

VISCOSITIES AND DENSITIES OF SOME MULTICHARGED ELECTROLYTES IN ISOPROPANOL-WATER MIXTURES

M L PARMAR* and ANITA KHANNA

Department of Chemistry, Himachal Pradesh University, Shimla 171 005, India

(Received 10 August 1986; Accepted 11 October 1988)

Viscosity and density data for aluminium ammonium sulphate and potassium aluminium sulphate in isopropanol-water (5, 10, 15 and 20 wt %) at different concentrations and temperatures are presented. The viscosity data have been analyzed by means of Jones-Dole equation. The activation parameters of viscous flow were obtained by the application of transition-state theory. The density data have been analysed by using the Masson's equation. The limiting apparent molar volume, ϕ_v^0 , and the slope S_v , have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The ϕ_v^0 values vary with temperature as a power series of temperature. Structure making/breaking capacities of the multi-charged electrolytes have been inferred from the sign of $(\partial^2\phi_v^0/\partial T^2)$. Both multi-charged electrolytes behave like the symmetrical tetra-alkyl ammonium salts and as structure makers/promoters.

Key Words : Viscosities; Densities; Multicharged Electrolytes; Isopropanol-Water Mixtures; Apparent Molar Volumes

INTRODUCTION

RECENTLY, Kay *et al.*¹ have concluded from the conductance behaviour of a number of tetra-alkyl ammonium salts in aqueous and various organic solvents that in a solvent with high solvating power, small ions are well solvated and therefore solvent-separated ion pairs are predominantly formed. On the other hand large ions are almost bare in solvents, such as water and alcohols, and form contact ion pairs.

The present studies have been undertaken with an aim of learning more about the nature of solute-solvent interactions from viscosity and partial molar volume studies of some multicharged electrolytes viz., aluminium ammonium sulphate and potassium aluminium sulphate in dilute solutions of isopropanol in water upon 20% (w/w) of isopropanol.

MATERIALS AND METHOD

Analar grade chemicals, aluminium ammonium sulphate and potassium aluminium sulphate, were used after drying over P_2O_5 . The isopropyl alcohol of Analar was refluxed over calcium oxide for several hours and then distilled. The middle fraction was stored in glass bottles over Linde type 5A molecular sieves. Freshly

*To whom all correspondence should be addressed.

distilled water of specific conductance of the order of $10^{-6} \sim 10^{-1} \text{ cm}^{-1}$ was used for preparing the aqueous mixtures of isopropanol and also used as a standard liquid for calibration purposes. All the aqueous-isopropanol mixtures as well as solutions of electrolytes were made by weight and conversion of molality into molarity was done by using the following expression² :—

$$C = \frac{d \cdot m \cdot 1000}{1000 + m M_2} \quad \dots(1)$$

where C is the molarity, d the density of the solution of electrolyte, m the molality and M_2 the molecular weight of electrolyte. Density was measured with an apparatus similar to the one reported by Ward and Millero³ and Parmar and Kundra.⁴ The kinematic viscosities were measured with the help of a capillary type viscometer⁵ with a flow time 283s for water at 303 K. Runs were repeated until three successive determinations were obtained within 0.1s. The relative viscosities of solutions were calculated using the following relation :

$$\eta_{1,2}/\eta_1 = d_{1,2} t_{1,2}/d_1 t_1, \quad \dots(2)$$

where the terms have their usual meaning. All flow times being greater than 100s, kinetic energy correction was not considered necessary. The apparent molar volumes of solute were calculated by using the following relation :

$$\phi_v = \frac{1000 (d_1 - d_{1,2})}{c d_1} + \frac{M_2}{d_1}, \quad \dots(3)$$

where M_2 is the molecular weight of the electrolyte and other symbols have their usual meaning.

The viscosity measurements were made in an air thermostat and the density measurements in water bath whose temperature was kept within $\pm 0.01^\circ \text{C}$.

