

# Excess Volumes of Mixing of Cl<sup>-</sup> and Br<sup>-</sup> with Na<sup>+</sup> and K<sup>+</sup> at 308.15 K in Aqueous Dioxane Mixed Solvent

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## ABSTRACT

Excess volumes of mixing for six possible binary combinations of solutions of NaCl, KCl, NaBr and KBr have been determined at constant ionic strengths of 1.000 and 2.000 mol kg<sup>-1</sup> at 308.15 K using a dilatometer in a water + 1,4-dioxane mixed solvent system. Pitzer's ion interaction model has been utilized to obtain binary and triplet interaction parameters, i.e.  $\theta^V$  and  $\psi^V$ . The data were also analysed in the light of the Friedman model. Data are dependent on the nature of the common ion and do not support the cross square rule (CSR). The deviation from the CSR increased with increasing ionic strength and is considered to arise from the appreciable contribution of triplet interactions and preferential solvation of the ions and ion-clusters in the mixed solvent system.

## KEYWORDS

Excess volumes of mixing, Friedman model, Pitzer model, cross square rule.

## 1. Introduction

Excess volumes of mixing ( $\Delta V_m$ ) data provide valuable information about ion-ion and ion-solvent interactions, which play an important role in the solution chemistry of solutes.<sup>1-6</sup> Most of the studies on excess thermodynamic functions have been carried out in water. A literature survey reveals that volume of mixing data of electrolyte solutions particularly in mixed solvent systems are lacking. Accurate electrolytic data in aqueous, as well as in mixed solvent systems, are required not only to understand the nature of ion-ion and ion-solvent interactions but also have practical applicability in various fields like geology,<sup>7</sup> oceanography,<sup>8</sup> boiler engineering,<sup>9</sup> water treatment and oil recovery.<sup>10</sup> The concentrated salt solutions are used to provide hydrostatic pressure in the drilling of oil and gas wells. Interest in calculating the various thermodynamic properties of concentrated electrolyte solutions has been created by the development of the ion-interaction model by Pitzer.<sup>11-14</sup> The binary and triplet interaction parameters in Pitzer's model can be calculated from excess thermodynamic property data.

The  $\Delta V_m$  data reflect the changes associated with intermolecular hydrogen bonding caused by the presence of ions. If the intermolecular hydrogen bonding in pure water is disturbed by the addition of any organic co-solvent, capable of forming hydrogen bonds with water, then the hydration of cations and anions is influenced to different extents. Therefore, volume of mixing data in the presence of common and non-common ions in a mixed solvent system should provide not only a deeper insight into the process of solvation, but also a means of checking the applicability of Young's cross square rule. The cross square rule (CSR) is one of the most important generalizations concerning the behaviour of mixed salt solutions, which was first developed by Young.<sup>15</sup> It has been shown to provide good modelling for a number of aqueous electrolytic solutions.<sup>16-20</sup> In our earlier studies<sup>21,22</sup> we have extended this generalization to mixed solvent systems as well. If the relative permittivity of the mixed solvent system does not deviate significantly from that of water,

then it is expected that electrostatic effects arising from it will remain almost the same and excess volume of mixing data in the mixed solvent system would highlight the ion-solvent interactions.

These considerations prompted us to determine the molar excess volumes of mixing of Cl<sup>-</sup> and Br<sup>-</sup> with Na<sup>+</sup> and K<sup>+</sup> in the aqueous dioxane mixed solvent system. 1,4-Dioxane is a dipolar aprotic solvent and was selected because of its strong donor properties due to the presence of two lone pairs of electrons on each of its own two oxygen atoms.

