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Enthalpy of mixing of univalent electrolyte solutions at different ionic strengths at 308.15 K in aqua–DMF mixed solvent system

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Abstract

Excess enthalpies of mixing for six possible binary combinations of solutions of NaCl, KCl, NaBr and KBr have been determined as a function of ionic strength. The experiments were performed at constant ionic strengths of 1.000 and 2.000 mol kg^{-1} at 308.15 K using flow micro calorimeter in water + *N*,*N*-dimethylformamide mixed solvent system. Data do not support Young's cross square rule. Pitzer's ion interaction model has been utilized to obtain binary and triplet interaction parameters i.e. Θ^{H} and ψ^{H}. The data were also analyzed in the light of Friedman model and it is suggested that interactions between solvated ions are dictated not only by coulombic interactions but also by appreciable asymmetric effects. The deviation from Young's cross square rule is considered to arise from significant contribution of triplet interactions and preferential solvation of the ions and ion-clusters, due to incorporation of organic co-solvent in the solvation shell.

Keywords: Enthalpy of mixing; Dimethylformamide; Pitzer model; Friedman model; Cross square rule

1. Introduction

Ion–ion and ion–solvent interactions play an important role in the solution chemistry of solutes [1–6]. Enthalpy of mixing (ΔH_m) is a sensitive tool, which provides valuable information about these interactions. Most of such studies have been carried out in water (W), which has well studied hydrogen bonded structure. Literature survey reveals that ΔH_m data of electrolyte 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" or "ion–interaction model" by Pitzer [11–14]. The binary and triplet interaction parameters in the Pitzer ion-interaction model can be calculated from the excess thermodynamic property data.

Molar excess enthalpy 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 perturbed 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 enthalpy 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 rule. Cross square rule (CSR) is one of the most important generalizations concerning the behavior of mixed salt solutions, which was first developed by Young [15]. This so called CSR has been shown to hold good for

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a number of aqueous electrolytic 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 electrostatic affects arising from it will almost remain same and ΔH_m data in the mixed solvent system would highlight the ion–solvent interactions.

These considerations prompted us to determine the molar excess enthalpy of mixing (ΔH_m) of Cl^- and Br^- of Na^+ and K^+ in water + *N*,*N*-dimethylformamide mixed solvent system. The proportion of dimethylformamide (DMF) in the mixed solvent system was adjusted in such a way that the dielectric constant of the resulting mixture was nearly the same as that of water at 308.15 K. DMF is a dipolar aprotic solvent and was selected because of its strong donor properties due to presence of two electron donating methyl groups attached to the nitrogen atom, which again bears a lone pair of electrons. It is very effective candidate in influencing the hydrogen bonding in water.

2. Materials and method

DMF (Ranbaxy, AR) was purified by a standard procedure [23]. Deionized water was mixed with some NaOH and a pinch of solid $KMnO_4$ and then doubly distilled. DMF (dielectric constant $\xi_D = 34.93$ at 308.15 K) [24a] was mixed with appropriate quantity of doubly distilled water ($\xi_w = 74.795$ at 308.15 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 subscripts (w) and (D) stands for water and DMF respectively and $w_w = 0.8797$ is the mass fraction of water. The validity of this assumption was checked in our previous work [21].

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 molar excess enthalpy of mixing (ΔH_m) data at 308.15 K were determined for the six possible binary combinations using flow isothermal micro calorimeter (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 308.15 ± 0.01 K. Two identical perfusor pumps (Braun, Melsungen, Germany) and gas tight Hamilton syringes were used to pump the solutions through the micro calorimeter. Number of moles and mole fraction of each component in the mixed stream were calculated from densities and volumetric flow rates of components pumped into the mixing cell. Details and the operating procedure of the apparatus have been reported elsewhere [25,26]. The ΔH_m data were calculated from:

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

Eq. (2) can be written as follows:

$$\Delta H_m = i^2 R \frac{\Delta h_1}{\Delta h_2} \times \frac{Y_1}{n_1} \tag{3}$$

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, Y_1 is the mole fraction of electrolyte 1 and, n_1 and n_2 are the number of moles of the electrolyte 1 and 2, respectively. The accuracy of the measurement 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. A brief view of Pitzer's equations