RESULTS AND DISCUSSION

The densities and relative viscosities of aluminium ammonium sulphate and potassium aluminium sulphate in 5, 10, 15 and 20 wt per cent solutions of isopropanol in water were determined at 298 K. The electrolytes aluminium ammonium sulphate and potassium aluminium sulphate exhibited an identical behaviour in the above different compositions of isopropanol-water mixture. To study the effect of temperature the relative viscosity for these electrolytes was determined only in 5 per cent iso-propanol-water mixture at 298, 303, 308 and 313 K. The data have been analyzed by using the Jones-Dole equation⁶

$$\eta_r = \eta_{1,2}/\eta_1 = 1 + AC^{1/2} + BC, \quad \dots(4)$$

where η_r is the relative viscosity of the solutions, A is the Falkenhagen⁷ coefficient that takes into account ionic interactions, and B is the Jones-Dole coefficient⁶ which is related to the size of the ions and to the different ion-solvent interactions. According to equation (4), $(\eta_r - 1)/\sqrt{c}$ when plotted as a function of \sqrt{C} would be a straight line. This was confirmed experimentally for both electrolytes in solutions having different compositions of isopropanol in water (cf. Figs. 1 and 2). The A and B coefficients were obtained from the intercepts and slopes of the linear curves and the values are given in Table I.

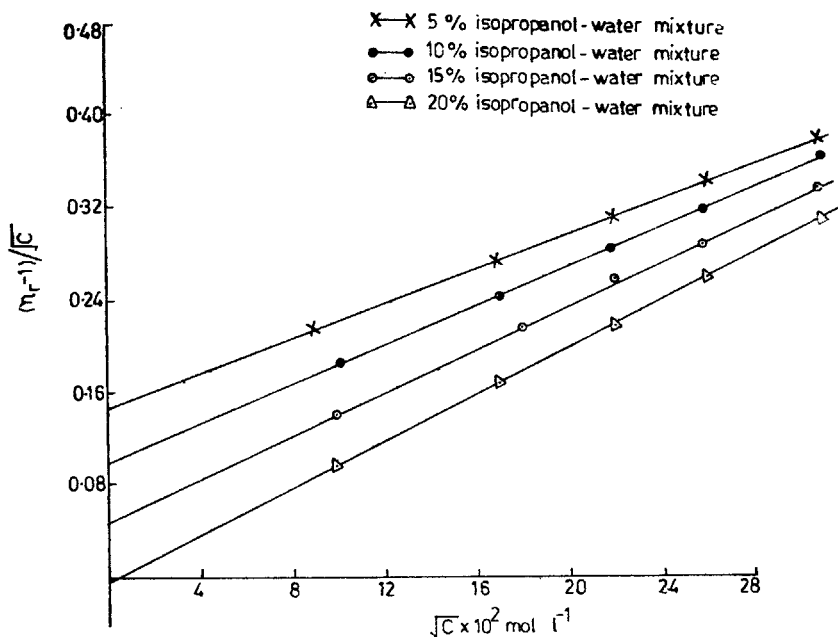


FIG 1 Plot of $(\eta_r - 1)/\sqrt{C}$ vs \sqrt{C} for aluminium ammonium sulphate at 298 K in different compositions of isopropanol-water mixture

