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Excess Enthalpies of Mixing of Binary Mixtures of NaCl, KCl, NaBr and KBr in Mixed Ternary Solvent Systems at 298.15 K

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ABSTRACT

Excess enthalpies of mixing for six possible binary combinations of solutions of NaCl, KCl, NaBr and KBr in mixed ternary solvents composed of formamide, 1,4-dioxane and water have been determined using a flow microcalorimeter at constant ionic strengths of 0.500 and 1.000 mol kg^{-1} at 298.15 K. Unlike the case of water, the data do not support Young's cross square rule. Pitzer's virial coefficient theory has been utilized to obtain binary and ternary interaction parameters, i.e. θ^H and ψ^H. The data were also analysed in terms of the Friedman model and it was found that interactions between solvated ions are dictated not only by coulombic interactions but also by appreciable asymmetric effects.

KEYWORDS

Enthalpy of mixing, ternary solvents, Pitzer theory, Friedman model, cross square rule.

1. Introduction

Enthalpy of mixing is a sensitive tool, which provides valuable information about ion–ion and ion–solvent interactions. These interactions play a key role in the solution chemistry of solutes.[1–6] Most thermodynamic studies have been carried out in water (*w*), which has a well-defined hydrogen-bonded structure. A literature survey reveals that enthalpy of mixing data of electrolytic solutions in mixed solvent systems are lacking. Accurate electrolytic data in aqueous as well as mixed solvent systems are required to understand not only the nature of ion–ion and ion–solvent interactions but also their practical applicability in various fields like geology,[7] oceanography,[8] boiler engineering,[9] water treatment and oil recovery.[10] Concentrated solutions of electrolytes are involved in many industrial processes, such as to provide hydrostatic pressure in the drilling of oil and gas wells. NaCl, NaBr, KCl and KBr are common salts in many natural and industrial waters and their thermodynamic properties are of practical interest for industrial and geochemical applications.

Interest in calculating various thermodynamic properties of concentrated electrolytic solutions has grown by the development of virial coefficient theory or the ion interaction model by Pitzer,[11–16] where the excess Gibbs energy of the system is represented by a combination of long-range attractive forces and short-range repulsive forces. The excess Gibbs energy for a solution containing n_w kg of solvent and n_i, n_j, n_k moles of solute species *i, j, k* is given[11,15] by

$$G^{ex}/(n_w RT) = f(I) + \sum_i \sum_j n_i n_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k n_i i_j n_k \mu_{ijk} \qquad (1)$$

where *f*(*I*) expresses the effect of the long-range electrostatic forces, $\lambda_{ij}(I)$ is the second virial coefficient for pair-wise interaction between ions *i* and *j* and is a function of the ionic strength (*I*), μ_{ijk} is the third virial coefficient for ternary interaction and its dependence on ionic strength is ignored. Equation (1) can be expressed in terms of the measurable coefficients *B* and θ and the corresponding third virial coefficients *C* and ψ as[15,17]

$$\begin{aligned} G^{ex}/(n_w RT) = {} & f(I) + 2\sum_c \sum_a m_c m_a \left[B_{ca} + \left(\sum_c m_c z_c\right) C_{ca}\right] \\ & + \sum_c \sum_{c'} m_c m_{c'} \left[\theta_{cc'} + \sum_a m_a \psi_{cc'a}/2\right] \\ & + \sum_a \sum_{a'} m_a m_{a'} \left[\theta_{aa'} + \sum_c m_c \psi_{aa'c}/2\right] \end{aligned} \qquad (2)$$