## 2. Experimental

1,4-Dioxane (Merck, AR) was purified by a standard method.<sup>23</sup> 1,4-Dioxane (relative permittivity  $\zeta_D = 2.039$  at 308.15 K)<sup>24</sup> was mixed with an appropriate quantity of doubly distilled water ( $\zeta_w = 74.495$  at 308.15 K)<sup>24</sup> to yield a mixed solvent having a relative permittivity ( $\zeta_{mix}$ ) of 70. It is assumed<sup>24</sup> that:

$$\zeta_{mix} = w_w \zeta_w + (1 - w_w) \zeta_D \quad (1)$$

where subscripts  $w$  and  $D$  represent water and 1,4-dioxane, respectively, and  $w_w$  (0.9383) is the mass fraction of water. Stock solutions (1.000 and 2.000 mol kg<sup>-1</sup> of mixed solvent) 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  $\Delta V_m$  data at 308.15 K were determined for the six possible binary combinations using a two limbed V-shaped dilatometer in the manner described by Singh and Sharma.<sup>25</sup> The dilatometer was placed in a water thermostat and temperature was controlled at 308.15 ± 0.01 K or better using 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 a cathetometer (OSAW, India), which could read to within ± 0.001 cm. The  $\Delta V_m$  data for the binary mixtures were calculated from the expression:

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

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where  $\pi r^2$  is the cross-sectional area of the capillary of the dilatometer,  $\Delta h$  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 numbers of moles of the electrolyte in solutions 1 and 2, respectively.

The capillary of the dilatometer was calibrated using the mass of the mercury column in it. The length of the mercury column in the capillary was read at various positions by a travelling microscope which could read to within  $\pm 0.001$  cm. The density of mercury ( $\rho$ ) was obtained from the literature at the respective temperature.<sup>26</sup> From the mass ( $w$ ) of the mercury column of length  $l$ , the area of the capillary ( $\pi r^2$ ) was calculated from the expression:

$$\pi r^2 = w/l(\rho) \quad (3)$$

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

### 2.1. Pitzer's Model

A system of equations for the thermodynamic properties of electrolytes is developed on the basis of theoretical insights from analysis of the Debye-Hückel model. Guggenheim proposed a system of equations<sup>28</sup> and applied it to dilute solutions which were later modified by Scatchard<sup>29</sup> for concentrated solutions. These equations are very complicated and consequently, it seems worthwhile to seek simpler equations with fewer and more meaningful parameters. Pitzer<sup>11,12,30,31</sup> suggested and set up a system of equations for the thermodynamic properties of pure and mixed electrolytes in a generalized form for the well-known virial coefficient theory, where the excess Gibbs 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 energy in terms of the measurable coefficients  $B$  and  $\theta$  and the corresponding third virial coefficients  $C$  and  $\psi$  of a mixture of electrolytes is given by:

$$\begin{aligned} G^{ex}/(n_w RT) = & -A_\phi (4I/b) \ln(1 + b\sqrt{I}) \\ & + 2 \sum_c \sum_a m_c m_a [B_{ca} + (\sum_c m_c z_c) C_{ca}] \\ & + \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'} + \sum_a m_a \psi_{cc'a} / 2] \\ & + \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'} + \sum_c m_c \psi_{aa'c} / 2] \quad (4) \end{aligned}$$

where all the terms have their usual significance as discussed earlier.<sup>30,31</sup>

The equation for the excess volume follows from differentiation of equation (4) with respect to pressure:<sup>32,33</sup>

$$\begin{aligned} V^{ex}/(n_w RT) = & \frac{A_\phi I}{RTb} \ln(1 + b\sqrt{I}) \\ & + 2 \sum_c \sum_a m_c m_a [B_{ca}^V + (\sum_c m_c z_c) C_{ca}^V] \\ & + \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'}^V + \sum_a m_a \psi_{cc'a}^V / 2] \\ & + \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'}^V + \sum_c m_c \psi_{aa'c}^V / 2] \quad (5) \end{aligned}$$

where  $A_\phi$  is the Debye-Hückel slope for the volume,  $b$  is a parameter having a constant value of  $1.2 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ ,  $n_w$  is the number of kilograms of solvent,  $m_i$  is the molality and  $z_i$  is the charge of a

particular cation (c) or anion (a),  $R$  is the universal gas constant ( $83.1441 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$ ),  $B^V$  and  $C^V$  are parameters related to short range interactions of ions of opposite sign,  $\theta^V$  is the ion-interaction parameter related to binary interactions and  $\psi^V$  is the ion interaction parameter related to triplet interactions.

