

TABLE 2 — VALUES OF CONSTANTS  $A$  AND  $B$  AT 25°

DMA wt %	$A$	$B$
0.0	0.0047	-0.0737
	(0.0050)*	(-0.0755)*
10.0	0.0023	-0.1019
20.0	0.0207	-0.1257
40.0	0.0264	-0.1181
60.0	0.0151	-0.0531
75.0	0.0196	0.1286
85.0	0.0181	0.5468

\*Values in parentheses are literature values at 25° (ref. 11).

attaining a maximum value. The maximum viscosity was found at about 62 wt % of DMA, which is in agreement with the reported data<sup>10</sup>.

The Jones-Dole equation in the form

$$(\eta/\eta^0 - 1)/c^{1/2} = A + Bc^{1/2}$$

has been used for the analysis of experimental data. The coefficients  $A$  and  $B$  have been calculated by the method of least squares and recorded in Table 2. It can be noted that the coefficient  $B$  for potassium iodide in mixed solvent diminishes with the addition of small amounts of DMA in water, reaches a minimum value and then starts increasing with further addition of DMA. The solvent dependence of  $B$  may be explained on the basis of the view of Stokes and Mills<sup>11</sup>, according to which the viscosity of dilute electrolyte solution is equated to the viscosity of solvent plus the contributions from solutes in the following manner:

$$\eta = \eta^0 + \eta^* + \eta^E + \eta^A + \eta^D \quad \dots(2)$$

where  $\eta^*$  is the positive increment in viscosity caused by coulombic interaction,  $\eta^E$  is the positive increment due to the shape and size of an ion,  $\eta^A$  is the increment due to the alignment or orientation of the polar molecules by the ionic field and  $\eta^D$  is the change in viscosity associated with distortion of the solvent structure leading to greater fluidity (structure breaking effect).

Combining Eqs. (1) and (2) and cancelling the term due to coulombic interaction from both we have

$$\eta^E + \eta^A + \eta^D = \eta^0 Bc \quad \dots(3)$$

Therefore, at a given concentration the  $B$  coefficient can be discussed in terms of different viscosity effects. It is known that  $K^+$  and  $I^-$  ion destroy the water structure and this property leads to their negative  $B$  values<sup>12</sup>. In KI both the  $K^+$  and  $I^-$  ions have large radius (within a group) and small surface charge density. Therefore, these would cause a very weak orientation effect in their immediate vicinity and consequently will lead to very small values of  $\eta^E$  and  $\eta^A$ . On the other hand, there is considerable distortion of solvent structure in the close proximity of such ions due to the competitive forces between the ionic field and the bulk structure. Thus,  $\eta^E + \eta^A < \eta^D$  and  $B$  coefficient will be negative for KI in aqueous solution. The addition of small amounts of DMA enhances the structure of water and a more dense liquid structure is obtained<sup>13</sup>. Therefore, ions responsible for break-

ing the structure would give much larger values of  $\eta^D$  in mixed solvents than in pure water. Thus,  $\eta^E + \eta^A \ll \eta^D$  and still lower (more negative) values of  $B$  coefficient are obtained. With further addition of DMA the water structure is broken and hence the change in  $\eta^D$  will be smaller than in the previous case. Therefore,  $\eta^E + \eta^A \approx \eta^D$  and we see that the values of coefficient  $B$  becomes less and less negative and finally positive when  $\eta^E + \eta^A > \eta^D$ .

It was noticed that a minimum in  $B$  value was obtained corresponding to about 30 wt % DMA. It may be concluded that the solvent at this composition is most structured. The minimum in  $B$  value can be interpreted as the maximum ion-solvent interaction and thus giving maximum breaking of the solvent structure on the addition of structure breaking electrolyte (KI).

In the solvents containing high wt % DMA the ions start orienting the solvent molecules and a considerable change in the value of  $\eta^E$  occurs. Therefore,  $\eta^E + \eta^A \gg \eta^D$  and we get high positive values of  $B$  coefficient.

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#### Conductance of Lithium Acetate in Water & Aqueous Methyl Acetate

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Conductance of lithium acetate in water and aq.-methyl acetate (20%, v/v) has been measured at 40°, 45° and 50° and in different concentrations of the electrolyte. Experimental data have been analysed on the basis of Onsager's equation and Onsager-Fuoss-Skinner equation. The ion-size parameter,  $a$  (Å) has also been obtained at different temperatures employing Onsager-Fuoss-Skinner equation. Temperature dependence of the Walden-products is also discussed in terms of the structure-breaking/making characteristics of the salt.

THE conductivity of lithium acetate in water and aqueous methyl acetate (20% v/v at 25°) have been measured at different temperatures with a view to (i) testing the validity of Onsager's equation<sup>1</sup> and the Onsager-Fuoss-Skinner<sup>2</sup> equations, (ii) estimating the solute-solvent interaction and (iii) evaluating the contact distance between the ions in the solution at infinite dilution.