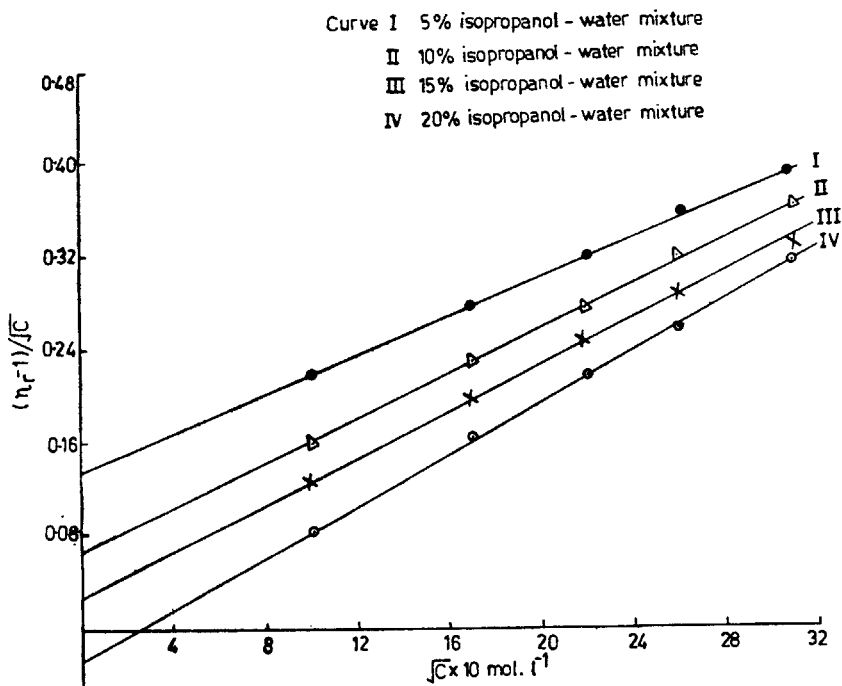


FIG 2 Plot of $(\eta_r - 1)/\sqrt{C}$ vs \sqrt{C} for potassium aluminium sulphate at 298 K in different compositions of isopropanol-water mixture

TABLE I

A. Values of A and B (coefficients of Jones-Dole Equation), ϕ_v^0 ($\text{cm}^3 \text{mol}^{-1}$) and S_v ($\text{cm}^3 \text{ l}^{1/2} \text{mol}^{-3/2}$) of multicharged electrolytes in iso-propanol-water mixtures at 298 K

% Composition of iso-propanol water mixture	Aluminium Ammonium Sulphate				Potassium Aluminium Sulphate			
	A	B	ϕ_v^0	S_v	A	B	ϕ_v^0	S_v
5	0.144	0.76	194.00	88.88	0.128	0.84	195.20	95.24
10	0.100	0.86	204.00	78.57	0.072	0.96	215.60	93.33
15	0.044	0.93	206.04	100.00	0.028	1.00	178.00	163.64
20	-0.004	1.04	209.04	69.56	-0.028	1.12	209.60	73.68

B. Values of A and B (coefficients of Jones-Dole Equation), ϕ_v^0 ($\text{cm}^3 \text{mol}^{-1}$) and S_v ($\text{cm}^3 \text{ l}^{1/2} \text{mol}^{-3/2}$) in 5 per cent isopropanol-water mixture at different temperatures

Temperature (K)	Aluminium Ammonium Sulphate				Potassium Aluminium Sulphate			
	A	B	ϕ_v^0	S_v	A	B	ϕ_v^0	S_v
298	0.144	0.76	194.00	88.88	0.128	0.84	195.20	95.24
303	0.120	1.34	203.60	138.46	0.008	1.61	187.20	181.82
308	0.050	1.31	230.00	66.66	0.050	1.33	188.00	228.57
313	0.030	1.03	269.20	94.11	0.140	1.04	197.20	100.00

A perusal of Table I shows that coefficient A decreases while coefficient B increases with increasing concentration of isopropanol in water for both electrolytes. The plots of $(\eta_r - 1)/\sqrt{C}$ vs. \sqrt{C} for aluminium ammonium sulphate and potassium aluminium sulphate in 5 per cent isopropanol-water mixture are also linear at all temperatures under study (cf. Figs. 3 and 4). The values of the coefficients A and B at different temperatures are given in Table I.

Recently, dB/dT has been observed⁸ as an important criterion for determining the solute-solvent interactions. The viscosity studies of a number of such solutions have shown that structure makers will have negative dB/dT value while structure-breakers will have a positive $\frac{dB}{dT}$ value. The present studies have shown the negative temperature coefficient of B for both the electrolytes in 5 per cent isopropanol-water. This suggests that these electrolytes behave like structure makers/promoters.

The viscosity data have been analysed on the basis of a transition state theory of the relative viscosities of electrolytic solutions.⁹ The application of this treatment gives rise to the following equation :

