

8. GOPAL, R. & SIDDIQUE, M. A., *J. phys. Chem.*, **72** (1968), 1814.
9. GOPAL, R. & SRIVASTAVA, R. K., *J. Indian chem. Soc.*, **40** (1963), 99.
10. MILLERO, F. J., *J. phys. Chem.*, **72** (1968), 3209.
11. MASSON, D. O., *Phil. Mag.*, **8** (1929), 218.
12. DAS, P. B., DAS, P. K. & PATNAIK, D., *J. Indian chem. Soc.*, (1960), 683.
13. PRASAD, B. & CHACKRAVARTY, A. S., *Trans. Faraday Soc.*, **35** (1939), 1466; PRASAD, B. & SRINIVASAN, M. K., *Trans. Faraday Soc.*, **35** (1939), 1442.
14. STOKES, R. H. & MILLS, R., *Viscosity of electrolyte and related properties* (Pergamon Press, New York), 1965, 39.
15. AKERLOF, G., *J. Am. chem. Soc.*, **54** (1932), 4125.
16. AKERLOF, G. & SHORT, O. A., *J. Am. chem. Soc.*, **58** (1936), 1241.

### Ion-Solvent Interaction Studies of Chlorides, Bromides & Nitrates of Sodium & Potassium in Dioxane-Water Mixtures at Different Temperatures

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The viscosities of NaCl, NaBr, NaNO<sub>3</sub>, KCl, KBr and KNO<sub>3</sub> in 10, 20 and 30% dioxane-water mixtures (w/w) have been measured at 30°, 35°, 40° and 45° and the results analysed in terms of Jones-Dole equation:  $\eta_r = 1 + AC^{\frac{1}{2}} + BC$ . The coefficients *A* and *B* have been obtained graphically from the plot of  $\eta_r - 1/C^{\frac{1}{2}}$  versus *C*<sup>1</sup>.

IN continuation of our earlier work<sup>1</sup> on the viscosity of electrolyte solution in aquo-organic mixtures, the viscosity of NaCl, NaBr, NaNO<sub>3</sub>, KCl, KBr and KNO<sub>3</sub> in different dioxane-water mixtures have been measured at 30°, 35°, 40° and 45° and the data analysed on the basis of Jones-Dole equation<sup>1</sup> to know the nature of ion-ion and ion-solvent interaction in solution<sup>2-8</sup>.

All the salts used were of E. Merck (extra pure) quality. The viscometric apparatus and technique were similar to those employed by Chackravarty and Prasad<sup>9</sup>. The densities of the solvents and solutions were determined with a pycnometer (50 ml) with buoyancy correction and were the same as those of Srinivasan and Prasad<sup>10</sup>. Necessary precautions were taken to prevent evaporation of the solvent<sup>11</sup>. The viscosities of the electrolyte solutions were measured in the dioxane-water mixtures containing 10, 20 and 30% of dioxane (w/w). The concentration range was from 0.1 to 0.001*M*.

From the conductance measurements (unpublished) electrolytes were found to be almost completely dissociated and hence the modified equation proposed by Das<sup>12</sup> was not applicable. The results have been analysed in terms of Jones-Dole equation since the plots of  $\eta_r - 1/C^{\frac{1}{2}}$  versus *C*<sup>1</sup> were linear. The intercepts and the slopes of the plots gave respectively the coefficients of *A* and *B*. The coefficient *B* thus obtained for various salts at different temperatures are given in Table 1. The calculated values<sup>13</sup> of *A* are in good agreement with the experimental values. The relative viscosity values calculated from the values of *A* and *B* thus

TABLE 1 — VALUES OF COEFFICIENT *B* AT DIFFERENT TEMPERATURES AND [DIOXANE]

Temp. °C	B × 10 <sup>2</sup> in dioxane-water mixtures (% wt/wt)					
	10	20	30	10	20	30
	NaCl			KCl		
30	8.1	10.0	15.5	1.9	3.4	4.8
35	9.1	11.2	16.6	2.0	4.0	5.2
40	14.0	15.0	20.0	3.3	5.0	6.1
45	15.0	16.2	22.0	3.6	5.8	6.9
	NaBr			KBr		
30	9.7	12.0	15.1	2.8	4.7	5.1
35	11.5	12.4	17.0	3.4	5.1	6.2
40	6.6	11.2	14.5	2.2	6.2	5.8
45	6.5	10.8	13.7	2.1	5.1	5.6
	NaNO <sub>3</sub>			KNO <sub>3</sub>		
30	7.1	9.6	13.0	1.1	3.2	4.2
35	8.5	10.9	14.2	1.5	3.9	5.0
40	10.2	11.5	15.3	1.8	4.3	5.7
45	11.2	12.5	16.0	1.9	4.7	6.1

obtained are found to be in fair agreement with the experimental values.

