PARTIAL MOLAR VOLUMES OF SOME MULTICHARGED ELECTROLYTES IN AQUEOUS DIMETHYLFORMAMIDE AT VARIOUS TEMPERATURES

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Partial molar volumes of ammonium aluminium sulfate and potassium aluminium sulfate in DMF–water mixtures (5–20 wt.% of DMF) have been determined from solution density measurements at various temperatures and electrolyte concentrations. The data were evaluated by using Masson equation and the obtained parameters were interpreted in terms of ion–solvent and ion–ion interactions. Both electrolytes have been found to act as the structure makers/promotors in DMF–water systems.
Key words: Multicharged electrolytes; Partial molar volume.

Partial molar volumes of electrolytes provide valuable information about the ion–ion, ion–solvent and solvent–solvent interactions[1,2]. This information is of fundamental importance for understanding the reaction rates and equilibria involving dissolved electrolytes. These interactions have in detailed been studied for many electrolytes dissolved in water and some single organic solvents. On the other hand, much less attention have been paid to electrolyte solutions in mixed solvents though interactions in such systems are of great practical importance. The addition of organic solvent to an electrolyte aqueous solution brings about a change in ions' solvation that often results in a large change in the reactivity of dissolved electrolyte[3,4]. Peculiarity of water–organic solvent mixtures is well demonstrated by dramatic changes in reaction rates that cannot be explained in terms of change in the permittivity of reaction surrounding only[5–8].

Dimethylformamide (DMF) has often been used as the model of peptide linkage in studies aimed at understanding of the protein denaturation ability[9,10]. Also some biological processes are known to prefer "amide-like" environment to the "water-like" one[11]. Accordingly, it is the aim of the present study to bring about new information on the interactions in DMF–water systems that are interesting from the both chemistry and biology points of view.

EXPERIMENTAL

Ammonium aluminium sulfate and potassium aluminium sulfate (both of Analytic Reagent grade) were used after drying over P_2O_5 in a desiccator. *N,N*-Dimethylformamide (Analysed Reagent) was kept over anhydrous sodium carbonate for about 48 h and then distilled under reduced pressure. Only the middle fraction was used. The physical constants of DMF used at 298 K, such as density and viscosity 0.94407 g cm^{-3} and 0.7971 cP, respectively, agree with literature values[12]. Doubly distilled water (specific conductivity 1 . 10^{-6} Ω cm^{-1}) was always prepared afresh.

All the aqueous dimethylformamide mixtures as well as the solution of electrolytes were made by weight and conversion of molality, *m*, into molar concentration, *c*, was done using the standard expression[13]: $c = 1\ 000\ dm/(1\ 000 + m\ M_2)$ where *d* is the solution density and M_2 molecular weight of the electrolyte (453.33 g mol^{-1} and 474.38 g mol^{-1} for ammonium aluminium sulfate and potassium aluminium sulfate, respectively). Density was measured by an apparatus of the Ward and Millero[14] type described elsewhere[15] and temperature was kapt within ±0.1 °C. Accuracy in density measurement was of ±1 . 10^{-5} g cm^{-3}.

The apparent molar volumes (Φ_V) were calculated from the density data using the following standard expression[16]: $\Phi_v = 1\ 000(d_0 - d)/d_0 c + M_2/d_0$, where d_0 is the mixed solvent density.

RESULTS AND DISCUSSION

The densities were measured for solutions of the electrolytes in aqueous DMF of the weight ratio of DMF, w_{DMF} equal to 5, 10, 15 and 20% (w/w) at 298 K, and in 5% (w/w) aqueous DMF on the temperature interval from 298 K to 313 K. The electrolyte concentrations have been varied from 0.99 . 10^{-2} mol dm^{-3} to 12.55 . 10^{-2} mol dm^{-3}.

The dependence of Φ_v on the square root of molar concentration of the electrolyte are plotted in Fig. 1 for potassium aluminium sulfate in different compositions of DMF–H_2O mixtures at 298 K. Similar plots have been found for the another electrolyte. The
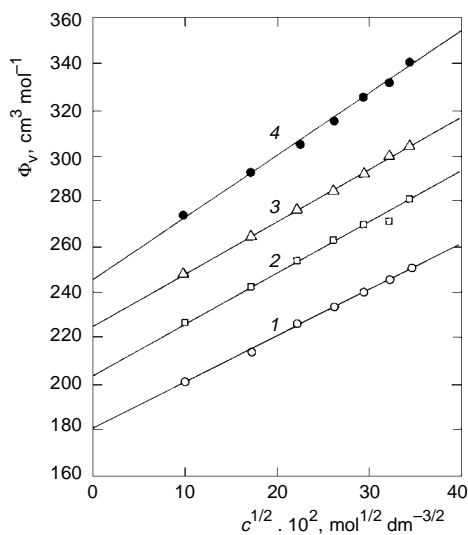