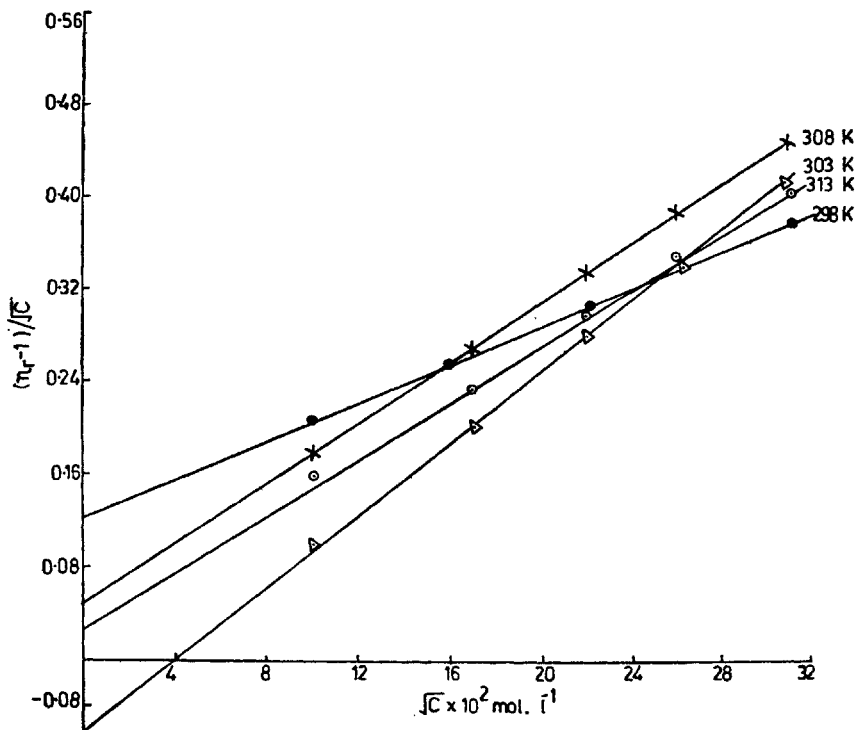


FIG 3 Plot of $(\eta_r - 1)/\sqrt{C}$ vs \sqrt{C} for aluminium ammonium sulphate in 5% isopropanol at different temperatures

$$B = \frac{\bar{V}_1^0 - \bar{V}_2^0}{1000} + \frac{\bar{V}_1^0}{1000} \left[\frac{\Delta\mu_2^0\# - \mu_1^0\#}{RT} \right], \quad \dots(5)$$

where \bar{V}_1^0 and \bar{V}_2^0 are the partial molar volumes of the solvent and solute (at infinite dilution) respectively. $\Delta\mu_2^0\#$ is the contribution per mole of solute to the free energy of activation for viscous flow of the solution. $\mu_1^0\#$ is the free energy of activation per mole of the pure solvent¹⁰

$$\Delta\mu_1^0\# = \Delta G_1\# = RT \ln (\eta_0 \bar{V}_1^0/hN), \quad \dots(6)$$

where η_0 is the viscosity of the solvent.

$\Delta\mu_2^0\#$ parameter has been calculated from relation (6) and its values are given in Table II for different compositions of isopropanol-water mixtures at 298 K. The values of \bar{V}_2^0 , the partial molar volume at infinite dilution for both the electrolytes have been determined and recorded in Table II. The standard partial molar volume \bar{V}_1^0 of isopropanol at infinite dilution, was found to be 60.30 cm³ mole⁻¹ at 298 K.

Table II shows very little change of $\Delta\mu_1^0\#$ within the range of the isopropanol concentrations under study. $\Delta\mu_2^0\#$ is determined from the coefficient B and $(\bar{V}_1^0 - \bar{V}_2^0)$. Table II also shows that $\Delta\mu_2^0\#$ increases for both the electrolytes with the increase in isopropanol content of the solvent at 298 K.

