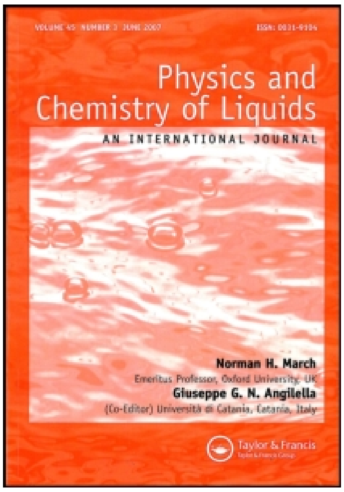

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Thermodynamics of 1 : 1 electrolyte solutions at 298.15 K in aqua-DMF mixed solvent system: excess volume of mixing

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Excess volumes of mixing for six possible binary combinations of solutions of NaCl, KCl, NaBr, and KBr have been determined at constant ionic strength of 1.000 and 2.000 $\mathrm{mol\,kg^{-1}}$ at 298.15 K using dilatometer in water + *N*,*N*-dimethylformamide mixed solvent system. Pitzer's virial coefficient theory has been utilized to obtain binary and triplet interaction parameters i.e., θ^V and ψ^V. Data do not support Young's cross square rule (CSR). The deviation from CSR is considered to arise from significant contributions of triplet interactions and preferential solvation of the ions and ion-clusters in the mixed solvent system.

Keywords: volume of mixing; *N*,*N*-dimethylformamide; Pitzer model; Young's cross square rule

1. Introduction

Ion–ion and ion–solvent interactions play an important role in the solution chemistry of solutes [1–6]. Volume of mixing provides valuable information about the interactions of ions in between and with the solvent used. Most of such studies have been carried out in water (W), which has well studied hydrogen bonded structure. Literature surveys reveal that volume of mixing data of electrolytic solutions, particularly in the mixed solvent systems are lacking. Accurate electrolytic data in aqueous as well as mixed solvent system are required not only to understand the nature of ion–ion and ion-solvent interactions but also have its practical applicability in various fields like geology [7], oceanography [8], boiler engineering [9], water treatment, and oil recovery [10]. Interest in calculating the various thermodynamic properties of concentrated electrolyte solutions has been aided by the development of virial coefficient theory by Pitzer [11–14]. The binary and triplet interaction parameters in the Pitzer theory can be calculated from the excess thermodynamic property data.

Molar excess volume of mixing reflects the changes associated with intermolecular hydrogen bonding caused by the presence of ions. If the intermolecular hydrogen bonding in pure water is disturbed by addition of any organic cosolvent, capable of forming H-bonding with water, then extend of hydration of the cations and anions is influenced to different extents. So molar excess volume data in presence of common and uncommon ion in a mixed solvent system should not only provide a deeper insight into the process of solvation, but also a means of checking the applicability of Young's cross square

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rule (CSR). CSR is one of the most important generalizations concerning the behaviour of mixed salt solutions, which was first developed by Young [15]. It has been shown to hold good for a number of aqueous electrolyte solutions [16–20]. In our recent work [21,22], we have extended these studies to the mixed solvent systems. If the dielectric constant of the mixed solvent system does not deviate significantly from that of water, then it is expected that the electrostatic affects arising from it will almost remain same and volume of mixing data in the mixed solvent system would highlight the ion–solvent interactions.

With this view, we determined the molar excess volume of mixing of Cl^- and Br^- of Na^+ and K^+ in water + *N*,*N*-dimethylformamide mixed solvent system. Dimethylformamide (DMF) is a dipolar aprotic solvent and was selected because of its strong donor properties due to the presence of two electron donating methyl groups attached to a nitrogen atom, which again bears a lone pair of electrons.

2. Experimental section

DMF (Ranbaxy, AR) was purified by a standard procedure [23]. DMF (dielectric constant $\xi_D = 36.71$ at 298.15 K) [24a] was mixed with appropriate quantity of doubly distilled water ($\xi_w = 78.39$ at 298.15 K) [24a] to yield mixed solvent system having ξ_{mix} of 70. It is assumed [24b]:

$$\xi_{mix} = w_w \xi_w + (1 - w_w)\xi_D, \tag{1}$$

where subscript (w) and (D) stands for water and DMF, respectively and $w_w = 0.7987$ is the mass fraction of water.