A system of equations for the thermodynamic properties of electrolytes is developed on the basis of theoretical insights from improved analysis of the Debye Hückel model. Guggenheim [28] proposed a system of equations and applied to dilute solutions which were later modified by Scatchard [29] for concentrated solutions. These equations are very complicated and consequently, it seems worthwhile to seek simpler equations with fewer and meaningful parameters. Pitzer [11,12,30–33] 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 combination of long range electrostatic interaction (Debye Hückel theory) and short range repulsive forces expressed as virial coefficients. The general equation for the excess enthalpy in terms of the measurable coefficients B^H and Θ^H and the corresponding third virial coefficients C^H and ψ^H of a mixture of electrolytes is given by:

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

where A_H is the Debye-Hückel slope for the enthalpy, b is a parameter having constant value of 1.2 kg$^{1/2}$ 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), B^H and C^H are parameters related to short range interactions of ions of opposite sign, Θ^H and ψ^H are ion interaction parameters related to binary and triplet interactions. The second virial coefficients (B^H and Θ^H) and third virial coefficients (C^H and ψ^H) are temperature derivatives of the ion interaction parameters of Pitzer's free energy equation [12,30,32,33].

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

$$\Delta H_m = H_{mix}^{ex} - Y_1 H_1^{ex} - (1 - Y_1) H_2^{ex} \tag{5}$$

where H_{mix}^{ex}, H_1^{ex} and H_2^{ex} 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 molecular weight.

In Pitzer's model, for a non common ion mixture of (1:1) MX and (1:1) NY salt, the heat of mixing is obtained by substituting Eq. (4) into Eq. (5), yielding:

$$\frac{\Delta H_m}{(n_w R T^2 I^2)} = Y_1(1 - Y_1)[2\Theta_{MN}^H + 2\Theta_{XY}^H + I(\Psi_{MNX}^H + \Psi_{MNY}^H + \Psi_{MXY}^H + \Psi_{NXY}^H)] \tag{6}$$

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

For a common-anion mixture of a (1:1) MX and (1:1) NX salt, Eq. (6) reduces to:

$$\frac{\Delta H_m}{(n_w R T^2 I^2)} = Y_1(1 - Y_1)[2\Theta_{MN}^H + I\Psi_{MNX}^H] \tag{7}$$

similarly, for a common-cation mixture of (1:1) MX and (1:1) MY salt, the heat of mixing equation is:

$$\frac{\Delta H_m}{(n_w R T^2 I^2)} = Y_1(1 - Y_1)[2\Theta_{XY}^H + I\Psi_{MXY}^H] \tag{8}$$

Eqs. (7) and (8) can be fit to the common-ion mixture data to yield the pair (Θ_{MN}^H, Θ_{XY}^H), and triplet (Ψ_{MNX}^H, Ψ_{MXY}^H), ion-interaction parameters. Since Pitzer's equations utilize ΔH_m data in joules per kilogram of solvent so conversion was performed by multiplying the ΔH_m values of (J mol^{-1}) by the ionic strength (mol kg^{-1}).

4. Results and discussion

The ΔH_m data for the six possible binary mixtures of NaCl, KCl, NaBr and KBr measured at 308.15 K, I = 1.000 and 2.000 mol kg^{-1} are reported in Table 1 and plotted in Figs. 1 and 2. The ΔH_m data for all the systems are positive at I = 1.000 mol kg^{-1}. When ionic strength is increased to 2.000 mol kg^{-1}, the ΔH_m values remained almost same in the KBr + NaBr and NaBr + NaCl systems, increased in the NaCl + KCl and NaCl + KBr systems and decreased in the KBr + KCl and NaBr + KCl systems.

