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Ion-Solvent Interaction of Potassium Iodide in N,N-Dimethylacetamide-Water Mixtures from Viscosity Data

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Viscosities in the concentration range 0·005-0·2 *m* of KI in N,N-dimethylacetamide-water mixtures have been measured at 25°C. The experimental data have been analysed in terms of *A* and *B* coefficients calculated from the Jones-Dole equation, $\eta/\eta_0 = 1 + Ac^{1/2} + Bc$. The value of *B*-coefficient in the mixed solvents first decreases and then increases after a minimum is observed at about 30 wt % of DMA.

THE viscosity of potassium iodide in the mixed solvents has been determined and analysed in terms of Jone-Dole[1] equation (1) to gain an insight into the ion-solvent interaction

$$\eta/\eta° = 1 + Ac^{1/2} + Bc \qquad \ldots(1)$$

The constant *A* in Eq. (1) refers to the long range interionic forces[2-4], which is important in the case of very dilute solutions. However, in present investigation it has no significance. The coefficient *B*, which represents ion-solvent interaction[5], has been used to interpret the experimental data obtained in this study.

Potassium iodide (analar) was purified by the method of Harold-Simmons-Booth[6]. N,N-Dimethyl-acetamide (DMA) (Eastman Kodak) was treated with KOH pellets for several hours and then distilled under reduced pressure (b.p. 66-68°/31 mm). The specific conductance of DMA thus obtained was $0·4 \times 10^{-6}$ mhos/cm (lit.[7] $3·0 \times 10^{-7}$ Scm⁻¹). Mixed solvents containing different weight % of DMA were prepared at least 6 hr in advance to avoid air bubbles which come out after mixing process. The temperature in the Gallenkamp thermostat was maintained at $25° \pm 0·01°$. Calibrated Cannon-Ubbelhode viscometer[8], with the viscosity constant of 0·003910 centistokes/sec was used for the measurements. The flow time was determined with a stopwatch of 0·1 sec least count. Densities of solutions were measured by a pyknometer of 20 ml capacity. The error in the viscosity values was within 0·1%. The viscosity (η) of the solvent and solutions were calculated from the relation $\eta = P \times t$ (0·00391) cp, where P is the density and t the flow time in seconds. The viscosity of pure water was taken to be 0·8937 cp at 25° as reported in the literature[9].

Viscosities of mixed solvents and of solutions containing KI are given in Table 1. The viscosity of DMA-water mixtures increases with the increase of DMA in the mixed solvents and decreases after

TABLE 1 — VISCOSITY OF POTASSIUM IODIDE IN DMA-WATER MIXTURES AT 25°C

Concentration $C \times 10^2$ (*M*)	$C^{1/2} \times 10^2$	η (cp)	$[(\eta - \eta°)/\eta°C^{1/2}] \times 10^2$
SYSTEM I (0·0 wt % DMA)			
0·000	0·000	0·8937	0·000
0·511	7·148	0·8938	0·156
1·022	10·110	0·8933	−0·442
2·044	14·397	0·8928	−0·704
4·088	20·219	0·8918	−1·051
6·132	24·763	0·8911	−1·174
8·176	28·593	0·8892	−1·761
10·220	31·968	0·8884	−1·855
20·441	45·210	0·8822	−2·846
SYSTEM II (10 wt % DMA)			
0·000	0·00	1·1983	0·000
0·510	7·145	1·1979	−0·467
1·021	10·105	1·9171	−0·991
2·042	14·289	1·1963	−1·168
4·084	20·208	1·1944	−1·610
6·125	24·750	1·1914	−2·326
8·168	28·579	1·1894	−2·598
10·209	31·951	1·1857	−3·290
20·419	45·187	1·1751	−4·284
SYSTEM III (20 wt % DMA)			
0·000	0·000	1·5990	0·000
0·512	7·152	1·6009	1·224
1·023	10·116	1·6003	0·803
2·046	14·306	1·5995	0·218
4·093	20·231	1·5974	−0·494
6·139	24·776	1·5948	−1·060
8·186	28·612	1·5919	−1·551
10·233	31·987	1·5893	−1·896
20·466	45·239	1·5728	−3·621
SYSTEM IV (40 wt % DMA)			
0·000	0·000	2·7654	0·000
0·507	7·121	2·7696	2·132
1·014	10·080	2·7688	1·219
2·028	14·242	2·7688	0·863
4·057	20·141	2·7662	0·143
6·085	24·667	2·7640	−0·205
8·113	28·483	2·7568	−0·710
10·141	31·844	2·7553	−1·146
20·283	45·036	2·7326	−2·633
SYSTEM V (60 wt % DMA)			
0·000	0·000	3·9563	0·000
0·492	7·014	3·9567	1·081
0·984	9·918	3·9575	0·969
1·967	14·027	3·9580	0·755
3·935	19·838	3·9577	0·509
5·903	24·296	3·9566	0·301
7·871	28·055	3·9546	0·081
9·838	31·367	3·9511	−0·209
19·677	44·359	3·9377	−0·912
SYSTEM VI (75 wt % DMA)			
0·000	0·000	3·5263	0·000
0·502	7·083	3·5333	2·802
1·003	10·017	3·5381	3·340
2·046	14·306	3·5451	3·726
4·014	20·035	3·5580	4·486
6·021	24·538	3·5729	5·385
8·028	28·334	3·5816	5·534
10·035	31·676	3·5927	5·944
SYSTEM VII (85 wt % DMA)			
0·000	0·000	2·4214	0·000
0·496	7·045	2·4305	5·334
0·993	9·964	2·4392	7·377
2·028	14·242	2·4546	9·627
3·972	19·929	2·4853	13·241
5·957	24·403	2·5107	15·112
7·943	28·183	2·5368	16·910

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[10].

The Jones-Dole equation in the form

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

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[11], 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:

$$\eta = \eta° + \eta^* + \eta^E + \eta^A + \eta^D \qquad ...(2)$$

where n^* is the positive increment in viscosity caused by coulombic interaction, η^E is the positive increment due to the shape and size of an ion, η^A is the increment due to the alignment or orientation of the polar molecules by the ionic field and η^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

$$\eta^E + \eta^A + \eta^D = \eta° \, Bc \qquad ...(3)$$

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[12]. 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 η^E and η^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[13]. Therefore, ions responsible for break-

ing the structure would give much larger values of η^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 η^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 η^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.