

Study of excess volume of mixing in mixed salt solution: The ternary systems involving tetramethylammonium bromide, alkali bromides and D₂O at 298·15 K

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Abstract. The densities of solutions of (CH₃)₄NBr + LiBr + D₂O, (CH₃)₄NBr + KBr + D₂O and (CH₃)₄NBr + CsBr + D₂O were determined at 298·15 K at a fixed ionic strength of 4·0 M and varying salt mole-fractions. Some results were also obtained at ionic strengths 2·0 and 3·0 for equimolar mixtures of the salts. The mean apparent molar volumes were calculated and used to obtain excess volumes of mixing. The results were compared with similar data in the literature and interpreted in terms of ion–ion interactions and Friedman's volume interaction parameters.

Keywords. Tetramethylammonium bromide-D₂O solutions; mixed salt solutions with alkali halides; mean apparent and excess volumes; ion–ion interaction.

1. Introduction

The studies of excess thermodynamic properties of mixed aqueous electrolyte solutions have assumed importance in recent years (Anderson and Wood 1973), since these provide useful information on the interaction of like-charge-ions and triplet interactions in general if measurements are made at a constant ionic strength with a common ion. Many thermodynamic properties like excess volume of mixing, excess free energy of mixing and excess compression of mixing for solutions involving tetraalkylammonium bromides and alkali bromides indicate extraordinarily large thermodynamic effects which were generally interpreted in terms of R₄N⁺ – R₄N⁺ pair interaction (Wen and Nara 1967; Wen 1971; Wen *et al* 1971; Rosenzweig *et al* 1976; Padova *et al* 1976; Patil and Mehta 1987, 1988) and significant modification of water structure around the cations.

In this communication, we report the density data of binary and ternary solutions containing tetramethylammonium bromide, LiBr, KBr and CsBr in D₂O at 298·15 K. The measurements for ternary solutions were made at a constant ionic strength of 4·0 M and varying the mixing ratio of the two constituent salts. The data at ionic strength 2·0 and 3·0 are also reported for equimolar solutions. The results of the investigation were analysed by using Friedman's (1962) equation.

2. Experimental

The heavy water of 99.75 and 99.9% D_2O content was used as such for binary and ternary solutions respectively. It was obtained from Merck, Sharp and Dohme, Canada. The salts LiBr, KBr and CsBr were from Merck, Darmstadt and of 'suprapur' quality, while Me_4NBr was Fluka 'purum' grade. They were used directly without any purification but after drying them in a vacuum oven (10^{-5} Torr) at $120^\circ C$ and at $65^\circ C$ for the required lengths of time.

All the binary and ternary solutions were prepared fresh by dissolving the appropriate amount of solutes in a known weight of D_2O in stoppered polythene bottles which were immediately sealed by 'Parafilm'. The maximum deviations in the value of ionic strength of 4.0 M (concentrations) were not more than 0.25%.

Densities were measured with an Anton Paar vibrating tube densimeter operating at $25 \pm 0.01^\circ C$. Calibration was performed with water and with air under ambient conditions. As far as we know, no literature data for the systems studied are available for comparison purposes. In the lower concentration region (upto 0.4 m), Fortier and coworkers have reported some data for alkali bromides (Fortier *et al* 1974). In order to compare our data with these workers we have extended our measurements upto 0.1 m for LiBr + D_2O systems. The data of density difference (i.e. $d - d_0$) for binary solutions of the salts studied are given in figure 1 along with the data of Fortier *et al* (1974). The agreement in the low concentration region is quite good considering the