The values of *A* coefficients for different electrolytes are positive indicating dependence of ionic interactions on the nature of the electrolytes. The radii of the anions Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> are almost of the same order<sup>14</sup>. Hence the ion-ion interaction is expected to be same and this is found to be true. The electrostatic ion-ion interaction and hence the value of *A* is found to increase with the decrease in dielectric constant of the medium, i.e. with an increase in dioxane content in the solvent mixture. As expected the values of *A* decrease with the rise in temperature for all the salts.

According to Stokes and Mill<sup>4</sup>, the viscosity of a dilute electrolytic solution incorporates that of the solvent plus the contribution from other factors viz. (i)  $\eta^E$ , the positive increase due to the shape and size of an ion (ii)  $\eta^A$ , the increase due to the alignment or orientation of the polar molecules by the ionic field and (iii)  $\eta^D$ , the decrease in the viscosity due to distortion of the solvent structure by the ions. Therefore the *B* coefficients can also be discussed in terms of the viscosity effects at different temperatures. With increase in temperature,  $\eta^D$  decreases because the competition between ionic field and bulk structure is less.  $\eta^E$  remains fairly constant and  $\eta^A$  decreases slowly, so that *B* is positive. The negative temperature coefficient of *B* is due to the fact that the oriented solvent molecules in the secondary layer will be less rigidly held due to the increased thermal motion. This will give a significant decrease in the value of  $\eta^A$ . Also with increase in temperature, the water structure is broken down and the fluidity is increased (i.e.  $\eta^D$  is large). The mobility of the ion to the first approximation is dependent on the fluidity of the medium in its immediate surroundings and hence there is a decrease in the *B* value.

In the present case, the *B* coefficients of the salts containing Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> increase with the increase in temperature (though the increase is less in case

of  $\text{NO}_3^-$ ) as the viscosity decrease due to the distortion of the solvent structure i.e.  $\gamma^D$  is small and  $\gamma^E + \gamma^A + \gamma^D$ . In the case of salts containing  $\text{Br}^-$ ,  $\gamma^D$  increases (excepting at  $35^\circ$ ) and hence the  $B$  coefficient decreases with the increase in temperature. The lesser the value of the  $B$  coefficient the greater is the structure breaking effect or ion-solvent interaction and solvation. Hence the structure breaking effect or ion-solvent interaction follows the order  $\text{Br}^- > \text{NO}_3^- > \text{Cl}^-$ , and in agreement with that of Kay<sup>15,16</sup> who distinguished between the structure breaking and structure making ions by plotting  $\Delta(\lambda_0\gamma_0)/\Delta T$  versus  $\Delta B/\Delta T$ .

Ions with greater crystal radii and small charge densities, would possibly have a weak orienting effect in the first layer. Therefore,  $\gamma^E$  and  $\gamma^A$  will be small. Also there exist a considerable amount of distortion in the vicinity of such ions due to the competition between the ionic field and bulk structure and consequently  $\gamma^D$  will be larger. Thus  $B$  will be smaller for  $\text{K}^+$  salts than for  $\text{Na}^+$  salts. Further investigation are in progress with that of other monovalent cations.

McRae<sup>17</sup> has suggested that the dioxane molecules has two nonadjacent dipolar groups whose moments cancel, so that the effective reaction is probably greater than is indicated by microscopic properties. Hence the frozen layer as suggested by Frank and Evans<sup>18</sup>, around the cation is expected to be constituted of both water and the dioxane molecules possibly consisting more of the former than of the latter. The diffused layer would consist of loosely oriented water and dioxane molecules, the extent of orientation decreasing with the distance from the ion till the outermost layer has the same structure and composition as that of the solvent. When the dioxane content of the solvent increases, more dioxane molecules take part in constituting the diffused layer thereby promoting a sort of ordering effect in the solvation sphere leading to larger value of  $\gamma^E$  and  $\gamma^A$ . This will be reflected in increase in  $B$  values with increase in dioxane content (Table 1).