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Plots of Φ_v *versus* $c^{1/2}$ for potassium aluminium sulfate in DMF–H_2O mixtures with different DMF content (in wt.%) at 298 K; *1* 5, *2* 10, *3* 15, *4* 20

limiting apparent molar volumes (Φ_v^0) were calculated using the least squares fit to the plots of Φ_V against the square root of molar concentration, c, using Masson's equation[17]

$$\Phi_v = \Phi_v^0 + s_v c^{1/2} \ , \qquad (1)$$

where Φ_v^0 is the partial molar volume at infinite dilution and s_v the experimental slope. The values of Φ_v^0 and s_v, along with standard errors, are listed in Table I.

It is evident from Table I that s_v is positive and large for both the multicharged electrolytes in aqueous DMF mixtures at 298 K. Since s_v is a measure of solute–solute/ion–ion interactions, these results indicate the presence of very strong ion–ion interactions. These interactions, however, increase with the increase of DMF content in water at 298 K. It is also evident from Table I that s_v changes its sign from negative to the positive one upon the addition of a small amount of DMF in water, which may be attributed to strong solvent–solvent interactions (*i.e.* between DMF and water). Also the relative values of s_v are higher in the case of potassium aluminium sulfate as compared with

TABLE I
Partial molar volumes (Φ_v^0), experimental slope (s_v) and partial molar volumes of transfer ($\Delta\Phi_{v,tr}^0$) for ammonium aluminium sulfate and potassium aluminium sulfate in DMF–H$_2$O mixtures at 298 K. The standard errors are given in parentheses

w_{DMF}, %w/w	Φ_v^0, cm^3 mol^{-1}	s_v, cm^3 dm$^{3/2}$ mol$^{-3/2}$	$\Delta\Phi_{v,tr}^0$, cm^3 mol^{-1}
	Ammonium aluminium sulfate		
0	291.3(2.1)	–200.9(2.5)	–
5	214.3(1.5)	96.0(2.1)	–76.8
10	228.0(0.5)	101.6(1.9)	–63.4
15	233.6(0.7)	116.7(2.3)	–58.1
20	235.9(0.5)	158.8(2.2)	–55.5
	Potassium aluminium sulfate		
0	288.7(1.6)	–149.7(2.9)	–
5	181.3(0.9)	198.6(3.5)	–107.5
10	205.1(0.5)	217.3(1.9)	–83.7
15	226.1(0.5)	223.3(2.0)	–62.6
20	254.8(1.4)	270.0(2.5)	–42.9

those of ammonium aluminium sulfate thereby suggesting that ion–ion interactions are stronger in the case of the former electrolyte.

Since the only difference in the two electrolytes pertains to the presence of NH_4^+ and K^+ ions, stronger ion interactions in potassium aluminium sulfate than those in ammonium aluminium sulfate suggest that NH_4^+ ions are more strongly solvated than K^+ ions in aqueous DMF.

These results in DMF–water mixtures suggest a possible explanation for the absence of the negative s_v values for both salts in DMF–water solvent mixtures. Although at infinite dilution both the salts are completely dissociated in all these solvent mixtures the situation would be different at higher concentrations. The salts are not completely ionized such that interionic penetration does not occur which may give rise to positive slope in the Φ_v *versus* $c^{1/2}$ curves.

The sharp decrease in Φ_v^0 (or more negative $\Delta\Phi_{v,tr}^0$) in going from water to 5% DMF may be due to very strong solvent–solvent (*i.e.* DMF–water) interactions that are sufficient to prevent preferential solvation of cations by DMF. In other words, preferential solvation by DMF molecules, particularly in solvent mixtures containing low fractions of DMF, would also be reduced by the strong DMF–water interactions thereby resulting in the sharp decrease in Φ_v^0 values.

The volumes of transfer calculated by using Eq. (*2*) are given in Table I.

$$\Delta\Phi_{v,tr}^0 = \Phi_v^0 \,(MS) - \Phi_v^0 \,(W) \tag{2}$$

Here $\Phi_v^0 \,(MS)$ and $\Phi_v^0 \,(W)$ are the apparent molar volumes at infinite dilution in mixed solvent and in pure water, respectively.

