

Limiting Partial Molar Volumes of Electrolytes in Dimethylformamide–Water Mixtures at 298.15 K

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Partial molar volumes at infinite dilution, V_2^∞ , are reported for some 1:1 electrolytes in dimethylformamide (DMF)–water mixtures covering the whole fraction range at 298.15 K. The results obtained show that the behaviour of V_2^∞ both for alkali-metal halides and for hydrophobic electrolytes is dependent on the added DMF. In the water-rich region, the alkali-metal halides exhibit small variations of V_2^∞ , but two extrema, a minimum and a maximum, in the case of the hydrophobic electrolytes, are observed. In the DMF-rich region, a drastic decrease of V_2^∞ for all electrolytes is exhibited. The results are discussed on the basis of ion–solvent and solvent–solvent interactions.

The properties of aqueous solutions containing amides have received considerable attention since they have the peptide linkage elements^{1,2} and they are used as model compounds to obtain information on biochemical systems. In relation to aqueous mixtures of *N,N*-dimethylformamide (DMF), several studies have been made in order to elucidate the mechanism of the interaction of DMF with water (relative permittivities,^{3,4} cryoscopic and calorimetric measurements,⁵ ultrasonic velocities,⁶ volumes and heat capacities,⁷ NMR,^{8–10} viscosities^{10,11} and enthalpies of dilution¹²) where strong hydrogen bonding to the carbonyl group of DMF produces associates of the DMF–(H₂O)_{*n*} type. On the other hand, studies of electrolytes in aqueous mixtures of DMF (NMR,¹³ enthalpies of solution,^{14–16} transfer Gibbs energies^{17–19} and viscosities^{20,21}) have also been published, but limiting partial molar volumes of electrolytes in these mixtures have been restricted to tetraalkylammonium bromides.^{21,22}

In this paper we report partial molar volumes at infinite dilution of 1:1 electrolytes in aqueous mixtures of DMF covering the whole mole fraction range in order to obtain a better insight into ion–solvent and solvent–solvent interactions in mixed aqueous solvents.

Experimental

DMF (Merck, stated purity 99.8%, maximum content H₂O 0.05%) was dried over a thermally activated 4A molecular sieve prior to use. Ph₄PCl (Janssen Chimica, G.R., stated purity 99%) and NaBPh₄ (Merck, G.R., stated purity ≥99.5%) were dried for three days at 343 K in a vacuum desiccator. LiCl, NaCl, KCl, NaBr and KI were reagent grade (Merck) and were used after drying them overnight in an oven at 393 K. All salts were kept in a vacuum desiccator prior to use. DMF and water were degassed prior to making up solutions by weight.

Measurements of densities were made using the apparatus and procedures described previously.²³

Densities have an uncertainty (95% confidence limits) of $\pm 7 \times 10^{-6}$ g cm⁻³.

Results and Discussion

Apparent molar volumes, $\phi_v/\text{cm}^3 \text{ mol}^{-1}$, were calculated from solution densities using the standard expression

$$\phi_v = \frac{M_2}{\rho} + \frac{\rho_0 - \rho}{m\rho_0\rho} \quad (1)$$

where M_2 is the molecular weight of the electrolyte, m its molality; ρ and ρ_0 represent the density of solution and

solvent, respectively. A compilation of ρ , ρ_0 and ϕ_v are available as a supplementary publication.†

The application of the Redlich–Meyer equation²⁴ was not possible owing to the lack of values of the theoretical limiting slopes, S_v , in these mixtures. However, ϕ_v were found to vary linearly with $m^{1/2}$ over the concentration range investigated (0–0.37 mol kg⁻¹). The limiting partial molar volume of the electrolytes, $V_2^\infty = \phi_v^\infty$, was obtained by least-squares fitting of the results to the Masson equation:

$$\phi_v = \phi_v^\infty + S_v^* m^{1/2} \quad (2)$$

where S_v^* is the experimental slope. Table 1 shows values of V_2^∞ together with their 95% confidence limits (in parentheses). As can be observed, the experimental results obey the additivity rule within $\pm 1.8 \text{ cm}^3 \text{ mol}^{-1}$.