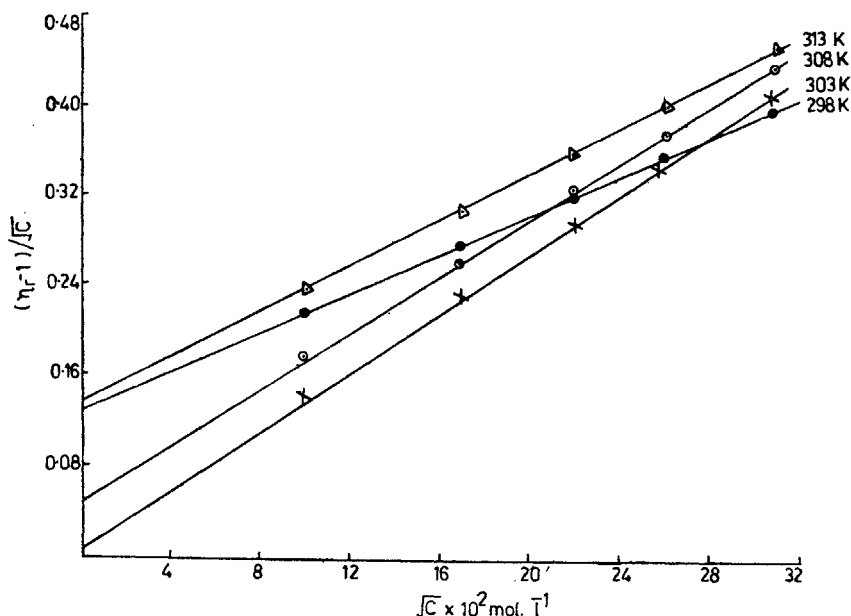


FIG 4 Plot of $(\eta_r - 1)/\sqrt{C}$ vs \sqrt{C} for potassium aluminium sulphate in 5% isopropanol water mixture at different temperatures

TABLE II

Values of \bar{V}_2^0 , $\Delta\mu_1^{0\#}$ and $\Delta\mu_2^{0\#}$ in iso-propanol-water mixture at 208 K

% composition of isopropanol water	\bar{V}_2^0 (cm ³ mol ⁻¹)		$\Delta\mu_1^{0\#}$ (KJ mol ⁻¹)	$\Delta\mu_2^{0\#}$ (KJ mol ⁻¹)	
	Aluminium ammonium sulphate	Potassium aluminium sulphate		Aluminium ammonium sulphate	Potassium aluminium sulphate
5	194.00	195.00	12.15	48.86	52.19
10	204.00	215.60	12.69	53.93	58.51
15	206.04	178.00	13.39	57.59	59.31
20	209.04	209.60	13.53	62.37	65.68

The apparent molar volume, ϕ_v , has been calculated from the density data by using relation (3). The apparent molar volume has been found to vary linearly with the square root of the concentration according to Masson's equation¹¹

$$\phi_v = \phi_v^0 + S_v \sqrt{C}, \quad \dots 7$$

where ϕ_v^0 the limiting apparent molar volume, is equal to the partial molar volume \bar{V}_2^0 at infinite dilution, and S_v is the experimental slope. The apparent/partial molar volume at infinite dilution and the slope S_v for different systems are given in Table I.

It is evident from Table I that S_v decreases with the increase of isopropanol content of the solvent but it has a maximum value in 15 per cent isopropanol-water mixture for both electrolytes at 298 K. This suggests a decrease in solute-solute interactions with the increase in isopropanol content of the solvent. The maximum of S_v in 15 per cent isopropanol solution indicates that the solute-solute interaction is greatest at this concentration of isopropanol in water.

It is also clear from Table I that ϕ_v^0 increases with the increase in isopropanol concentration of the solvent in case of aluminium sulphate, whereas it has minimum