The volume of mixing ( $\Delta V_m$ ) is equal to the difference between the excess volume of the mixture and the excess volumes of the pure electrolyte solutions, i.e.

$$\Delta V_m = V_{mix}^{ex} - Y_1 V_1^{ex} - (1 - Y_1) V_2^{ex} \quad (6)$$

where  $V_{mix}^{ex}$ ,  $V_1^{ex}$  and  $V_2^{ex}$  are the excess volumes of the mixture and pure electrolyte solutions, respectively, and  $Y_1$  is the ionic strength fraction of electrolyte (1), the electrolyte with the higher molar mass.

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

$$\begin{aligned} \Delta V_m / (n_w RTI^2) = & Y_1 (1 - Y_1) [2\theta_{MN}^V \\ & + 2\theta_{XY}^V + I(\psi_{MNX}^V + \psi_{MNY}^V + \psi_{MXY}^V + \psi_{NXY}^V)] \quad (7) \end{aligned}$$

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 salts, equation (7) reduces to:

$$\Delta V_m / (n_w RTI^2) = Y_1 (1 - Y_1) [2\theta_{MN}^V + I\psi_{MNX}^V] \quad (8)$$

Similarly, a for common-cation mixture, equation (7) reduces to:

$$\Delta V_m / (n_w RTI^2) = Y_1 (1 - Y_1) [2\theta_{XY}^V + I\psi_{MXY}^V] \quad (9)$$

Equations (8) and (9) can be fitted to the common-ion mixture data to yield the binary ( $\theta_{MN}^V$ ,  $\theta_{XY}^V$ ) and ternary ( $\psi_{MNX}^V$ ,  $\psi_{MXY}^V$ ) ion-interaction parameters. Since Pitzer's equations utilize  $\Delta V_m$  data in  $\text{cm}^3 \text{ kg}^{-1}$  of solvent, unit conversion was thus performed by multiplying the  $\Delta V_m$  values in  $\text{cm}^3 \text{ mol}^{-1}$  by the ionic strength in  $\text{mol kg}^{-1}$ .

### 3. Results and Discussion

The molar excess volumes of mixing for the six possible binary mixtures of NaCl, KCl, NaBr and KBr measured at 308.15 K,  $I = 1.000$  and  $2.000 \text{ mol kg}^{-1}$  are reported in Table 1 and plotted in Figs 1 and 2. The  $\Delta V_m$  data are positive at  $I = 1.000 \text{ mol kg}^{-1}$  for all the systems. When the ionic strength was increased to  $2.000 \text{ mol kg}^{-1}$ , the  $\Delta V_m$  values decreased in all systems and became negative in the systems having common anions, i.e. NaCl + KCl and NaBr + KBr.

Friedman's equation<sup>34-36</sup> was fitted to the experimental data, where the molar excess volume of mixing is expressed by:

$$\Delta V_m = I^2 Y_1 (1 - Y_1) [v_0 + v_1 (1 - 2Y_1) + v_2 (1 - 2Y_1)^2] \quad (10)$$

