated by means of equation (5) using the tabulated values of $\log K$ and E. It is evident from the tables that

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[2] From the thesis presented to the Graduate Committee of Canisius College by Arthur Schramm in partial fulfilment of the requirements for the degree, Master of Science, June, 1937. Presented at the Rochester meeting of the A. C. S., Sept., 1937.

[3] Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935).

[4] (a) Warner and Stitt, *ibid.*, **55**, 4807 (1933); (b) Warner and Warrick, *ibid.*, **57**, 1491 (1935).

[5] Åkerlöf, *ibid.*, **54**, 4125 (1932).

[6] Scatchard, *ibid.*, **52**, 52 (1930).

[7] Table I. (a) Data in water, and in water–alcohol mixtures at dielectric values of 63.5 and 55 were obtained from ref. 3. (b) Data at 50°, dielectric values of 50 and 45 were obtained from ref. 4b.

[8] Scatchard, *Chem. Rev.*, **10**, 229 (1932).

the log K's for the constant dielectric constant mixtures are approximately constant, the average value being 11.77. This leads to a collision factor of ~5.8 × 10^{11}. It thus seems that the collision factor is, within experimental error, independent of both the dielectric constant and the ionic strength in methanol–water mixtures of constant dielectric constant.

Svirbely and Warner[3] obtained a relationship between the critical increment in a solvent of fixed composition and a medium of constant dielectric constant, namely

$$(E^0)_{\text{fixed comp.}} = (E^0_D{}^*) + 2.3\,RT^2 \left(\frac{\partial \log k_0}{\partial D}\right)_T \frac{dD}{dT} \qquad (6)$$

For water, equation (6) becomes

$$(E^0)_{H_2O} - (E^0_D{}^*) = (1050T/D) \qquad (7)$$

Using equation (7) one calculates the difference between the critical increment in water and in media of fixed dielectric constant to be 4860 calories at 50°. Using the experimental values of the E^0's given in Table I, one observes that the differences between the critical increments in water and in media of fixed dielectric constant vary from 4740 cal. at D = 63.5 to 6210 cal. at D = 35. The increase in the differences between the experimental values as one approaches the lower dielectrics is due to the continued decrease in the value of $E^0_D{}^*$. The decrease in $E^0_D{}^*$ amounts to 1500 calories. It should be pointed out, however, that some of the decrease in $E^0_D{}^*$ may be due to the method of calculating the k_0's. In the derivation of equation (1) essentially it is assumed that equation (4) not only holds throughout the experimental range but that it also holds to zero concentration. This extrapolation to zero concentration, particularly as the (DT) product decreases, appears to be somewhat uncertain. However, one cannot estimate at present just how much if any of the decrease in $E^0_D{}^*$ is due to errors of extrapolation. If $E^0_D{}^*$ is plotted against D, a linear relation-

TABLE I

SUMMARY OF DATA AT ZERO IONIC STRENGTH

	Variable dielectric constant media				Constant dielectric constant media																	
	H_2O k_0		28.3 % MeOH–H_2O k_0		63.5			55			50			45			40			35		
Temp., °C.	Direct	Eq. 5	Direct	Eq. 5	Wt. % MeOH	k_0 Direct	Eq. 5	Wt. % MeOH	k_0 Direct	Eq. 5	Wt. % MeOH	k_0 Direct	Eq. 5	Wt. % MeOH	k_0 Direct	Eq. 5	Wt. % MeOH	k_0 Direct	Eq. 5	Wt. % MeOH	k_0 Direct	Eq. 5
30	0.00625	0.00615	0.0159	0.0155	28.3	0.0159	0.0156	46.6	0.0304	0.0294	57.1	0.0455	0.0457	67.2	0.0777	0.0785	77.8	0.125	0.124	89.1	0.185	0.183
40	.0217	.0214	.0498	.0506	21.4	.0413	.0424	39.6	.0785	.0785	50.8	.121	.119	61.4	.198	.202	72.4	.315	.302	84.0	.475	.460
50	.0680	.0691	.154	.154	14.8	.106	.108	33.4	.192	.197	45.0	.299	.294	56.1	.489	.490	67.3	.742	.757			
60	.205	.208	.440	.440	8.1	.263	.261	27.5	.468	.468	38.9	.680	.685	50.6	1.120	1.130	62.7	1.720	1.730	74.3	2.470	2.460
70	.584	.589			0.0	.584	.598															
log. K_0 (Eq. 5)	14.78		14.33				11.77		11.80			11.71			11.75			11.77			11.78	
E (Eq. 5)	23,580		22,400				18,840		18,500			18,110			17,840			17,590			17,370	

