Limiting Partial Molar Volumes of Ions in Water-Methanol and Water-Acetonitrile

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Measurements of densities of solution of $AgNO_3$ and $Ca(NO_3)_2$ in the mixed solvents water-methanol and water-acetonitrile were carried out at 25 °C and the partial molar volumes V_2^∞ of these electrolytes were determined by taking account of the concentration dependence of the apparent molar volumes predicted by the Debye-Hückel theory. The ionic partial molar volumes of Ag^+, Ca^{2+}, and NO_3^- were evaluated and compared with those of other ions in the two mixed solvent systems. The solvent composition dependence is more remarkable in water-acetonitrile than in water-methanol, and characteristic behavior was observed for Ag^+ and Ca^{2+} ions in water-acetonitrile system.

First light was shed on the selective solvation of ions in mixed solvent wate-acetonitrile(AN) by Schneider and Strehlow[1] more than 30 years ago. These authors argued that the ion Ag^+ is preferentially solvated by acetonitrile, while in the solvation shell of the ion NO_3^- the solvation of water molecules is preferential. In the second paper,[2] they reported the preferential solvation of water to Ca^{2+} and Cl^- ions in water-methanol mixtures. However, this second paper seems to draw less attention than their first paper. Following Schneider and Strehlow[1] a number of workers have investigated the problem of selective solvation of ions in water-acetonitrile mixture. The quantities investigated are, for example, transfers of thermodynamic function,[3-5] $\Delta_t X$ (X=G, H, S), transport numbers,[6,7] and ionic molar conductivities.[8,9]

In our series of work on solute-solvent interaction in mixed solvents,[10-13] special emphasis has been placed on the determination of the partial molar volume and partial molar adiabatic compressibility of ionic solutes and the splitting of these partial molar quantities into cationic and anionic contributions. In this paper, we will report the partial molar volumes of silver nitrate and calcium nitrate in water-methanol and water-acetonitrile systems. The dielectric behavior of these two systems is quantitatively similar up to ca. 70 mol% of water. As for solutes we must add that use of other divalent nitrates as samples was unsuccessful on account of the difficulty in obtaining completely anhydrous sample (case for $Mg(NO_3)_2$) or the limited solubility of the salts for precise measurements of the solution density (case for $Zn(NO_3)_2$, $Ba(NO_3)_2$, and $Pb(NO_3)_2$). Even for $Ca(NO_3)_2$ measurement in pure acetonitrile was impossible on account of its low solubility.

To determine the V_2^∞ values from apparent molar volumes, we adopted the theoretical coefficient S_V, the values of which for water-acetonitrile were calculated as part of this work.

To date, the partial molar volumes of electrolytes in water-acetonitrile system have been treated in the three papers.[14-16] The V_2^∞ values of 1-1 electrolytes up to 25 mol% of acetonitrile was reported recently.[14] In pure acetonitrile the ultrasonic vibration potential measurement[15] was done for the ionic division of V_2^∞ of 1-1 type salt. Using the roughly evaluated V_2^∞ values, Singh et al. reported the $\Delta_t V_2^\infty$ ($H_2O \rightarrow H_2O/AN$) for univalent ions over the whole composition of the solvent system.[16]

Experimental

Samples. Anhydrous calcium nitrate was obtained from $Ca(NO_3)_2 \cdot 4H_2O$ by keeping it in vacuo for more than 48 hours over P_2O_5. The guaranteed grade reagent methanol was dried using the molecular sieves activated at 350 °C for more than three hours. The molecular sieves were set into the solvent methanol two or three days before use and the molecular sieves were eliminated by decantation. The solvent acetonitrile was distilled with phosphorus pentaoxide which was added to the solvent in the ratio of 5 g of P_2O_5 to one dm^3 of solvent. As the anhydrous calcium nitrate is extremely hygroscopic, the sample solution of this product was prepared in a dry-box.

Measurements. As in our recent work,[11-13] densities of solution were measured with a digital vibrating density meter Anton Paar DMA-02C. All measurements were done at 298.15 K.