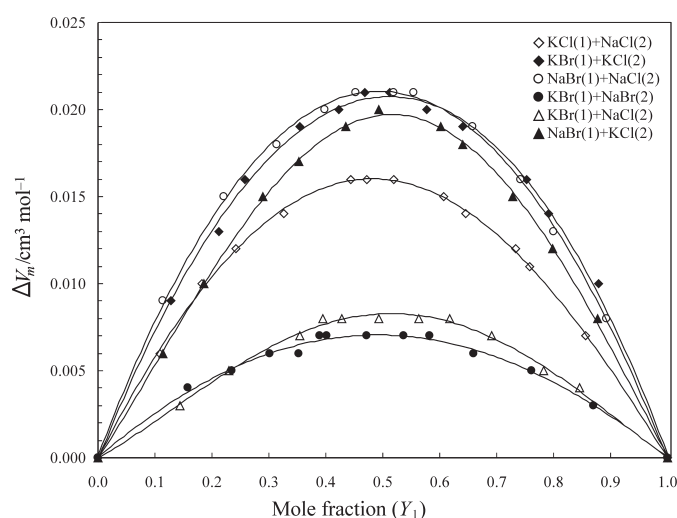
where  $\Delta V_m$  is the volume of mixing in  $\text{cm}^3$  per kg of solvent,  $I$  is the ionic strength of the mixture given by  $I = \frac{1}{2} \sum m_i z_i^2$ , and  $Y_1$  is the mole fraction of the heavier salt. The parameters  $v_0$ ,  $v_1$  and  $v_2$  are mixing parameters related to the pair, triplet and higher interactions, respectively, which were calculated by fitting equation (10) to the  $\Delta V_m$  data using the least squares method and are reported in Table 2 along with the standard deviations ( $\sigma$ ), defined by:

$$\sigma^2 = \frac{\sum [\Delta V_m(\text{exp.}) - \Delta V_m(\text{calc. from eq. (10)})^2]}{m - n} \quad (11)$$

where  $m$  is the number of data points and  $n$  is the number of variables in equation (10). The term  $v_0$  in equation (10) is a measure of the magnitude of the height of the parabola at  $Y_1 =$

**Table 1** Experimental  $\Delta V_m$  data for six pairs of 1:1 electrolyte solutions in aqueous dioxane mixed solvent system as a function of mole fraction ( $Y_1$ ) of electrolyte (1) at 308.15 K.

$Y_1$	$\Delta V_m$ /cm <sup>3</sup> mol <sup>-1</sup>	$Y_1$	$\Delta V_m$ /cm <sup>3</sup> mol <sup>-1</sup>	$Y_1$	$\Delta V_m$ /cm <sup>3</sup> mol <sup>-1</sup>
$I = 1.000 \text{ mol kg}^{-1}$					
KCl (1) + NaCl (2)		KBr (1) + KCl (2)		NaBr (1) + NaCl (2)	
0.1082	0.006	0.1281	0.009	0.1144	0.009
0.1828	0.010	0.2115	0.013	0.2214	0.015
0.2416	0.012	0.2579	0.016	0.3138	0.018
0.3264	0.014	0.3542	0.018	0.3984	0.020
0.4438	0.016	0.4233	0.020	0.4535	0.021
0.4713	0.016	0.4679	0.021	0.5194	0.021
0.5192	0.016	0.5117	0.021	0.5548	0.021
0.6068	0.015	0.5777	0.020	0.6583	0.019
0.6459	0.014	0.6407	0.019	0.7422	0.016
0.7327	0.012	0.7519	0.016	0.7994	0.013
0.7579	0.011	0.7909	0.014	0.8928	0.008
0.8564	0.007	0.8789	0.010		
KBr (1) + NaBr (2)		KBr (1) + NaCl (2)		NaBr (1) + KCl (2)	
0.1586	0.004	0.1436	0.003	0.1136	0.006
0.2349	0.005	0.2299	0.005	0.1868	0.010
0.3012	0.006	0.3539	0.007	0.2901	0.015
0.3524	0.006	0.3943	0.008	0.3534	0.017
0.3901	0.007	0.4288	0.008	0.4357	0.019
0.4022	0.007	0.4932	0.008	0.4932	0.020
0.4712	0.007	0.5628	0.008	0.6012	0.019
0.5366	0.007	0.6180	0.008	0.6399	0.018
0.5817	0.007	0.6914	0.007	0.7288	0.015
0.6601	0.006	0.7819	0.005	0.7986	0.012
0.7612	0.005	0.8462	0.004	0.8777	0.008
0.8709	0.003				
$I = 2.000 \text{ mol kg}^{-1}$					
KCl (1) + NaCl (2)		KBr (1) + KCl (2)		NaBr (1) + NaCl (2)	
0.1516	-0.005	0.2119	0.001	0.1298	0.003
0.2189	-0.006	0.3083	0.001	0.2131	0.004
0.2924	-0.007	0.3716	0.002	0.2828	0.005
0.3488	-0.009	0.4428	0.002	0.3933	0.005
0.4522	-0.009	0.4891	0.002	0.4502	0.005
0.5286	-0.009	0.5544	0.002	0.5085	0.005
0.5732	-0.008	0.5986	0.002	0.5524	0.005
0.6609	-0.007	0.6104	0.002	0.6286	0.004
0.7288	-0.006	0.6959	0.001	0.6808	0.004
0.7921	-0.005	0.8078	0.001	0.7418	0.004
0.8573	-0.004	0.8578	0.001	0.8426	0.003
KBr (1) + NaBr (2)		KBr (1) + NaCl (2)		NaBr (1) + KCl (2)	
0.1412	-0.010	0.1714	0.006	0.1389	0.007
0.1762	-0.013	0.2436	0.007	0.2085	0.010
0.2422	-0.015	0.2968	0.009	0.2928	0.012
0.3026	-0.018	0.3502	0.009	0.3709	0.014
0.3411	-0.020	0.4083	0.010	0.4381	0.015
0.3915	-0.022	0.4706	0.011	0.4933	0.016
0.4715	-0.023	0.5388	0.010	0.4586	0.016
0.5314	-0.022	0.6006	0.009	0.5976	0.016
0.5884	-0.022	0.6814	0.009	0.6608	0.014
0.6902	-0.020	0.7586	0.008	0.6966	0.014
0.7557	-0.018	0.8236	0.006	0.7586	0.011
0.8372	-0.012			0.8208	0.009

