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

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Due to the pronounced influence of the properties of the medium upon the rate of reactions involving ions[1] and the fact that in all solvents these properties are usually functions of the temperature, it seems certain that these factors should be considered in discussions of the critical increment or energy of activation[2] of reactions in solution.

**Influence of Dielectric Constant.**—Salt effects may be eliminated by considering the velocity constant at zero ionic strength ($k^0$). In ionic reactions, the factor having the most pronounced influence upon $k^0$ at constant temperature is very likely the dielectric constant of the solvent. With this assumption, we may write

$$\log k^0 = f(D,T)$$

and

$$\frac{d \log k^0}{dT} = \left(\frac{\partial \log k^0}{\partial T}\right)_D + \left(\frac{\partial \log k^0}{\partial D}\right)_T \frac{dD}{dT} \qquad (1)$$

Multiplying Eq. (1) by $2.3RT^2$, one obtains a relation between the critical increment in a solvent of fixed composition and a medium of constant dielectric constant.

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

For all common solvents and solvent mixtures, the dielectric constant decreases with increasing temperature and Eq. (2) predicts that if an increase in $D$ causes a decrease in $k^0$, $E^0$ will be greater than $E^{0*}$. In attempting to decide which value should be considered the true energy of activation, one encounters the fundamental difficulty of splitting the rate equation into the customary kinetic and energy of activation terms. The success of the Brönsted–Christiansen–Scatchard theory would lead one to believe that changes in $k^0$ due to change of $D$ with $T$ should be included in the kinetic term. One should, therefore, consider $E^*$ the true energy of activation since it arises from $(\partial \log k^0/\partial T)_D$. To the best of our knowledge, all investigators in the field of solution kinetics have called $E$, which is obtained from d log $k^0/dT$ or d log $k/dT$, the energy of activation. However, Eq. (2) is independent of any theory and gives the relation between the two critical increments when rate constants depend only on $D$ and $T$.

The dielectric constants of most solvents and solvent mixtures may be expressed[3] in the form

$$D = ae^{-bT} \qquad (3)$$

where $a$ and $b$ are empirical constants. Hence, at any given temperature

$$dD/dT = -bD \qquad (4)$$

From experiments to determine the variation of $k^0$ with $D$ at constant temperature, one may evaluate $(\partial \log k^0/\partial D)_T$ and then calculate $E^*$ from $E$ using Eqs. (2) and (4). For reactions between two ions, the Scatchard theory[1a] yields the relations

$$\log k^0 = -\frac{\epsilon^2 Z_A Z_B}{2.3rkDT} + C \qquad (5)$$

and

$$\left(\frac{\partial \log k^0}{\partial D}\right)_T = \frac{\epsilon^2 Z_A Z_B}{2.3rkD^2T} \qquad (6)$$

This predicts for reactions between ions of unlike sign $E > E^*$ and for reactions between ions of like sign $E < E^*$.

The whole treatment may be made more general, but more difficult to apply, by obtaining $E^*$ from $(\partial \log k^0/\partial T)_{x_1, x_2 \ldots x_n}$ where $x_1, x_2 \ldots x_n$ represent all properties of the solvent which influence the rate and vary with the temperature.

**Influence of Ionic Strength.**—Knowing the velocity constants, at fixed temperature and dielectric constant as a function of the ionic strength ($\mu$), one may find a relation between the critical increments at zero ionic strength ($E^0$) and at some fixed ionic strength by methods similar to those used in the previous section. For reactions between ions and uncharged molecules, the primary salt effect is generally small, and $E$ should not change much with ionic strength. For reactions between ions, the usually valid Brönsted–Christiansen relation may be used.

$$\log k = \log k^0 + \log \frac{f_A f_B}{f_X} \qquad (7)$$

Assuming that the ion activity coefficients may

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[1] (a) Scatchard, *Chem. Rev.*, **10**, 229 (1932); (b) Harned and Samaras, THIS JOURNAL, **54**, 1, 9 (1932); (c) Warner and Warrick, *ibid.*, **57**, 1491 (1935).

[2] (a) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, 1933; (b) La Mer, *J. Chem. Phys.*, **1**, 289 (1933).