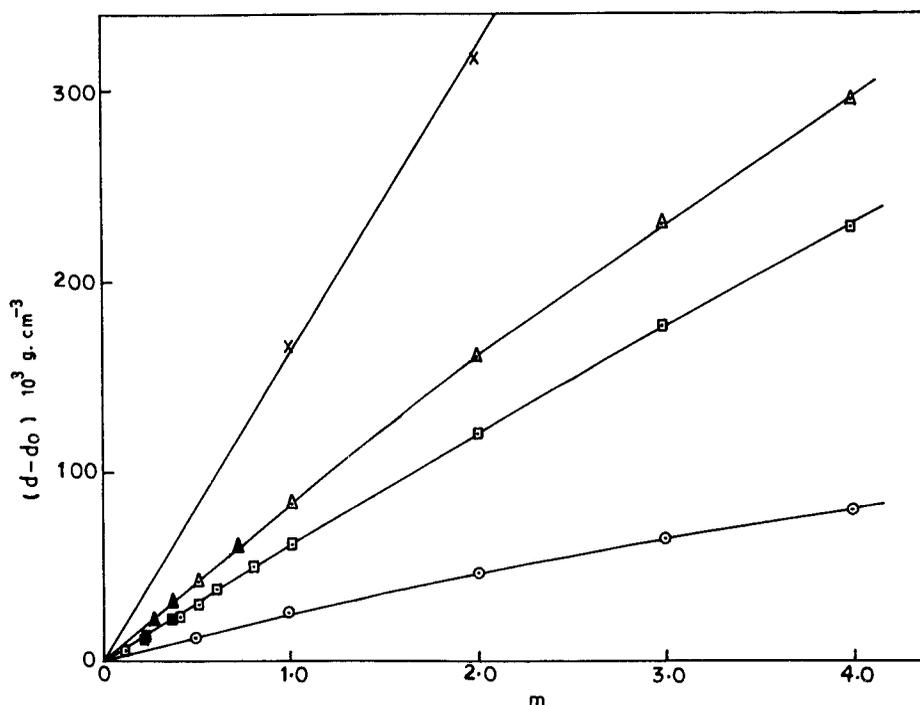


Figure 1. The density differences ($d-d_0$) as a function of molality of the salt in D_2O , at $298.15 K$; $\circ-\circ$ $(CH_3)_4NBr$, $\square-\square$ LiBr, $\Delta-\Delta$ KBr and $\times-\times$ CsBr. The filled symbols represent the literature data (Fortier *et al* 1974).

hygroscopic nature and different enrichment percentage of D₂O for the two sets of data. Our density values for 99.75 and 99.9% D₂O were 1.10445 ± 0.00003 and 1.10468 ± 0.00004 g cm⁻³, respectively. The overall accuracy in the density determinations is of the order of 2×10^{-5} g cm⁻³.

3. Results and treatment

The apparent molal volumes (ϕ_V) were calculated from density data using the equation:

$$\phi_V = \frac{M}{d} + \frac{(d_0 - d) \cdot 10^3}{m \cdot d_0 \cdot d}, \quad (1)$$

where d_0 is the density of D₂O, m is the molality (number of moles per kilogram of D₂O) and M is the molecular weight of the solute. The ϕ_V data are usually expressed as a function of molality, by the Redlich–Meyer equation:

$$\phi_V = \phi_V^0 + A_V(d_0 \cdot m)^{1/2} + B_V \cdot m, \quad (2)$$

where ϕ_V^0 is the standard partial molal volume at infinite dilution, A_V is the limiting slope of the Debye–Huckel theory, while, B_V is deviation parameter signifying the solute–solute interaction. The A_V parameter cannot be evaluated, since the variation of the dielectric constant of heavy water with pressure is not known, but it is usually assumed that A_V is equal to that in H₂O (= 1,868). The plots of the function $\phi_V - A_V(d_0 m)^{1/2}$ as a function of concentration are shown in figure 2. The uncertainty in the ϕ_V values at the lowest concentration of interest (0.4 M) is 0.05 cm³ mol⁻¹. Our ϕ_V^0 values obtained by linear extrapolation from high concentration data are 25.35, 33.55, 45.8 and 115.2 cm³ mol⁻¹ for LiBr, KBr, CsBr, and (CH₃)₄NBr, respectively. The ϕ_V^0 values for KBr and CsBr are in good agreement with the data of Conway and Liliberte (1970) (for KBr) and Fortier *et al* 1974 (for CsBr), respectively. Our ϕ_V^0 values for LiBr and Me₄NBr are somewhat higher than the values reported in the literature (24.97 and 114.26 cm³ mol⁻¹, respectively, Fortier *et al* 1974, and Conway and Liliberte 1970), which we attribute to the high concentrations employed in this study. The density data obtained for ternary systems (CH₃)₄NBr + CsBr + D₂O, (CH₃)₄NBr + KBr + D₂O and (CH₃)₄NBr + LiBr + D₂O are given graphically in figure 3 as a function of ionic strength fraction of (CH₃)₄NBr at total molality of 4.0 and at 298.15 K. The mean apparent molal volumes $\phi_{V_{\text{mix}}}$ (y, m) of the aqueous (D₂O) tetramethyl–ammonium bromide and alkali bromide mixtures were calculated using the equation,