Stock solutions (1.000 and 2.000 mol kg^{-1} of mixed solvent) of each of NaCl, KCl, NaBr, and KBr were prepared by dissolving the appropriate quantities of each of the dried analytical reagent grade (>99.5%) salts in the above mixed solvent. The ΔV_m data at 298.15 K were determined for the six possible binary combinations using a two limbed V-shaped dilatometer in the manner described by Singh and Sharma [25]. The dilatometer was placed in water thermostat and temperature was maintained at 298.15 ± 0.01 K or better by a mercury-in-toluene regulator. The reference mark and the liquid level in the dilatometer capillary were noted after attaining thermal equilibrium with the help of cathetometer (OSAW-India), which could read up to ±0.001 cm. The ΔV_m data for the binary mixtures were calculated from the expression:

$$\Delta V_m = \pi r^2 \Delta h (n_1 + n_2)^{-1}, \tag{2}$$

where πr^2 is the area of the capillary of dilatometer, Δh is the change in the liquid level in the capillary after mixing, r is the radius of the capillary, and n_1 and n_2 are the number of moles of the electrolyte in the solution 1 and 2, respectively.

The capillary of the dilatometer was calibrated from the weight of the mercury column in it. The length of the mercury column in the capillary at various positions was read by a traveling microscope which could read upto ±0.001 cm. The density of mercury (ρ) was taken from the literature [26] at that particular temperature. From the weight (w) of the mercury column of length (l), the area of the capillary (πr^2) was calculated from the expression:

$$\pi r^2 = w(l\rho)^{-1}. \tag{3}$$

The accuracy of the measurement was checked by measuring the molar excess volume of mixing for cyclohexane + benzene mixture at 298.15 K. The results agreed well with the literature [27] values.

3. Review of Pitzer's equations

Pitzer [11,12,28–31] suggested and set up a system of equations for the thermodynamic properties of pure and mixed electrolytes in a generalized form in the well known virial-coefficient theory, where the excess free energy of the system is represented by a combination of long range electrostatic interactions (Debye–Hückel theory) and short range repulsive forces expressed as virial coefficients. The general equation for the excess Gibbs free energy in terms of the measurable coefficients B and θ and the corresponding third virial coefficients C and ψ of a mixture of electrolytes is given by:

$$\begin{aligned} G^{ex}/(n_{\mathrm{w}}RT) = {} & -\frac{4A_{\phi}I}{b}\ln\left(1+b\sqrt{I}\right) + 2\sum_{c}\sum_{a} m_c m_a\left[B_{ca} + \left(\sum_{c} m_c z_c\right)C_{ca}\right] \\ & + \sum_{c}\sum_{c'} m_c m_{c'}\left[\theta_{cc'} + \sum_{a}\frac{m_a\psi_{cc'a}}{2}\right] \\ & + \sum_{a}\sum_{a'} m_a m_{a'}\left[\theta_{aa'} + \sum_{c}\frac{m_c\psi_{aa'c}}{2}\right], \end{aligned} \tag{4}$$

where all the terms have the usual significance as given by Pitzer and Phutela [30,31].

The equation for the excess volume follows from differentiation of equation (4) with respect to pressure:

$$\begin{aligned} V^{ex}/(n_{\mathrm{w}}RT) = {} & \frac{A_V I}{RTb}\ln\left(1+b\sqrt{I}\right) + 2\sum_{c}\sum_{a} m_c m_a\left[B^V_{ca} + \left(\sum_{c} m_c z_c\right)C^V_{ca}\right] \\ & + \sum_{c}\sum_{c'} m_c m_{c'}\left[\theta^V_{cc'} + \sum_{a}\frac{m_a\psi^V_{cc'a}}{2}\right] \\ & + \sum_{a}\sum_{a'} m_a m_{a'}\left[\theta^V_{aa'} + \sum_{c}\frac{m_c\psi^V_{aa'c}}{2}\right] \end{aligned} \tag{5}$$

where A_V is the Debye–Hückel slope for the volume, b is a parameter having constant value of 1.2 $\mathrm{kg}^{1/2}\,\mathrm{mol}^{-1/2}$, n_w is number of kilograms of solvent, m_i and z_i are the molality and charge of a particular cation (c) or anion (a), R is the universal gas constant, 83.1441 $\mathrm{cm}^3\,\mathrm{bar}\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$, B^V and C^V are parameters related to short range interactions of ions of opposite sign, and θ^V and ψ^V are ion interaction parameters related to binary and triplet interactions.