Results and Discussion

Partial Molar Volumes. The apparent molar volumes V_ϕ were calculated using the conventional equation

$$V_\phi = 1000(d_1 - d)/cd_1 + M/d_1, \tag{1}$$

where c is the concentration of solute in mol dm^{-3} and the subscript 1 refers to solvent. The concentration dependence of V_ϕ in the experimental concentration ranges is expressed in terms of the equation

$$V_\phi - S_V c^{1/2} = V_2^\infty + hc. \tag{2}$$

In Eq. 2 the parameter S_V is equal to $kw^{3/2}$ and the quantities w and k are expressed as

$$w=(1/2)\sum \nu_i z_i^2, \quad (3)$$

and

$$k=2N_o^2e^3(2\pi/1000RT)^{1/2}\varepsilon^{-3/2}\{(\mathrm{d}\ln\varepsilon/\mathrm{d}P)-(\kappa_T/3)\}, \quad (4)$$

where κ_T is the isothermal compressibility and other symbols have their usual meaning. The values of κ_T were obtained from the reported data.[17] From the Tait-form equation for dielectric constants found elsewhere,[18] we calculated the pressure derivatives of the dielectric constant at 0.1 MPa. Values of ε, $\mathrm{d}\ln\varepsilon/\mathrm{d}P$ and κ_T at rounded solvent composition are summarized in Table 1.

Figures 1 and 2 show the plot of Eq. 2 for the samples $AgNO_3$ and $Ca(NO_3)_2$, respectively. The parameter h of Eq. 2 is negative except for $AgNO_3$ in water-acetonitrile system. The values of h of the solute $Ca(NO_3)_2$ become negatively larger with increasing content of methanol or acetonitrile. An increase in the negative deviation from Eq. 2 with the content of organic solvent in aqueous mixed solvents has also been observed for $CaCl_2$ in water-methanol

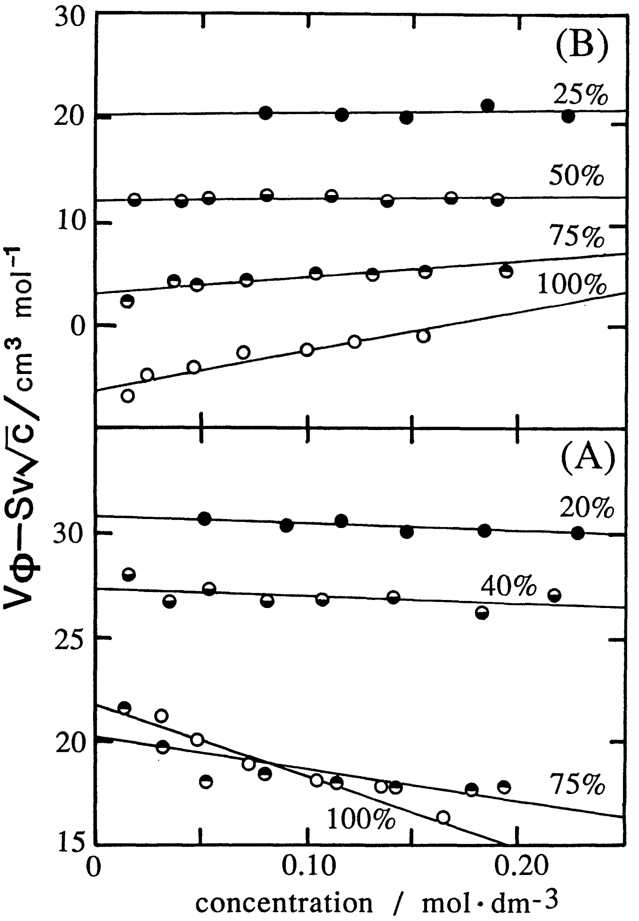

Fig. 1. Plots of $V_\phi - S_v c^{1/2}$ versus concentration c for $AgNO_3$ dissolved in the mixed solvent water-methanol(A) and water-acetonitrile(B) at 25 °C. The % in the figure refers to the acetone content (mol%) of the solvent system.

