TABLE II

THE CONDUCTIVITY OF AQUEOUS POTASSIUM HYDROFLUORIDE AT 25°

C	0.020	0.006	0.005	0.002	0.001
Λ exptl.	138	150	167	217	270
Λ calcd.	136.0	163.3	169.6	217.7	265.5
% Dev.	1.45	8.87	1.56	0.32	1.67

complicate the analysis. The relatively large deviation at $C = 0.006$ is, of course, due to the error introduced by neglecting the concentration of the hydrofluoride ion; at lower concentrations this error becomes of less importance.

Summary

It has been shown that the conductance function for unilateral triple ion formation applies satisfactorily to the conductance data for aqueous hydrofluoric acid at 25 and at 0°. The constants determined in this way are consistent with the substantially independent values which may be obtained from transference measurements and they may be employed successfully to calculate the conductivity of potassium hydrofluoride solutions.

PROVIDENCE, R. I. RECEIVED APRIL 20, 1938

[JOINT CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF CANISIUS COLLEGE AND OF THE UNIVERSITY OF MARYLAND]

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

BY JAMES LANDER[1] AND W. J. SVIRBELY

Recently,[2] equations were derived which predicted the influence of dielectric constant and ionic strength upon the critical increments of ionic reactions. The critical increments obtained by means of the theoretical equations were then compared with the experimental critical increments obtained for the reaction between ammonium and cyanate ions in methanol–water mixtures of constant dielectric constants. In the present investigation, the same reaction was studied over a temperature range of 30 to 60° in mixtures of water with ethylene glycol at the fixed dielectric constants of 63.5, 60, 55, 50, 45 and 40 in order to observe if there would be any specific medium effects due to the use of a different solvent. The experimental critical increments were then compared with the values obtained by means of the theoretical equations.[2]

Experimental

The ethylene glycol used was Eastman Best Grade (Highest Purity). The glycol was distilled and the fraction boiling sharply at 197° (uncorr.) was used. All other materials were prepared or purified as described in previous papers[3] which also describe the procedure used in this investigation. All temperatures were checked against a thermometer calibrated by the Bureau of Standards. Thermostat temperatures were maintained constant within ±0.01°. Dielectric constants for glycol–water mixtures were taken from the work of Åkerlöf.[4]

Average values of the limiting velocity constants were determined by means of the equation[3b,2]

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

and are listed in Table I. Deviations (δ) of the experimental value of $C/(1 + 4A\sqrt{C})$ from the value calculated from the average k_0 are plotted[3b] against the experimental values of this function in Figs. 1 and 2. The filled circles represent values of $C^0/(1 + 4A\sqrt{C^0})$. In Table II, we give velocity constants (k_1) at $\sqrt{\mu} = 0.194$ obtained from k_0 by the relation[3b]

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

In Fig. 3, log k_0 is plotted against $1/T$ for the various media. These lines, as well as those obtained by plotting log k_1 against $1/T$, can be expressed by the general equation

$$\log k = \log K - (E/4.58T) \quad (3)$$

Values of log K_0 and E_0 and of log K_1 and E_1 obtained by means of equation (3) are listed in Tables I and II, respectively. The tables also contain values of k_0 and k_1 calculated by equation (3) using the tabulated values of log K and E.

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[1] From the thesis presented to the Graduate Committee of Canisius College by James Lander in partial fulfilment of the requirements for the degree of Master of Science, June, 1938.

[2] (a) Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935); (b) Svirbely and Schramm, *ibid.*, **60**, 330 (1938).