TABLE II

SUMMARY OF DATA AT $\sqrt{\mu}$ = 0.194

	Variable dielectric constant media				Constant dielectric constant media											
	H_2O k_1		28.3% MeOH–H_2O k_1		63.5 k_1		55 k_1		50 k_1		45 k_1		40 k_1		35 k_1	
Temp., °C.	Direct	Eq. 5	Direct	Eq. 5	Direct	Eq. 5	Direct	Eq. 5	Direct	Eq. 5	Direct	Eq. 5	Direct	Eq. 5	Direct	Eq. 5
30	0.00429	0.00420	0.0099	0.0095	0.0099	0.0095	0.0173	0.0169	0.0243	0.0245	0.0385	0.0383	0.0564	0.0552	0.0743	0.0748
40	.0148	.0144	.0306	.0308	.0262	.0263	.0457	.0458	.0662	.0653	.1005	.1009	.146	.144	0.1955	0.193
50	.0460	.0458	.0937	.0927	.0683	.0680	.114	.117	.167	.165	.254	.246	.353	.353		
60	.137	.133	.265	.261	.172	.166	.283	.282	.388	.393	.594	.604	.838	.822	1.078	1.088
70	.388	.377			.388	.386										
log K_1 (Eq. 5)	14.37		13.94		11.77		11.81		11.77		11.77		11.77		11.78	
E (Eq. 5)	23,240		22,150		19,140		18,850		18,570		18,300		18,080		17,910	
E (Eq. 9 at 50° C.)	23,380		22,180		19,180		18,890		18,540		18,300		18,100		17,920	

ship is obtained which may be expressed by the equation

$$E_D^{0*} = -15{,}460 - 53.19D \qquad (12)$$

By combining equations (5) and (12) one obtains an empirical equation for $\log k_0$ in media of fixed dielectric constant, namely

$$\log k_0 = 11.75 - \frac{(15{,}460 + 53.19D)}{4.58T} \qquad (13)$$

Values of $\log k_0$ obtained by equation (13) are compared with the experimental values in Fig. 3.

