

## Solvation of Ions. XXXI\* Partial Molal Volumes of Sodium, Silver(I) and Copper(I) Ions in Acetonitrile/Water Mixtures

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### Abstract

The partial molal volumes of Na<sup>+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup>, Ph<sub>4</sub>As<sup>+</sup>, BPh<sub>4</sub><sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> are reported for transfer from water to various acetonitrile/water (MeCN/H<sub>2</sub>O) mixtures by using the tatb assumption that  $\Delta V_t(\text{Ph}_4\text{As}^+) = \Delta V_t(\text{BPh}_4^-)$ . The results, which show a complex dependence of ionic partial molal volumes on MeCN/H<sub>2</sub>O solvent composition, are discussed in terms of ion-solvent and solvent-solvent interactions. This study complements earlier work on the energetics of transfer (tatb assumption) of these ions from water to aqueous acetonitrile solutions.

### Introduction

Acetonitrile/water mixtures (MeCN/H<sub>2</sub>O) are interesting in relation to studies on ion-solvent interactions because of the contrasting behaviour of alkali-metal cations, which interact more strongly with water, and silver(I) and copper(I) cations, which are more strongly solvated by acetonitrile.<sup>1</sup> In the past, we have investigated the energetics of transfer<sup>2</sup> and the conductivities of transfer<sup>3</sup> of these ions from H<sub>2</sub>O to MeCN/H<sub>2</sub>O to obtain information on ion-solvent interactions and on solvent structure itself. These studies enabled us to understand and optimize various hydro-metallurgical processes in which the MeCN/H<sub>2</sub>O solutions of these ions have found extensive applications.<sup>4,5</sup> The partial molal volume of an ion at infinite dilution is a non-energetic function, and depends on the magnitude of the intrinsic volume of the ion and on the ability of the solvent to change its volume through processes such as electrostriction. The electrostriction is governed by the strength of ion-solvent interactions and by the ease with which the bulk solvent can contract around the ion. Thus the same two factors, ion-solvent interactions and solvent-solvent interactions, are important to both the energetics and the partial molal volumes of ions.

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† P.S. and I.D.M. dedicate this paper to the memory of their coauthor who died on 30 August 1982.

<sup>1</sup> MacLeod, I. D., Muir, D. M., Parker, A. J., and Singh, P., *Aust. J. Chem.*, 1977, **30**, 1423.

<sup>2</sup> Singh, P., MacLeod, I. D., and Parker, A. J., *J. Solution Chem.*, 1982, **11**, 495.

<sup>3</sup> Singh, P., MacLeod, I. D., and Parker, A. J., unpublished data.

<sup>4</sup> Parker, A. J., Waghorne, W. E., Giles, D. E., Sharp, J. H., Alexander, R., and Muir, D. M., U.S. Pat. 2,865,744 (1975).

<sup>5</sup> Parker, A. J., Diggle, J. W., and Avraamides, J., *Aust. J. Chem.*, 1974, **27**, 721.

We have already demonstrated the usefulness of the tetraphenylarsonium tetraphenylborate (tatb) assumption in obtaining standard free energies, enthalpies and entropies of transfer of ions from water to various pure organic, organic/organic and organic/water mixtures.<sup>2,6</sup> We have also used the same assumption in the past to obtain ionic partial molal volumes of transfer from water to various protic and dipolar aprotic solvents.<sup>7</sup> In the present paper, we report the partial molal volumes of transfer ( $H_2O \rightarrow MeCN/H_2O$ ) of sodium, silver(I), copper(I), chloride and nitrate ions as obtained through the same (tatb) assumption. The results are discussed in terms of the Frank and Evans model<sup>8</sup> of ionic solvation.

### Experimental

Pure dry samples of  $NaNO_3$ ,  $AgNO_3$ ,  $NaCl$ ,  $NaBPh_4$  and  $Ph_4AsI$  were prepared as described previously.<sup>2,3</sup>  $Ph_4AsNO_3$  was prepared metathetically in aqueous solution from  $Ph_4AsCl$  and  $AgNO_3$ .  $AgCl$  was removed by filtration, and the  $Ph_4AsNO_3$  crystallized from the filtrate. The product so formed was recrystallized from hot acetone, and dried at room temperature under vacuum (1 mmHg) for 24 h. Because of the difficulty of preparing  $Ph_4AsCl$  in the anhydrous state, the  $MeCN/H_2O$  solutions of  $Ph_4AsCl$  were prepared by weight (Fluka pa) and standardized by potentiometric titration of  $Cl^-$  against a standard  $AgNO_3$  solution.