$$\phi_{V_{\text{mix}}}(y, m) = \frac{1}{m} \left\{ (1000 + mM + mM)/d - \frac{1000}{d_0} \right\} \quad (3)$$

where y is the mole fraction of tetramethylammonium bromide and m_i and M_i are the molality and molar mass, respectively, of the alkali (Li or K or Cs) and tetramethylammonium bromide at a total molality of $m = m_2 + m_3$. The mean apparent molal volumes were not corrected for the Debye–Huckel limiting law effect since we have handled comparatively high concentrations.

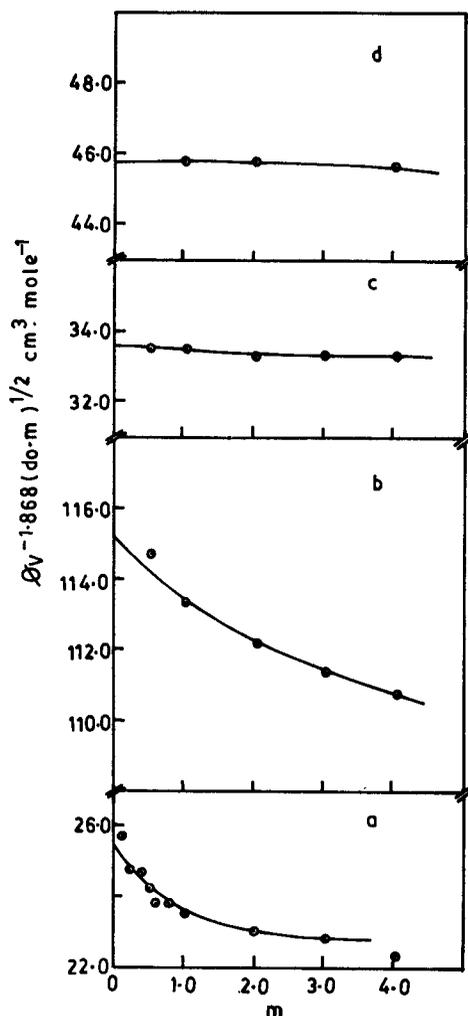


Figure 2. The parameter $\phi_V - 1.868(d_0 - m)^{1/2}$ as a function of molality of the salts in binary solutions: *a*—LiBr, *b*— $(\text{CH}_3)_4\text{NBr}$, *c*—KBr and *d*—CsBr at 298.15 K.

Errors in $\phi_{V_{\text{mix}}}$ may be estimated from Redlich and Biegeleisen's equation (Redlich and Biegeleisen 1942)

$$\phi_{V_{\text{mix}}} = -10^3 \frac{\delta d}{m d_0} + \frac{10^3 (d - d_0) \cdot \delta m}{m}, \quad (4)$$

where $\phi_{V_{\text{mix}}}$, δd and δm are the uncertainties in apparent molal volume, density and concentration respectively. Our estimated error in $\phi_{V_{\text{mix}}}$ at the lowest ionic strength in the studied system is of the order of $0.01 \text{ cm}^3 \text{ mol}^{-1}$.

