

The Coefficients of the Jones-Dole Equation for the Viscosity of Solutions of Potassium Iodide in Mixtures of Water and Dimethylacetamide at 35°C

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Abstract

The viscosities of solutions of KI in binary mixtures of water and dimethylacetamide at 35°C in the concentration range 0.005–0.2 mol dm⁻³ are reported. The data are analysed in terms of the *A* and *B* parameters of the Jones-Dole equation. The value of the *B* coefficient first decreases and then increases after attaining a minimum at about 0.05 mole fraction of dimethylacetamide.

Introduction

The viscosity η of dilute solutions of electrolytes varies with concentration *c* according to the Jones-Dole¹ equation:

$$\eta/\eta^\circ = 1 + Ac^{1/2} + Bc$$

The constant *A* is related to the long-range interionic forces,²⁻⁴ and the term $Ac^{1/2}$ is predominant in very dilute solutions. The coefficient *B* is related to the interaction between the ions and the solvent and is interpreted as a measure of the structure-forming and structure-breaking capacity of an electrolyte in solution.⁵ This communication reports measurements of the viscosities of dilute solutions of potassium iodide in dimethylacetamide-water mixtures at 35°C, in order to determine the variation of structure in the mixed-solvent system.

Experimental

The apparatus and procedures for the viscosity and density measurements were the same as those described earlier.^{6,7} Measurements were made at 35 ± 0.01°C. AnalaR grade potassium iodide was purified by the method of Simmons-Booth.⁸ Dimethylacetamide (dma) (Eastman Kodak, U.S.A.) 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 4.0 × 10⁻⁵ S m⁻¹ (lit.⁹ 3.0 × 10⁻⁵ S m⁻¹).

¹ Jones, G., and Dole, M., *J. Am. Chem. Soc.*, 1929, **51**, 2950.

² Falkenhagen, H., and Dole, M., *Phys. Z.*, 1929, **30**, 611.

³ Falkenhagen, H., *Phys. Z.*, 1931, **32**, 745.

⁴ Falkenhagen, H., and Vernon, E. L., *Philos. Mag.*, 1932, **14**, 537.

⁵ Feakins, D., and Lawrence, K. G., *J. Chem. Soc. A*, 1966, 212.

⁶ Singh, D., Singh, N. P., and Lal Bahadur, *Indian J. Chem.*, 1975, **13**, 1177.

⁷ Prasad, B. N., Singh, N. P., and Singh, M. M., *Indian J. Chem. A*, 1976, **14**, 322.

⁸ Simmons-Booth, H., *Inorg. Synth.*, 1939, **1**, 163.

⁹ Paul, R. C., Banait, J. S., and Narula, S. P., *Aust. J. Chem.*, 1975, **28**, 321.

Table 1. Viscosity (η) of potassium iodide in dma-water mixtures at 35°C

Concn (mol dm ⁻³)	10 ³ η (kg m ⁻¹ s ⁻¹)	Concn (mol dm ⁻³)	10 ³ η (kg m ⁻¹ s ⁻¹)	Concn (mol dm ⁻³)	10 ³ η (kg m ⁻¹ s ⁻¹)
0.0 mole fraction dma		0.0224 mole fraction dma		0.0491 mole fraction dma	
0.00000	0.7194	0.00000	0.9411	0.00000	1.2237
0.00545	0.7196	0.00549	0.9415	0.00546	1.2250
0.01090	0.7196	0.01097	0.9416	0.01093	1.2251
0.02180	0.7193	0.02195	0.9414	0.02186	1.2259
0.04361	0.7191	0.04390	0.9402	0.04372	1.2249
0.06541	0.7186	0.06586	0.9402	0.06557	1.2234
0.08722	0.7183	0.08781	0.9393	0.08743	1.2218
0.10902	0.7177	0.10976	0.9383	0.10929	1.2207
0.21804	0.7143	0.21952	0.9333	0.21858	1.2138
0.1211 mole fraction dma		0.2361 mole fraction dma		0.3826 mole fraction dma	
0.00000	2.0011	0.00000	2.7460	0.00000	2.5395
0.00541	2.0022	0.00484	2.7496	0.00460	2.5462
0.01081	2.0023	0.00968	2.7510	0.00920	2.5495
0.02163	2.0019	0.01934	2.7540	0.01840	2.5546
0.04326	2.0008	0.03869	2.7586	0.03681	2.5631
0.06489	1.9991	0.05804	2.7633	0.05521	2.5728
0.08652	1.9974	0.07738	2.7659	0.07302	2.5791
0.10815	1.9953	0.09678	2.7797	0.09202	2.5882
0.21630	1.9879	0.19345	2.7792	0.18404	2.6333
		0.5393 mole fraction dma			
		0.00000	1.8610		
		0.00721	1.8770		
		0.01442	1.8860		
		0.02885	1.9005		
		0.04327	1.9102		
		0.05770	1.9201		
		0.07212	1.9319		
		0.14425	1.9847		

Table 2. Values of constants A and B at 35°C x , mole fraction of dma

x	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)	x	A (dm ^{3/2} mol ^{-1/2})	B (dm ³ mol ⁻¹)
0.0000	0.0072 ± 0.0007	-0.046 ± 0.003	0.2361	0.0174 ± 0.0011	0.027 ± 0.004
0.0224	0.0105 ± 0.0009	-0.059 ± 0.004	0.3826	0.0270 ± 0.0025	0.126 ± 0.010
0.0491	0.0230 ± 0.0015	-0.089 ± 0.006	0.5393	0.0809 ± 0.0039	0.236 ± 0.017
0.1211	0.0112 ± 0.0006	-0.057 ± 0.002			

The viscosities, η , of the solvents and solutions were calculated from the relation

$$\eta = 0.003910\rho t$$

where ρ is the density in gm cm⁻³, t is the efflux time in seconds and 0.003910 is the viscometer constant. The overall uncertainty in the viscosity was estimated to be less than 0.1%. The viscosity of pure water at 35°C was taken to be 0.7194×10^{-3} kg m⁻¹ s⁻¹.¹⁰

¹⁰ Stokes, R. H., and Mills, R., 'The International Encyclopedia of Physical Chemistry and Chemical Physics' p. 39 (Pergamon: London 1965).

Results and Discussion

The results of viscosity measurements of dma-water mixtures and of solutions containing potassium iodide in the concentration range $0.005\text{--}0.2\text{ mol dm}^{-3}$ have been recorded in Table 1. Jones-Dole parameters (Table 2) were derived by fitting the experimental data to the equation

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

by the method of least squares.

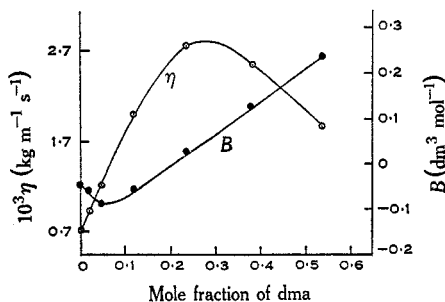


Fig. 1. Variations of the viscosity of dma-water mixtures and B coefficients of KI with solvent composition at 35°C .

When dma is added to water at 35°C the viscosity passes through a maximum at about 0.25 mole fraction of dma (Fig. 1, η curve). The B coefficient, for solutions of potassium iodide in the mixed solvents, passes through a minimum at 0.05 mole fraction dma. This behaviour is readily explained in terms of the discussion of Stokes and Mills;¹⁰ the solvent mixture with the minimum value of B would be the most structured, with the 'structure-breaking' electrolyte potassium iodide having its maximum effect.

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