The  $CuNO_3$  solutions were prepared by the quantitative cementation of copper with  $AgNO_3$  solutions of known concentrations in  $MeCN/H_2O$ . The solutions so obtained were restandardized by titration with acidified standard  $KMnO_4$  solution. The densities of solutions were measured with a digital density meter (Anton Parr DMA 02D). The temperature of the instrument cell holding the solution sample was kept constant at  $25 \pm 0.001^\circ C$ . The densities are reliable to  $\pm 1 \times 10^{-6} g cm^{-3}$ . Each sample solution was allowed to stand for at least 24 h before the density measurement was made. Averaged densities from at least five independent measurements were used in the calculations of partial molal volumes.

### Results

The apparent molal volume ( $V$ ) of each electrolyte has been calculated from the measured density of its solution through the equation<sup>7</sup>

$$V = M/d_0 - 1000(d - d_0)/d_0c \quad (1)$$

where  $d_0$  and  $d$  are the densities of the solvent and the solution respectively,  $M$  is the molecular weight of the solute, and  $c$  is its concentration in  $mol l^{-1}$ . The concentration dependence of the  $V$  values in the range  $0.001-0.01 M$  was very small; therefore, the measurements were repeated over a narrow range of the concentration until at least five results agreed to within  $\pm 1.0 cm^3$ . The average of these values was taken to be the partial molal volume of the electrolyte in the solvent. The values for various electrolytes are shown in Table 1.

The ionic partial molal volumes of transfer were calculated by using the tatb assumption, i.e.

$$\Delta V_t(Ph_4As^+) = \Delta V_t(BPh_4^-) = \frac{1}{2}\Delta V_t(Ph_4AsBPh_4) \quad (2)$$

The values of  $\Delta V_t(Ph_4AsBPh_4)$  were obtained indirectly from combinations as in

$$\Delta V_t(Ph_4AsBPh_4) = \Delta V_t(Ph_4AsX) + \Delta V_t(NaBPh_4) - \Delta V_t(NaX) \quad (3)$$

where X is an anion.

<sup>6</sup> Cox, B. G., Hedwig, G. R., Parker, A. J., and Watts, D. W., *Aust. J. Chem.*, 1974, **27**, 477.

<sup>7</sup> Dack, M. R. J., Bird, K. J., and Parker, A. J., *Aust. J. Chem.*, 1975, **28**, 955.

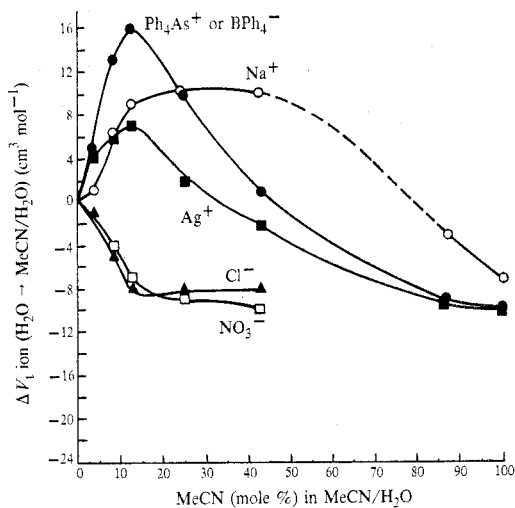
<sup>8</sup> Frank, H. S., and Evans, M. W., *J. Chem. Phys.*, 1945, **13**, 507.

**Table 1.** Partial molal volumes ( $\text{cm}^3 \text{mol}^{-1}$ ) of various electrolytes at  $25^\circ\text{C}$  in MeCN/ $\text{H}_2\text{O}$  mixtures  
 $X$  denotes the amount (mole %) of MeCN in MeCN/ $\text{H}_2\text{O}$