Lithium acetate (BDH, England) was used after crystallization from ethanol. Methyl acetate was purified by treating it with potassium carbonate and distilling after keeping overnight over P<sub>2</sub>O<sub>5</sub>. Anhydrous methyl acetate had the following physical characteristics: density = 0.9206 g ml<sup>-1</sup>,  $\eta = 0.00351$  poise, conductance =  $3.8 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup> at 30° and the values are comparable with the literature values<sup>3,4</sup>. Water of conductivity of the order of 10<sup>-6</sup> ohm<sup>-1</sup> cm<sup>-1</sup> was used for making solutions of lithium acetate in methyl acetate. Aqueous mixture of methyl acetate was prepared at 25°. All solutions were made by weight. Conversion between equivalent concentration and molality was done from the usual relationship<sup>5</sup>. Measurements were carried out at 40°, 45° and 50°. Densities of the solutions ( $\bar{d}$ ) were determined with the help of a method described elsewhere<sup>6</sup>. Conductance measurements were carried out in the manner reported in our earlier publications<sup>7-9</sup>.

The equivalent conductance values of lithium acetate in water and in aq.-methyl acetate at different temperatures are summarized in Table 1.

The values of the constant  $\theta$  in the Onsager's equation for solutions of lithium acetate at 40°, 45° and 50° are 0.2344, 0.2369 and 0.2396 respectively whereas those of the constant  $\sigma$  at these temperatures are 82.38, 90.58 and 99.09 respectively. For solutions of lithium acetate in aq.-methyl the values of  $\theta$  at 40°, 45° and 50° are 0.3097, 0.3125 and 0.3154 respectively whereas those of  $\sigma$  at these temperatures are 72.09, 81.06 and 89.74 respectively.

The plots of  $\Lambda$  versus  $\sqrt{C}$  are linear for solutions in water, but for solutions in aq.-methyl acetate, linear plots are obtained only up to the concentration  $\approx 0.01N$ . The values of the limiting conductances,  $\Lambda_0$ , obtained on extrapolation of  $\Lambda$  versus  $\sqrt{C}$  plots to  $\sqrt{C} \rightarrow 0$ , for solutions in water and in aq.-methyl acetate at 40°, 45° and 50° respectively along with theoretical and experimental Onsager slopes are given in Table 2.

Table 2 shows that the deviation in the Onsager slopes are less in aqueous solutions than in aqueous methyl acetate. The large discrepancies in the slopes in solutions of aq.-methyl acetate can be attributed to the incomplete dissociation of lithium acetate and formation of ion-pairs. To prove the formation of ion-pairs in this solution, a plot between  $\log \Lambda$  and  $\log C$  is drawn according to the theory of Fuoss-Kraus<sup>10</sup>. Further, according to Bjerrum<sup>11</sup>, the limiting slope ( $d \log \Lambda / d \log C$ ) should be equal to -0.5 and the experimentally observed value is found to be -0.46, indicating a fair agreement between the theory and the experiment. Further, the conductance equation is also related<sup>11</sup>

TABLE 1 — EQUIVALENT CONDUCTANCE OF SOLUTIONS OF LITHIUM ACETATE IN WATER AND Aq.-METHYL ACETATE AT 40°, 45° AND 50°

Water		Aq.-methyl acetate	
$C \times 10^3$ (g. eq./litre)	$\Lambda$ obs. ohm <sup>-1</sup> cm <sup>2</sup>	$C \times 10^3$ (g. eq./litre)	$\Lambda$ obs. ohm <sup>-1</sup> cm <sup>2</sup>
40°			
7.65	107.50	6.12	124.61
14.99	103.02	8.13	119.58
22.50	100.00	13.82	104.58
38.43	94.02	32.85	89.21
55.68	88.04	51.51	80.28
76.44	83.51	71.55	78.00
99.22	79.06	90.96	70.19
45°			
9.02	113.50	7.09	130.24
15.62	109.50	9.66	120.53
23.25	106.02	20.67	108.78
37.51	101.68	39.82	98.81
55.01	95.61	61.74	89.09
78.34	91.20	81.88	82.38
123.07	78.30	115.10	76.74
50°			
3.30	128.50	5.84	136.13
7.65	124.50	7.76	129.34
13.22	121.02	9.95	125.09
19.53	118.13	18.86	119.22
40.35	107.46	39.63	105.36
79.00	100.63	59.94	96.46
107.26	95.00	80.84	87.41
0.00	0.00	110.86	80.13

TABLE 2 — LIMITING CONDUCTANCE ( $\Lambda_0$ ) AND ONSAGER'S SLOPES IN WATER AND IN Aq.-METHYL ACETATE AT 40°, 45° AND 50°

Temp. (°C)	$\Lambda_0$ (ohm <sup>-1</sup> cm <sup>2</sup> )	K		Deviation (%)
		Onsager	Obs.	
40	119.0	110.2	125.0	13.0
	(163.5)	(122.7)	(511.1)	(316.3)
45	126.0	120.4	128.5	6.0
	(165.5)	(130.7)	(433.3)	(231.3)
50	135.0	131.4	128.5	2.0
	(169.0)	(143.0)	(433.3)	(202.9)

Values in aq.-methyl acetate are given in parentheses.

to the dissociation function, ( $K^1$ ) and the mass law constant, ( $k$ ) according to the relation<sup>11</sup>:

$$\bar{\Lambda}\sqrt{C} = \Lambda_0\sqrt{K^1} + \sqrt{K^1} \frac{\Lambda_0\sigma}{k} C \quad \dots(1)$$

According to Eq. (1), plot of  $\Lambda\sqrt{C}$  versus  $C$  should be linear and it has been found to be so in the dilute region. At higher concentrations, curvature is obtained which suggests<sup>12,13</sup> that some associated complex formation has occurred in aq.-methyl acetate.