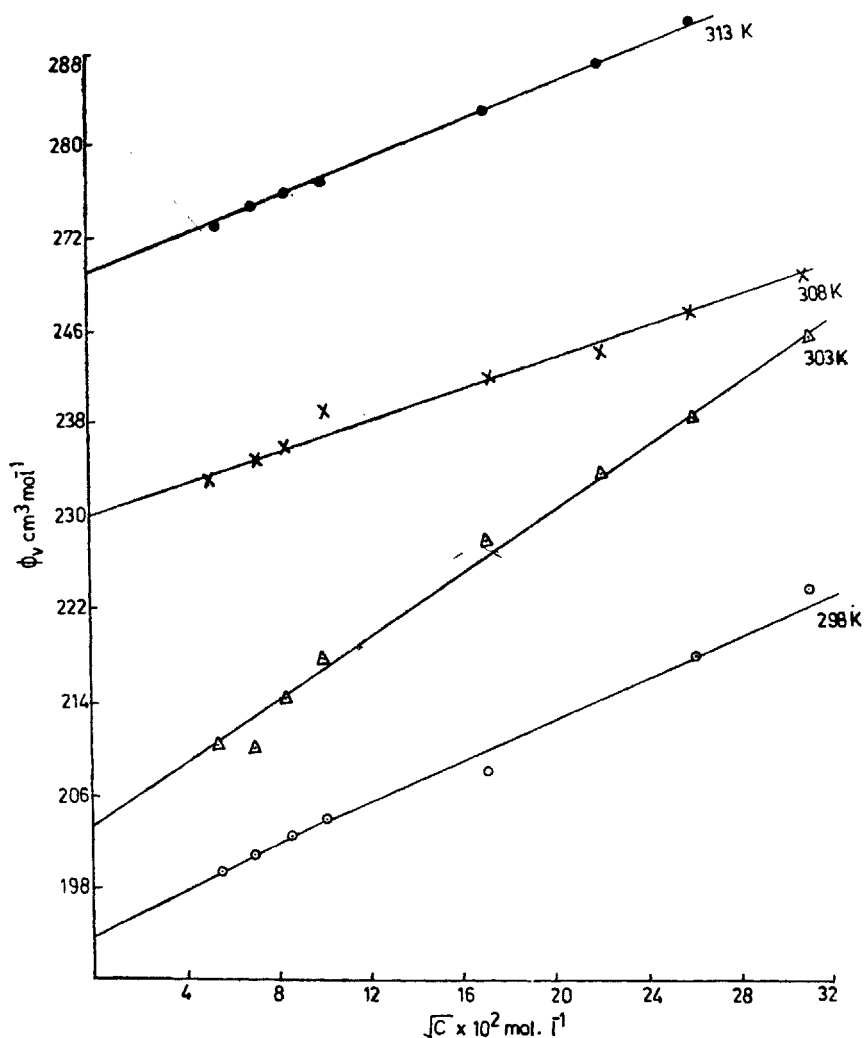


FIG 5 Plot of ϕ_v vs \sqrt{C} for aluminium ammonium sulphate at different temperatures in 5% isopropanol-water mixture

value in 15 per cent of isopropanol for potassium aluminium sulphate. This indicates that the solute-solvent interaction is least at this concentration of isopropanol.

Effect of Temperature

The linear plots of ϕ_v versus \sqrt{C} at different temperatures (298, 303, 308 and 313 K) in 5 per cent isopropanol-water mixture for aluminium ammonium sulphate and potassium aluminium sulphate are shown in Figs. 5 and 6 respectively. The values of limiting apparent molar volume ϕ_v^0 and the slope S_v at different temperatures are recorded in Table I.

It is evident from Table I that the value of S_v is minimum for aluminium ammonium sulphate at 308 K while it has a maximum value for potassium