[3] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

TABLE I

LIMITING VELOCITY CONSTANTS IN WATER AND IN MEDIA OF FIXED DIELECTRIC CONSTANT

| | $H_2O$ Variable $D$ | | | $CH_3OH-H_2O$ $D = 63.5$ | | | $CH_3OH-H_2O$ $D = 55.0$ | |
|---|---|---|---|---|---|---|---|---|
| Temp., °C. | $k_s^0$ | $k_G^0$ | Wt. % $CH_3OH$ | $k_s^0$ | $k_G^0$ | Wt. % $CH_3OH$ | $k_s^0$ | $k_G$ |
| 30 | 0.00625 | 0.00647 | 28.3 | 0.0159 | 0.0166 | 46.6 | 0.0304 | 0.0330 |
| 40 | .0217 | .0227 | 21.4 | .0413 | .0432 | 39.6 | .0785 | .0833 |
| 50 | .0680 | .0710 | 14.8 | .106 | .110 | 33.4 | .192 | .207 |
| 60 | .205 | .212 | 8.1 | .263 | .270 | 27.5 | .468 | .502 |
| 70 | .584 | .609 | 0.0 | .584 | .609 | .. | .... | .... |

TABLE II

VELOCITY CONSTANTS AT $\sqrt{\mu}$ = 0.194 IN WATER AND IN MEDIA OF FIXED DIELECTRIC CONSTANT

| | $H_2O$ Variable $D$ | | | $CH_3OH-H_2O$ $D = 63.5$ | | | $CH_3OH-H_2O$ $D = 55.0$ | | |
|---|---|---|---|---|---|---|---|---|---|
| Temp., °C. | $k_1$ | $k_2$ | $k_3$ | $k_1$ | $k_2$ | $k_3$ | $k_1$ | $k_2$ | $k_3$ |
| 30 | 0.00429 | 0.00432 | 0.00435 | 0.00990 | 0.00989 | 0.00963 | 0.0173 | 0.0175 | 0.0166 |
| 40 | .0148 | .0150 | .0149 | .0262 | .0261 | .0265 | .0457 | .0446 | .0445 |
| 50 | .0460 | .0465 | .0469 | .0683 | ..... | ..... | .114 | .114 | .113 |
| 60 | .137 | .137 | .137 | .172 | .171 | .170 | .283 | .283 | .284 |
| 70 | .388 | ..... | .385 | .388 | ..... | .385 | .... | .... | .... |

be expressed by the Debye theory, taking into account ion diameters, Eq. (7) becomes[1a,c]

$$\log k = \log k^0 + \frac{\epsilon^2 Z_A Z_B \kappa}{DkT(1 + \kappa b)} \qquad (8)$$

By differentiating Eq. (8) and multiplying by $RT^2$, one obtains a relation between $E^0$ and $E$ at a fixed ionic strength. This treatment permits the interesting observation that for reactions between ions of unlike sign in solvents such as water, alcohols and water–alcohol mixtures, an increase in ionic strength should increase the critical increment in media of fixed dielectric constant but decrease it in solvents of fixed composition.

In the following sections these predictions concerning the influence of dielectric constant and ionic strength upon the critical increment will be compared with observed effects in the conversion of ammonium cyanate into urea.

## Experimental

In this part, experiments are reported on the rate of reaction between ammonium ion and cyanate ion over the temperature range 30 to 70° in water (dielectric constant varying with temperature) and in mixtures of water with methyl alcohol at constant dielectric constants for the mixtures of 63.5 and 55.0. All materials were prepared or purified as described in previous papers,[4,1c] 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 ±0.03°. Dielectric constants for water and for water–methyl alcohol mixtures were taken from the work of Åkerlöf.[3]

The limiting velocity constants ($k^0$) were calculated by Scatchard's[5] method which yields the integrated velocity equation[1c]

$$k^0 t = \left\{\frac{1 + 4A\sqrt{C}}{C}\right\} - \left\{\frac{1 + 4A\sqrt{C^0}}{C^0}\right\} \qquad (9)$$