Here all the terms have their usual significance.[11,15–17] The term *f*(*I*) in Equations (1) and (2) can be expressed in terms of the Debye-Hückel parameter, A_ϕ, and a parameter *b* (having a constant value of 1.2 kg$^{1/2}$ mol$^{-1/2}$) as follows

$$f(I) = -A_\phi \left(4I/b\right) \ln(1 + bI^{1/2}) \qquad (3)$$

Differentiation of Equation (2) with respect to temperature yields:

$$\begin{aligned} H^{ex}/(n_w RT^2) = {} & \frac{A_H I}{RT^2 b} \ln\left(1 + b\sqrt{I}\right) \\ & - 2\sum_c \sum_a m_c m_a \left[B^H_{ca} + \left(\sum_c m_c z_c\right) C^H_{ca}\right] \\ & - \sum_c \sum_{c'} m_c m_{c'} \left[\theta^H_{cc'} + \sum_a m_a \psi^H_{cc'a}/2\right] \\ & - \sum_a \sum_{a'} m_a m_{a'} \left[\theta^H_{aa'} + \sum_c m_c \psi^H_{aa'c}/2\right] \end{aligned} \qquad (4)$$

Here A_H is the Debye-Hückel slope for the enthalpy. The second virial coefficients, i.e. *B*, B^H, θ and θ^H in Equations (2) and (4), have an ionic strength dependence as shown elsewhere.[15,17]

The enthalpy of mixing (ΔH_m) is the difference between the excess enthalpy of the mixture and the excess enthalpies of the pure electrolytes

$$\Delta H_m = H^{ex}_{mix} - Y_1 H^{ex}_1 - \left(1 - Y_1\right) H^{ex}_2 \qquad (5)$$

where H^{ex}_{mix}, H^{ex}_1 and H^{ex}_2 are the excess enthalpies 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 (1:1) MX

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and (1:1) NY salts, the excess enthalpy of mixing is obtained by substituting Equation (4) into Equation (5), yielding

$$\Delta H_m / \left(n_w RT^2 I^2\right) = Y_1\left(1 - Y_1\right)\left[2\theta^H_{MN} + 2\theta^H_{XY} + I(\psi^H_{MNX} + \psi^H_{MNY} + \psi^H_{MXY} + \psi^H_{NXY})\right] \qquad (6)$$

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 (6) reduces to

$$\Delta H_m / \left(n_w RT^2 I^2\right) = Y_1(1 - Y_1)\left[2\theta^H_{MN} + I\psi^H_{MNX}\right] \qquad (7)$$

Similarly, for a common-cation mixture of (1:1) MX and (1:1) MY salts

$$\Delta H_m / \left(n_w RT^2 I^2\right) = Y_1\left(1 - Y_1\right)\left[2\theta^H_{XY} + I\psi^H_{MXY}\right] \qquad (8)$$

Equations (7) and (8) can be fitted to the common-ion mixture data to yield the binary, $(\theta^H_{MN}, \theta^H_{XY})$ and ternary $(\psi^H_{MNX}, \psi^H_{MXY})$ ion interaction parameters.

The cross square rule (CSR), which was first developed by Young,[18] is yet another important generalization concerning the behaviour of mixed salt solutions. It has been reported to hold good for a number of aqueous electrolyte solutions.[19–23]

Enthalpy of mixing reflects the changes associated with intermolecular hydrogen bonding caused by the presence of ions. If the hydrogen bonding in pure water is disturbed by the addition of an organic solvent, then the hydration of cations and anions will be influenced to different extents. So enthalpy of mixing data in the presence of common and non-common ions in a mixed solvent should provide not only a deeper insight into the process of solvation, but also a help in checking the applicability of the CSR. If the relative permittivity of the mixed solvent does not deviate significantly from that of water, then it is expected that electrostatic affects arising from it will remain almost the same and the enthalpy of mixing data in the mixed solvent would highlight the ion-solvent interactions.

In view of the above, we measured the excess enthalpies of mixing of binary combinations of NaCl, NaBr, KCl and KBr solutions in mixed ternary solvents containing formamide (*F*) + 1,4-dioxane (*D*) + water (*w*). The relative permittivity of the mixed ternary solvent was fixed at 70 at 298.15 K. Formamide and 1,4-dioxane were selected because of their strong electron-donor properties and abilities to perturb the hydrogen bonding in water.