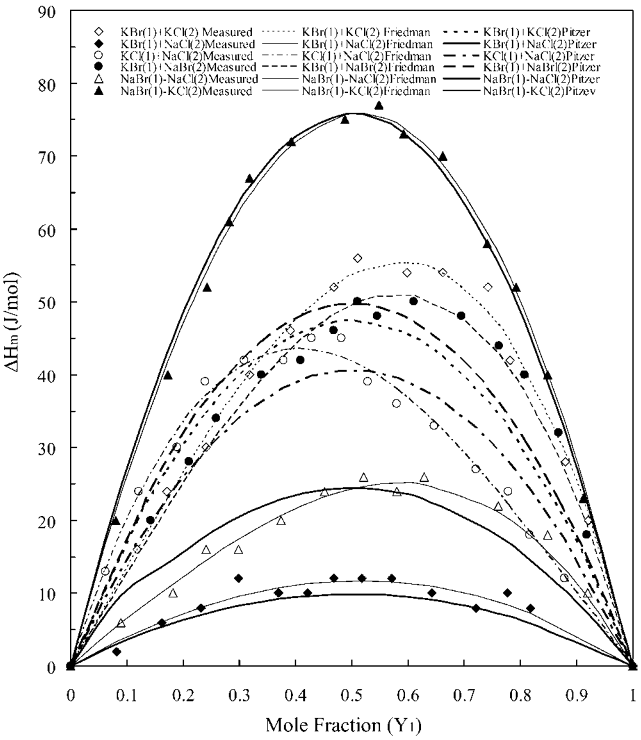

Fig. 1. Experimental ΔH_m data in water + DMF mixed solvent system at I = 1.000 mol kg^{-1} and temperature of 308.15 K. The curves represent the calculated ΔH_m values from Friedman (Eq. (9)) and Pitzer's equations (Eqs. (7) and (8)).

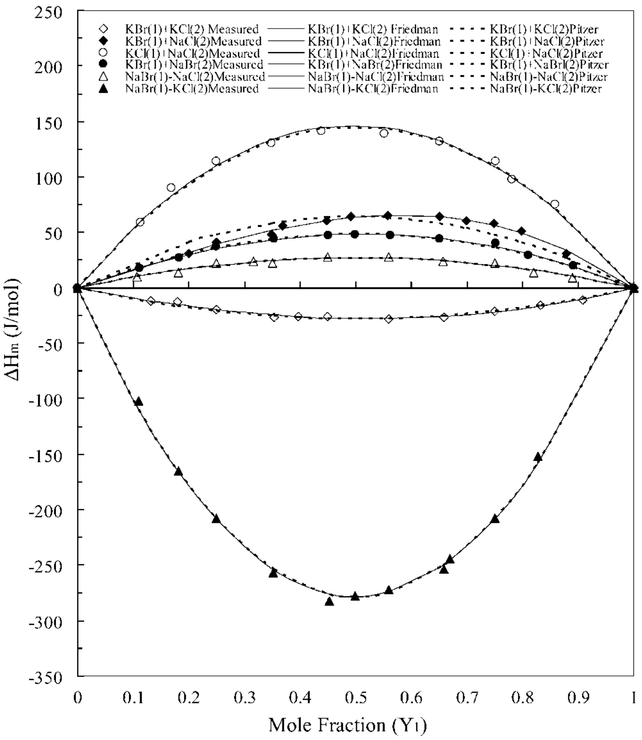

Fig. 2. Experimental ΔH_m data in water + DMF mixed solvent system at I = 2.000 mol kg^{-1} and temperature of 308.15 K. The curves represent the calculated ΔH_m values from Friedman (Eq. (9)) and Pitzer's equations (Eqs. (7) and (8)).

Table 1
Experimental ΔH_m data for six pairs of univalent electrolyte solutions in water + DMF mixed solvent as a function of mole fraction (Y_1) of solute (1) at 308.15 K