The excess volume of mixing per kilogram of solvent is defined as (Wen and Nara 1967)

$$\Delta V^{\text{ex}}(y, m) = m \{ \phi_V(y, m) - (1 - y) \phi_V(0, m) - y \phi_V(1, m) \}, \quad (5)$$

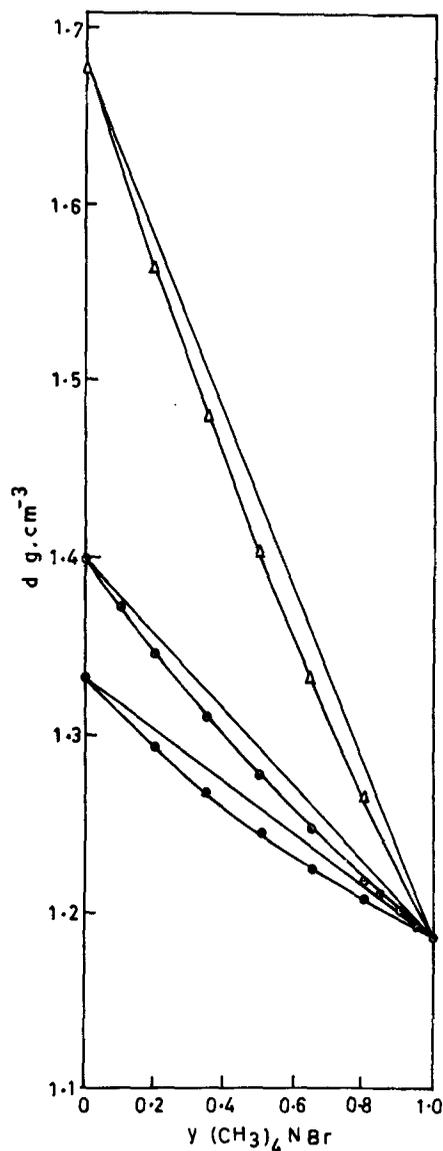


Figure 3. Density data (d) as a function of mole-fraction of $(\text{CH}_3)_4\text{NBr}$ in ternary solutions; at 298.15 K and fixed ionic strength of 4.0 M. ●—● $(\text{CH}_3)_4\text{NBr} + \text{LiBr} + \text{D}_2\text{O}$, ○—○ $(\text{CH}_3)_4\text{NBr} + \text{KBr} + \text{D}_2\text{O}$; and Δ—Δ $(\text{CH}_3)_4\text{NBr} + \text{CsBr} + \text{D}_2\text{O}$.

where $\phi_V(0, m)$ and $\phi_V(1, m)$ apply to solutions of the pure salts and of which values were obtained from the data of binary solutions. From (5), the excess volume of mixing is obtained directly. The values obtained are plotted in figure 4 at constant total molality against y , the mole fraction of $(\text{CH}_3)_4\text{NBr}$.

According to Friedman's theory (Friedman 1962), the excess volume of mixing is given by:

$$\Delta V^{\text{ex}}(y, m) = m^2 y(1 - y) \{ V_0 + V_1(1 - 2y) + V_2(1 - 2y)^2 + \dots \}, \quad (6)$$