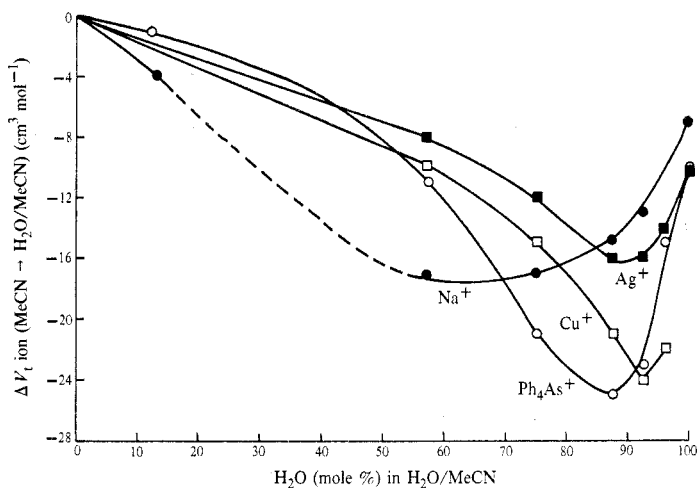
$X$	$\text{Ph}_4\text{AsCl}$	$\text{NaBPh}_4$	$\text{NaCl}$	$\text{NaNO}_3$	$\text{AgNO}_3$	$\text{CuNO}_3$	$\text{Ph}_4\text{AsI}$	$\text{Ph}_4\text{AsNO}_3$	$\text{NaI}$
0	315	276	16	28	28	—	—	327 <sup>A</sup>	—
3.6	319	281	16	30	33	29	—	333 <sup>A</sup>	—
7.7	323	294	17	30	30	26	—	336 <sup>A</sup>	—
12.4	323	299	17	30	28	21	—	336 <sup>A</sup>	—
24.7	317	295	18	29	21	12	—	328 <sup>A</sup>	—
42.9	308	286	18	28	16	6	—	318 <sup>A</sup>	—
86.7	—	263	—	—	—	—	310	311	17
100	284 <sup>B</sup>	258 <sup>B</sup>	-12	0	-3	-15	307	296	11

<sup>A</sup> Calculated from the equation  $V(\text{Ph}_4\text{AsNO}_3) = V(\text{Ph}_4\text{AsX}) + V(\text{NaNO}_3) - V(\text{NaX})$ .

<sup>B</sup> Ref. 7.



**Fig. 1.** The partial molal volumes of transfer ( $\Delta V_t$ ) of various ions from water to acetonitrile/water mixtures ( $25^\circ\text{C}$ ).



**Fig. 2.** The partial molal volumes of transfer ( $\Delta V_t$ ) of various ions from acetonitrile to water/acetonitrile mixtures ( $25^\circ\text{C}$ ).

$V_3$  is the volume change associated with the water molecules in the zone of disorder, i.e., zone 3, and its magnitude is a function of the number of water molecules and their packing density in the region. As an estimate, if the water molecules in this region are assumed to be randomly packed then their packing fraction can be taken to be  $c. 0.63$ .<sup>12</sup> Therefore  $V_3$  will be equal to  $18.5(n-n_h) \text{ cm}^3 \text{ mol}^{-1}$ . [The factor 18.5 represents  $V_{\text{H}_2\text{O}}$  (van der Waals) divided by the packing fraction.] Thus  $V_3$  has a positive contribution to equation (4). Since the combined result of  $V_e + V_{1,2}$  is negative, the overall sign of  $V_e + V_{1,2} + V_3$  depends on the relative magnitudes of  $V_e + V_{1,2}$  and  $V_3$ . For small ions with high charge density, the  $V_e + V_{1,2}$  terms dominate, so that  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  is negative. For bulky ions of low charge density the  $V_3$  term is predominant, and hence  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  is positive. Thus the model which explains the ionic size dependence of entropies in aqueous solutions also explains the dependence of ionic partial molal volumes.

**Table 2.** Ionic entropies of hydration ( $\Delta S_{\text{hyd}}$ ), entropies of transfer ( $\Delta S_t$ ), and  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  values in water at 25°C

$\Delta S_{\text{hyd}}$  values taken from Franks, F., (Ed.) 'Water—A Comprehensive Treatise' Ch. 1 (Plenum: New York 1973). See ref. 11 for details of  $\Delta S_t$ , the entropy of transfer from a hypothetical ideal water to real water.  $V_{\text{ion}(\text{cryst})}$  represents the crystallographic volume of the ion as calculated from the Pauling crystal radii quoted in Nightingale, E. R., *J. Phys. Chem.*, 1959, 63, 1381.  $V_{\text{ion}}$  values ( $V_{\text{ion}(\text{aq})}$ ) were taken from Millero, F. J., *Chem. Rev.*, 1971, 71, 147