In Fig. 1 we have plotted trends of V_2^∞ with the mixed solvent composition for alkali-metal halides. At low DMF composition, up to $x_{\text{DMF}} \approx 0.3$, the influence of added DMF does not produce significant changes on V_2^∞ , except for LiCl where the effect of DMF begins to be noteworthy from $x_{\text{DMF}} \approx 0.17$. On the other hand, as the DMF content increases, the effect of DMF produces a drastic decrease in V_2^∞ up to pure DMF, taking even negative values for LiCl in the DMF-rich region.

It is known that interactions between alkali-metal ions and dipolar aprotic solvents occur at the negative pole of the DMF dipole while the positive end of the dipole is sterically hindered from interacting with halide ions. In principle, this fact makes interaction of alkali-metal ions with both water and DMF possible, but that of halide ions is restricted to water only. However, on the basis of the Jones–Dole coefficients of alkali-metal halides in water–amide mixtures, Woldan²⁸ has noted that in the water-rich region both alkali-metal ions and halide ions are solvated selectively by water, irrespective of the amide used. However, there is little evidence from standard functions of transfer for the preferential solvation of alkali-metal halides in dipolar aprotic aqueous solvents. On the other hand, Gallardo-Jiménez and Lilley²⁹ have studied enthalpies of interaction of alkali-metal halides with DMF in terms of the enthalpic virial second coefficient, $h_{\text{salt-DMF}}$, which is a measure of the water-mediated salt–DMF interactions. Note that in the case of our electrolytes, $h_{\text{salt-DMF}}$ is negative both in the anionic and cationic series and becomes more negative as the ion size increases, except for LiCl, which seems to indicate that from a

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Table 1 Partial molar volumes at infinite dilution, $V_2^\infty/\text{cm}^3 \text{ mol}^{-1}$, for some electrolytes in $x\text{DMF}-(1-x)\text{water}$ mixtures at 298.15 K

x	LiCl	NaCl	KCl	NaBr	KBr	KI	Ph_4PCl	NaPh_4B
0.0	16.91 ^a	16.62 ^a	26.87 ^a	23.48 ^a	33.73 ^a	45.6 ^a	310 ^b	276.4 ^b
0.0196	17.4 (0.4)	15.6 (0.3)	27.9 (0.3)	24.3 (0.1)	34.9 (0.7)	45.1(0.7)	310.1 (0.7)	274.5 (0.4)
0.0417	16.6 (0.4)	17.4 (0.3)	26.6 (0.1)	23.8 (0.3)	33.2 (0.3)	46.4 (0.3)	309.5 (0.8)	278.5 (0.6)
0.0955	16.9 (0.4)	16.7 (0.3)	27.3 (0.1)	24.2 (0.3)	33.8 (0.3)	47.2 (0.2)	307.3 (0.2)	288.9 (0.5)
0.1241							306.9 (0.5)	
0.1678	14.9 (0.4)	16.9 (0.9)	28.1 (0.3)	24.6 (0.5)	34.7 (0.2)	48.1 (0.8)	305.9 (0.4)	296.9 (0.3)
0.2227							307.9 (0.4)	
0.2699	13.2 (0.3)	16.9 (0.5)	27.0 (0.4)	23.1 (0.7)	34.5 (0.6)	47.5 (1.0)	307.7 (0.8)	299.4 (0.3)
0.3003							306.2 (0.3)	
0.3415							304.0 (1.0)	297.9 (1.0)
0.4232							302.1 (0.6)	295.6 (0.4)
0.4965	8.6 (0.3)	14.5 (0.4)	23.2 (0.4)	21.5 (0.5)	31.3 (0.4)	44.1 (1.0)	301.2 (0.2)	294.6 (0.6)
0.6598	5.4 (0.9)			17.0 (0.4)				
0.6705		11.3 (1.0)	21.0 (0.9)		27.2 (1.0)	41.7 (1.1)	297.3 (1.1)	288.3 (0.3)
0.8299	1.7 (0.5)	— ^c	— ^c	14.0 (1.0)	25.2 (1.2)	35.0 (0.9)	292.6 (0.8)	282.9 (1.0)
1.0	−4.4 ^d	5.9 ^d	13.0 ^d	6.6 ^d	14.1 ^d	30.5 ^d	282.6 (1.0)	278.0 (0.5)
								280 ^e