2. Experimental

Formamide (Ranbaxy, AR)[24a] and 1,4-dioxane (Merck, AR)[24b] were purified by standard procedures. The densities of the purified organic solvents are reported and compared with literature values in Table 1. Formamide (ε_F = 111.0 at 298.15 K) and 1,4-dioxane (ε_D = 2.209 at 298.15 K) were mixed with an appropriate quantity of doubly distilled water (ε_w = 78.39 at 298.15 K)[25a] to yield a mixed solvent system having ε_{mix} of 70. It is assumed[25b] that

$$\varepsilon_{mix} = \sum_a^b w_a \varepsilon_a \qquad (9)$$

The mass fractions of formamide, 1,4-dioxane and water in the mixed ternary solvent are $w_F = 0.273$, $w_D = 0.227$ and $w_w = 0.500$, respectively.

Stock solutions (0.500 and 1.000 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 grade salts in the above mixed solvent. The ΔH_m data at 298.15 K were determined for the six possible binary combinations using a flow microcalorimeter (LKB-2107, Sweden), which consists of a mixing cell, a reference cell, a thermostatic water bath and a data acquisition unit. The thermostatic water bath controls the temperature of the heat sink where both the mixing cell and the reference cell are located. The temperature of the instrument was maintained at 298.15 ± 0.01 K. Two identical perfusor pumps (Braun, Melsungen, Germany) and gas-tight Hamilton syringes were used to pump the solutions through the microcalorimeter. The number of moles and mole fraction of each component in the mixed stream were calculated from the densities and volumetric flow rates of the components pumped into the mixing cell. Details of the apparatus and the operating procedure have been reported elsewhere.[26] The ΔH_m data were calculated from

Table 1 Comparison of experimental and literature densities of pure solvents.

Solvent	Density /kg m^{-3}	
	Experimental	Literature
1,4-Dioxane	1027.83	1027.92 [26]
Formamide	1129.22	1129.18 [27]

$$\Delta H_m = i^2 R \frac{\Delta h_1}{\Delta h_2}(n_1 + n_2)^{-1} \qquad (10)$$

where *i* is the electrical current (amperes), *R* is the resistance of the microcalorimeter heater (ohms), Δh_1 and Δh_2 are the baseline shifts on mixing and in the calibration experiments respectively on achieving the steady state, and n_1 and n_2 are the numbers of moles of the electrolytes 1 and 2, respectively. The accuracy of the measurements was checked by measuring the enthalpy of mixing for benzene (1) + carbon tetrachloride (2) mixtures at 298.15 K. The results agreed with literature[27] values within ±2 J mol^{-1}.

3. Results and Discussion

Excess enthalpies of mixing for the six possible binary mixtures of NaCl, KCl, NaBr and KBr were measured at 298.15 K and at ionic strengths of 0.500 and 1.000 mol kg^{-1}. The ΔH_m data are reported in Table 2 and are plotted against the mole fraction of electrolyte 1 (Y_1) in Figs 1 and 2. The ΔH_m values were found to be negative at an ionic strength of 0.500 mol kg^{-1} for all the systems. When the ionic strength was increased to 1.000 mol kg^{-1}, the ΔH_m values increased and became positive. The excess enthalpy of mixing (ΔH_m) in terms of the Friedman model[28,29] can be expressed as follows:

$$\Delta H_m = RTI^2 Y_1\left(1 - Y_1\right)\left[h_0 + h_1\left(1 - 2Y_1\right) + ...\right] \qquad (11)$$