Ion	$V_{\text{ion}(\text{cryst})}$ ( $\text{cm}^3 \text{ mol}^{-1}$ )	$\Delta S_{\text{hyd}}$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	$\Delta S_t$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )	$V_{\text{ion}(\text{aq})} - V_{\text{ion}(\text{cryst})}$ ( $\text{cm}^3 \text{ mol}^{-1}$ )
H <sup>+</sup>	—	-131	-57.3	-5.4
Li <sup>+</sup>	0.5	-141	-65.7	-6.8
Na <sup>+</sup>	2.2	-110	-31.8	-8.8
K <sup>+</sup>	5.9	-74	-1.3	-2.3
Rb <sup>+</sup>	8.1	-62	+11.3	0.6
Cs <sup>+</sup>	12.1	-59	+14.2	3.8
Ag <sup>+</sup>	5.0	-115	-39	-12
F <sup>-</sup>	6.3	-133	-65.7	-2.1
Cl <sup>-</sup>	14.9	-76	-18.0	8.3
Br <sup>-</sup>	18.6	-61	-3.8	11.5
I <sup>-</sup>	25.3	-38	+14.2	16.3
NO <sub>3</sub> <sup>-</sup>	46.2	—	+28.5	-11.8
ClO <sub>4</sub> <sup>-</sup>	62.6	—	+41.0	-13.1
ClO <sub>3</sub> <sup>-</sup>	60.1	—	+35.6	-18.0
Me <sub>4</sub> N <sup>+</sup>	105.0	—	—	-20.8
Et <sub>4</sub> N <sup>+</sup>	160.8	—	—	-17.1
Pr <sub>4</sub> N <sup>+</sup>	232.1	—	—	-22.8
Bu <sub>4</sub> N <sup>+</sup>	303.0	—	-105.9	-32.7
Ph <sub>4</sub> As <sup>+</sup>	312.0 <sup>A</sup>	—	-102.1	-20.0
BPh <sub>4</sub> <sup>-</sup>	295.0 <sup>A</sup>	—	-102.1	-12.0

<sup>A</sup> Kim, J. I., *J. Phys. Chem.*, 1978, 82, 191.

### (ii) Ions Undergoing Solvation of the Second Kind (Hydrophobic Hydration)

This kind of solvation has been proposed<sup>6,9-11</sup> for bulky ions carrying large alkyl groups to explain their thermodynamic properties in water. According to this model the water structure rejects the solute, but accommodates it inside the solvent-developed surface of low entropy but favourable enthalpy.<sup>6,10,11</sup> The charge density of these

ions is insufficient to overcome solvent-solvent interactions, and thus regions 1-3 as discussed earlier are effectively not formed. This model successfully explains the energetics of these ions in aqueous solution.<sup>6,10,11</sup> For example, as shown in Table 2, the entropy of transfer of  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{As}^+$  from ideal to real water is very strongly negative; this results from the reinforcement of the water structure by the bulky hydrophobic ions.

In terms of this model, the ionic partial molal volume in water will be a function of the following three factors:

$V_e$ , a slight decrease in volume due to a very weak electrostriction of water

$V_{st}$ , an increase in volume of bulk water due to the reinforcement of its structure

$V_{cage}$ , a decrease in volume due to the fitting of ions into the open three-dimensional structure of water

As before, these terms may be equated to  $V_{ion} - V_{ion(cryst)}$  through the equation

$$V_{ion} - V_{ion(cryst)} = V_e + V_{st} + V_{cage} \quad (5)$$

Since the charge density of the ion is very low,  $V_e$  is negligible. Likewise, the contribution of  $V_{st}$  to equation (5) is quite small because the molar volume of fully developed water structure such as in ice ( $19.71 \text{ cm}^3 \text{ mol}^{-1}$ ) is only slightly higher than the normal molar volume of bulk water ( $18.07 \text{ cm}^3 \text{ mol}^{-1}$ ). Thus  $V_{cage}$  predominantly determines the partial molal volume of these ions in water. This explains why the  $V_{ion} - V_{ion(cryst)}$  values in  $\text{H}_2\text{O}$  for the tetraalkylammonium ions, and  $\text{Ph}_4\text{As}^+$  and  $\text{BPh}_4^-$  are quite negative<sup>13</sup> (see Table 2).

### (b) Molal Volumes of Specific Ions

Having discussed partial molal volumes of ions in terms of solvation of the first or second kind, we can explain the effect of addition of MeCN to  $\text{H}_2\text{O}$  on the partial molal volumes of ions.