**Fig. 1** Experimental  $\Delta V_m$  data in aqueous dioxane mixed solvent at  $I = 1.000 \text{ mol kg}^{-1}$  and  $T = 308.15 \text{ K}$ .

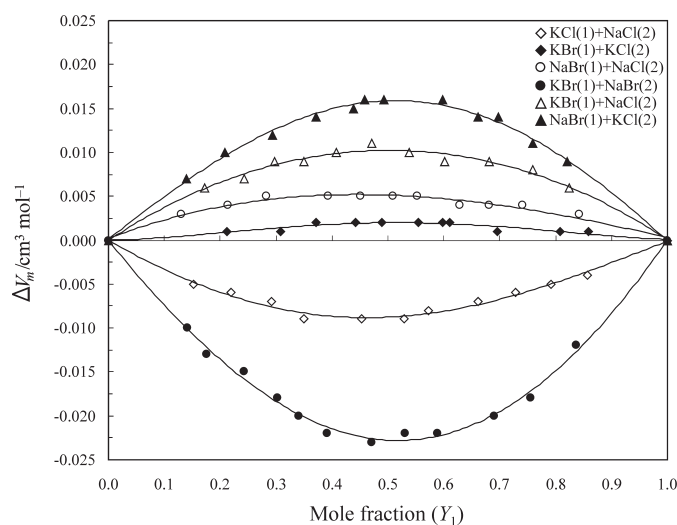
0.5 and  $\nu_1$  is a measure of the asymmetry of the curve. Equation (10) gave a good fit of the data. The comparison of experimental  $\Delta V_m$  values with those calculated using Equation (10) is shown in Fig. 3. An examination of the  $\nu_i$  parameters reveals that  $\nu_0$  is greater than  $\nu_1$  for the systems showing a positive value of volume of mixing and  $\nu_0$  is smaller than  $\nu_1$  for systems showing a negative value of volume of mixing. Furthermore, the greater the value of the excess volume of mixing the greater the value of  $\nu_0$  and *vice versa*.