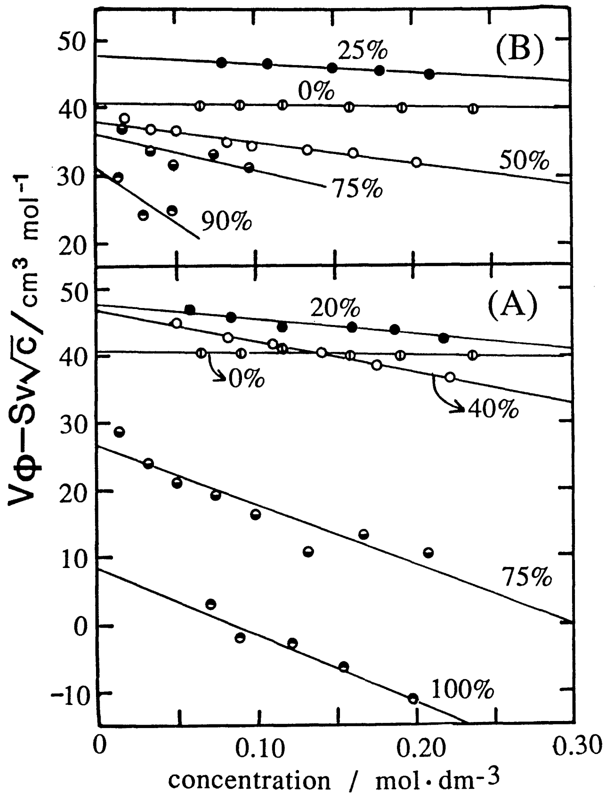

Fig. 2. Plots of $V_\phi - S_v c^{1/2}$ versus concentration c for $Ca(NO_3)_2$ dissolved in the mixed solvent water-methanol (A) and water-acetonitrile (B) at 25 °C. The % in the figure refers to the acetone content (mol%) of the solvent system.

Table 1. Numerical Values of the Coefficient k Calculated by the Debye-Hückel Theory for the Mixed Solvent Water-Acetonitrile at 25 °C

[Acetonitrile]	k	[Acetonitrile]	k
mol%	$cm^3\,mol^{-3/2}\,dm^{3/2}$	mol%	$cm^3\,mol^{-3/2}\,dm^{3/2}$
0	1.868	60	8.118
10	2.863	70	9.507
20	3.700	75	10.20
25	4.256	90	12.81
40	6.164	100	15.08
50	7.104		

Table 2. Partial Molar Volumes of $AgNO_3$ and $Ca(NO_3)_2$ in H_2O-MeOH System at 25 °C

[Methanol]	V_2^∞/cm^3 mol^{-1}		[Acetonitrile]	V_2^∞/cm^3 mol^{-1}	
mol%	$AgNO_3$	$Ca(NO_3)_2$	mol%	$AgNO_3$	$Ca(NO_3)_2$
0	27.9 28.02[a]	40.7 40.164[b]	0	27.9 28.02[a]	40.7 40.164[b]
20	30.8	47.7	25	20.3	47.9
40	27.4	46.6	50	12.3	38.0
75	20.2	26.5	75	3.3	36.1
100	21.8	8.7	90	—	31.2
			100	−6.4 −3[c]	—

a) Ref. 19. b) Ref. 20. c) Ref. 16.

system.[11] Such a negative deviation observed for $Ca(NO_3)_2$ is perhaps due to the ion association, the amount of which increases with decreasing dielectric constant of the solvent. In every case represented in Figs. 1 and 2, extrapolation of V_ϕ to infinite dilution was carried out by the first order least mean-squares fitting to the experimental data.

The partial molar volumes of $AgNO_3$ and $Ca(NO_3)_2$ at infinite dilution obtained are given in Table 2 and are plotted against solvent composition in Fig. 3. In water, our partial molar volumes agree satisfactorily with those found in the literature.[19,20] Among the four systems studied, direct comparison is possible only for $AgNO_3$ in water-acetonitrile. As seen in Fig. 3, our V_2^∞ ($AgNO_3$) falls fairly well on the line connecting the values reported earlier.[16] The difference in the value of V_2^∞ ($AgNO_3$) in pure acetonitrile obtained in this work (−6.4 cm^3 mol^{-1}) and that found in the literature (−3 cm^3 mol^{-1}) is too large to accept in the discussion of the V_2^∞ values in aqueous solutions. In the case of V_2^∞ values in nonaqueous solvents, however, such a degree of difference is not rare. For example, two distinctly different values 4.73[15] and 11[16] cm^3 mol^{-1} have been reported by different authors for the V_2^∞ of sodium iodide in acetonitrile.