The volume of mixing, ΔV_m, is the difference between the excess volume of the mixture and the excess volumes of the pure electrolytes:

$$\Delta V_m = V^{ex}_{\mathrm{mix}} - Y_1 V^{ex}_1 - (1 - Y_1)V^{ex}_2 \tag{6}$$

where V^{ex}_{mix}, V^{ex}_1, and V^{ex}_2 are the excess volumes of the mixture and pure electrolyte solutions, respectively, and Y is the ionic strength fraction of electrolyte (1), the electrolyte with the higher molecular weight.

In Pitzer's model, for a noncommon ion mixture of a (1 : 1) MX salt and (1 : 1) NY salt, the volume of mixing is obtained by substituting equation (5) into equation (6), yielding:

$$\Delta V_m = n_{\mathrm{w}} RTI^2 Y_1(1 - Y_1)\lfloor 2\theta^V_{\mathrm{MN}} + 2\theta^V_{\mathrm{XY}} + I(\psi^V_{\mathrm{MNX}} + \psi^V_{\mathrm{MNY}} + \psi^V_{\mathrm{MXY}} + \psi^V_{\mathrm{NXY}})\rfloor, \tag{7}$$

where Y_1 is the ionic strength fraction of MX in the solution.

For a common-anion mixture of (1 : 1) MX and (1 : 1) NX salt, equation (7) reduces to:

$$\Delta V_m = n_{\mathrm{w}} RTI^2 Y_1(1 - Y_1)\left[2\theta^V_{\mathrm{MN}} + I\psi^V_{\mathrm{MNX}}\right]. \tag{8}$$

Similarly, for a common-cation mixture of (1 : 1) MX and (1 : 1) MY salt, equation (7) reduces to:

$$\Delta V_m = n_{\mathrm{w}} RTI^2 Y_1(1 - Y_1)\left[2\theta^V_{\mathrm{XY}} + I\psi^V_{\mathrm{MXY}}\right]. \tag{9}$$

Equations (8) and (9) can be fit to the common-ion mixture data to yield the binary $(\theta^V_{\mathrm{MN}}, \theta^V_{\mathrm{XY}})$ and ternary $(\psi^V_{\mathrm{MNX}}, \psi^V_{\mathrm{MXY}})$ ion-interaction parameters. Since Pitzer's equations utilize ΔV_m data in cm^3 per kilogram of solvent, so conversion was performed by multiplying the ΔV_m values of $(\mathrm{cm}^3\,\mathrm{mol}^{-1})$ by the ionic strength $(\mathrm{mol\,kg}^{-1})$.

4. Results and discussion

The molar excess volume of mixing, ΔV_m, for the six possible binary mixtures of NaCl, KCl, NaBr, and KBr measured at 298.15 K, $I = 1.000$ and $2.000\,\mathrm{mol\,kg}^{-1}$ are reported in Table 1 and plotted in Figures 1 and 2. The volume of mixing data can be represented by:

$$\Delta V_m = Y_1 Y_2\left[A + B(Y_1 - Y_2) + C(Y_1 - Y_2)^2\right] \tag{10}$$

where Y_1 and Y_2 are the mole fractions of component 1 and 2 in the mixture, A, B, and C are the disposable parameters, which are evaluated by fitting equation (10) into ΔV_m data by least square method and are reported in Table 2 along with SD (σ), defined by:

$$\sigma_{(\Delta V_m)} = \left[\frac{\Sigma\{(\Delta V_{m(\mathrm{exp.})}) - \Delta V_{m(\mathrm{Calcd\ from\ equation\ 10})}\}^2}{(m - n)}\right]^{1/2} \tag{11}$$

where 'm' is the number of data points and 'n' is the number of variables in equation (10).