It has been demonstrated earlier<sup>19,20,37,38</sup> that the excess thermodynamic properties for the common ion mixing equals the sum of the excess thermodynamic properties of the non-common ion mixings. This postulate is referred as CSR and can be expressed as follows:

$$\frac{1}{2} \Sigma \square + \varepsilon = \frac{1}{2} \Sigma \times \quad (12)$$

where  $\Sigma \square$  represents the sum of the volumes of common ion mixing shown along the respective sides of the square in Fig. 4, i.e.,

$$\Sigma \square = \Delta V_m(\text{KCl} + \text{NaCl}) + \Delta V_m(\text{NaBr} + \text{NaCl}) + \Delta V_m(\text{KBr} + \text{KCl}) + \Delta V_m(\text{KBr} + \text{NaBr}) \quad (13)$$

**Fig. 2** Experimental  $\Delta V_m$  data in aqueous dioxane mixed solvent at  $I = 2.000 \text{ mol kg}^{-1}$  and  $T = 308.15 \text{ K}$ .

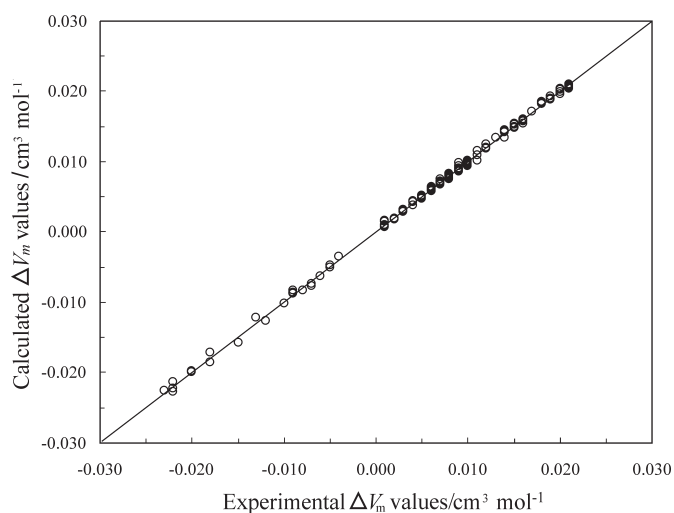


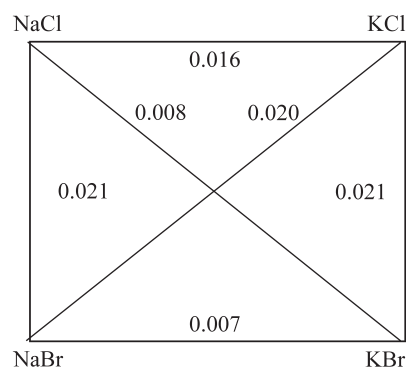
Fig. 3 Comparison of experimental  $\Delta V_m$  values with those calculated from equation (10) of the Friedman model.

and  $\Sigma \times$  represents the sum of the volumes of non-common ion mixing shown along the respective diagonals in Fig. 4, i.e.,

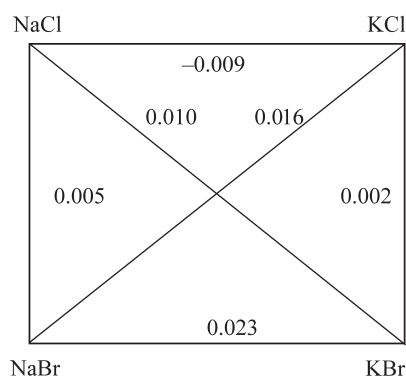
$$\Sigma \times = \Delta V_m(\text{KBr} + \text{NaCl}) + \Delta V_m(\text{NaBr} + \text{KCl}) \quad (14)$$

The term  $\varepsilon$  is often zero or very small in aqueous solutions. The present  $\Delta V_m$  data do not follow this generalization. The CSR diagrams are presented in Fig. 4. Examination of these diagrams demonstrates that the  $\Delta V_m$  data are not independent of the common ion as suggested by CSR. Furthermore, the higher the ionic strength, the greater is the deviation from the cross square rule. These deviations in the mixed solvent system indicate that triplet or higher interactions may be quite appreciable in the mixed solvent system. These deviations seem to arise from the preferential solvation of the ions and ion clusters in the mixed solvent system as reported earlier.<sup>39</sup>