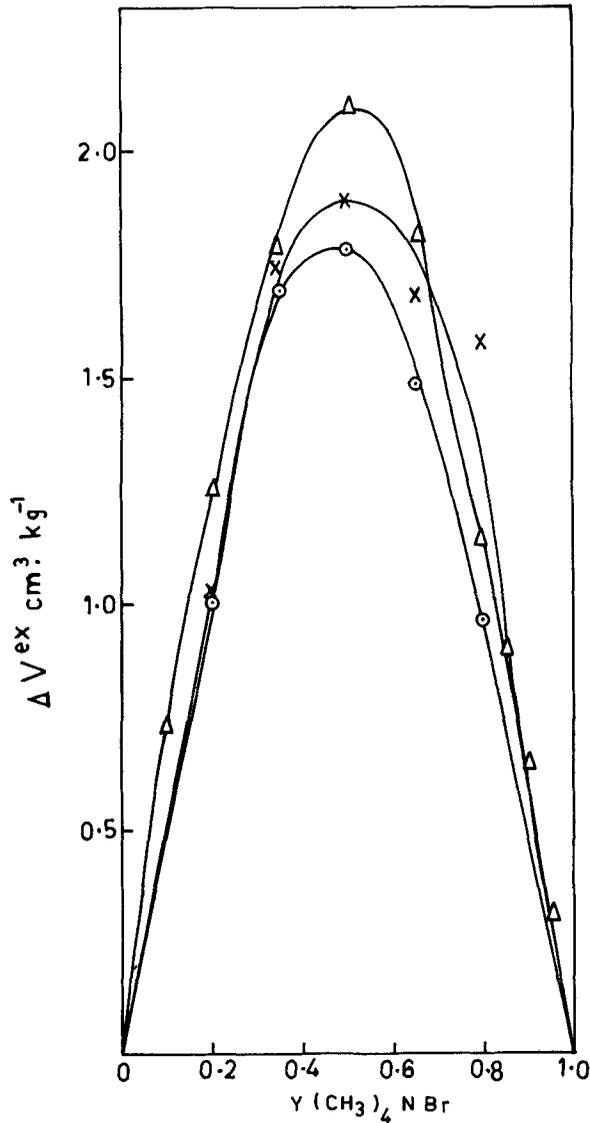


Figure 4. Excess volumes of mixing (ΔV^{ex}) in ternary solutions of constant molality 4.0 at 298.15 K as function of mole-fraction of $(\text{CH}_3)_4\text{NBr}$. $\circ-\circ$ $(\text{CH}_3)_4\text{NBr} + \text{LiBr} + \text{D}_2\text{O}$ $\triangle-\triangle$ $(\text{CH}_3)_4\text{NBr} + \text{KBr} + \text{D}_2\text{O}$; and $\times-\times$ $(\text{CH}_3)_4\text{NBr} + \text{CsBr} + \text{D}_2\text{O}$.

where V_i 's are interaction parameters that represent the various changes in volume incurred when particles interact. We define a parameter $Z [= \Delta V^{\text{ex}}(y, m)/I^2 \cdot y \cdot (1 - y)]$ whose values are calculated at different mole fractions of $(\text{CH}_3)_4\text{NBr}$. At 0.5y, the value of Z is equal to V_0 of Friedman's equation (6) and signifies the extent of cation-cation interaction. The variation of Z with ionic strength gives information about the triplet interactions in general as

$$V_0 = V_{02} + mV_{03}. \quad (7)$$

Table 1. ΔV^{ex} values and the derived parameter 'Z' applying Friedman's equation.

Systems	ΔV^{ex} ($\text{cm}^3 \text{kg}^{-1}$)			Z ($\text{cm}^3 \text{mol}^{-2} \text{kg}^{-1}$)		
	a	b	c	a	b	c
$(\text{CH}_3)_4\text{NBr-LiBr}$	0.022	0.595	1.785	0.02	0.26	0.45
$(\text{CH}_3)_4\text{NBr-KBr}$	0.272	0.561	2.100	0.27	0.25	0.52
$(\text{CH}_3)_4\text{NBr-CsBr}$	0.807	1.428	1.89	0.81	0.63	0.47

$a = 2.0 \text{ M}$, $b = 3.0 \text{ M}$ and $c = 4.0 \text{ M}$.

We have not attempted to calculate the values of V_1 , V_2 , the higher order interaction parameters as the data are of limited accuracy. The values of ΔV^{ex} at 0.5 mole-fraction of $(\text{CH}_3)_4\text{NBr}$ for the studied systems are collected in table 1.