The data have been further analysed by the Fuoss-Onsager-Skinner equation for the dissociated salts. The values of the limiting equivalent conductances,  $\Lambda_0$ , the contact distances  $a$  ( $\text{\AA}$ ) of the ions in solution along with the Walden product<sup>1</sup>,  $\Lambda_0\eta$ , at different temperatures are given in Table 3.

TABLE 3 — VALUES OF  $\Lambda_0$ ,  $\Lambda_0\eta$  AND  $a$  (Å) AT DIFFERENT TEMPERATURES FOR LITHIUM ACETATE IN WATER AND AQUEOUS METHYL ACETATE OBTAINED FROM THE TEST OF THE FUOSS-ONSAGER-SKINNER EQUATION

Temp. (°C)	$\Lambda_0$ (ohm <sup>-1</sup> cm <sup>2</sup> ) Water	$\Lambda_0$ (ohm <sup>-1</sup> cm <sup>2</sup> ) Aq.-methyl acetate	$\Lambda_0\eta$		$a$ (Å)	
			Water	Aq.-methyl acetate	Water	Aq.-methyl acetate
40	121.9	128.4	0.80	1.06	1.4	1.7
45	130.2	135.5	0.78	0.99	1.6	1.9
50	133.2	143.6	0.73	0.95	2.2	2.0

The data in Table 3 reveal that the limiting equivalent conductances obtained by Onsager extrapolation method and Fuoss-Onsager-Skinner equation differ slightly for solution in water, but for solutions in aq.-methyl acetate, there is large difference in  $\Lambda_0$  values. This large difference may be due to the fact that (a) the Fuoss-Onsager-Skinner conductance equation takes into account the points at higher concentrations also whereas these points show deviations from simple Onsager plots and (b) manual extrapolation in Onsager plots may be the source of error.

The structural effects on the conductance of ions in aqueous solutions are derived by a comparison of their Walden-products in aqueous and non-aqueous solutions at different temperatures<sup>14,15</sup>. From the Table 3, it is clear that as the temperature increases the Walden-product goes on decreasing. The  $\Lambda_0\eta$  versus  $t$  plots are almost linear for both the solutions and have negative temperature coefficient. The negative temperature coefficient<sup>7</sup> suggests that the lithium acetate acts as a structure-breaker both in water and in aq.-methyl acetate. The slight increase in the ion size parameter  $a$  (Å) with temperature for lithium acetate in water and aqueous methyl acetate may be interpreted<sup>7</sup> as an indication of the structure-breaking tendency of the electrolyte in a solvent.

The structure-breaking capacity of lithium acetate in water and aqueous methyl acetate is also supported from the viscosity measurements<sup>16</sup>.

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#### Study of Hydrolysis Kinetics & Lactone-Acid-Salt Equilibria of $\gamma$ -D-Mannonolactone

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Specific rate constant ( $k_H$ ) for the hydrolysis of  $\gamma$ -D-mannonolactone in aqueous solution has been determined conductometrically, the values at 25° and 37° are 2.04 and  $5.37 \times 10^{-5} \text{ sec}^{-1}$  respectively. Activation energy ( $E_a = 14.73 \text{ kcal mole}^{-1}$ ) has been found from the Arrhenius plot. The overall equilibrium constant ( $K_{eq}$ ) for the hydrolysis of the lactone,  $k_A$  for mannonic acid and the equilibrium constant  $k_L$  for the hydrolysis of the lactone have been determined from pH and optical rotation measurements and are found to be  $2.48 \pm 0.10 \times 10^{-5}$ ,  $1.60 \pm 0.16 \times 10^{-4}$  and 0.18 respectively. Lactonization constants  $k_1$  for mannonic acid at 25° and 37° are  $1.34$  and  $2.98 \times 10^{-5} \text{ sec}^{-1}$  respectively.

THE hydrolysis kinetics of industrially important aldonolactones, viz. D-glucono- $\delta$ -lactone<sup>1</sup>, lactobionolactone<sup>2</sup>, maltobionolactone<sup>3</sup>, cellobionolactone<sup>4</sup> and  $\gamma$ -D-galactonolactone<sup>5</sup> have been reported earlier, but such data on  $\gamma$ -D-mannonolactone are wanting. A systematic study of the hydrolysis kinetics of this lactone and lactone-acid-salt equilibria are reported in this note.

$\gamma$ -D-Mannonolactone — D-Mannose (45 g) was electrolytically oxidized in the presence of  $\text{NaHCO}_3$  (25 g) and 1% sodium bromide in 800 ml water

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