It is postulated that excess thermodynamic properties of mixing are not only affected by an electrostatic contribution but also by overlap of ionic solvation shells.<sup>40</sup> The interference between the solvated shells of the ions leads to the extrusion of the solvent overlap volume. This displaced volume then relaxes to its normal bulk state. The solvation of an ion in any solvent depends upon several factors like electron pair donation (measured by the Gutman donor number<sup>24</sup>), electron pair acceptance (indicated by the electron pair acceptance polarity index,  $E_T$ ), structural (categorized by softness, openness and ordering<sup>41</sup>), and self-association characteristics of the solvent molecules. Our mixed solvent system contains 6.166% by mass of



(a)  $I = 1.000 \text{ mol kg}^{-1}$   
 $\frac{1}{2} \Sigma \times = 0.014$   
 $\frac{1}{2} \Sigma \square = 0.032$   
 $\varepsilon = -0.018$



(b)  $I = 2.000 \text{ mol kg}^{-1}$   
 $\frac{1}{2} \Sigma \times = 0.013$   
 $\frac{1}{2} \Sigma \square = -0.012$   
 $\varepsilon = 0.025$

Fig. 4 Cross square rule diagrams for various 1:1 electrolyte solutions in aqueous dioxane mixed solvent system at 308.15 K at different ionic strengths.

1,4-dioxane, whose Gutman donor number ( $61.923 \text{ kJ mol}^{-1}$ )<sup>24</sup> is smaller than that of water ( $75.312 \text{ kJ mol}^{-1}$ )<sup>24</sup> and moreover the electron pair acceptance polarity index ( $E_T$ ) value of 1,4-dioxane ( $150.624 \text{ kJ mol}^{-1}$ ) is also smaller than that of water ( $264.010 \text{ kJ mol}^{-1}$ ). Therefore, due to the difference in donor numbers and softnesses of the  $\text{Cl}^-$  and  $\text{Br}^-$  ions, it is believed that 1,4-dioxane

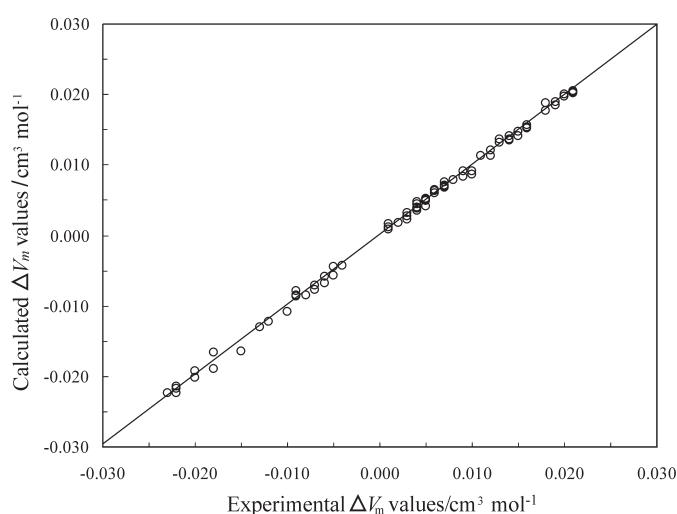
Table 2 Mixing parameters of equation (10) for 1:1 electrolyte solutions in aqueous dioxane mixed solvent system at 308.15 K along with standard deviations.