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

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

TABLE I

SUMMARY OF DATA AT ZERO IONIC STRENGTH IN GLYCOL–WATER MEDIA

Constant dielectric constant media

Temp., °C.	63.5			60			55			50			45			40		
	Wt. % of gly.	k_0 Eq. 1	k_0 Eq. 3	Wt. % of gly.	k_0 Eq. 1	k_0 Eq. 3	Wt. % of gly.	k_0 Eq. 1	k_0 Eq. 3	Wt. % of gly.	k_0 Eq. 1	k_0 Eq. 3	Wt. % of gly.	k_0 Eq. 1	k_0 Eq. 3	Wt. % of gly.	k_0 Eq. 1	k_0 Eq. 3
30	44.25	0.0113	0.0113	54.20	0.0141	0.0139	68.0	0.0191	0.0191	76.15	0.0265	0.0264	85.75	0.0384	0.0372	94.10	0.0509	0.0508
40	33.56	.0321	.0329	44.90	.039	.040	58.8	.0533	.0548	70.35	.0756	.0746	82.18	.106	.106	90.8	.141	.146
50	22.70	.0910	.089	34.90	.1096	.108	50.6	.148	.148	64.0	.202	.203	75.64	.280	.287	86.65	.380	.393
60	11.55	.230	.227	24.20	.279	.275	41.6	.387	.376	56.6	.528	.515	69.95	.730	.727	81.70	.996	.995
log K_0 (eq. 3)		12.51			12.54			12.67			12.76			12.91			13.06	
E (eq. 3)		20,060			19,980			19,970			19,900			19,900			19,920	

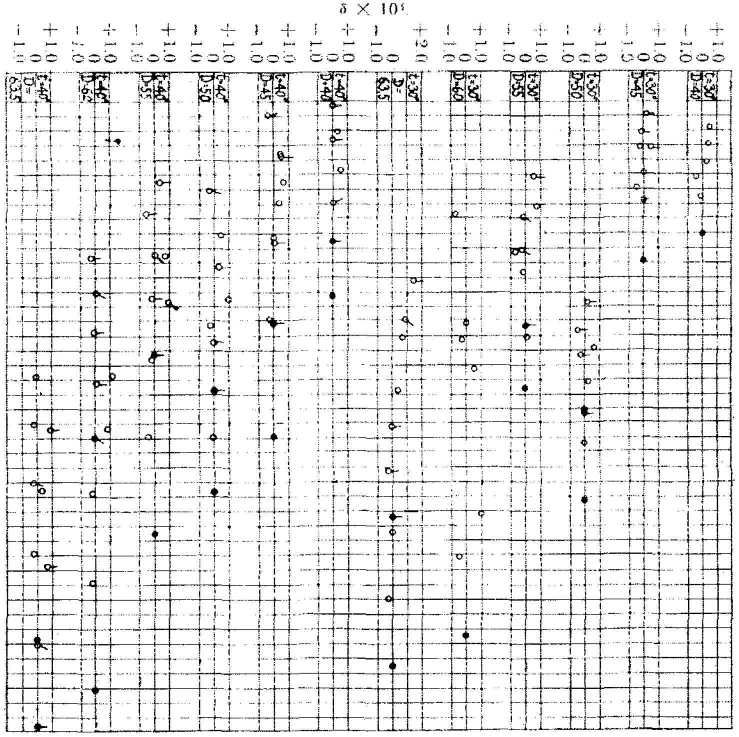

Fig. 1.—Glycol–water mixtures.

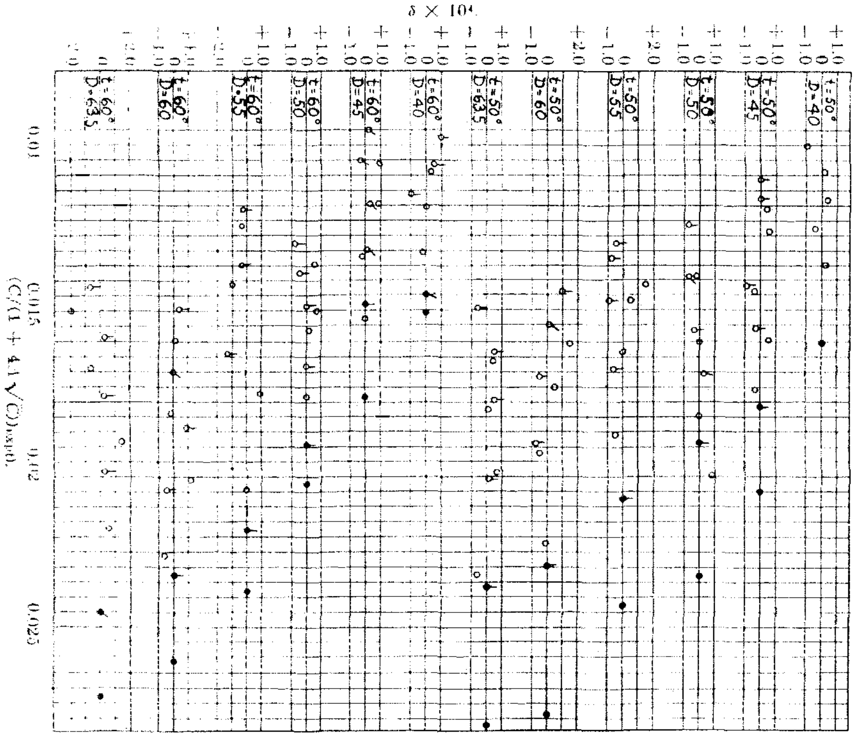

Fig. 2.—Glycol–water mixtures.