The CSR [15,19,20,32,33] suggests that the sum of excess thermodynamic properties for the reciprocal salt pairs of common ion mixings should be equal to the sum of the excess thermodynamic properties of the uncommon ion mixings, i.e.,

$$\frac{1}{2}\sum \square + \varepsilon = \frac{1}{2}\sum \times, \tag{12}$$

where ε is often very small leads to the corollary that $1/2\ \Sigma\square \cong 1/2\ \Sigma\times$. The CSR diagrams are presented in Figure 3. Examination of these diagrams demonstrates that the present ΔV_m data do not follow Young's rule. These deviations in the mixed solvent system indicate that although the rule applies to the pair interactions, it does not seem to be applicable to triplet or higher interactions. These deviations seem to arise from the preferential solvation of the ions and ion clusters in the mixed solvent system.

Friedman and Ramanathan [34] have postulated that excess volumes of mixing are not only affected by an electrostatic contribution but also by overlap of ion solvation shells.

Table 1. Experimental ΔV_m data for six pairs of 1 : 1 electrolyte solutions in aqua-DMF mixed solvent system as a function of mole fraction (Y_1) of solute (1) at 298.15 K and ionic strengths of 1.000 and 2.000 mol kg^{-1}.

Y_1	ΔV_m (cm^3 mol^{-1})	Y_1	ΔV_m (cm^3 mol^{-1})	Y_1	ΔV_m (cm^3 mol^{-1})
At $I = 1.000$ mol kg^{-1}					
KCl (1) + NaCl (2)		KBr (1) + NaCl (2)		KBr (1) + KCl (2)	
0.1372	0.002	0.1713	0.004	0.1012	0.003
0.2241	0.003	0.2194	0.005	0.1824	0.003
0.2808	0.004	0.2860	0.006	0.2251	0.004
0.3985	0.005	0.3191	0.006	0.3372	0.005
0.4504	0.005	0.3986	0.007	0.4172	0.006
0.5048	0.005	0.4852	0.007	0.4896	0.006
0.5687	0.005	0.5356	0.007	0.5652	0.006
0.6371	0.004	0.6016	0.006	0.6580	0.005
0.6572	0.004	0.6943	0.006	0.6841	0.005
0.7594	0.003	0.7430	0.005	0.7841	0.004
0.8001	0.003	0.8678	0.003	0.8576	0.003
0.8576	0.002				
KBr (1) + NaBr (2)		NaBr (1) + KCl (2)		NaBr (1) + NaCl (2)	
0.1187	0.003	0.1622	−0.006	0.1126	0.006
0.2233	0.004	0.2582	−0.008	0.1911	0.009
0.2929	0.004	0.2694	−0.008	0.2486	0.010
0.3582	0.005	0.3371	−0.011	0.2928	0.011
0.4195	0.005	0.3802	−0.011	0.3838	0.013
0.4665	0.006	0.4479	−0.012	0.4569	0.013
0.5090	0.006	0.5162	−0.012	0.5341	0.013
0.5378	0.006	0.5981	−0.012	0.6238	0.012
0.5998	0.005	0.6801	−0.010	0.6941	0.011
0.6856	0.005	0.7574	−0.009	0.7698	0.009
0.7456	0.004	0.8332	−0.006	0.8289	0.008
0.8177	0.004	0.8946	−0.005	0.8688	0.006
At $I = 2.000$ mol kg^{-1}					
KCl (1) + NaCl (2)		NaBr (1) + NaCl (2)		NaBr (1) + KCl (2)	
0.1058	−0.005	0.1403	0.012	0.1273	0.009
0.1586	−0.006	0.2177	0.016	0.2089	0.013
0.2210	−0.007	0.2986	0.021	0.2988	0.016
0.2928	−0.009	0.3981	0.023	0.3706	0.019
0.3931	−0.010	0.4888	0.024	0.4258	0.019
0.4181	−0.010	0.5283	0.025	0.4924	0.020
0.4716	−0.010	0.5892	0.024	0.5456	0.020
0.5406	−0.010	0.6186	0.023	0.6059	0.019
0.6336	−0.009	0.6666	0.020	0.6356	0.019
0.7086	−0.008	0.7506	0.019	0.7276	0.015
0.7586	−0.007	0.8083	0.016	0.7766	0.013
0.8614	−0.005	0.8686	0.011	0.8359	0.011
KBr (1) + KCl (2)		KBr (1) + NaBr (2)		KBr (1) + NaCl (2)	
0.1718	0.010	0.1669	−0.004	0.1242	0.007
0.2298	0.014	0.2586	−0.005	0.1856	0.009
0.2821	0.016	0.3218	−0.005	0.2111	0.011
0.3434	0.018	0.3786	−0.005	0.3076	0.014
0.3983	0.018	0.4488	−0.006	0.3981	0.016
0.4813	0.020	0.4928	−0.006	0.4576	0.016
0.5178	0.019	0.5186	−0.006	0.4978	0.016
0.5703	0.019	0.5888	−0.006	0.5481	0.016
0.6116	0.018	0.6309	−0.005	0.6323	0.015
0.7096	0.016	0.7126	−0.005	0.7076	0.014
0.7589	0.014	0.7783	−0.004	0.7556	0.012
0.8409	0.011	0.8508	−0.004	0.8632	0.009