System	$I/\text{mol kg}^{-1}$	$\nu_0 \times 10^2/\text{cm}^3 \text{ kg mol}^{-2}$	$\nu_1 \times 10^3/\text{cm}^3 \text{ kg mol}^{-2}$	$\nu_2 \times 10^3/\text{cm}^3 \text{ kg mol}^{-2}$	$\sigma^V \times 10^4/\text{cm}^3 \text{ kg}^{-1}$
KCl (1) + NaCl (2)	1.000	6.398	5.00	-5.58	1.8
KBr (1) + KCl (2)	1.000	8.239	-5.15	3.53	4.5
NaBr (1) + NaCl (2)	1.000	8.417	2.30	1.30	2.5
KBr (1) + NaBr (2)	1.000	2.818	1.15	-1.11	2.2
KBr (1) + NaCl (2)	1.000	3.307	-2.76	-11.91	2.1
NaBr (1) + KCl (2)	1.000	7.874	-6.56	-21.85	2.1
KCl (1) + NaCl (2)	2.000	-1.751	-2.91	1.96	4.2
KBr (1) + KCl (2)	2.000	0.397	-0.48	-2.87	2.7
NaBr (1) + NaCl (2)	2.000	0.983	2.05	4.62	2.4
KBr (1) + NaBr (2)	2.000	-4.55	3.38	2.90	6.0
KBr (1) + NaCl (2)	2.000	2.045	-0.18	0.74	4.7
NaBr (1) + KCl (2)	2.000	3.173	-1.92	-4.57	4.4



**Table 3** Ion interaction parameters of Equations (8) and (9) for various 1:1 electrolyte solutions in aqueous dioxane mixed solvent system at 308.15 K along with standard deviations.

System	$\theta^V \times 10^3 / \text{kg mol}^{-1} \text{ bar}^{-1}$	$\psi^V \times 10^3 / \text{kg}^2 \text{ mol}^{-2} \text{ bar}^{-1}$	$\sigma^V \times 10^4 / \text{cm}^3 \text{ kg}^{-1}$
<i>I</i> = 1.000 mol kg <sup>-1</sup>			
KCl (1) + NaCl (2)	25.001	-49.999	5.9
KBr (1) + KCl (2)	25.001	-49.998	6.4
NaBr (1) + NaCl (2)	25.001	-49.998	6.0
KBr (1) + NaBr (2)	25.000	-49.999	2.5
	$\theta^V \times 10^7 / \text{kg mol}^{-1} \text{ bar}^{-1}$	$\psi^V \times 10^7 / \text{kg}^2 \text{ mol}^{-2} \text{ bar}^{-1}$	$\sigma^V \times 10^4 / \text{cm}^3 \text{ kg}^{-1}$
<i>I</i> = 2.000 mol kg <sup>-1</sup>			
KCl (1) + NaCl (2)	1.679	-1.679	6.6
KBr (1) + KCl (2)	3.614	3.614	3.3
NaBr (1) + NaCl (2)	1.007	1.007	5.2
KBr (1) + NaBr (2)	-4.386	-4.386	8.7

**Fig. 5** Comparison of experimental  $\Delta V_m$  values with those calculated from equations (8) and (9) of Pitzer's ion interaction model.

may preferentially solvate certain ions and ion clusters in the mixed solvent system. In addition, because  $\text{Na}^+$  is a water structure-maker and the water structure-breaking ability<sup>42</sup> of  $\text{K}^+$ ,  $\text{Br}^-$  and  $\text{Cl}^-$  ions vary as  $\text{Cl}^- < \text{K}^+ < \text{Br}^-$ , 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 solvents may not be independent of the nature of the common ion.

In view of the above, 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, along with the standard deviations. From Table 3, it can be seen that the triplet interactions have higher magnitude and opposite sign, at an ionic strength of 1.000 mol kg<sup>-1</sup> and the same magnitude and sign at an ionic strength of 2.000 mol kg<sup>-1</sup>, compared with the binary interaction terms. Furthermore, the magnitude of both the binary and triplet interaction terms is much smaller at *I* = 2.000 mol kg<sup>-1</sup> compared with those at *I* = 1.000 mol kg<sup>-1</sup>. Generally, triplet interactions are negligible compared with binary interactions in pure water. Pitzer's model gave a good representation of the data as can be seen from Fig. 5, in which the experimental  $\Delta V_m$  values have been compared with those calculated from equations (8) and (9).

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