TABLE II

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

Constant dielectric constant media

Temp., °C.	63.5		60		55		50		45		40	
	k_1		k_1		k_1		k_1		k_1		k_1	
	Eq. 2	Eq. 3	Eq. 2	Eq. 3	Eq. 2	Eq. 3	Eq. 2	Eq. 3	Eq. 2	Eq. 3	Eq. 2	Eq. 3
30	0.00703	0.00703	0.00847	0.00829	0.0109	0.0107	0.0142	0.0142	0.0190	0.0183	0.0230	0.0228
40	.0203	.0211	.0239	.0245	.0311	.0319	.0413	.0418	.0538	.0539	.0655	.0667
50	.0586	.0586	.0684	.0680	.0878	.0882	.113	.115	.145	.148	.180	.183
60	.151	.153	.177	.177	.234	.230	.301	.297	.387	.383	.486	.469
log K (eq. 3)	12.68		12.69		12.79		12.80		12.91		12.95	
E(eq. 3)	20,580		20,500		20,480		20,330		20,320		20,250	
E(eq. 6 at 50°)	20,400		20,330		20,360		20,330		20,360		20,310	

From the equation[2a]

$$(E^0)_{\text{fixed comp.}} = (E_{\mathrm{D}}^{0*}) + 2.3RT^2\left(\frac{\partial \log k_0}{\partial D}\right)_T \frac{\mathrm{d}D}{\mathrm{d}T} \qquad (4)$$

one obtains in this case using water as the solvent of fixed composition

$$(E^0)_{\mathrm{H_2O}} - (E_{\mathrm{D}}^{0*}) = 605\,\frac{T}{D} \qquad (5)$$

Using equation (5) one calculates the difference between the critical increments in water and in glycol–water media of fixed dielectric constant to be 2800 cal. at 50°. Using the experimental values of the E_0s given in Table I and taking E_0 in water[2] to be 23,580 cal. one observes that the difference between the critical increments in water and in glycol–water media of fixed dielectric constant has an average value of 3620 cal. Thus E_{D}^{0*} is here apparently independent of dielectric constant.

By taking logarithms and differentiating equation (2) one obtains a relationship between E_0 and E at a fixed ionic strength, namely

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

Using equation (6) 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 fair agreement with the Es obtained by equation (3).

An equation for ionic reactions has been developed by Scatchard[5] from consideration of the dielectric effect of the medium, namely

$$\log k - \log k_0^* = \frac{e^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{2.3KTr}\left(\frac{1}{D^0} - \frac{1}{D}\right) \qquad (7)$$

where k_0^* is the rate constant at zero ionic strength in a standard solvent of dielectric constant D^0 and k_0 is the corresponding rate constant at zero ionic strength in a solvent of dielectric constant D. Using water as the standard solvent we have plotted in Fig. 4 the values of ($\log k_0 - \log k_0^*$) against the corresponding differences in the reciprocals of D^0 and D at the different temperatures. The plots, according to equation (7), should be linear and have slopes varying from -108 at 60° to -119 at 30° (assuming $r = 2 \times 10^{-8}$ cm.). The curves depart from the predicted linearity. The limiting slopes of the curves are in fair agreement with the predicted values, increasing from ~ -88 at 60° to ~ -96 at 30°.