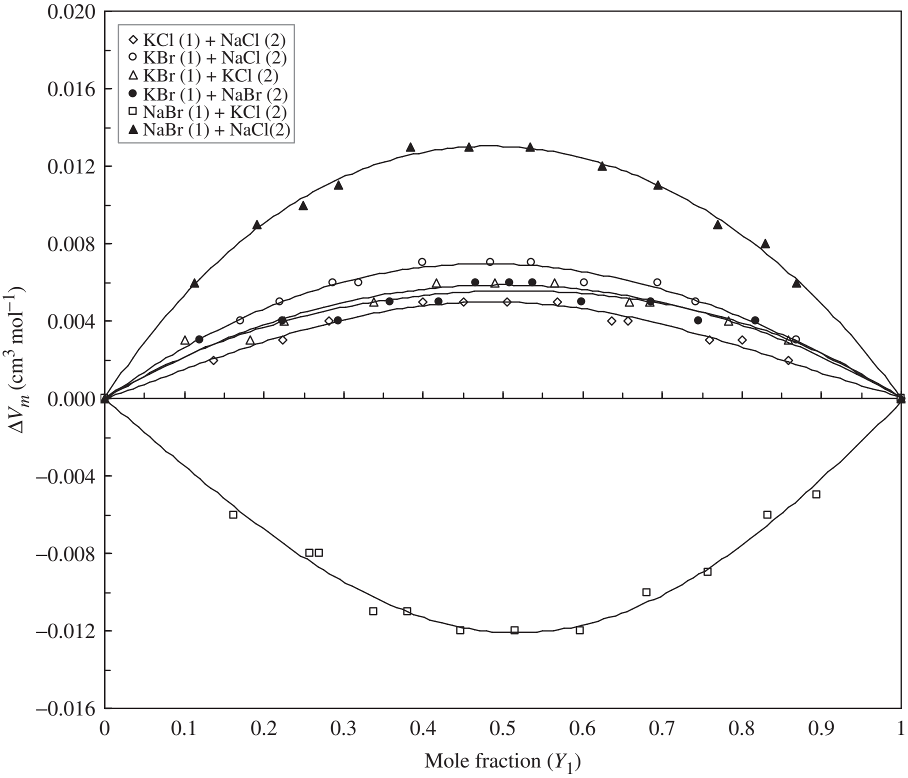


Figure 1. Experimental ΔV_m data in aqua-DMF mixed solvent system at $T = 298.15\,\mathrm{K}$ and $I = 1.000\,\mathrm{mol\,kg^{-1}}$.

The interference between the solvated shells leads to extrusion of the solvent overlap volume as shown in Figure 4. This displaced volume then relaxes to its normal bulk state.

Solvation of an ion in any solvent depends upon several factors like electron pair donation (measured by Gutman donor number), electron pair acceptance (indicated by electron pair acceptance polarity index), structural (categorized by softness, openness, and ordering), and self association characteristics of the solvent molecules. Since the present mixed solvent system contains 20.13% by weight of DMF (i.e., ~2.76 moles of DMF/kg of solvent) and Gutman donor number [24c] of water ($\mathrm{DN} = 75.3\,\mathrm{kJ\,mol^{-1}}$) is different from that of DMF ($\mathrm{DN} = 111.29\,\mathrm{kJ\,mol^{-1}}$), so the solvation of ions of 1 : 1 electrolytes in the water + DMF mixed solvent system would not be the same as in pure water. In addition, $\mathrm{Na^+}$ is a water-structure maker and the water structure-breaking ability [35] of $\mathrm{K^+}$, $\mathrm{Br^-}$, and $\mathrm{Cl^-}$ ions vary as $\mathrm{Cl^-} < \mathrm{K^+} < \mathrm{Br^-}$, so it may be reasonable to assume that solvent overlap volume in the interference between the solvated shells of these ions does not relax in the same manner as that in pure water, hence volume of mixing data in mixed solvent may not be independent of the nature of the common ion as suggested by CSR for the dilute aqueous solutions.