The values of $\Delta\Phi_{v,tr}^0$ are negative for both the electrolytes in different compositions of DMF–H_2O mixtures and increase in magnitude with the increase in DMF content. The increase in Φ_v^0 and $\Delta\Phi_{v,tr}^0$ may be due to the decrease in electrostriction in the presence of DMF. Thus, the electrostriction effect which brings about the shrinkage in the volume of the solvent is decreased in mixed solvents as compared with that in pure water. Since, electrostriction primarily reflects electrolyte–solvent interactions, it can be inferred that electrolyte–solvent interactions increase with the increase in DMF. Further, the value of $\Delta\Phi_{v,tr}^0$ do not differ much for both the electrolytes in a particular composition suggesting that cations are preferentially solvated by DMF and this preference increases with the increase in DMF thereby reducing the strong[18] solvent–solvent interactions between water and dimethylformamide.

Effect of temperature: Since the behaviour of both the electrolytes in different compositions of DMF–H_2O mixture was found to be identical at 298 K, only 5% (w/w) DMF–H_2O composition was selected for studying the effect of temperature. Hence the densities were determined for various concentrations of ammonium aluminium sulfate and potas-

sium aluminium sulfate in 5% (w/w) DMF–H$_2$O mixture at different temperatures (298, 303, 308 and 313 K). Linear plots of Φ_v *versus* $c^{1/2}$ were obtained at different temperatures in 5 wt.% DMF–H$_2$O mixture for both the electrolytes studied here. A sample plot for ammonium aluminium sulfate is shown in Fig. 2. The values of limiting apparent molar volumes (Φ_v^0) and the experimental slopes (s_v) obtained by using least squares fit to above plots of the experimental values of Φ_v *versus* $c^{1/2}$ (using Eq. (*1*)) are given in Table II.

The values of s_v for both the electrolytes at all temperatures are positive and large (Table II) which indicate that ion–ion interactions are strong in 5 wt.% DMF–H$_2$O mixture at all temperatures and these increase with the increase in temperature.

The value of Φ_v^0 also increases with increase in temperature. This increase may be attributed to increase in solvation. The temperature dependence of Φ_v^0 in 5 wt.% DMF–H$_2$O mixture for ammonium aluminium sulfate can be expressed by Eq. (*3*).

$$\Phi_v^0 = 42\,717 - 288.17\,T + 0.489\,T^2 \ , \tag{3}$$

whereas in the case of potassium aluminium sulfate, the variation of Φ_v^0 with temperature (in K) can be represented by Eq. (*4*)
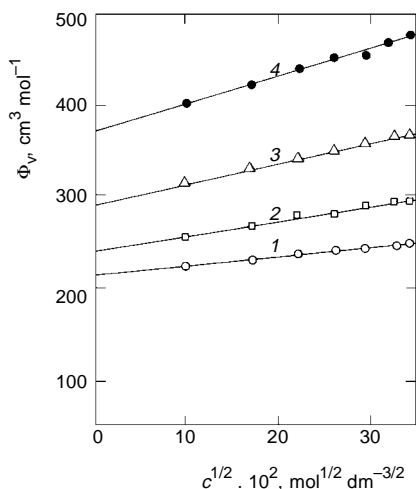
$$\Phi_v^0 = 38\,124 - 257.79\,T + 0.438\,T^2 \ . \tag{4}$$

Fig. 2

Plots of Φ_v *versus* $c^{1/2}$ for ammonium aluminium sulfate in 5 wt.% DMF–H$_2$O mixture at different temperatures (in K): *1* 298, *2* 303, *3* 308, *4* 313

The partial molar expansibilities $\Phi_E^0 = (\partial \Phi_v^0 / \partial T)$ calculated from Eqs (*3*) and (*4*) for aluminium ammonium sulfate and potassium aluminium sulfate, respectively, are also given in Table II. It is evident from this table that the value of Φ_E^0 increases with the increase in temperature. The increase in magnitude is positive indicating thereby that

Partial molar volumes, Φ_v^0 (cm^3 mol^{-1}), experimental slope, s_v (cm^3 dm$^{3/2}$ mol$^{-3/2}$) and partial molar expansibilities, Φ_E^0 (cm^3 mol^{-1} K^{-1}) for ammonium aluminium sulfate and potassium aluminium sulfate in 5 wt.% DMF–H$_2$O at different temperatures. The standard errors are given in parentheses

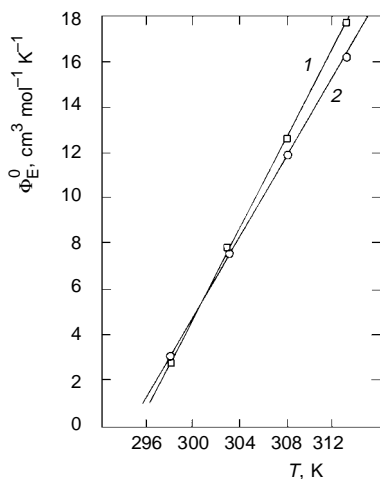| Parameter	Temperature			
	298	303	308	313
Ammonium aluminium sulfate				
Φ_v^0	214.3(1.5)	241.1(1.9)	292.2(1.0)	369.2(1.0)
s_v	96.0(2.1)	156.5(3.4)	212.7(4.0)	308.2(4.0)
Φ_E^0	3.27	8.16	13.05	17.94
Potassium aluminium sulfate				
Φ_v^0	181.3(0.9)	207.9(1.5)	256.4(2.4)	326.0(3.0)
s_v	198.6(3.5)	264.4(5.8)	273.8(4.3)	360.0(5.4)
Φ_E^0	3.26	7.64	12.02	16.39