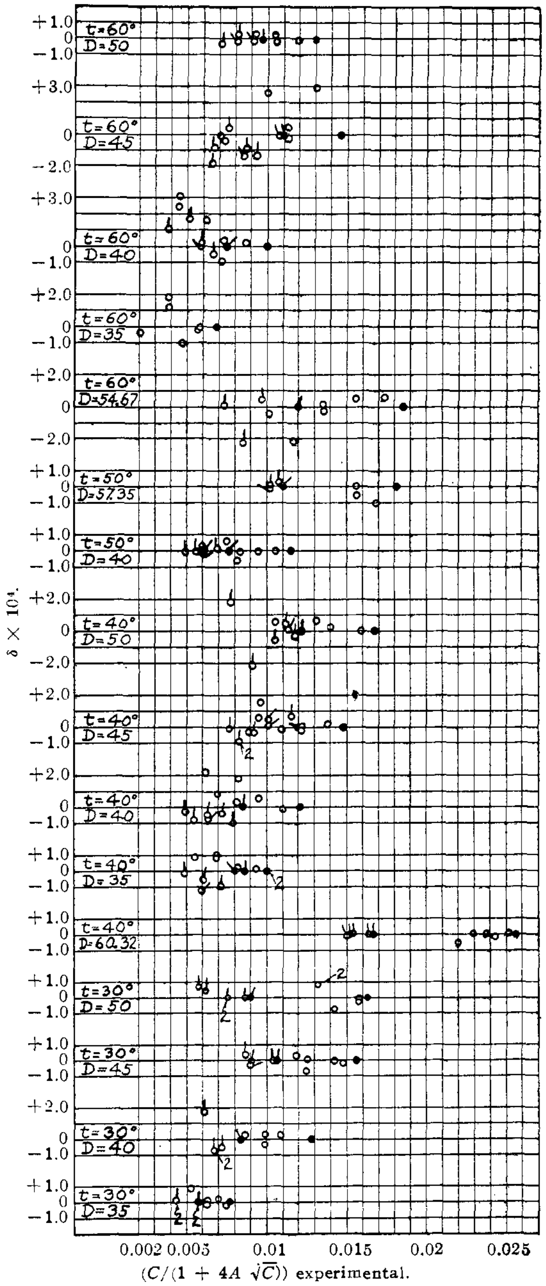

Fig. 1.—Methanol–water mixtures.

For 28.3% alcohol, equation (6) becomes

$$(E^0)_{28.3\%\,\mathrm{CH_3OH}} - (E_D^{0*}) = 735T/D \qquad (8)$$

This leads[3] to a calculated value of $E^0_{28.3\%\ \mathrm{CH_3OH}} = 22{,}970$ cal. Using equation (8) one calculates the difference between the critical increment in 28.3% methanol and in media of fixed dielectric constant to be 4130 cal. at 50°. Using the experimental E^0's, one observes that $(E^0)_{28.3\%\mathrm{CH_3OH}} - (E_D^{0*})$ varies from 3560 cal. at $D = 63.5$ to 5030 cal. at $D = 35$.

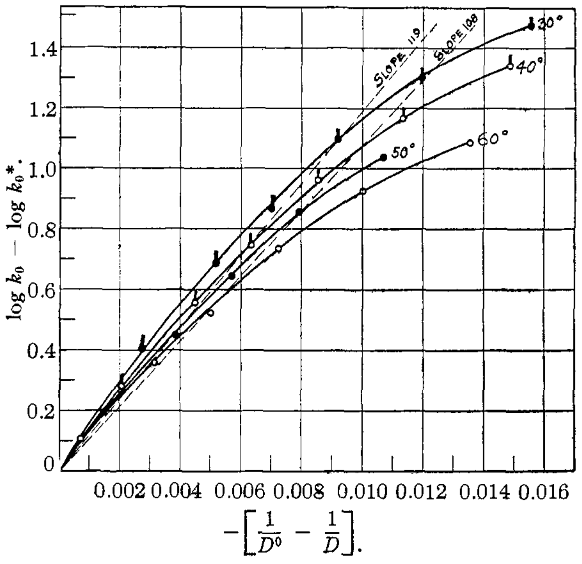

Fig. 2.

By taking logarithms and differentiating equation (4) one obtains a relationship between E^0 and E at a fixed ionic strength, namely

$$E = E^0 + \frac{(12.5 \times 10^6\sqrt{\mu}\,RT)}{(TD)^{3/2} + 8.36 \times 10^6\sqrt{\mu}}\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right) \qquad (9)$$

Using equation 9, we have calculated E at $\sqrt{\mu} = 0.194$ from E^0 of the various media. The results are listed in Table II and are in good agreement with the E's obtained by equation (5). Furthermore, it is observed that in agreement with equation (9), the critical increments increased with ionic strength in the media of fixed dielectric constant but decreased with ionic strength in the media of fixed composition.

The following equation for ionic reactions has been developed by Scatchard[8] from consideration of the dielectric effect of the medium, namely

$$\log k_0 - \log k_0^* = \frac{e^2 Z_A Z_B}{2.3kTr}\left(\frac{1}{D^0} - \frac{1}{D}\right) \qquad (10)$$

where k_0^* is the rate constant at zero ionic strength in a standard solvent of dielectric constant D^0, k_0 is the corresponding rate constant at zero ionic strength in a solvent of dielectric constant D. If we use water as the standard solvent and we assume $r = 2 \times 10^{-8}$ cm., then we obtain from equation 10 the following equations for this reaction

$$\begin{aligned} t = 60^\circ \quad & \log k_0 - \log k_0^* = -108\left(\frac{1}{66.62} - \frac{1}{D}\right) \\ t = 30^\circ \quad & \log k_0 - \log k_0^* = -119\left(\frac{1}{76.73} - \frac{1}{D}\right) \end{aligned} \qquad (11)$$