#### (i) $\text{Ph}_4\text{As}^+$ and $\text{BPh}_4^-$ Ions

Since  $\text{Ph}_4\text{As}^+$  and  $\text{BPh}_4^-$  ions undergo solvation of the second kind, the cage effect is predominant and hence the  $V_{ion} - V_{ion(cryst)}$  is negative ( $-12 \text{ cm}^3 \text{ mol}^{-1}$  for  $\text{BPh}_4^-$ , Table 2). If the water structure is broken, the cage effect will be lowered, and hence  $V_{ion} - V_{ion(cryst)}$  becomes less negative and should reach a maximum when all the water structure disappears. This is actually observed for these ions and other similar ions such as  $\text{R}_4\text{N}^+$  when water is heated.<sup>13</sup> Heating of water progressively breaks down the three-dimensional clusters of water thereby eliminating the cage effect. The addition of MeCN to water is known to break the 'ice-like' structure of water. Most of the polymeric structure of water is broken even in *c.* 10 mole % MeCN in MeCN/ $\text{H}_2\text{O}$ .<sup>14,15</sup> The fact that  $\Delta V_t(\text{Ph}_4\text{As}^+ \text{ or } \text{BPh}_4^-)$  for transfer from  $\text{H}_2\text{O}$  to MeCN/ $\text{H}_2\text{O}$  increases initially and then goes through a maximum at about 12 mole % MeCN in MeCN/ $\text{H}_2\text{O}$  is consistent with the effect of structural changes of the solvent on the partial molal volume of hydrophobic ions. Increasing MeCN beyond 10 mole % in MeCN/ $\text{H}_2\text{O}$  progressively imparts organic characteristics to

<sup>13</sup> Millero, F. J., and Drost-Hansen, W., *J. Phys. Chem.*, 1968, **72**, 1758.

<sup>14</sup> Armitage, D. A., Blandamer, M. J., Foster, M. J., Hidden, N. J., Morcom, K. W., Symons, M. C. R., and Wothen, M. J., *Trans. Faraday Soc.*, 1968, **64**, 1193.

<sup>15</sup> Grant-Taylor, D. F., and Macdonald, D. D., *Can. J. Chem.*, 1976, **54**, 2813.

the solvent mixture.<sup>15</sup> The uniqueness of bulk water is destroyed at about 30 mole % MeCN, and the mixture behaves more like a 'normal' organic solvent. Dack *et al.*<sup>7</sup> have shown that the partial molal volumes of bulky hydrophobic ions such as  $\text{Ph}_4\text{As}^+$  or  $\text{R}_4\text{N}^+$  in dipolar aprotic solvents are governed by the solvent compressibility. A plot of  $\Delta V_t(\text{Ph}_4\text{As}^+)$  ( $\text{H}_2\text{O} \rightarrow \text{MeCN}/\text{H}_2\text{O}$ ) against solvent compressibility (Fig. 4) indicates that, as in pure dipolar aprotic solvents, the partial molal volume of  $\text{Ph}_4\text{As}^+$  in MeCN/ $\text{H}_2\text{O}$  mixtures containing more than *c.* 30 mole % MeCN is also governed by the solvent compressibility. Thus the mechanism which controls the partial molal volumes of these ions in MeCN/ $\text{H}_2\text{O}$  mixtures containing less than *c.* 30 mole % MeCN is quite different from that in mixtures containing more than *c.* 30 mole % MeCN.

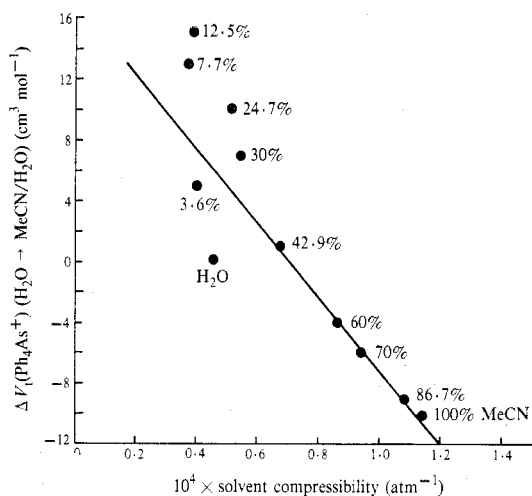


Fig. 4. The partial molal volume of transfer ( $\Delta V_t$ ) of  $\text{Ph}_4\text{As}^+$  ion from water to various acetonitrile/water mixtures against solvent compressibility (25°C). The percentages shown on the diagram represent amounts (mole %) of MeCN in the MeCN/ $\text{H}_2\text{O}$  mixtures. (Data for the solvent compressibility are taken from ref. 15.)