Y_1	ΔH_m	Y_1	ΔH_m	Y_1	ΔH_m
At ionic strength = 1.000 mol kg^{-1}					
KBr (1) + KCl (2)		KBr (1) + NaCl (2)		KCl (1) + NaCl (2)	
0.1189	16	0.0823	2	0.0622	13
0.1716	24	0.1621	6	0.1212	24
0.2416	30	0.2324	8	0.1888	30
0.3182	40	0.2988	12	0.2394	39
0.3909	46	0.3698	10	0.3087	42
0.4684	52	0.4210	10	0.3788	42
0.5112	56	0.4677	12	0.4292	45
0.5986	54	0.5186	12	0.4813	45
0.6624	54	0.5713	12	0.5283	39
0.7426	52	0.6422	10	0.5802	36
0.7816	42	0.7212	8	0.6467	33
0.8801	28	0.7766	10	0.7212	27
0.9213	20	0.8186	8	0.7786	24
				0.8174	18
				0.8782	12
KBr (1) + NaBr (2)		NaBr (1) + NaCl (2)		NaBr (1) + KCl (2)	
0.1419	20	0.8889	6	0.0802	20
0.2113	28	0.1820	10	0.1722	40
0.2598	34	0.2411	16	0.2421	52
0.3388	40	0.2988	16	0.2822	61
0.4088	42	0.3741	20	0.3187	67
0.4678	46	0.4514	24	0.3917	72
0.5099	50	0.5212	26	0.4877	75
0.5456	48	0.5808	24	0.5489	77
0.6113	50	0.6287	26	0.5920	73
0.6962	48	0.7601	22	0.6623	70
0.7614	44	0.8488	18	0.7414	58
0.8074	40	0.9192	10	0.7918	52
0.8679	32			0.8488	40
0.9179	18			0.9122	23
At ionic strength = 2.000 mol kg^{-1}					
KBr (1) + KCl (2)		NaBr (1) + NaCl (2)		KBr (1) + NaCl (2)	
0.1313	−12	0.1066	10	0.1998	31
0.1802	−13	0.1808	14	0.2490	41
0.2499	−20	0.2490	22	0.3495	48
0.3533	−27	0.3166	24	0.3687	56
0.3972	−26	0.3505	22	0.4484	60
0.4498	−26	0.4502	28	0.4915	64
0.5590	−28	0.5601	28	0.5586	65
0.6583	−27	0.6567	24	0.6506	64
0.7502	−21	0.7506	22	0.6999	60
0.8318	−16	0.8208	14	0.7491	58
0.9078	−11	0.8902	9	0.7992	51
				0.8790	31
NaBr (1) + KCl (2)		KBr (1) + NaBr (2)		KCl (1) + NaCl (2)	
0.1108	−102	0.1122	18	0.1128	59
0.1818	−165	0.1833	27	0.1683	90
0.2490	−208	0.2498	37	0.2498	114
0.3518	−257	0.3534	44	0.3494	130
0.4533	−282	0.4509	47	0.4384	141
0.4999	−278	0.4988	48	0.5515	139
0.5598	−272	0.5623	47	0.6513	132
0.6593	−254	0.6518	44	0.7515	114
0.6693	−244	0.7512	40	0.7812	98
0.7498	−208	0.8102	29	0.8583	75
0.8284	−152	0.8912	20		

Unit of ΔH_m: J mol^{-1}.

Table 2
Mixing parameters of Eq. (9) for various electrolyte solutions in water + DMF mixed solvent system at 308.15 K along with standard deviation (σ)

System	Ionic strength[a]	h_0 (10^2)[b]	h_1(10^3)[b]	σ[c]
KBr (1) + KCl (2)	1.000	8.36	−31.85	1.5
KBr (1) + NaCl (2)	1.000	1.83	−1.24	1.1
KCl (1) + NaCl (2)	1.000	6.53	27.23	1.4
KBr (1) + NaBr (2)	1.000	7.74	−27.55	2.0
NaBr (1) + NaCl (2)	1.000	3.80	−13.74	2.2
NaBr (1) + KCl (2)	1.000	11.83	−5.85	1.4
KBr (1) + KCl (2)	2.000	−1.09	1.22	1.2
NaBr (1) + NaCl (2)	2.000	1.05	−0.04	1.6
KBr (1) + NaCl (2)	2.000	2.48	−8.79	1.9
NaBr (1) + KCl (2)	2.000	−10.86	−0.54	3.9
KBr (1) + NaBr (2)	2.000	1.88	−1.04	1.3
KCl (1) + NaCl (2)	2.000	5.71	0.84	4.1

[a] Unit: mol kg^{-1}.
[b] Units: kg mol^{-1}.
[c] Units:J kg^{-1}.

Friedman's equation was fit to the enthalpy of mixing data, where the excess enthalpy of mixing is expressed as [18,34–37]:

$$H_m = RTI^2 Y_1(1 - Y_1)[h_0 + h_1(1 - 2Y_1) + \dots] \quad (9)$$

where ΔH_m is excess enthalpy of mixing in joules per kilogram of solvent, I is the molal ionic strength, R is the gas constant (8.31441 J mol^{-1} K^{-1}), Y_1 is the ionic strength fraction of the heavier salt and, T is the temperature in Kelvin. The h_0 and h_1 are mixing parameters related to the pair and triplet interactions respectively which were calculated by fitting the Eq. (9) into ΔH_m data using least square method and are reported in Table 2 along with standard deviation. 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 skew or asymmetry of the curve. Eq. (9) gives a good fit of the data as can be seen in the figures. An examination of h_n parameters reveals that h_0 is greater than h_1 for the system showing positive value of enthalpy of mixing and h_0 is smaller than h_1 for systems showing negative value of enthalpy of mixing. Further, greater is the value of excess enthalpy of mixing; greater is the value of h_0 and vice versa.