$A$ is the Debye–Hückel constant in $\ln f_i = -AZ_i^2 \sqrt{\mu}$. Average values of the limiting velocity constant ($k_s^0$) obtained by this method are listed in Table I. Deviations ($\delta$) of the experimental value of $C/(1+4A\sqrt{C})$ from the value calculated from the average $k_s^0$ are plotted against the experimental value of this function in Fig. 1.[1c] The filled circles represent values of $C^0/(1+4A\sqrt{C^0})$. Limiting velocity constants were also calculated from bimolecular constants determined by the method of slopes[1c,4] by Eq. (8) which applied to our reaction becomes

$$\log k^0 = \log k + \frac{3.63 \times 10^6 \sqrt{\mu}}{(TD)^{3/2} + 100.6\, DT \sqrt{\mu}} \qquad (10)$$

Average values of these limiting rate constants ($k_G^0$) are also given in Table I. In Table II, we give velocity constants at $\sqrt{\mu} = 0.194$ obtained by three methods: $k_1$ is obtained from $k_s^0$ by the relation[1c]

$$k_1 = k_s^0/(1 + 2A\sqrt{\mu}) \qquad (11)$$

$k_2$ from $k_G^0$ by Eq. (10), and $k_3$ is obtained directly from the slope[1c] of $t$ (minutes) against $1/C$ at $\sqrt{\mu} = 0.194$. All data at 50° are taken from the work of Warner and Warrick[1c] and velocity constants at 70° were recalculated from the data of Warner and Stitt.[4] In Fig. 2, log $k_s^0$ and log $k_1$

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[4] Warner and Stitt, THIS JOURNAL, **55**, 4807 (1933).

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

are plotted against $1/T$ for water and the methyl alcohol–water mixtures of $D = 63.5$ and $55.0$. (Lines obtained by plotting $\log k^0_G$ against $1/T$ are parallel to those obtained using $\log k^0_s$.) In each case, the deviations of experimental points from the best straight line are almost within the possible experimental error. There is, however, some indication of a trend toward decreased slopes in the lower temperature range. The linear relations shown in Fig. 2 may be expressed by the equations

$H_2O$, variable $D$

$$\log k^0_s = 14.77 - 23{,}580/4.58T$$
$$\log k_1 = 14.36 - 23{,}240/4.58T \quad (12)$$

$CH_3OH$–$H_2O$, $D = 63.5$

$$\log k^0_s = 11.79 - 18{,}840/4.58T$$
$$\log k_1 = 11.92 - 19{,}380/4.58T \quad (13)$$

$CH_3OH$–$H_2O$, $D = 55.0$

$$\log k^0_s = 11.79 - 18{,}500/4.58T$$
$$\log k_1 = 11.80 - 18{,}850/4.58T \quad (14)$$