FIG. 3
Variation of Φ_E^0 with temperature for *1* ammonium aluminium sulfate, *2* potassium aluminium sulfate; Φ_E^0 (ammonium aluminium sulfate) = Φ_E^0 (potassium aluminium sulfate) = 5.4 cm^3 mol^{-1} K^{-1} at 301 K

the behaviour of both the electrolytes is similar to that of symmetrical tetraalkyl ammonium salts[19] and unlike that of common electrolytes[20,21]. The positive increase in Φ_E^0 with increase in temperature for both the multicharged electrolytes may be ascribed to "caging effect" (refs[19,21]). Further, the variation of Φ_E^0 with temperature for both the electrolytes has been found to be linear as shown in Fig. 3. At 301 K, both the electrolytes have the same molar expansibilities (5.40 cm^3 mol^{-1} K^{-1}).

During past few years it has been emphasised by different workers that s_v is not the sole criterion for determining the structure making or breaking nature of any solute. Hepler[22] 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 solutes in aqueous solutions using the general thermodynamic expression:

$$[\partial\bar{c}_p/\partial p]_T = -[\partial^2\Phi_v^0/\partial T^2]_p \ . \tag{5}$$

On the basis of this expression it has been deduced that structure making solute should have positive value, whereas structure breaking solute negative value. In the present system it is observed from Eqs (3) and (4) that $[\partial^2\Phi_v^0/\partial T^2]_p$ is positive for solutions of both multicharged electrolytes in 5% (w/w) DMF–H_2O mixture which means that they behave as structure makers/promotors in the present system.

REFERENCES

1. McDowali J. M., Vincent C. A.: *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1862.
2. Dack M. R. J., Bird K. J., Parker A. J.: *Aust. J. Chem.* **1975**, *28*, 955.
3. Cox B. G., Waghorne W. E.: *Chem. Soc. Rev.* **1980**, *9*, 381.
4. Lau Y. K., Saluja P. P. S., Kelearle P.: *J. Am. Chem. Soc.* **1980**, *102*, 7429.
5. Parker A. J.: *Q. Rev. (London)* **1962**, 163; *Chem Rev.* **1969**, *69*, 1.
6. Wells D. W. in: *Physical Chemistry of Organic Solvent Systems* (A. K. Convington and T. Dickinson, Eds), Chap. 6. Plenum Press, London 1973.
7. Bladamer M. J., Burgess J., Clark B., Duce P. P., Hakin A. W., Gospal N., Rodulovic S., Guardado P., Sanchez F., Hubbrand C. D., Abu Gharib E. A.: *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1471.
8. Hedwing G. R., Queensby D. A., Parker A. J.: *J. Am. Chem. Soc.* **1980**, *97*, 3888.
9. Henson D. B., Swensen C. A.: *J. Phys. Chem.* **1973**, *77*, 2401.
10. Balasubramanium D., Shaikh R.: *Biopolymers* **1973**, *12*, 1639.
11. Parker A. J.: *Electrochim. Acta* **1976**, *21*, 671.
12. Riddick J. A., Bunger W. B.: *Organic Solvents*, Wiley, New York 1970.
13. Shoemaker D. P., Garland C. W.: *Experiments in Physical Chemistry*, 131. McGraw–Hill, New York 1967.
14. Ward G. K., Millero F. J.: *J. Solution Chem.* **1974**, *3*, 417.
15. Parmar M. L., Kundra A.: *Electrochim. Acta* **1983**, *28*, 1655.
16. Millero F. J. in: *Structure and Transport Processes in Water and Aqueous Solutions* (R. A. Horne, Ed.), Chap. 13, p. 521. Wiley, New York 1971.

17. Masson D. O.: *Philos. Mag*. **1929**, *8*, 218.
18. Cox B. G., Natarajan R., Waghorne W. E.: *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1780.
19. Ref.[16], Chap. 15, p. 622.
20. Millero F. J., Drost Hansen W.: *J. Phys. Chem*. **1968**, *72*, 1758.
21. Millero F. J.: *Chem. Rev*. **1971**, *71*, 147.
22. Hepler L. G.: *Can. J. Chem*. **1969**, *47*, 4617.