^a Ref. 24. ^b Ref. 25. ^c The solubility is too low to obtain accurate V_2^∞ . ^d Ref. 26. ^e Ref. 27.

thermochemical point of view a favourable interaction between the ions and DMF occurs. This is not in accordance with the idea that halide ions cannot interact with DMF because of steric hindrance at the positive pole of the DMF dipole. From the above considerations we could assume that alkali-metal ions and halide ions interact with DMF through their respective surrounding water cospheres in a water-rich region. The observed trends for V_2^∞ could be attributed to modifications in DMF–water interactions made by the presence of the ions in the mixed aqueous solvent. After this water-rich region the water around the ions is progressively being replaced by DMF in the mixture and less water remains to solvate the ions. This fact makes the interactions predominantly of cation–DMF type, because halide ions are sterically hindered from interacting with DMF molecules when the DMF content is high and, therefore, V_2^∞ behaviour is mainly determined by the electrostriction effect of the alkali-metal ions. In this sense, Zana and Yeager³⁰ have

obtained ionic partial molar volumes at infinite dilution, V_i^∞ , of alkali-metal ions and halide ions in pure DMF from the ultrasonic vibration potentials method. Note that V_i^∞ values in water and in DMF are very similar for the halide ions, except for the Br^- ion, but those corresponding to alkali-metal ions differ markedly. This means that the difference observed in V_2^∞ between water and DMF for alkali-metal halides in pure DMF is chiefly a consequence of cation–DMF interactions.

Fig. 2 shows trends of V_2^∞ with mole fraction of DMF for Ph_4PCl , NaBPh_4 and Bu_4^+NBr ,²² the latter being included for comparison. In contrast to alkali-metal halides, the three hydrophobic electrolytes exhibit significant changes of V_2^∞ in the water-rich region, with a minimum and a maximum whose positions seem to be dependent on the type of electrolyte. Thus, the maximum is located at approximately the same mole fraction of DMF for Ph_4PCl and NaBPh_4 , whereas for Bu_4^+NBr it extends up to the intermediate composition region. From this extrema region the effect of DMF

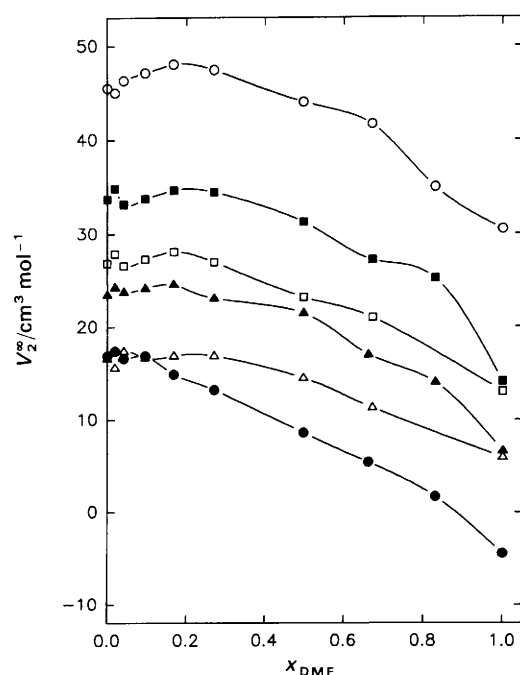


Fig. 1 Variation of limiting partial molar volumes, V_2^∞ , of electrolytes with DMF composition for: KI (○), KBr (■), NaBr (▲), KCl (□), NaCl (△), LiCl (●)