The mixing parameters related to the binary and ternary interactions, i.e. h_0 and h_1, were calculated by fitting the ΔH_m data to Equation (11) using the least squares method and are reported in Table 3. The parameter RTh_0 is a measure of the height of the parabola at Y_1 = 0.5 and RTh_1 is a measure of the asymmetry of the curve. An examination of the mixing parameters reveals that h_0 is greater than h_1 for the systems showing positive values of the enthalpy of mixing and h_0 is smaller than h_1 for systems showing negative values of the enthalpy of mixing. Furthermore, the greater the value of the enthalpy of mixing, the greater is the value of h_0 and *vice versa.*

Unlike the results obtained in pure water[22,23] at 298.15 K, the present ΔH_m data are dependent on the common ion and do not follow the well-known cross square rule (CSR).[18] It has been demonstrated earlier[22,23,30,31] that the sum of the excess thermodynamic properties for the common ion mixings equals the sum of

Table 2 Experimental ΔH_m data (J mol^{-1}) for six pairs of univalent electrolyte solutions in formamide + dioxane + water mixed ternary solvents as a function of mole fraction (Y_1) of solute 1 at 298.15 K.

Y_1	ΔH_m	Y_1	ΔH_m	Y_1	ΔH_m
		I = 0.500 mol kg^{-1}			
KBr (1) + KCl (2)		KBr (1) + NaCl (2)		KCl (1) + NaCl (2)	
0.1720	–33	0.1323	–13	0.1216	–32
0.2285	–45	0.2011	–15	0.1918	–52
0.3081	–53	0.2442	–21	0.2501	–61
0.3438	–63	0.3494	–24	0.3535	–82
0.4390	–67	0.4342	–25	0.4385	–97
0.4944	–71	0.4782	–26	0.5108	–101
0.5514	–77	0.5512	–23	0.5942	–101
0.6502	–72	0.6411	–19	0.6520	–98
0.6968	–73	0.6811	–19	0.7495	–86
0.7506	–66	0.7410	–17	0.8426	–65
0.8183	–56	0.8184	–13	0.8936	–49
0.8898	–37				
KBr (1) + NaBr (2)		NaBr (1) + NaCl (2)		NaBr (1) + KCl (2)	
0.1412	–21	0.1686	–17	0.2441	–19
0.2191	–25	0.251	–20	0.3293	–23
0.2510	–31	0.3394	–23	0.4384	–23
0.3441	–32	0.4436	–28	0.5013	–25
0.4384	–37	0.4949	–29	0.5533	–24
0.4984	–40	0.5536	–27	0.6586	–23
0.5455	–39	0.6509	–25	0.7494	–20
0.6514	–32	0.7091	–21	0.8082	–17
0.6989	–31	0.7388	–23	0.8786	–12
0.7616	–28	0.8182	–17		
0.8412	–20				
		I = 1.000 mol kg^{-1}			
KBr (1) + KCl (2)		NaBr (1) + NaCl (2)		KBr (1) + NaCl (2)	
0.1093	22	0.1208	10	0.1128	19
0.1582	36	0.2118	14	0.1818	28
0.2487	45	0.2480	18	0.2467	35
0.3348	56	0.3455	19	0.3438	42
0.3958	59	0.4418	24	0.3588	46
0.4386	62	0.4974	25	0.4401	49
0.4972	62	0.5530	24	0.4956	51
0.5586	58	0.5952	24	0.5512	49
0.6483	56	0.6498	20	0.6482	45
0.7476	44	0.7480	18	0.7467	38
0.8185	32	0.8088	14	0.8180	32
0.8677	26	0.8702	12	0.8592	26
0.9198	18				
NaBr (1) + KCl (2)		KBr (1) + NaBr (2)		KCl (1) + NaCl (2)	
0.1238	17	0.0808	28	0.1578	74
0.2079	26	0.1686	44	0.2474	106
0.2507	33	0.2487	59	0.3302	131
0.3486	38	0.3318	70	0.3975	142
0.4453	41	0.3832	71	0.4388	149
0.5009	42	0.4577	72	0.4965	150
0.5564	42	0.4982	74	0.5371	149
0.6530	34	0.5388	68	0.6263	141
0.6932	34	0.6651	59	0.6635	130
0.7504	28	0.7433	52	0.7474	106
0.8577	17	0.7918	42	0.8191	83
		0.8613	32	0.8823	57