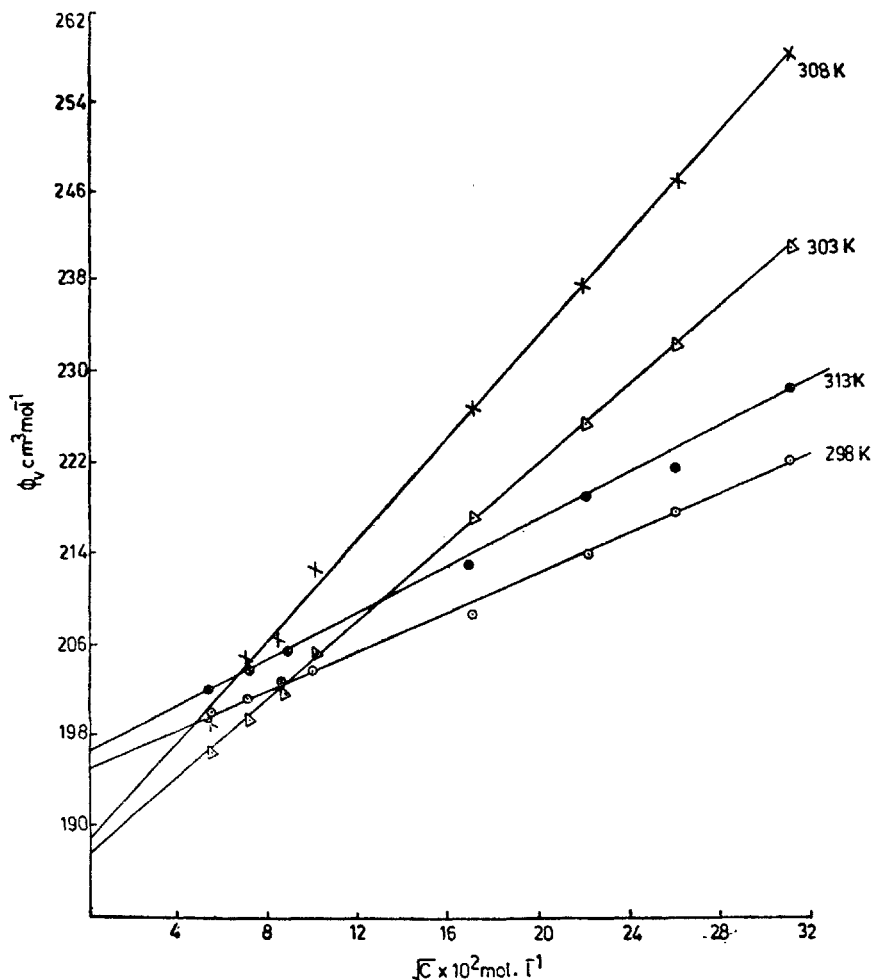


FIG 6 Plot of ϕ_v vs \sqrt{C} for potassium aluminium sulphate at different temperatures in 5% isopropanol-water mixture

aluminium sulphate at 308 K in 5 per cent isopropanol. This suggests that solute-solute interactions are minimum in case of aluminium ammonium sulphate while these are maximum for potassium aluminium sulphate at 308 K.

The temperature dependence of ϕ_v^0 for aluminium ammonium sulphate in 5 per cent isopropanol can be expressed by the following equation :

$$\phi_v^0 = 2.99606 \times 10^4 - 200.016 T + 0.336 T^2, \quad \dots(8)$$

whereas in case of potassium aluminium sulphate the variation of ϕ_v^0 with temperature can be represented by the following expression :

$$\phi_v^0 = 1.65637 \times 10^4 - 107.376T + 0.176T^2, \quad \dots(9)$$

where the temperature T is measured in Kelvin.