## (ii) $\text{Na}^+$ Ion

The sodium ion is a small hydrophilic ion which is preferentially solvated by  $\text{H}_2\text{O}$  in MeCN/ $\text{H}_2\text{O}$ .<sup>2,3</sup> Its partial molal volume is expected to be controlled by the solvation of the first kind mechanism. Due to the predominance of the  $V_e$  term of equation (4), its  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  value in water is negative ( $-8.8 \text{ cm}^3 \text{ mol}^{-1}$ , Table 2). Since the addition of MeCN breaks the structure of water, the sodium ion has to break fewer hydrogen bonds to form the same solvation shell in MeCN/ $\text{H}_2\text{O}$  than in pure water. Thus the  $V_e$  term has a lower magnitude in MeCN/ $\text{H}_2\text{O}$  than in pure water; this should result in a positive value of  $\Delta V_t(\text{Na}^+)$  for transfer from water to MeCN/ $\text{H}_2\text{O}$ . Fig. 1 shows that the observed  $\Delta V_t(\text{Na}^+)$  is consistent with this expectation. Since the structure-breaking effect of MeCN on  $\text{H}_2\text{O}$  is almost complete at about 30 mole % MeCN in MeCN/ $\text{H}_2\text{O}$ ,<sup>15</sup> the  $\Delta V_t(\text{Na}^+)$  reaches a maximum at about the same solvent composition and then shows little change between 25 and 40 mole % MeCN.

At higher concentrations of MeCN the  $\Delta V_t(\text{Na}^+)$  value decreases. The conductance,<sup>3</sup> free energies of transfer<sup>2</sup> and n.m.r. studies<sup>16</sup> indicate that, at very high concentrations of MeCN in MeCN/ $\text{H}_2\text{O}$ , the MeCN replaces  $\text{H}_2\text{O}$  in the  $\text{Na}^+$  solvation

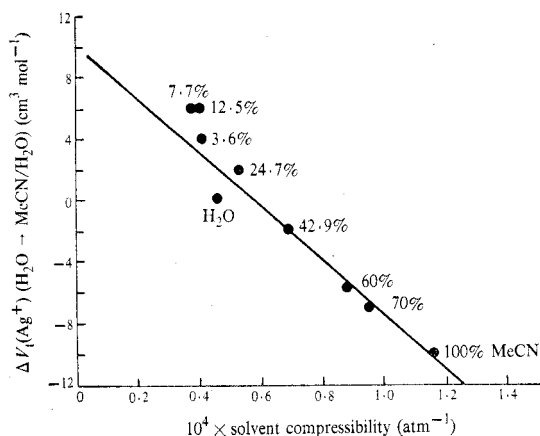
<sup>16</sup> Cox, B. G., Parker, A. J., and Waghorne, W. E., *J. Phys. Chem.*, 1974, **78**, 1731.

shell. Thus the nitrile-solvated  $\text{Na}^+$  ion behaves like the  $\text{Ph}_4\text{As}^+$  ion, and in this situation its partial molal volume is controlled by the solvent compressibility and so  $\Delta V_t$  decreases (Fig. 1).

### (iii) $\text{Ag}^+$ Ion

As noted earlier, the solvation behaviour of  $\text{Ag}^+$  in pure  $\text{H}_2\text{O}$  is similar to that of  $\text{Na}^+$ , and its partial molal volume in water is controlled by the solvation of first kind mechanism. On transfer from water to  $\text{MeCN}/\text{H}_2\text{O}$ , the solvation shell of  $\text{Ag}^+$  undergoes a complete reorganization, i.e., water in the solvation shell is replaced by  $\text{MeCN}$  and the solvated ion which has hydrophobic interactions with the solvent.<sup>1-3</sup> Thus, in  $\text{MeCN}/\text{H}_2\text{O}$ , the solvation behaviour of  $\text{Ag}^+$  is expected to follow solvation of the second kind.

Fig. 5. The partial molal volume of transfer ( $\Delta V_t$ ) of  $\text{Ag}^+$  ion from water to various acetonitrile/water mixtures against solvent compressibility (25°C). The percentages shown on the diagram represent amounts (mole %) of  $\text{MeCN}$  in the  $\text{MeCN}/\text{H}_2\text{O}$  mixtures. (Data for the solvent compressibility are taken from ref. 15.)