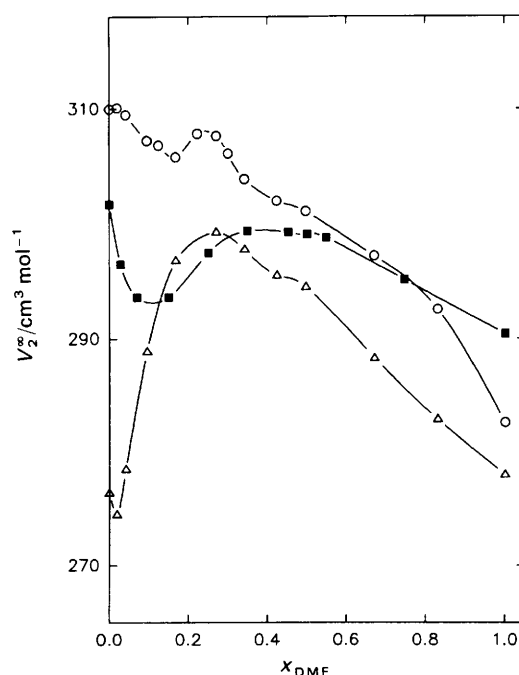


Fig. 2 Variation of limiting partial molar volumes, V_2^∞ , with DMF composition for: Ph_4PCl (○), NaBPh_4 (△), Bu_4^+NBr (■)

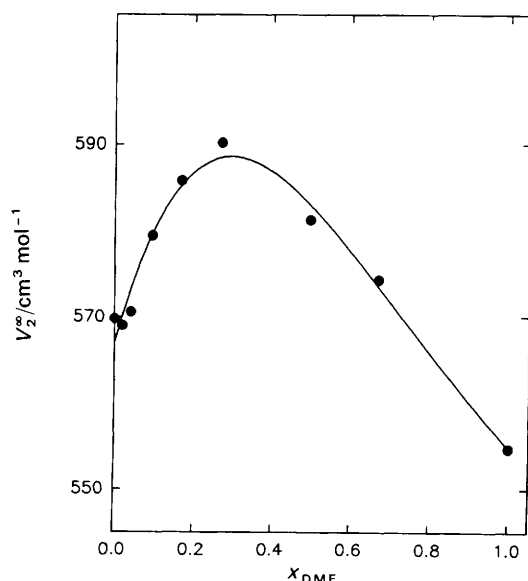


Fig. 3 Variation of limiting partial molar volume, V_2^∞ , with DMF composition for Ph_4PBPh_4

produces a marked decrease of V_2^∞ , similar to that for alkali-metal halides.

The existence of a minimum and a maximum suggests that combined opposing effects between hydrophilic ion-solvent and hydrophobic ion-solvent interactions occur. Since the maximum is located at $x_{\text{DMF}} \approx 0.27$ for Ph_4PCl and NaBPh_4 and considering that the Ph_4P^+ and BPh_4^- ions have a similar size and comparable hydrophobic characteristics and, moreover, with negligible electrostriction effects due to their weak electric field, we could assign the behaviour of V_2^∞ in the maximum as due to hydrophobic ion-solvent interactions. In contrast, the minima must predominantly be determined by the corresponding counter-ion-solvent interactions. In order to confirm that the assignments of both extrema are correct, we can cancel the respective contributions of the Cl^- and Na^+ ions to V_2^∞ of Ph_4PCl and NaBPh_4 , respectively, by considering the Ph_4PBPh_4 electrolyte, which can be achieved using the additivity rule in Table 1 according to the expression

$$V_2^\infty(\text{Ph}_4\text{PBPh}_4) = V_2^\infty(\text{Ph}_4\text{PCl}) + V_2^\infty(\text{NaBPh}_4) - V_2^\infty(\text{NaCl}) \quad (3)$$

In Fig. 3 we have plotted the dependence of V_2^∞ on the mole fraction of DMF for Ph_4PBPh_4 . The plot shows that the minimum has disappeared and only the maximum at $x_{\text{DMF}} \approx 0.27$ prevails. On the other hand, the drastic decrease of V_2^∞ with increasing content of DMF for the three hydrophobic electrolytes (Fig. 2) has been attributed in the case of $\text{Bu}_4\text{NBr}^{22}$ to structural interactions between this and the DMF. Nevertheless, on the basis of the above considerations for alkali-metal halides, the behaviour of V_2^∞ in the DMF-rich region must be determined by the hydrophobic cation

effect with Ph_4PCl and Bu_4NBr electrolytes, and by the combined effects of the cation and the anion with NaBPh_4 electrolyte.