These equations (also those for $t = 40^\circ$ and 50°) predict an increase in velocity with decrease in dielectric constant for this reaction. Reference to Table I shows that the experimental results are in agreement with theory. In Fig. 2 values of ($\log k_0 - \log k_0^*$) have been plotted against the corresponding differences in the reciprocals of D^0 and D at the different temperatures. The resulting plots, according to equations 11, should be linear with slopes equal to the constants in the corresponding equations and increasing with decreasing temperatures. The curves depart, however, from the predicted linearity, the slopes decreasing as the amount of alcohol is increased at each temperature. The limiting slopes of the curves are in fair agreement with the predicted values, increasing from ~ -113 to ~ -147 with decreasing temperatures. Better agreement between experiment and theory is hardly to be expected due to the approximate nature of equation 10 as others have pointed out.[4b,8] It should also be pointed out that much of the curvature in Fig. 2 may be due to the possible errors of extrapolation previously mentioned.

Finally, we desire to call attention to an empirical relationship between the dielectric effect and the temperature effect on the value of the limiting velocity constant for this reaction in methanol-water mixtures of constant dielectric constant. From the partial differentials of equation (13) one obtains

$$\left(\frac{\partial k_0}{\partial T}\right)_D = -\left(\frac{\partial k_0}{\partial D}\right)_T \left(\frac{290.7 + D}{T}\right) \qquad (14)$$

The third term in equation (14) varies from 0.98 to 1.17 over the complete temperature and dielectric range. One may then say that as an approximation

$$\left(\frac{\Delta k_0}{\Delta T}\right)_D = -\left(\frac{\Delta k_0}{\Delta D}\right)_T \qquad (15)$$

Reference to Table I shows that this empirical equation is obeyed since one obtains approximately the same k_0 value by either decreasing the dielectric constant by 10 at a constant temperature or by increasing the temperature by 10 at constant dielectric constant.

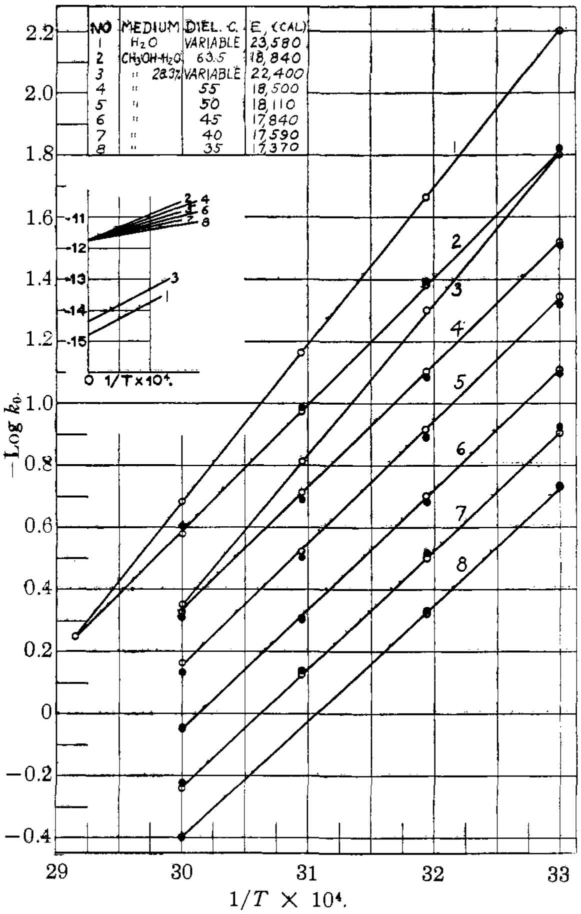

Fig. 3.—Influence of temperature on the rate of conversion of ammonium cyanate to urea in different media at zero ionic strength. ○, experimental points; ●, calcd. by equation 13.