In pure water, the  $V_e$  effect is predominant so that  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  is  $-12 \text{ cm}^3 \text{ mol}^{-1}$ . On transfer to  $\text{MeCN}/\text{H}_2\text{O}$ , the cage effect is predominant, resulting in a negative value for  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$ . If  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  in  $\text{MeCN}/\text{H}_2\text{O}$  is more negative than  $-12 \text{ cm}^3 \text{ mol}^{-1}$ , the  $\Delta V_t(\text{Ag}^+)$  on transfer from  $\text{H}_2\text{O}$  to  $\text{MeCN}/\text{H}_2\text{O}$  will be negative, otherwise it will be positive. For comparison, the  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  value of  $\text{Ph}_4\text{As}^+$  in 10 mole %  $\text{MeCN}/\text{H}_2\text{O}$  is  $-6 \text{ cm}^3$  (from Fig. 1) which is mainly due to the cage effect, as discussed earlier. If as an estimate the magnitude of the cage effect for  $\text{Ag}(\text{MeCN})_x^+$  in 10 mole %  $\text{MeCN}/\text{H}_2\text{O}$  is taken to be the same as that for  $\text{Ph}_4\text{As}^+$ , then  $\Delta V_t(\text{Ag}^+)$  for transfer from  $\text{H}_2\text{O}$  to 10 mole %  $\text{MeCN}/\text{H}_2\text{O}$  should be  $+6 \text{ cm}^3 \text{ mol}^{-1}$ . This is very close to the experimental value (Fig. 1). Thus the initial increase in  $\Delta V_t(\text{Ag}^+)$  on addition of  $\text{MeCN}$  to  $\text{H}_2\text{O}$  is due to the change from solvation of the first kind to solvation of the second kind. The maximum value of  $\Delta V_t(\text{Ag}^+)$  observed at *c.* 10 mole %  $\text{MeCN}$  in  $\text{MeCN}/\text{H}_2\text{O}$  corresponds to the structure-breaking effect of  $\text{MeCN}$  on  $\text{H}_2\text{O}$ . At higher concentrations of  $\text{MeCN}$ , the monotonic decrease of  $\Delta V_t(\text{Ag}^+)$  is again due to the solvent compressibility effect (Fig. 5).

### (iv) $\text{Cu}^+$ Ion

Chemically, the behaviour of  $\text{Cu}^+$  is similar to that of  $\text{Ag}^+$ , since both are preferentially solvated by  $\text{MeCN}$  in  $\text{MeCN}/\text{H}_2\text{O}$ . Thus the  $\Delta V_t(\text{Cu}^+)$  for transfer from

MeCN to H<sub>2</sub>O/MeCN is similar to that of Ag<sup>+</sup> (Fig. 2). The relative magnitude of  $\Delta V_t(\text{Cu}^+)$  is generally higher than  $\Delta V_t(\text{Ag}^+)$  due to the greater hydrophobicity of  $\text{Cu}(\text{MeCN})_y^+$  species as compared to that of  $\text{Ag}(\text{MeCN})_x^+$  species.

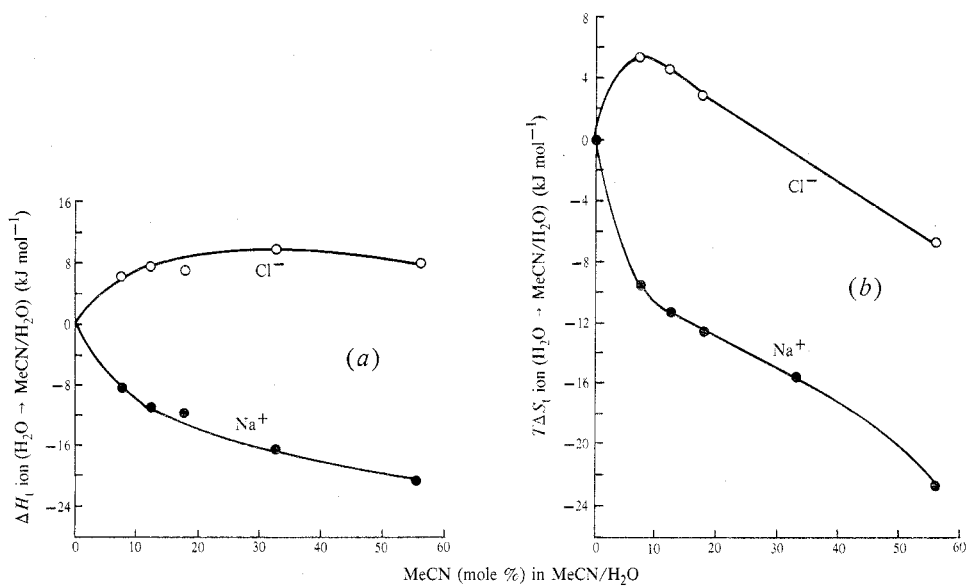


Fig. 6. (a) Enthalpies of transfer ( $\Delta H_t$ ); (b) entropies of transfer (given as  $T\Delta S_t$ ) of Na<sup>+</sup> and Cl<sup>-</sup> from water to various acetonitrile/water mixtures (25°C). (Values based on the tab assumption<sup>2,6</sup> as applied to the data quoted in Cox, B. G., Natarajan, R., and Waghorne, W. E., *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 86.)