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References

- 1 G. Somsen, *Pure Appl. Chem.*, 1991, **63**, 1687.
- 2 G. R. Hedwig, T. H. Lilley and H. Linsdell, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2987, and references therein.
- 3 G. Douhéret and M. Morenas, *C. R. Acad. Sci., Ser. C*, 1967, **2**, 729.
- 4 R. Reynaud, *C. R. Acad. Sci., Ser. C*, 1968, **266**, 489.
- 5 J. Bougard and R. Jadot, *J. Chem. Thermodyn.*, 1975, **7**, 185.
- 6 F. Kawaizumi, M. Ohno and Y. Miyahara, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2229.
- 7 C. De Visser, G. Perron and J. E. Desnoyers, *J. Chem. Eng. Data*, 1977, **22**, 74.
- 8 Y. I. Mitchenko, V. A. Fenin and E. P. Krasnov, *Russ. J. Chem.*, 1978, **52**, 163.
- 9 V. Zelano, *Z. Phys. Chem. N. F.*, 1983, **138**, 31.
- 10 C. M. Kinart, W. J. Kinart and L. Shulski, *Pol. J. Chem.*, 1985, **59**, 597.
- 11 C. Della Volpe, G. Guarino, R. Sartorio and V. Vitagliano, *J. Chem. Eng. Data*, 1986, **31**, 37.
- 12 R. H. Wood and L. H. Hiltzik, *J. Solution Chem.*, 1980, **9**, 45.
- 13 A. Fratiello, R. E. Lee, D. P. Miller and V. M. Nishida, *Mol. Phys.*, 1967, **13**, 349.
- 14 S. Taniowska-Osinska and A. Piekarska, *Bull. Acad. Pol. Sci., Sér. Sci. Chim.*, 1978, **26**, 613.
- 15 L. Thakur and R. Prasad, *Indian J. Chem.*, 1980, **19A**, 520.
- 16 W. J. M. Heusvelsland, C. de Visser and G. Somsen, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1191.
- 17 S. P. Rudra, B. P. Chakravarty, K. Kundu and I. N. Basu-Mallick, *Z. Phys. Chem. N. F.*, 1986, **150**, 211.
- 18 E. A. Goma, *Thermochim. Acta*, 1989, **142**, 19.
- 19 K. Das, K. Bose and K. Kundu, *Electrochim. Acta*, 1981, **26**, 479.
- 20 B. N. Prasad, N. P. Singh and M. M. Singh, *Indian J. Chem.*, 1976, **14A**, 332.
- 21 N. C. Dey, G. Kumar, B. K. Saikia and I. Haque, *J. Solution Chem.*, 1985, **14**, 49.
- 22 W. J. M. Heusvelsland and G. Somsen, *J. Chem. Thermodyn.*, 1977, **9**, 231.
- 23 C. Yanes, P. Pérez-Tejeda, E. García-Pañeda and A. Maestre, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 223.
- 24 F. J. Millero, in *Water and Aqueous Solutions. Structure, Thermodynamics and Transport Processes*, ed. E. A. Horne, Wiley, New York, 1972, ch. 13.
- 25 C. Jolicoeur, P. R. Philip, G. Perron, P. A. Leduc and J. E. Desnoyers, *Can. J. Chem.*, 1972, **50**, 3167.
- 26 F. Kawaizumi and R. Zana, *J. Phys. Chem.*, 1974, **78**, 1099.
- 27 M. R. J. Dack, K. J. Bird and A. J. Parker, *Aust. J. Chem.*, 1975, **28**, 955.
- 28 M. Woldan, *Z. Phys. Chem. N. F.*, 1986, **150**, 201.
- 29 M. A. Gallardo-Jiménez and T. H. Lilley, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 2909.
- 30 R. Zana and E. B. Yeager, in *Modern Aspects of Electrochemistry*, ed. J. O'M. Bockris, B. E. Conway and R. E. White, Plenum Press, New York, 1982, vol. 14, ch. 1.

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