Wu et al. [19,20] reported that the heat of mixing in aqueous solution is independent of the common ion. Thus h_0 should also be independent of common ion [34]. On the contrary, the present ΔH_m data deviate substantially from this conclusion. These deviations indicate that the triplet or higher interactions may be quite significant in the mixed solvent and it has indeed been observed as can be seen in Table 2. The skew term contribute significantly suggesting that the triplet interactions involving two ions of like charge with common ion has appreciable contribution along with like-charged pair interaction term. Similar differences from the results of Wu et al. [19,20] were seen in an earlier study [22] too in an aqua-dioxane mixed solvent.

To confirm the role of triplet interactions, we also fitted Pitzer's equations i.e. Eqs. (7) and (8) to our common ion mixture data and calculated the binary and triplet ion–interaction parameters, which are presented in Table 3 along with standard deviation. From Table 3, it can be seen that the triplet interactions have higher magnitude and opposite sign at ionic strength of 1.000 mol kg^{-1} and same magnitude as well as sign at ionic strength of 2.000 mol kg^{-1} compared to the binary interaction terms. Though both models successfully explained the ΔH_m data yet Friedman model proved better when standard deviations were compared.

Young and co-workers [19,20,38,39], have demonstrated that the excess thermodynamic properties for the reciprocal salt pairs of common ion mixings equals the sum of the excess thermodynamic properties of the uncommon ion mixings, i.e.

$$\tfrac{1}{2}\sum \square + \varepsilon = \tfrac{1}{2}\sum X \quad (10)$$

where ε is zero or often very small. The cross-square rule diagrams are presented in Fig. 3, where ΔH_m values at $Y_1 = 0.5$, are shown for six possible mixings of the four electrolytes. Examination of these diagrams demonstrates that the present results deviate from Young's Rule. Furthermore, higher is the ionic strength more is the deviation from 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. A reasonable explanation for these deviations is the preferential solvation of the ions and ion clusters in the mixed solvent, which has an effect on the interactions of pairs and triplets of ions.

Friedman and Ramanathan [40] 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 solvated shells leads to extrusion of the solvent overlap volume as shown in Fig. 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) [24c], electron pair acceptance (indicated by

Table 3
Pitzer's parameters of Eqs. (7) and (8) for various electrolyte solutions in water + DMF mixed solvent system at 308.15 K along with standard deviation (σ)

$I = 1.000$ mol kg^{-1}				$I = 2.000$ mol kg^{-1}			
System	$\Theta \times 10^2$	$\psi \times 10^2$	σ	System	$\Theta \times 10^5$	$\psi \times 10^5$	σ
KBr (1) + KCl (2)	2.507	−4.99	7.8	KBr (1) + KCl (2)	−1.76	−1.76	3.0
KCl (1) + NaCl (2)	2.505	−4.989	5.4	NaBr (1) + NaCl (2)	1.71	1.71	3.1
KBr (1) + NaBr (2)	2.506	−4.987	5.4	KBr (1) + NaBr (2)	3.06	3.06	3.0
NaBr (1) + NaCl (2)	2.503	−4.994	3.5	KCl (1) + NaCl (2)	9.26	9.26	8.4

Units of Θ, ψ and, σ are kg mol^{-1} K^{-1}, kg^2 mol^{-2} K^{-1} and J kg^{-1} respectively.