#### (v) Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> Ions

The orientation of the water dipoles around the anions is opposite to that around cations. Both Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> are large ions of low charge density relative to Na<sup>+</sup> and form hydrogen bonds with water. Thus, even though both the ions solvate water through solvation of the first kind, the number of hydrogen bonds broken from the bulk water is much lower for Cl<sup>-</sup> than for Na<sup>+</sup>. This is consistent with the known hydration numbers of these ions.<sup>17,18</sup> It is also reflected in their respective values of  $V_{\text{ion}} - V_{\text{ion}(\text{cryst})}$  in H<sub>2</sub>O, i.e., Na<sup>+</sup>, -8.8; Cl<sup>-</sup>, +8.3 cm<sup>3</sup> mol<sup>-1</sup> (Table 2). Figs 6a and 6b suggest that the addition of up to 60 mole % MeCN to H<sub>2</sub>O affects the thermodynamic properties of Na<sup>+</sup> and Cl<sup>-</sup> ions differently. The  $\Delta H_t(\text{Na}^+)$  for transfer from H<sub>2</sub>O to MeCN/H<sub>2</sub>O is exothermic, whereas the corresponding value for  $\Delta H_t(\text{Cl}^-)$  is endothermic. The  $T\Delta S_t(\text{Na}^+)$  value for the same transfer decreases sharply up to *c.* 10 mole % MeCN in MeCN/H<sub>2</sub>O and then decreases more smoothly over the rest of the range of the solvent composition. The  $T\Delta S_t(\text{Cl}^-)$  for transfer from H<sub>2</sub>O to MeCN/H<sub>2</sub>O increases sharply up to *c.* 10 mole % MeCN in MeCN/H<sub>2</sub>O and then decreases as more MeCN is added to H<sub>2</sub>O.

<sup>17</sup> Robinson, R. A., and Stokes, R. H., 'Electrolyte Solutions' 1st Edn, Ch. 6 (Butterworths: London 1955).

<sup>18</sup> Amis, E. S., and Hinton, J. F., (Eds), 'Solvent Effects on Chemical Phenomena' Ch. 3 (Academic Press: New York 1973).



The enthalpy and entropy considerations suggest that, unlike  $\text{Na}^+$ , the  $\text{Cl}^-$  ion breaks more hydrogen bonds in  $\text{MeCN}/\text{H}_2\text{O}$  than in pure  $\text{H}_2\text{O}$ , and this increases its solvation number to some extent. Presumably due to the low charge density of  $\text{Cl}^-$ , it is unable to compete with the strong intermolecular hydrogen bonding of bulk water. However, the presence of  $\text{MeCN}$  weakens the intermolecular hydrogen bonding of water which enables the  $\text{Cl}^-$  ion to orient more water around it in  $\text{MeCN}/\text{H}_2\text{O}$  than in pure  $\text{H}_2\text{O}$ . The sharp decrease in  $\Delta V_t(\text{Cl}^-)$  shown in Fig. 1 is consistent with this argument. Thus the difference in the volumetric behaviour of  $\text{Na}^+$  and  $\text{Cl}^-$  in  $\text{MeCN}/\text{H}_2\text{O}$  is related to the differences in the ion-solvent and solvent-solvent interactions. A similar minimum in the  $\Delta V_t(\text{Cl}^-)$  for transfer from  $\text{H}_2\text{O}$  to  $\text{EtOH}/\text{H}_2\text{O}$  has been postulated by Lee and Hyne<sup>19</sup> to be related to a minimum in the degree of structure of  $\text{EtOH}/\text{H}_2\text{O}$  mixtures.

The  $\Delta V_t$  behaviour of  $\text{NO}_3^-$  for transfer from  $\text{H}_2\text{O}$  to  $\text{MeCN}/\text{H}_2\text{O}$  is similar to that of  $\text{Cl}^-$  and can be explained in the same way as for  $\text{Cl}^-$ .

### Conclusion

The partial molal volumes of ions, like other thermodynamic properties, show a complex dependence upon the  $\text{MeCN}/\text{H}_2\text{O}$  solvent composition, reflecting the interactions between the ions and the neighbouring solvent molecules as well as the effect of the solvated ions on the bulk solvent properties. The observed solvent dependence of partial molal volumes of ions can be explained in terms of the Frank and Evans solvation model at low concentration of  $\text{MeCN}$  in  $\text{MeCN}/\text{H}_2\text{O}$ . At higher concentrations of  $\text{MeCN}$ , the volume parameter is directly related to the solvent compressibility.

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<sup>19</sup> Lee, I., and Hyne, J. B., *Can. J. Chem.*, 1968, **46**, 2333.