Ionic Partial Molar Volumes. At present, experimental techniques for the ionic division of V_2^∞ of a salt are limited to the ultrasonic vibration potential and the sedimentation potential measurements. In a previous paper[12] we measured the sedimentation potential (SP) in solutions of LiCl, NaCl, and KCl dissolved in water-methanol mixtures and split V_2^∞ of these chlorides into cationic and anionic parts. In that paper, the variation of the partial molar volumes of Cl^- as well as Li^+, Na^+, and K^+ in water-methanol system with solvent composition was represented graphically. Combination of the values V_2^∞ (MX) determined in our laboratory[10-12] and those obtained in this work with the numerical values of V_2^∞ (Cl^-) obtained in our previous work[12] permits us to evaluate the partial molar volumes of various ions in water-methanol system. The calculation procedure for the nitrate and silver ions is as follows: first, we calculate V_2^∞ (Ca^{2+}) by subtracting V_2^∞ (Cl^-) from V_2^∞ ($CaCl_2$), then calculate V_2^∞ (NO_3^-) from V_2^∞ ($Ca(NO_3)_2$), and finally obtain V_2^∞ (Ag^+) from V_2^∞ ($AgNO_3$). The ionic partial molar volumes thus evaluated are shown in Table 4 in which the V_2^∞ values in water are included; the values in water are based on the V_2^∞ values of

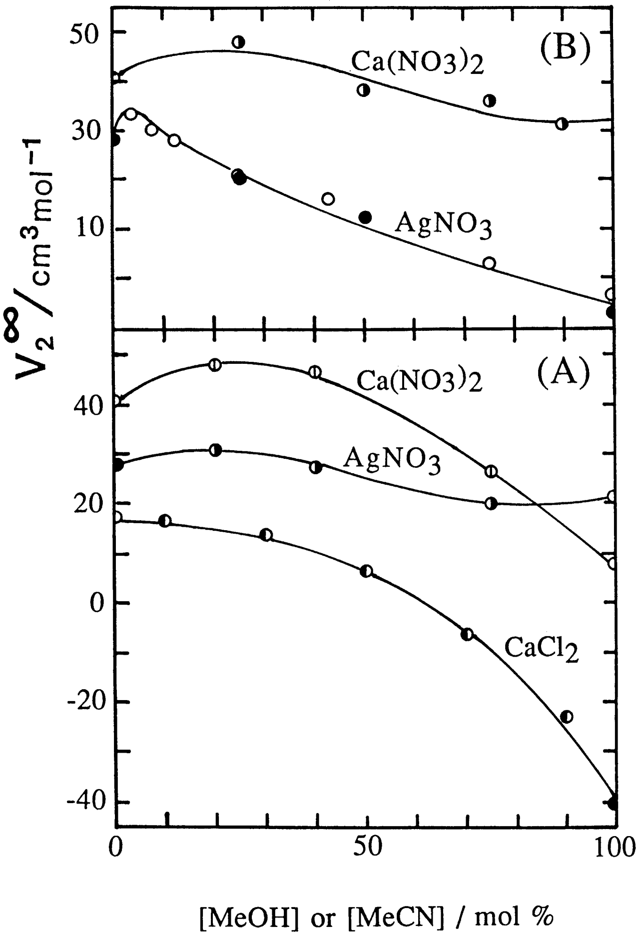

Fig. 3. Variation of the partial molar volumes with solvent composition at 25 °. (A): $Ca(NO_3)_2$, $CaCl_2$, and $AgNO_3$ in water-methanol. (B); $Ca(NO_3)_2$ and $AgNO_3$ (●; this work, ○; reported value) in water-acetonitrile.

Table 3. Ionic Partial Molar Volumes in Water-Methanol System Based on the Measurements of Sedimentation Potentials at 25 °C

[MeOH]	V_2^∞/cm^3 mol^{-1}							
mol%	Li^+	Na^+	K^+	Cs^+	Ag^+	Ca^{2+}	Cl^-	NO_3^-
0	−3.01	−3.39	6.85	19.15	−3.7	−22.22	20.0[a] 23.5[b]	31.5 34.9[b]
10						−26.5	21.5[a]	
20					−7.7	(−29.4)		38.5
30	−6.9	−6.5	4.9	16.4		−32.0	22.8[a]	
40					−13.7	(−35.6)		41.1
50	−9.2	−8.5	4.7	14.9		−39.0	22.6[a]	
70	−12.3	−12.7	1.6	11.8		−48.1	20.8[a]	
75					−18.7	(−51.2)		38.9
90	−12.7	−16.1	−3.5	8.4		−57.0	16.9[a]	
100	−16.9	−15.6	−6.1	2.7	−14.9	−64.6	12.0[a] 12.6[c] 13.0[d]	36.7

a) Reference for the ionic division of V_2^∞(MX). b) Ref. 22. c) Ref. 23. d) Ref. 24.