In view of the earlier discussion, we fitted Pitzer's equations to our common ion mixture data and calculated the binary and triplet ion-interaction parameters, which are presented in Table 3. Pitzer's model gave a good representation of data as can be seen in

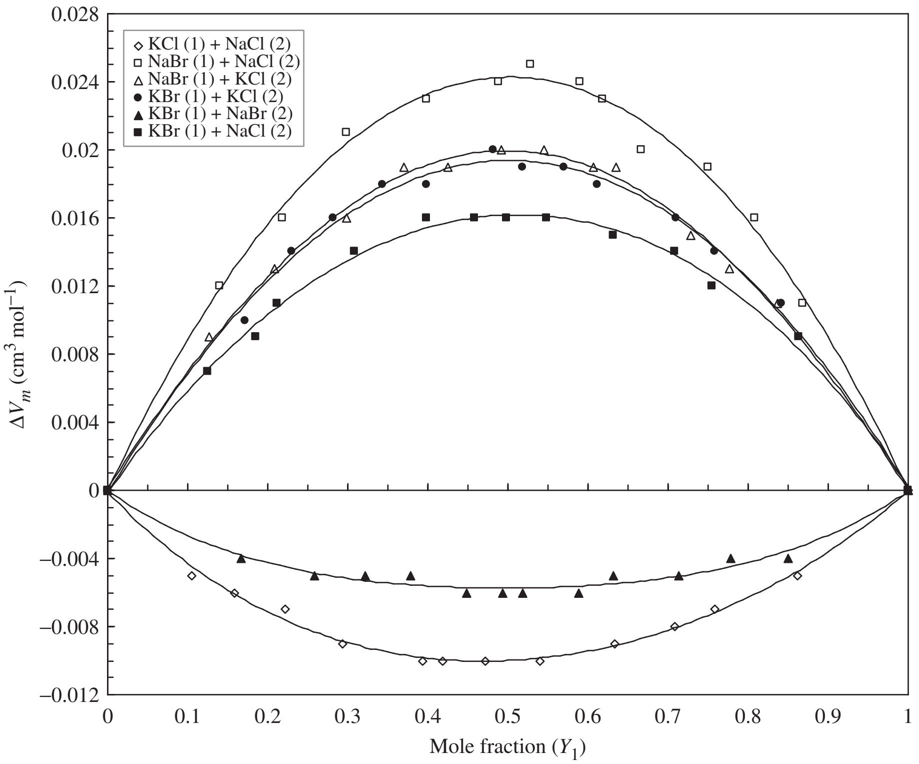
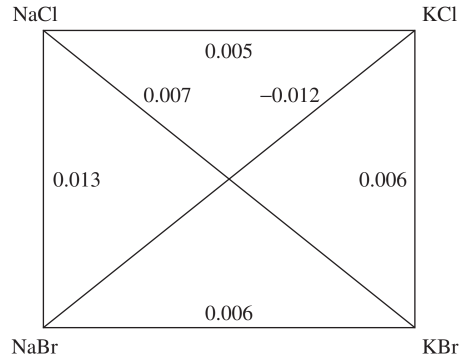


Figure 2. Experimental ΔV_m data in aqua-DMF mixed solvent system at $T = 298.15$ K and $I = 2.000$ mol kg^{-1}.

Table 2. Adjustable parameters of equation (10) for various 1 : 1 electrolyte solutions in aqua-DMF mixed solvent system at 298.15 K and ionic strengths of 1.000 and 2.000 mol kg^{-1}.