Summary

1. The rate of conversion of ammonium cyanate to urea has been studied over the temperature range 30 to 60° in 28.3% methanol, dielectric constant varying with temperature, and in mixtures of water with methanol at constant dielectric constants for the mixtures of 50, 45, 40 and 35.

2. The value of the collision factor Z in the Arrhenius equation appears to be independent of dielectric constant and ionic strength in methanol-water media of constant dielectric constant. In methanol-water media of constant composition, the collision factor varies with the media and with the ionic strength.

3. The influence of dielectric constant of the

solvent upon the rate constants is in fair agreement with the Scatchard–Christiansen theory.

4. Empirically it is shown that for this reaction in methanol–water mixtures of constant dielectric constant the following relation holds

$$\left(\frac{\Delta k_0}{\Delta T}\right)_D = -\left(\frac{\Delta k_0}{\Delta D}\right)_T$$

5. The influence of ionic strength upon the observed critical increments at zero ionic strength is in good agreement with equations previously derived. It is observed that the critical increment decreases with decreasing dielectric constant in media of constant dielectric constant.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. II. Density Data

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As a part of the general investigation of the thermodynamics of hydrochloric acid in dioxane–water mixtures, it is necessary to know the concentration of the electrolyte, c, in moles per liter of solution. Extensive measurements of cells suitable for studying the properties of hydrochloric acid in these solutions have been made in this Laboratory and, for practical reasons, the concentrations of the acid have been expressed in molalities, m. Since c is related to m by the equation

$$c/m = 1000d/(1000 + mM) \qquad (1)$$

where d is the density and M the molecular weight of the solute, density determinations of the solutions are required. This communication contains the result of density determinations of 20, 45, 70 and 82% dioxane in water solutions covering a range in temperature from 0 to 50° and ranges of concentration from 0 to 3 M hydrochloric acid for the first two mixtures, from 0 to 1.5 M for the third, and from 0 to 0.7 M in the case of the fourth mixture, respectively.

Experimental Measurements and Density Data

The materials were purified and the solutions were prepared according to the directions given by Harned and Morrison.[1] For the determinations of the 20, 45 and 70% solutions, both pycnometers and dilatometers were employed. The density of each solution was determined at 25° by pycnometers of about 30-cc. capacity, and the densities of the solutions at other temperatures were computed from volume changes measured by dilatometers. The volumes of the dilatometers were about 110 cc. and the capillaries were 3 mm. in diameter and one meter in length. The volumes of the dilatometers were determined by means of conductivity water. The temperature control was better than ±0.02°. The thermometers used were calibrated against a standard resistance thermometer.

In the case of the 82% dioxane solutions, only the dilatometers were used. The pure solvent was used to standardize the apparatus. The densities of the pure solvent, d_0, necessary for this purpose were obtained from the data of Hovorka, Schaefer, and Dreisbach[2] by plotting the isothermal values against mole fraction of dioxane. From these curves, d_0 was obtained at 10° intervals from 10 to 60°. By means of Newton's extrapolation formula values of d_0 were obtained at 5° intervals from 5 to 45°.

By these means, density measurements were obtained at molalities 0.1, 0.2, 0.3, 0.5, 0.7, 1, 1.5, 2 and 3 M in the cases of the 20 and 45% dioxane mixtures, at 0.1, 0.2, 0.3, 0.5, 0.7, 1 and 1.5 M for the 70% mixtures, and at 0.002, 0.003, 0.005, 0.007, 0.015, 0.02, 0.03, 0.05, 0.07, 0.1, 0.3, 0.5 and 0.7 M in the case of the 82% dioxane mixtures.

Since the results were so voluminous, they have been expressed by equations which give the densities, d, at each temperature as a function of the molality of the acid. It was found that a linear equation was not sufficient to represent the results to within ±0.03% except in one case, nor were quadratic equations adequate. The best simple representation of the results is given by the equation

$$d = d_0 + am - bm^3 + em \log m \qquad (2)$$

where d_0 is the density of solvent, and a, b, e are

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[1] Harned and Morrison, THIS JOURNAL, **58**, 1908 (1936); *Am. J. Sci.*, **33**, 161 (1937).

[2] Hovorka, Schaefer and Dreisbach, *ibid.*, **58**, 2264 (1936).