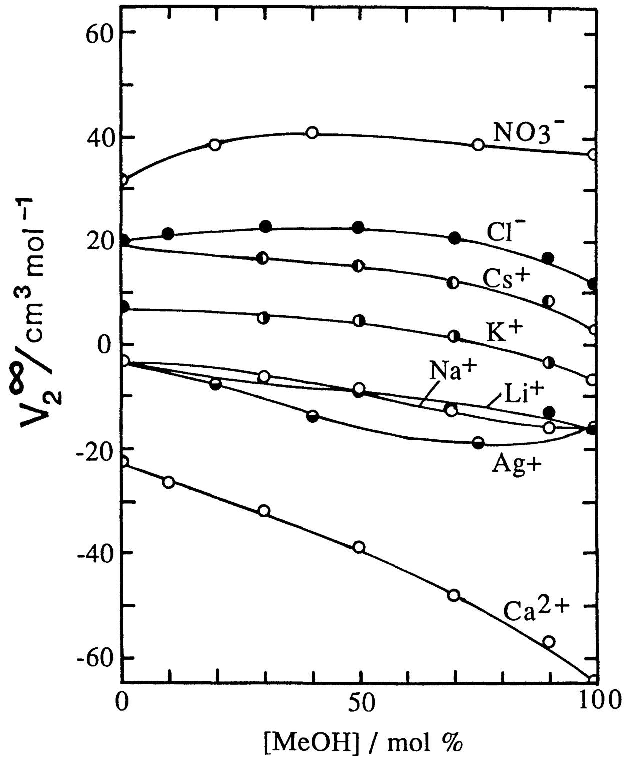

Fig. 4. Partial molar volumes of various ions dissolved in water-methanol at 25 °C.

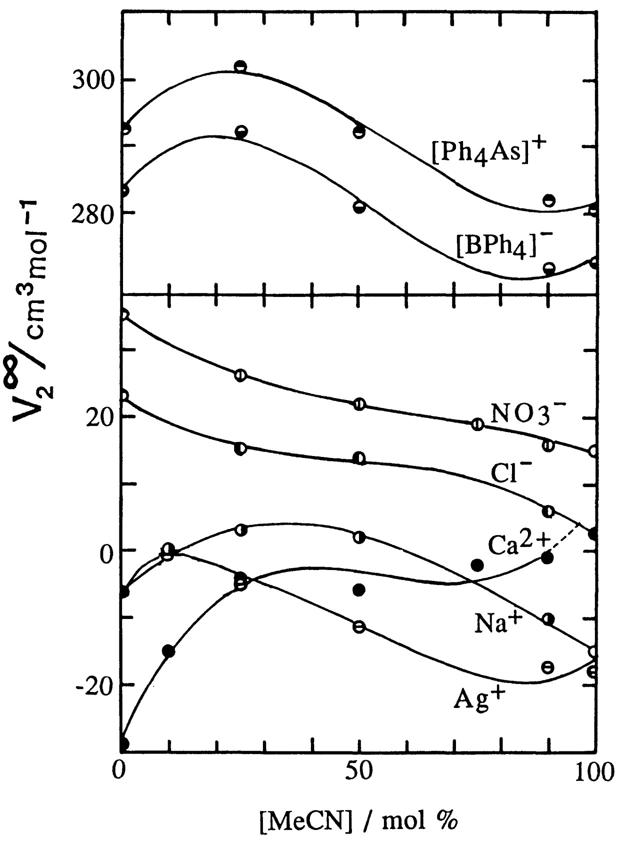

Fig. 5. Partial molar volumes of various ions dissolved in water-acetonitrile at 25 °C. The dotted line for the ion Ca^{2+} means that the partial molar volume in pure acetonitrile is unknown.

electrolytes recommended by Millero,[21] while the V_2^∞ values of salt in methanol used are those obtained by adding the most recent values of ionic partial molar volumes listed by French and Criss.[23]

The ultrasonic vibration potential or sedimentation potential method has not been applied to the system water-acetonitrile system. Here, we evaluate the partial molar volumes of ion first by interpolating the V_2^∞ values reported by Singh et al.[16] and then by using the the assumption that

$$\frac{V_2^\infty(Ph_4As^+)}{V_2^\infty(BPh_4^-)}=\frac{V_{vw}(Ph_4As^+)}{V_{vw}(BPh_4^-)}=1.0337, \qquad (6)$$

where V_{vw} means the van der Waals volume. Results of this ionic division are summarized in Table 4 and also represented in Fig. 5.