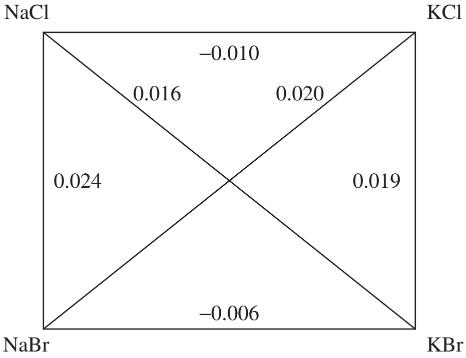
System	A × 10^2	B × 10^3	C × 10^3	$\sigma \times 10^4$
At $I = 1.000$ mol kg^{-1}				
KCl (1) + NaCl (2)	1.990	−1.458	−6.838	2.2
KBr (1) + NaCl (2)	2.778	−2.345	−4.640	2.3
KBr (1) + KCl (2)	2.345	−0.551	7.971	3.6
KBr (1) + KCl (2)	2.222	1.125	4.088	4.3
KBr (1) + NaBr (2)	−4.827	−4.202	9.522	4.9
NaBr (1) + NaCl (2)	5.205	−3.109	7.323	2.7
At $I = 2.000$ mol kg^{-1}				
KCl (1) + NaCl (2)	−3.996	4.441	−5.947	2.8
NaBr (1) + NaCl (2)	9.711	0.859	3.277	7.2
NaBr (1) + KCl (2)	7.979	−0.719	−5.125	4.4
KBr (1) + KCl (2)	7.750	0.725	−0.144	5.2
KBr (1) + NaBr (2)	−2.297	0.211	−9.868	3.7
KBr (1) + NaCl (2)	6.472	3.399	5.197	4.4



(a) I = 1.000 mol kg^{-1} $\frac{1}{2}\Sigma\times = -0.002$

$\frac{1}{2}\Sigma\square = 0.015$

$\varepsilon = -0.017$



(b) I = 2.000 mol kg^{-1} $\frac{1}{2}\Sigma\times = 0.018$

$\frac{1}{2}\Sigma\square = 0.014$

$\varepsilon = 0.004$

Figure 3. Young's cross square rule diagrams for various 1 : 1 electrolyte solutions in aqua-DMF mixed solvent at 298.15 K.

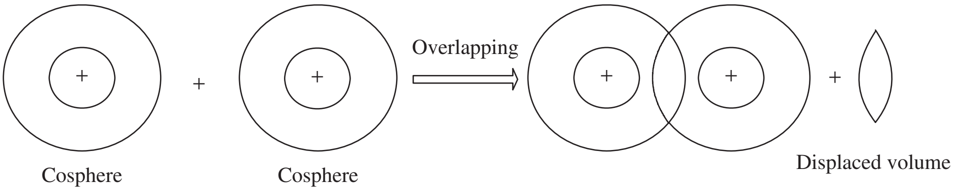


Figure 4. Overlapping of hydration cospheres of two ions giving rise to displaced volume.

Figure 5, wherein the experimental ΔV_m values have been compared with those calculated from equations (8) and (9). From Table 3, it can be seen that the triplet interactions are twice in magnitude and opposite in sign compared to binary interaction parameters at $I = 1.000\,\text{mol kg}^{-1}$ and have same magnitude as well as sign as the binary interaction terms