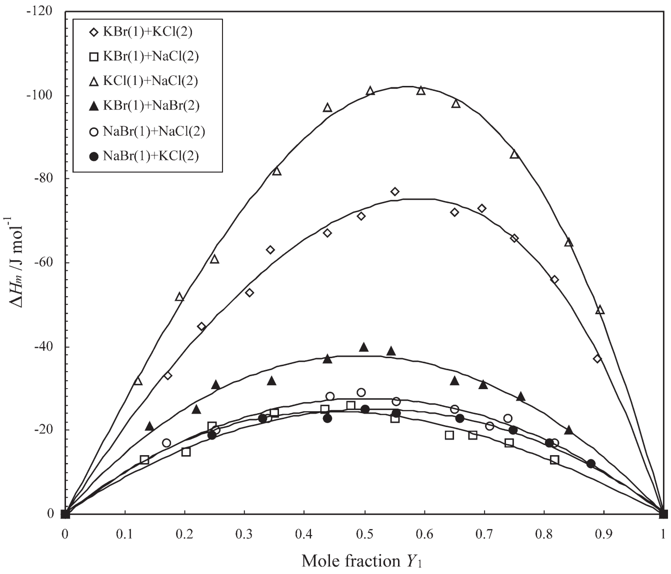

Figure 1 Experimental ΔH_m data in formamide + dioxane + water mixed solvent systems at I = 0.500 mol kg^{-1}: ◇ KBr (1) + KCl (2), □ KBr (1) + NaCl (2), △ KCl (1) + NaCl (2), ▲ KBr (1) + NaBr (2), ○ NaBr (1) + NaCl (2), ● NaBr(1) + KCl (2) at 298.15 K.

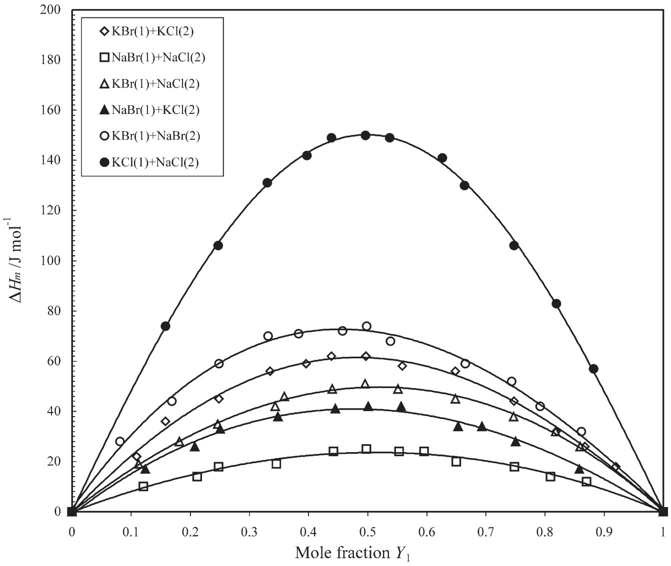

Figure 2 Experimental ΔH_m data in formamide + dioxane + water mixed solvent systems at I = 1.000 mol kg^{-1}: ◇ KBr (1) + KCl (2), □ NaBr (1) + NaCl (2), △ KBr (1) + NaCl (2), ▲ NaBr (1) + KCl (2), ○ KBr (1) + NaBr (2), ● KCl (1) + NaCl (2) at 298.15 K.

the excess thermodynamic properties of the non-common ion mixings. This generalization is termed the CSR and can be expressed as[23]

$$\tfrac{1}{2}\Sigma\square + \alpha = \tfrac{1}{2}\Sigma X \tag{12}$$

where $\Sigma\square$ represents the sum of the excess enthalpies of common ion mixings shown along the respective sides of the square in Fig. 3, i.e.