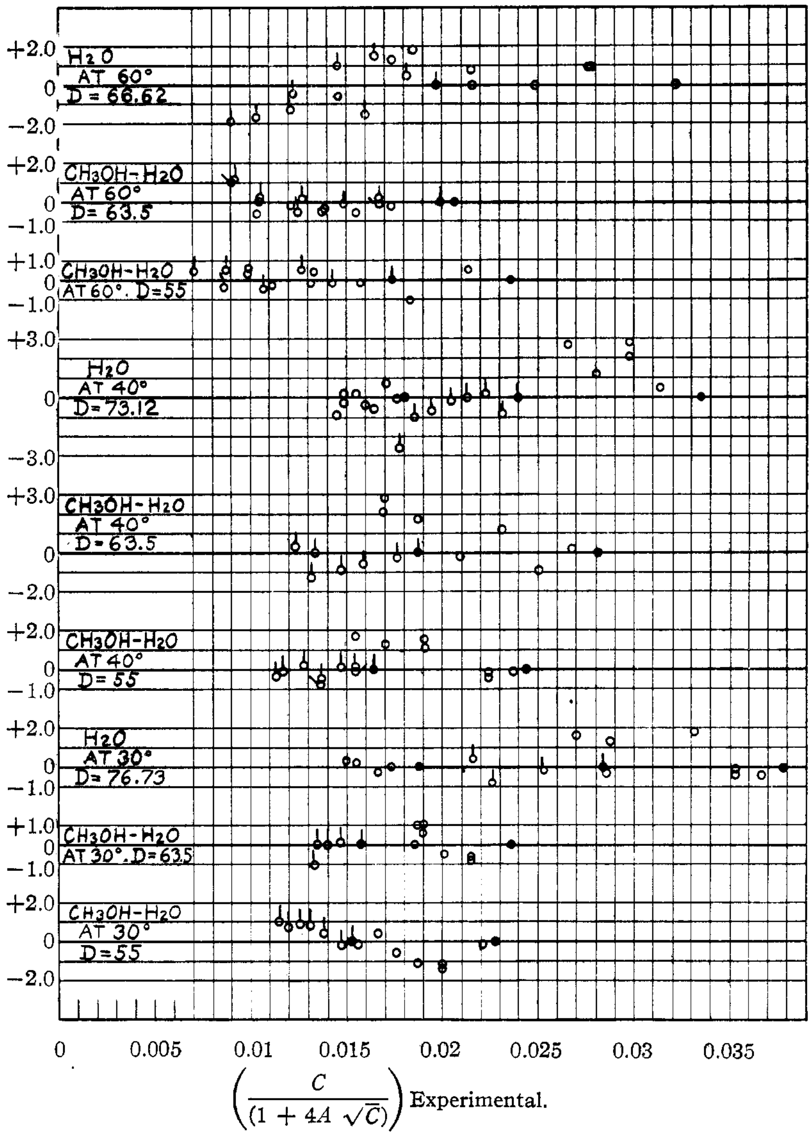

Fig. 1.

The difference between the zero ionic strength critical increments at the fixed dielectric constants of (Table III) 63.5 and 55.0 is within the possible experimental error of ±150 cal. Due to salting out there is some uncertainty as to the actual dielectric constants of these mixed solvents which may contribute to the difference in critical increments. However, these experiments do lend some support to the hypothesis that the critical increment of reactions between ions should be fairly independent of the dielectric constant when the dielectric constant does not change with temperature. There is a large and significant difference between the critical increment in water and in the media of fixed dielectric constant. These differences are compared with the difference calculated by Eq. (2) in Table III. Eq. (2) applied to the conversion of ammonium cyanate into urea becomes

$$(E^0)_{H_2O} - E^{0*} = \frac{1050\,T}{D} \quad (15)$$

In obtaining Eq. (15), $(\partial \log k^0_s/\partial D)_T$ is the experimental limiting slope of $\log k^0_s$ against $D$ in $CH_3OH$–$H_2O$ mixtures. $dD/dT$ for water is taken from the work of Åkerlöf.[3] Since $D$ decreases with increase in $T$, Eqs. (2) and (15) imply that if $E^{0*}$ is constant $(E^0)_{H_2O}$ will increase with $T$. Unfortunately our experiments are not sufficiently precise to test this implication. Eq. (2) also predicts that $E^0$ will change from one solvent of fixed composition to another through changes in $(\partial \log k^0/\partial D)_T$ and $dD/dT$. By interpolation of our

TABLE III

SUMMARY OF CRITICAL INCREMENT DATA

| | $H_2O$ | $CH_3OH$–$H_2O$ $D = 63.5$ | $CH_3OH$–$H_2O$ $D = 55.0$ |
|---|---|---|---|
| $E^0$ (Exptl. at $\sqrt{\mu} = 0$) | 23,580 | 18,840 | 18,500 |
| $(E^0)_{H_2O} - E^{0*}$(Exptl.) | | 4,740 | 5,080 |
| $(E^0)_{H_2O} - E^{0*}$(Calcd. by Eq. 2 at 50°) | | 4,860 | 4,860 |
| $E$(Exptl. at $\sqrt{\mu} = 0.194$) | 23,240 | 19,380 | 18,850 |
| $E$(Calcd. from $E^0$'s Eq. 17 at 50°) | 23,360 | 19,280 | 18,950 |
| $E$(Calcd. from $E^0$'s using Eq. (11) at 50°) | 23,380 | 19,270 | 19,000 |

data at 40 and 50° and a slight extrapolation at 60° we are able to obtain values of $k_s^0$ for 28.3 wt. per cent. of methyl alcohol as solvent. From these data we obtain $(E^0)_{28.3\%\ CH_3OH} = 23{,}050$ cal., which is approximately 500 cal. less than $(E^0)_{H_2O}$.