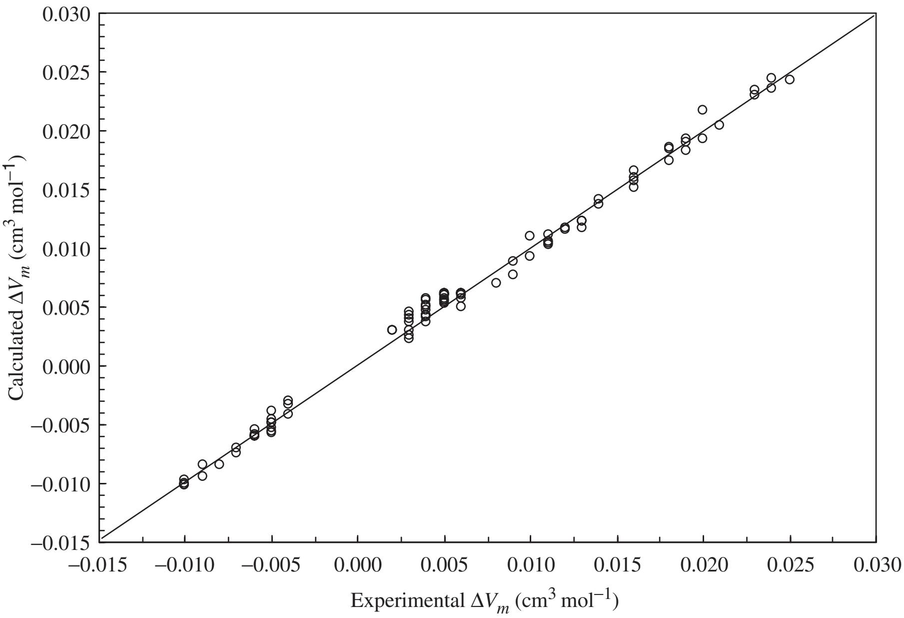


Figure 5. Comparison of experimental ΔV_m data with the values calculated from Pitzer's model.

Table 3. Pitzer's parameters of equations (8) and (9) for various 1 : 1 electrolyte solutions in aqua-DMF mixed solvent system at 298.15 K along with SD (σ).

System	$\theta^V \times 10^2$ (kg mol^{-1} bar^{-1})	$\psi^V \times 10^2$ (kg^2 mol^{-2} bar^{-1})	$\sigma^V \times 10^4$ (cm^3 kg^{-1})
At $I = 1.000$ mol kg^{-1}			
KCl (1) + NaCl (2)	2.509	−4.982	3.2
KBr (1) + KCl (2)	2.511	−4.978	3.5
KBr (1) + NaBr (2)	2.511	−4.978	4.3
NaBr (1) + NaCl (2)	2.525	−4.949	4.2
System	$\theta^V \times 10^7$ (kg mol^{-1} bar^{-1})	$10^4\,\psi^V \times 10^7$ (kg^2 mol^{-2} bar^{-1})	$\sigma^V \times 10^4$ (cm^3 kg^{-1})
At $I = 2.000$ mol kg^{-1}			
KCl (1) + NaCl (2)	−2.060	−2.060	4.7
NaBr (1) + NaCl (2)	4.920	4.920	6.9
KBr (1) + KCl (2)	3.906	3.906	5.0
KBr (1) + NaBr (2)	−1.211	−1.211	4.5

at $I = 2.000$ mol kg^{-1}. Further the magnitude of both binary and triplet interaction terms is smaller at $I = 2.000$ mol kg^{-1} compared to those at $I = 1.000$ mol kg^{-1}.

An examination of the nature of DMF suggests that the interactions of Na$^+$ or K$^+$ ions with DMF occur at its negative pole and the positive pole of DMF is sterically hindered from interaction with Cl$^-$ or Br$^-$ [36]. It makes the interactions of Na$^+$ or K$^+$ ions possible with both water and DMF but restricts the interactions of Cl$^-$ or Br$^-$ ions only to water. Furthermore, as the water around ion is progressively replaced by DMF, the cation–DMF interactions will become more predominant [37]. This suggests that DMF preferentially solvates certain ions and ion clusters in the mixture which has an effect on the interactions of pairs and triplets of ions.

Furthermore, there are 2.76 DMF molecules available to solvate an ion at $I = 1.000\,\mathrm{mol\,kg^{-1}}$ and the difference between $\Sigma\times$ and $\Sigma\square$ is -0.017, however at $I = 2.000\,\mathrm{mol\,kg^{-1}}$, number of DMF molecules available to solvate an ion reduces to half (i.e., 1.38) and the difference between $\Sigma\times$ and $\Sigma\square$ reduced to 0.004. So it can be concluded that more is the number of DMF molecules available to solvate an ion, more is the deviation from CSR. It is also supported by the fact that magnitude of triplet interaction terms is higher at $I = 1.000\,\mathrm{mol\,kg^{-1}}$ compared to those at $I = 2.000\,\mathrm{mol\,kg^{-1}}$.

5. Conclusions

The present study highlights the role of DMF in the process of solvation of the ions in the binary mixtures of 1 : 1 electrolytes in the water + DMF mixed solvent system. The ΔV_m data is dependent on the nature of the common ion and CSR does not hold. Pitzer's model has been successfully extended and utilized to calculate the binary and triplet interaction parameters. Triplet interactions are quite significant in the mixed solvent system. It is observed that more is the number of DMF molecules in the solvation shell of an ion; more is the deviation from CSR.

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