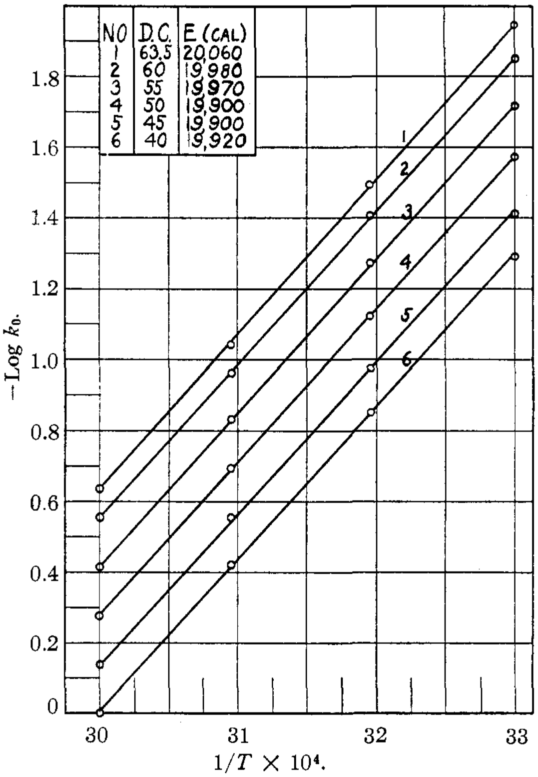

Fig. 3.—Influence of temperature on the rate of conversion of ammonium cyanate to urea in ethylene glycol–water media at zero ionic strength.

By reference to Table I, one observes that an empirical relation can be obtained between the dielectric effect and the temperature effect on the value of the limiting velocity constant for this reaction in glycol–water mixtures of constant dielectric constant, namely

$$\left(\frac{\Delta k_0}{\Delta D}\right)_T = -0.70\left(\frac{\Delta k_0}{\Delta T}\right)_D \qquad (8)$$

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(5) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

In the case of the methanol–water media, the constant on the right side of the equation was equal to unity.[2b]

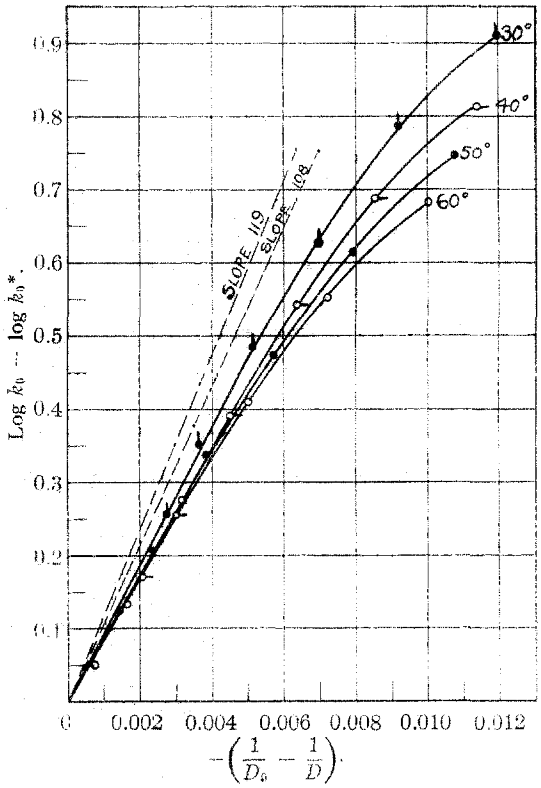

Fig. 4.

Discussion

It will be recalled that the equations previously derived[2] and used in this investigation were based on the assumption that the rate of reaction between ions depends only upon the temperature, the dielectric constant of the medium and the ionic strength. From previous investigations,[3b] and from the comparison of rates of the ammonium cyanate reaction in methanol–water media[2b] and in glycol–water media, we know that this assumption is only approximately true. However, considering these limitations the experimental data presented for this reaction in methanol–water media and in glycol–water media are in satisfactory agreement with those calculated by means of the equations and thus they very definitely show the influence of the dielectric constant and of the ionic strength upon critical increments.

We have summed up all of our observations in the two different solvent–water mixtures including some specific solvent influences:

(a) In methanol–water mixtures the log Ks for the constant dielectric constant media were constant, the average value being 11.77. In glycol–water media, however, the log Ks for the constant dielectric constant mixtures increase with decreasing dielectric constant.

(b) In methanol–water mixtures E_D^{0*} decreased with decreasing dielectric constant. In glycol–water media, however, E_D^{0*} is apparently independent of dielectric constant.

(c) In agreement with equation (6) the critical increments increased with ionic strength in both solvent–water mixtures of constant dielectric constant. In both cases calculated and experimental critical increments are in good agreement.