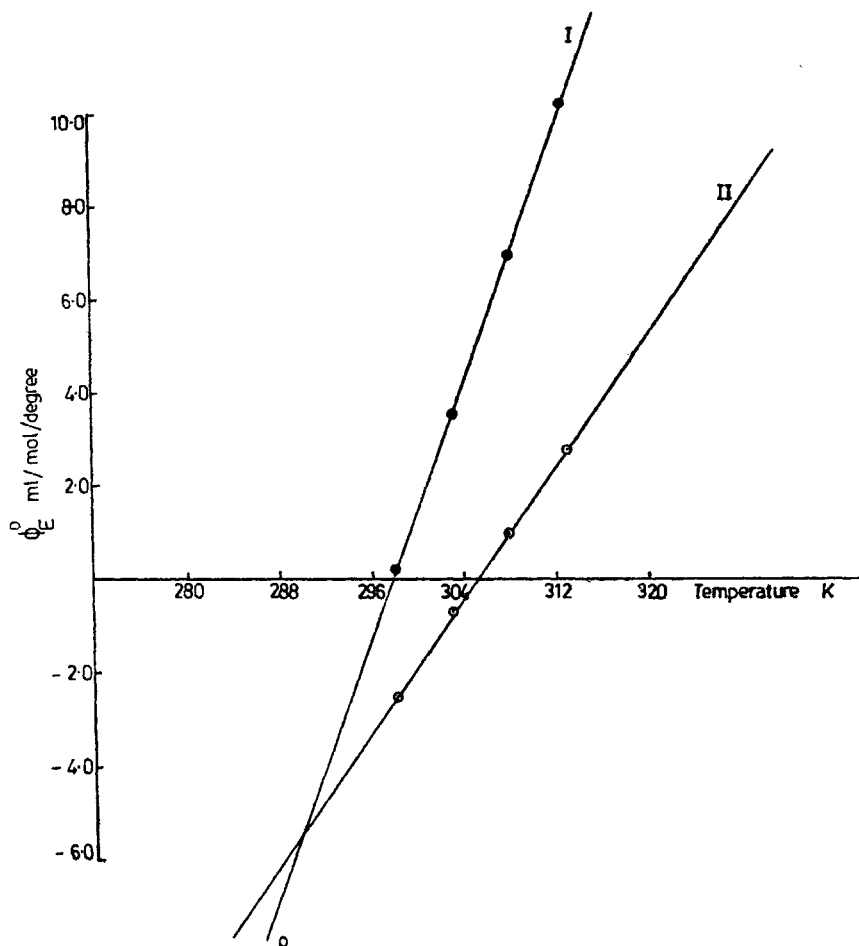


FIG 7 Variation of ϕ_E with temperature, curve I for aluminium ammonium sulphate and curve II for potassium aluminium sulphate

The increase in ϕ_v^0 of both electrolytes with increase of temperature can be attributed to the increase in solvation. The apparent molar expansibilities $\phi_E^0 = [\partial\phi_v^0/\partial T]$ calculated from (8) and (9) indicate that ϕ_E^0 increases with the increase of temperature. The increase in magnitude per degree temperature is positive indicating that both electrolytes behave like symmetrical tetra-alkylammonium salts,¹² but unlike common electrolytes where in the molar expansibility should decrease with increase of temperature.^{13,14}

The variation of ϕ_E^0 with temperature for both the electrolytes is linear (Fig. 7). This positive increase of ϕ_E^0 with the increase of temperature for both the electrolytes may be ascribed to "Caging effect".^{12,14} At 290 K both electrolytes have the same molar expansibilities, $\{5.4 \text{ ml mol}^{-1} \text{ K}^{-1}$ (cf. Fig. 7).

The positive values of S_v of both electrolytes in all the compositions of isopropanol-water mixture suggest that both electrolytes behave as structure makers. Recently, Hepler¹⁵ has developed a technique of examining the sign of $[\partial^2 \phi_v^0/\partial T^2]_P$ for various solutes in terms of long range structure making and breaking capacity of the solute in aqueous solutions using the following general expression :

$$[\partial C_P/\partial P]_T = - [\partial^2 \phi_v^0/\partial T^2]_P \quad \dots(10)$$

On this basis it has been deduced that structure making solutes should have positive values while structure breakers should have negative values. In the present study it has been observed from equations (9) and (10) that $(\partial^2 \phi_v^0/\partial T^2)_P$ is positive for both electrolytes in 5 per cent isopropanol-water mixture and therefore indicates that both the multicharged electrolytes behave as structure makers/promoters. This conclusion from molar volume studies is in excellent agreement with that drawn from viscosity measurements.

ACKNOWLEDGEMENT

One of the authors (A K) is grateful to the Council of Scientific and Industrial Research, New Delhi for the award of Senior Research Fellowship.

REFERENCES

- 1 R L Kay, D F Evans and Cunningham *J phys Chem* **73** (1969) 3322
- 2 D P Shoemaker and C W Garland *Experiments in Physical Chemistry* Mc Graw-Hill New York (1967) 131
- 3 G K Ward and F J Millero *J Soln Chem* **3** (1974) 417
- 4 M L Parmar and Anita Kundra *Electrochim Acta* **28** (1983) 1655
- 5 R L Blokhra and M L Parmar *Aust J Chem* **27** (1974) 1407
- 6 G Jones and M Dole *J Am chem Soc* **51** (1929) 2950
- 7 H Falkenhagen and E L Vernon *Z Phys* **33** (1932) 140
- 8 T S Sharma and J C Ahluwalia *Rev chem Soc* **2** (1973) 217
- 9 D Feakins D J Freemantle and K G Lawrence *J chem Soc Faraday Trans I* **70** (1974) 795
- 10 S Glasstone, K J Laidler and H Eyring *The Theory of Rate Processes* Mc Graw Hill New York (1941) 477

- 11 D O Masson *Phil Mag* **8** (1929) 218
- 12 F J Millero In *Structure and Transport Processes in Water and Aqueous Solutions* (Ed R A Horne) Ch 15 Wiley-Inter Science New York (1971)
- 13 F J Millero and Dorst Hansen *J phys Chem* **72** (1968) 1758
- 14 F J Millero *Chem Rev* **71** (1971) 147
- 15 L G Hepler *Can J Chem* **47** (1969) 4613