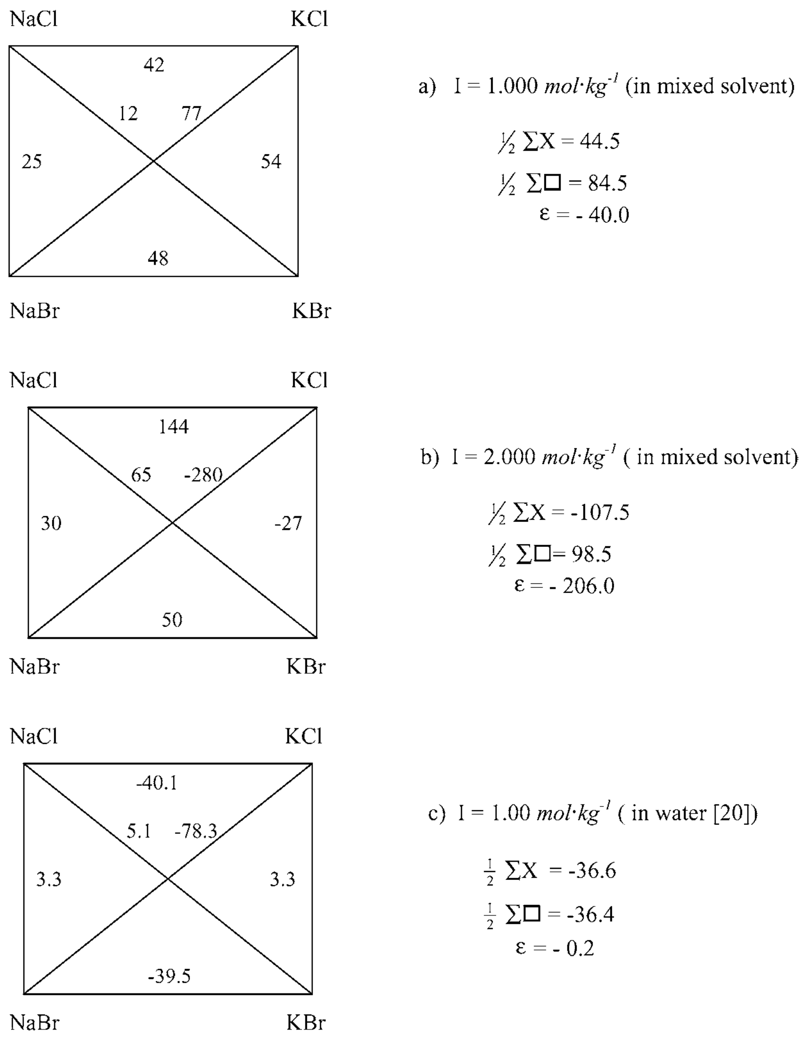

Fig. 3. Young's cross square rule diagrams for various univalent electrolyte solutions in water + *N*,*N*-DMF mixed solvent at 308.15K and in pure water.

electron pair acceptance polarity index) [41], structural (categorized by softness, openness and ordering) [42] and self association characteristics of the solvent molecules. Since our mixed solvent system contains 12.03% by weight of DMF and Gutman donor number (DN) of water (75.3 kJ mol^{-1}) is different from that of DMF (111.3 kJ mol^{-1}), so the solvation of ions of 1:1 electrolytes in the water + DMF mixed solvent system would not be of the same magnitude and sign as in pure water. In addition, because, Na^+ is a water-structure maker and the water structure-breaking ability [43] of K^+, Br^-, and Cl^- ions vary as $\mathrm{Cl}^- < \mathrm{K}^+ < \mathrm{Br}^-$, 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 enthalpy of mixing data in mixed solvent may not be independent on the nature of the common ion (unlike that in water).

Further examination of the nature of DMF and its concentration in the mixed solvent reveals that there are about 1.7 moles of DMF in 1 kg of solvent. This means that at $I = 1.00\,\mathrm{mol\,kg}^{-1}$, there are approximately two DMF molecules available to solvate an ion. Paneda et al [44] observed that the interactions of Na^+ or K^+ ions with DMF occur at the negative pole of DMF dipole and positive pole of dipole is sterically hindered from interaction with Cl^-

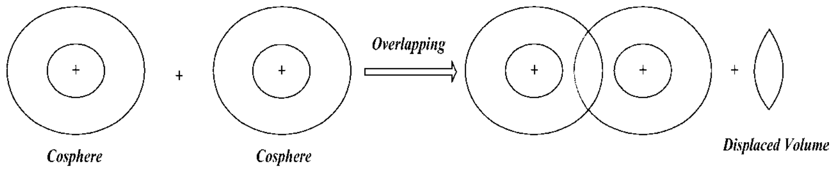

Fig. 4. Overlapping of solvation co-spheres of two ions giving rise to displaced volume.

or Br^-. 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 [45] because anions (Cl^- or Br^-) are sterically hindered from interaction with DMF molecules. This suggests that DMF may preferentially solvate certain ions and ion clusters in the mixture. Marcus [46,47] has used the idea of preferential solvation of ions in mixed solvent systems. In his linear solvation energy relationship, he includes solvent properties like polarity and hydrogen bond donation number and ion properties like size (ionic radius), charge, and softness. Given the differences in donor number and the variation in softness of Cl^- and Br^- ions, it seems reasonable to assume that the DMF preferentially solvates certain ions and ion clusters.

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 ΔH_m data is dependent of the common ion and Young's cross square rule does not hold. Both Friedman and Pitzer's model have been utilized successfully to determine the magnitude of binary and triplet interactions. The triplet interactions have appreciable contribution. Variations in solvation of the ions and ion clusters, including preferential solvation of certain species explain the deviation of the results from cross square rule. The deviation from CSR increases with the increasing ionic strength.

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