(d) The limiting slopes of the plots of (log k_0 – log k_0^*) against ($1/D^0$ – $1/D$) are in fair agreement with the predicted values in both cases.

(e) At 50° the rate constants in glycol–water mixtures are very nearly the same as those in isopropyl alcohol–water media and in dioxane–water media[3b] for the same constant dielectric constant mixtures.

As a result of the constancy of E_D^{0*} in glycol–water media, the suggestion previously made[2b] that possibly some of the decrease in E_D^{0*} with decreasing dielectric constant in methanol–water media was due to the method of calculating the k_0s, must either be dismissed or we must assume compensating medium effects operating in the glycol–water media. Unfortunately we cannot satisfactorily decide this question at present.

Summary

1. The rate of conversion of ammonium cyanate to urea has been studied over the temperature range 30 to 60° in glycol–water mixtures at the constant dielectric constants of 63.5, 60, 55, 50, 45 and 40.

2. 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 is apparently independent of the dielectric constant in glycol–water media of constant dielectric constant.

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

$$\left(\frac{\Delta k_0}{\Delta D}\right)_T = -0.70\left(\frac{\Delta k_0}{\Delta T}\right)_D$$

4. The influence of the dielectric constant

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

5. The experimental results for this reaction are compared in methanol-water and in glycol-water mixtures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

On the Mechanism of the Catechol-Tyrosinase Reaction. II. The Hydrogen Peroxide Question

BY CHARLES R. DAWSON AND BERNARD J. LUDWIG

The dihydric phenol catechol has been used widely as an experimental substrate in the study of phenolic-oxidase action. These studies, and the widespread occurrence of catechol derivatives in nature, have motivated the suggestion that the utilization of molecular oxygen during the respiration of certain types of plants probably is largely dependent on this type of enzymatic action.[1] Robinson and McCance[2] in 1925 were among the first to show that the enzymatic oxidation of catechol results in the absorption of two atoms of oxygen per molecule of the dihydric phenol. Although it has been established definitely that *o*-benzoquinone is one of the initial products formed during the action of a phenolic oxidase such as tyrosinase on catechol,[3-5] the nature of the enzymatic action and the chemical mechanisms involved have not yet been explained satisfactorily.

The conversion of catechol to *o*-benzoquinone is an oxidation requiring theoretically only one atom of oxygen, and thus much of the controversy during the past decade has been in reference to the fate of the second oxygen atom. Since aerobic oxidations are attended frequently by the initial formation of hydrogen peroxide, it is not surprising that one of the first mechanisms, as suggested by Onslow and Robinson,[6] accounted for the second atom of oxygen by the formation of hydrogen peroxide, *i. e.*

$$C_6H_4(OH)_2 + O_2 \longrightarrow C_6H_4O_2 + H_2O_2$$

These investigators, and others,[7] have claimed to have detected traces of hydrogen peroxide in the reaction mixture resulting from the enzymatic oxidation of catechol, and they attributed the difficulty in detecting this substance to the presence of peroxidase and catalase in their tyrosinase or oxidase preparations. Others have attributed the difficulty of detecting hydrogen peroxide in many catalytic oxidations to the presence of small amounts of certain metals.[8,9]

The reliability of the methods used by Onslow and Robinson, and others,[7] for the detection of hydrogen peroxide has been questioned, and several workers have expressed doubt concerning the formation of hydrogen peroxide during the enzymatic oxidation of catechol. Pugh and Raper[4] studied the oxidation of catechol using tyrosinase preparations that possessed appreciable catalase activity, and observed that the total oxygen uptake did not deviate from two atoms per molecule of substrate. They pointed out that the presence of catalase would tend to decompose any hydrogen peroxide formed during the enzymatic oxidation and would thereby return the second atom of oxygen to the reaction mixture. These workers suggested that the second oxygen atom is consumed during further oxidation of *o*-benzoquinone. Furthermore, Nobutani[10] found that catalase has no effect on the oxygen consumption during the enzymatic oxidation of *p*-cresol, and therefore concluded that hydrogen peroxide is not formed during this reaction.

A study of the reports of Pugh and Raper and of Nobutani, however, reveals that their conclusions have been based on evidence that is not entirely convincing. These investigators did not indicate the strengths of the catalase preparations used nor did they demonstrate that the catalase remains active throughout the oxidation process.

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