$$\Sigma\square = \Delta H_m(\mathrm{KCl + NaCl}) + \Delta H_m(\mathrm{NaBr + NaCl}) + \Delta H_m(\mathrm{KBr + KCl}) + \Delta H_m(\mathrm{KBr + NaBr}) \tag{13}$$

and ΣX represents the sum of the excess enthalpies of non-common ion mixings shown along the respective diagonals in Fig. 3, i.e.

$$\Sigma X = \Delta H_m(\mathrm{KBr + NaCl}) + \Delta H_m(\mathrm{NaBr + KCl}) \tag{14}$$

The term α is often zero or very small in aqueous solutions.[23]

The CSR diagrams in the mixed ternary solvents are presented and compared with that of water in Fig. 3. Examination of these diagrams demonstrates that the present results deviate from the

CSR. Further, the higher the ionic strength, the greater is the deviation from the CSR. These deviations indicate that ternary or higher interactions may be quite significant in the mixed solvent. Similar differences from the results of Wu *et al.*[22,23] were also seen in our earlier studies.[17,32,33]

Table 3 Mixing parameters of Equation (11) for various electrolyte solutions in formamide + dioxane + water mixed ternary solvent systems at 298.15 K.

System	I /mol kg^{-1}	h_0 /kg^2 mol^{-2}	h_1 /kg^2 mol^{-2}	σ^H /J mol^{-1}
KBr (1) + KCl (2)	0.500	–0.4785	0.1665	2
KBr (1) + NaCl (2)	0.500	–0.1562	–0.0344	1
KCl (1) + NaCl (2)	0.500	–0.6443	0.2027	1
KBr (1) + NaBr (2)	0.500	–0.2454	–0.0105	2
NaBr (1) + NaCl (2)	0.500	–0.1787	0.0021	1
NaBr (1) + KCl (2)	0.500	–0.1626	0.0104	1
KBr (1) + KCl (2)	1.000	0.0981	0.0070	2
NaBr (1) + NaCl (2)	1.000	0.0380	–0.0021	1
KBr (1) + NaCl (2)	1.000	0.0800	–0.0062	1
NaBr (1) + KCl (2)	1.000	0.0656	0.0060	1
KBr (1) + NaBr (2)	1.000	0.1167	0.0218	2
KCl (1) + NaCl (2)	1.000	0.2375	0.0040	3

Table 4 Pitzer's parameters of Equations (7) and (8) for various electrolyte solutions having common ions in formamide + dioxane + water mixed ternary solvent systems at 298.15 K and their standard deviations (σ^H).

System	I /mol kg^{-1}	θ^H /kg mol^{-1} K^{-1}	ψ^H /kg^2 mol^{-2} K^{-1}	σ^H /J kg^{-1}
KBr (1) + KCl (2)	0.500	0.1020	–0.5254	8
KCl (1) + NaCl (2)	0.500	0.1070	–0.5854	9
KBr (1) + NaBr (2)	0.500	0.0948	–0.4392	2
NaBr (1) + NaCl (2)	0.500	0.0928	–0.4148	1
KBr (1) + KCl (2)	1.000	0.0030	0.0060	2
NaBr (1) + NaCl (2)	1.000	0.00115	0.0023	1
KBr (1) + NaBr (2)	1.000	0.0036	0.0071	4
KCl (1) + NaCl (2)	1.000	0.0072	0.0145	3

Friedman and Ramanathan[34] have postulated that excess enthalpies of mixing are not only affected by an electrostatic contribution but also by overlap of ionic solvation shells. The interference between the solvation shells leads to extrusion of the solvent overlap volume that relaxes to its normal bulk state. This relaxation phenomenon is different in aqueous and mixed solvent systems.