Table 4. Rounded Values of the Ionic Partial Molar Volumes in Water-Acetonitrile System at 25 °C Based on the V_2^∞ (Ph_4AsCl) and V_2^∞ ($NaBPh_4$) Data

[MeCN]	V_2^∞/cm³ mol⁻¹						
mol%	Ph_4As^+	BPh_4^-	Na^+	Ag^+	Ca^{2+}	Cl^-	NO_3^-
0	292	283	−7	−7	−29	23	35
10	306	296	0	−1	−15	17	30
25	302	292	3	−5	−4	15	26
50	292	281	2	−11	−6	14	22
75					−2		19
90	282	272	−10	−17	1	6	16
100	281	273	−15	−18		3	15
			−21.4[a)]			6.4[a)]	

a) Ref. 15 determined by the ultrasonic vibration potential method.

Making allowance for uncertainties due to various factors (V_2^∞, use of the two different methods for ionic division, etc.) we can mention at least the following several characteristic features of the ion-solvents interactions in water-methanol and water-acetonitrile.

1) The partial molar volumes of metallic ions decrease with the methanol content, except for V_2^∞ (Ag^+) in solvents with 80—100 mol% of methanol. The decrease of V_2^∞ with the methanol content is most remarkable for the divalent cation Ca^{2+} indicating that the decrease of V_2^∞ is mainly electrostatic. The increase of V_2^∞ ($Ca(NO_3)_2$) observed in Fig. 3(A) is totally ascribable to the ion NO_3^-. Roughly speaking, in the mixed solvent water-methanol, the change of partial molar volume accompanying the solvent change, $\Delta_t V_2^\infty$, is similar for all the alkali metal ions (see Fig. 4).

2) In water-acetonitrile system, the solvent composition dependences of ionic partial molar volumes are drastically different from those in water-methanol. As mentioned earlier, for water-methanol and water-acetonitrile the bulk dielectric constants (ε) are similar in magnitude; the only difference is that ε is 35.9 for pure acetonitrile and 32.6 for methanol. The interpretation of the differences in the behavior of various ions represented in Figs. 4 and 5 in terms of the bulk dielectric constant of the solvents is obviously impossible. It must be stressed that the V_2^∞ of ions depends strongly on the degree of steric hindrance of the poles of the solvent molecule dipole and the properties of the solvent layer around the ion.15,24) The acetonitrile molecule has the dipole moment μ equal to 3.913 Debye (1 Debye=3.336×10^{-30} Cm), while those of methanol and water are 1.69 and 1.94 Debye, respectively. The negative pole of the acetonitrile is located at the nitrogen atom of the -C≡N group, and in both methanol and water, the negative and positive poles are on oxygen and hydrogen atoms, respectively. Hence, the nature of solvation at the microscopic level varies to a lesser extent with the solvent composition in water-methanol than in water-acetonitrile.

3) For large univalent ions [Ph_4As^+] and [BPh_4^-] the differences between V_2^∞ ([Ph_4As^+]) and V_2^∞ ([BPh_4^-]) are independent of the solvent composition.

4) The V_2^∞ (NO_3^-) and V_2^∞ (Cl^-) decrease in a similar way with the acetonitrile content. The increase of V_2^∞ ($AgNO_3$) observed in the water-rich region in the water-acetonitrile system (see Fig. 3) is attributed not to the anion NO_3^- but to the cation Ag^+, in contrast to the case of $Ca(NO_3)_2$ in the water-methanol system mentioned above. For the ions Ag^+ and Na^+, the extremum appears in the relationship between the respective V_2^∞ values and the acetonitrile content in the solvent system. The acetonitrile content giving the maximum V_2^∞ value corresponds to the solvent composition at which the values of isothermal compressibility κ_T pass through a minimum. The fact that the acetone content for the maximum of V_2^∞ (Ag^+) is far lower than that of V_2^∞ (Na^+) demonstrates the different behavior of ion Ag^+ from the alkali metal ion.

5) The result for Ca^{2+} in water-acetonitrile is the most striking one detected by the ionic splitting of V_2^∞ of the electrolytes investigated.

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