## References

1. DAS, N. C. & DAS, P. B., *Indian J. Chem.*, **15A** (1977), in press.
2. GURNEY, R. W., *Ionic processes in solutions* (McGraw-Hill, New York), 1953, 159.
3. HARNED, H. S. & OWEN, B. B., *Physical chemistry of electrolytic solutions* (McGraw-Hill, New York), 1958, 117.
4. STOKES, R. H. & MILLS, R., *Viscosity of electrolytes and related properties* (Pergamon Press, New York), 1965, 39.
5. KAY, R. L., VITUCIO, T., ZAWOSHI, C. & EVANS, D. F., *J. phys. Chem.*, **70** (1970), 2336.
6. KRICHKARD, K. & SKINNER, J. F., *J. phys. Chem.*, **73** (1969), 2060.
7. YAO, N. P. & BENNION, D. N., *J. phys. Chem.*, **75** (1971), 1927.
8. BARE, J. P. & SKINNER, J. F., *J. phys. Chem.*, **76** (1972), 434.
9. CHACKRAVARTY, A. S. & PRASAD, B., *Trans. Faraday Soc.*, **35** (1939), 1466.
10. SRINIVASAN, M. K. & PRASAD, B., *Trans. Faraday Soc.*, **35** (1939), 1442.
11. DAS, P. B., DAS, P. K. & PATNAIK, D., *J. Indian chem. Soc.*, **37** (1960), 683.
12. DAS, P. B., *J. Instn Chem.*, **48** (1976), 207.
13. FALKENHAGEN, H., *Z. Phys.*, **32** (1931), 745.
14. AGRAWAL, D. K. & SINGH, K., *J. Indian chem. Soc.*, **53** (1975), 482.
15. KAY, R. L., *In water, a comprehensive treatise*, Vol. 3, edited by R. Frank (Plenum Press, New York), 1973, 194.
16. KAY, R. L., *Advance chemical series*, No. 73, edited by R. F. Gould (American Chemical Society, Washington DC), 1968, 1.
17. MCRAE, E. G., *Chem. Rev.*, **18** (1936), 349.
18. FRANK, H. S. & EVANS, M. W., *J. chem. Phys.*, **13** (1945), 507.

## Kinetic Evidence for Fast Protonation Pre-equilibrium in the Acid Hydrolysis of Acetamide: Evaluation of Protonation Constant

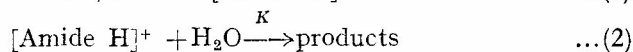
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**Over an extended acetamide concentration range (1-6M), the acid hydrolysis obeys the rate law, Rate =  $kK[\text{H}^+][\text{Amide}]/(1+K[\text{Amide}])$ , which provides a direct kinetic evidence for the step  $\text{CH}_3\text{CONH}_2 + \text{H}^+ \rightleftharpoons \text{CH}_3\text{CONH}_3^+$ . The values of protonation constant,  $K$ , determined kinetically are in good agreement with those obtained by other methods.**

THE hydrolysis of acetamide has been the subject of several studies<sup>1</sup> from various points of view, e.g. effect of different acids<sup>1,2</sup> and acidity<sup>3</sup>, solvent effects<sup>4,5</sup>, activation parameters<sup>2,5,6</sup> and correlation of rate using Taft equation<sup>7</sup> have been investigated. Surprisingly the most important aspect of hydrolysis, the variation of amide over an extended concentration range, has not been studied so far. The accepted  $A-2$  mechanism (Eqs. 1 and 2)



should lead to the familiar Michaelis-Mention rate law (3) or (4) when  $[\text{amide}] \gg [\text{H}^+]$

$$\text{Rate} = kK[\text{H}^+][\text{Amide}]/(1+K[\text{Amide}]) \quad \dots(3)$$

$$k_{\text{obs}} = kK[\text{Amide}]/(1+K[\text{Amide}]) \quad \dots(4)$$

$k_{\text{obs}}$  is the first-order rate constant. We studied the hydrolysis of acetamide in the concentration range 1-6M at  $55^\circ$ ,  $60^\circ$  and  $65^\circ$ . The kinetics were followed by estimating ammonia by formal titration method<sup>8</sup>. The results were reproducible to  $\pm 5\%$ . In all kinetic runs acetamide was in excess over hydrochloric acid such that the reaction followed a pseudo first order kinetics. The maximum concentration of acetamide employed, was limited by its solubility in water. The results are shown in Table 1.

The plots of  $1/k_{\text{obs}}$  versus  $1/[\text{Acetamide}]$  were linear, the intercepts and slopes of which gave the values of  $k$  and  $K$  respectively.  $k$  (litre  $\text{mol}^{-1} \text{sec}^{-1}$ ) and  $K$  (litre  $\text{mol}^{-1}$ ) were found to be  $(7.1 \pm 0.1) \times 10^{-4}$  and  $(0.31 \pm 0.03)$  at  $55^\circ$ ,  $(11.0 \pm 0.5) \times 10^{-4}$  and  $(0.33 \pm 0.02)$  at  $60^\circ$ , and  $(18.5 \pm 0.5) \times 10^{-4}$  and  $(0.36 \pm 0.03)$  at  $65^\circ$ .  $K$  appears to be independent of temperature. The value of  $K$  is in good agreement with the reported values from other sources, i.e.  $0.33^9$  ( $60^\circ$ ),  $0.42^{10}$  ( $25^\circ$ ),  $0.37^{11}$  ( $25^\circ$ ) and  $0.31^{12}$  ( $25^\circ$ ). The energy of activation was found to be  $18.7 \text{ kcal mol}^{-1}$  which also was in good