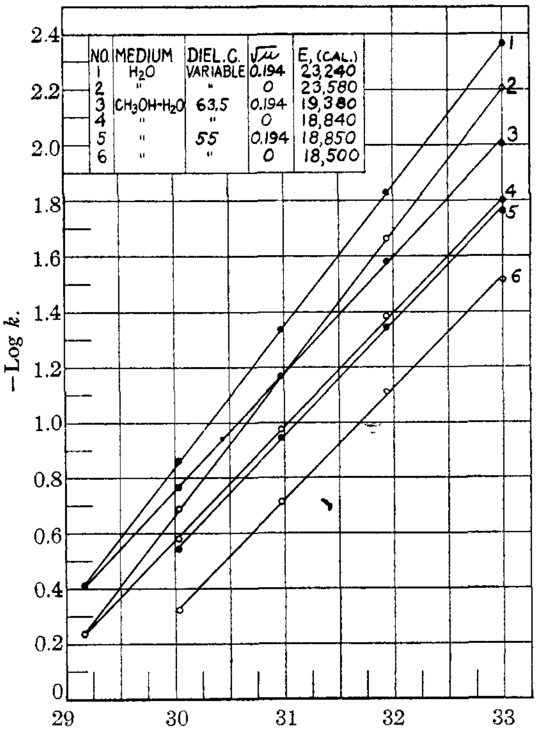

Fig. 2.—Influence of temperature on the rate of conversion of ammonium cyanate to urea in different media.

If $(\partial \log k_s^0/\partial D)_T$ is obtained from the experimental slope of log $k_s^0$ against $D$ at 28.3% of methyl alcohol and $dD/dT$ is obtained by interpolation of Åkerlöf's[3] data, Eq. (2) becomes

$$(E^0)_{28.3\%\ CH_3OH} - E^{0*} = 735\ T/D \qquad (16)$$

Assuming $E^{0*} = (E^0)_{D = 63.5}$, one calculates by Eq. (16), $(E^0)_{28.3\%\ CH_3OH} = 22{,}970$ cal.

By differentiating Eq. (10) and multiplying by $RT^2$, one obtains the following relation between the critical increments at $\sqrt{\mu} = 0$ ($E^0$) and at some fixed ionic strength

$$E = E^0 + 8.35 \times 10^6\ RT^2 \sqrt{\mu} \left\{ \frac{{}^3/{}_2 T^{1/2} D^{3/2} + 100.6\ D \sqrt{\mu}}{(T^{3/2} D^{3/2} + 100.6\ DT \sqrt{\mu})^2} \right\} \left\{ 1 + \frac{\mathrm{d} \ln D}{\mathrm{d} \ln T} \right\} \qquad (17)$$

Using Eq. (17), we have calculated $(E)_{\sqrt{\mu} = 0.194}$ from $E^0$ for water and the two media of fixed dielectric constant. These calculated critical increments are compared to experimental values in the fourth and fifth rows of Table III. $E$ and $E^0$ may also be related by taking logarithms and differentiating Eq. (11). Values of $E$ calculated from $E^0$ by this method are given in the last row of Table III. There are no significant differences between these values and those calculated by Eq. (17). If $E$ at $\mu = 0.1$ is calculated from $E^0$ for water, one obtains $(E)_{\mu = 0.1} = 23{,}280$ cal., which differs by about 0.5% from the values obtained by Walker and Hambly[6] and by Doyle[2a] at approximately the above ionic strength.

In conclusion, we must call attention to the approximate character of the relationships which have been derived and used. They are based upon the assumption that the rate of reactions between ions depends only upon the temperature, the dielectric constant of the medium and the ionic strength. From previous investigations,[1c,4] we know that this assumption is only approximately true for the rate of reaction between ammonium and cyanate ions. Considering these limitations, we believe we have satisfactorily accounted for the influence of dielectric constant and ionic strength upon the critical increments in this one case. The ideas presented in this paper are being tested with data on the rates of other ionic reactions which can be followed with greater precision.

## Summary

1. On the assumption that the rates of ionic reactions are functions only of the temperature, dielectric constant and ionic strength, equations are derived which predict the influence of dielectric constant and ionic strength upon critical increments.

2. These predictions are in satisfactory agreement with observed effects in the reaction between ammonium and cyanate ions which was studied over the temperature range 30 to 70° in water, dielectric constant varying with temperature, and in mixtures of water with methyl alcohol at fixed dielectric constants for the mixtures of 63.5 and 55.0.

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[6] Walker and Hambly, *J. Chem. Soc.*, **67**, 746 (1895).