Solvation of an ion in any solvent depends upon several factors like electron pair donation (measured by the Gutman donor number),[25c] electron pair acceptance (indicated by the electron pair acceptance polarity index),[35] structural (categorized by softness, openness, and orderdness),[36] and self-association characteristics of the solvent molecules. Our mixed solvent system contains 27.3 and 22.7% by mass of formamide and dioxane respectively. Further the Gutman donor number (DN) of water (75.3 kJ mol^{-1}) is different from that of formamide (150.6 kJ mol^{-1}) and dioxane (61.9 kJ mol^{-1}).[25c] The electron pair acceptance (E_T) value of water (264.0 kJ mol^{-1}) is also different from those of formamide (236.8 kJ mol^{-1}) and 1,4-dioxane (150.6 kJ mol^{-1}).[25d] Therefore it is envisaged that the interactions of cations or anions with organic solvents will influence the ion–water interactions and the ΔH_m data of the present electrolytes in mixed ternary solvents would correspond neither with that in water nor with each other in magnitude or in sign. This is also supported by the different water structure-orienting effects of Na^+, K^+, Br^- and Cl^- ions; Na^+ is a water structure-maker while the water structure-breaking ability[37] of K^+, Br^- and Cl^- ions varies as $Cl^- < K^+ < Br^-$. Hence, 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, thus enthalpy of mixing data in a mixed solvent may not be independent of the nature of the common ion (unlike that in water).

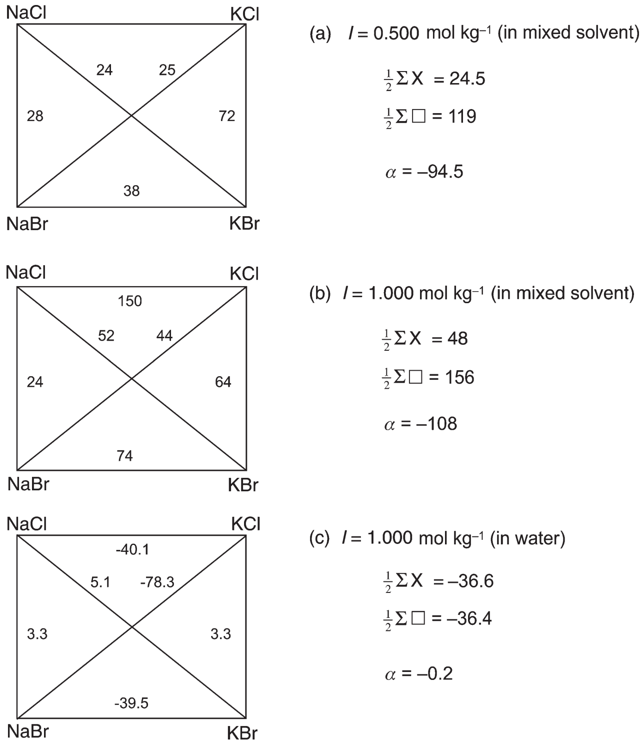

Figure 3 Cross square rule diagrams for various univalent electrolyte solutions in formamide + dioxane + water mixed ternary solvents and water at 298.15 K.

In view of the above, we fitted Pitzer's equations to our common ion mixture data and calculated the binary and ternary ion interaction parameters, which are presented in Table 4. From Table 4, it can be seen that the ternary interaction terms are quite high in magnitude and cannot be ignored. The deviations from the CSR in the mixed solvent systems indicate that although the rule applies to the binary interactions, it does not seem to be applicable to ternary or higher interactions.

4. Conclusions

The present study highlights the role of organic solvents in the process of solvation of the ions in binary mixtures of 1:1 electrolytes in the formamide + 1,4-dioxane + water mixed solvent system. The data differ appreciably from the corresponding data in water and Young's cross square rule does not hold valid. Pitzer's virial coefficient theory and Friedman's model have been successfully applied to represent the ΔH_m data. It was observed that ternary interactions are quite significant in magnitude.

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