4. Discussion

The apparent molal volume data in binary solutions (figure 2) for all the salts studied indicate negative values for the parameter B_V of (2) which signify the ion-ion interactions. A tentative conclusion from the magnitude of B_V appears to be that LiBr and $(\text{CH}_3)_4\text{NBr}$ are structure forming salts while CsBr and KBr are not so effective as the magnitudes of B_V are in the order of $(\text{CH}_3)_4\text{NBr} > \text{LiBr} > \text{KBr} > \text{CsBr}$. Similar trends have been observed by Desnoyer's and others in D_2O and H_2O in the dilute concentration region for alkali halides (Fertier *et al* 1974).

Observation of figure 3 reveals that density parameters for the ternary solutions exhibit negative deviation from linearity in all the three systems at ionic strength of 4.0 M. As shown in figure 4, ΔV^{ex} values are positive and when plotted against 'y' the mole-fraction of $(\text{CH}_3)_4\text{NBr}$ gives parabolic curves similar to those obtained in normal water (Wen and Nara 1967; Padova *et al* 1976; Patil and Mehta 1987). It is also noted that the magnitude of ΔV^{ex} increases with ionic strength in all systems studied (at 0.5 y). This suggests that cation-cation interactions increase with concentration as expected. Another interesting observation is that at ionic strength 2.0 the excess volume is almost zero for $(\text{CH}_3)_4\text{NBr} + \text{LiBr}$ system. It is known from the literature that the viscosity B coefficient and viscosity behaviour for $(\text{CH}_3)_4\text{N}^+$ and Li^+ ions in water are almost the same (Stokes and Mills 1965). Thus, one can conclude that the hydration properties of these ions are similar in aqueous solutions although many authors have classified $(\text{CH}_3)_4\text{N}^+$ as a structure breaking and Li^+ as a structure forming ion. The definite answer to this problem can be obtained only if the structural details of the hydration shell around these ions are understood. Recent studies of neutron scattering spectra of $(\text{CH}_3)_4\text{N}^+$ ions in D_2O also suggest that $(\text{CH}_3)_4\text{N}^+$ ion is a weak structure maker (Brown *et al* 1988).

Variation of Z (see table 1) with ionic strength reveals the different behaviour of the cations Li^+ and Cs^+ when mixed with $(\text{CH}_3)_4\text{N}^+$ ions. It is observed that Z increases with concentration in the case of $(\text{CH}_3)_4\text{NBr} + \text{LiBr}$ system while it decreases with concentration in the $(\text{CH}_3)_4\text{NBr} + \text{CsBr}$ system. Application of (7) shows that in the cases of the $(\text{CH}_3)_4\text{NBr} + \text{LiBr}$ system, the contribution to volume

due to triplet interactions ($(\text{CH}_3)_4\text{N}^+ - \text{Br}^- - \text{Li}^+$) is predominant and V_{02} (cation-cation interaction contribution) is only positive at the higher ionic strength of 4.0 M. In the case of the $(\text{CH}_3)_4\text{NBr} + \text{CsBr}$ system, it seems that cation pair interactions are more favoured at low concentrations compared to mixed ion triplets while at the higher ionic strength of 4.0 M, triplets also contribute to the observed excess volume of mixing. The behaviour of the system $(\text{CH}_3)_4\text{NBr} + \text{KBr}$ is intermediate between these two extremes. Wen *et al* (1968) have compared ΔmV^{ex} of $\text{Me}_4\text{NBr}-\text{KBr}-\text{D}_2\text{O}$ mixtures at ionic strength of 1.0 M with that of ΔmV^{ex} in normal water and found that it is smaller in magnitude for the former case. At present the data of ΔV^{ex} in normal water at higher ionic strength are not available for comparison purposes.

The observed specificity of the ion-pair and ion-triplet interactions in the systems studied suggest the importance of water structural interactions in the vicinity of these ions. With the help of NMR relaxation data and association constant parameter for water in binary solutions, Hertz has suggested that the structure breaking salts like RbBr and CsBr are hydrophobic while LiBr and NaBr are hydrophilic (Hertz 1985). The application of such an approach has recently been made for ternary solutions handled in this work and the results have been discussed elsewhere (Holz and Patil 1991).

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