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Thermodynamics of 1:1 electrolyte mixtures in aquo-1,4-dioxane solvent system: molar excess enthalpy

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Abstract

Molar excess enthalpy data at 308.15 K for 1 M binary solutions of MX + NY (or NX), MY + NX (or NY), M(or N)X + M(or N)Y (where M is Na^+, N is K^+, X is Cl^-, Y is Br^-) electrolytes in 1,4-dioxane (D) + water ($x_D = 0.0142$, dielectric constant 70 at 308.15 K) solvent (S) system have been determined using an LKB flow microcalorimeter. The data, which differ appreciably from the corresponding data in water and which depend, unlike those in water, on the nature of the common cation and common anion, do not support Young's cross square rule; this failure has been attributed to the dependence of the hydration of the ions of the MX + NX or MX + NY, etc., 1:1 electrolyte mixtures in S on the nature of (i) the common cation and common anion and (ii) the mixture of anions and of cations. The H^E data of the present systems have been attributed to both the coulombic interactions and the asymmetric effects, and this has been substantiated by an analysis of the data in terms of Friedman's cluster theory. The importance of the virial theory of Pitzer in the determination of the relative magnitudes of the coulombic and asymmetric interactions on H^E data, is also highlighted.

INTRODUCTION

Li^+, Na^+, K^+ are hard Lewis acids, while Cl^- and water are hard Lewis bases; Br^- lies on the borderline [1]. Because reaction takes place preferentially between soft acids and soft bases and hard acids and hard bases [2], Wu et al.'s [3] observation that the molar excess enthalpies of Cl^- and Br^- ion pairs in water are small and not influenced by the common cation suggests that the magnitude of the interactions between Cl^- and Br^- pairs of ions in an aqueous medium are dictated by the relative softness parameters of the anion concerned. Furthermore, because the enthalpy changes in aqueous solutions of mixed strong electrolytes reflect the heat effects associated with changes [4] in intermolecular hydrogen bonding caused by the presence of the ions, the small excess enthalpy of the Cl^- and

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Br^- ion pairs in water in the presence of the same cation suggests only very small changes in intermolecular H-bonding caused by these ions. If the intermolecular hydrogen bonding in pure water is disturbed by addition of an organic co-solvent capable of forming hydrogen bonds with water, the extend of hydration of the cations and anions is influenced to different extents, so that the molar excess enthalpy data of the Cl^- and Br^- ion pairs (in the presence of a common cation) in a mixed aqueous solvent system should provide not only deeper insight into the process of hydration of these ions, but also a means of checking the applicability of Young's cross square rule [5].

These considerations prompted us to determine molar excess enthalpy data of the Cl^- and Br^- of Na^+ and K^+ in the water + 1,4-dioxane solvent system; the proportion of 1,4-dioxane 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.

1,4-Dioxane was selected as a solvent because it was considered that the presenced of 2 lone pairs of electrons on each of its two oxygen atoms would make it a fit candidate to influence hydrogen bonding in water.

EXPERIMENTAL

1,4-Dioxane (Merck AR) was purified as suggested by McGlashan and Rastogi [6]. Deionized water was mixed with some solid NaOH and a pinch of solid $KMnO_4$, and was double-distilled from an all-glass assembly. The NaCl, KCl, NaBr and KBr were analytical grade reagents (% purity > 99.5). 1,4-Dioxane was mixed with an appropriate amount of the double-distilled water so as to yield a solvent of dielectric constant 70 ($x_{\mathrm{Dioxane}} = 0.0142$).

Preparation of stock solutions

Stock solutions (1 M) of each of NaCl, KBr, KCl, NaBr, etc., were prepared in the above solvent system. Before preparing the solutions, each salt was dried at 120.0°C for 24 h to remove moisture.

Excess enthalpy H^E data at 308.15 K of the 1 M mixtures of the NaCl (or KCl) + NaBr (or KBr) solutions in the present solvent were determined by an LKB flow microcalorimeter (LKB – 2107, Sweden) in the manner described by Monk and Wadsö [7]. The temperature of the instrument can be set with a precision of 0.1 K and its stability is 0.02 K over 24 h. Two identical Braun perfusor pumps (Braun, Melsungen, Germany) and gas-tight Hamilton syringes were employed to pump liquids through the calorimeter. Using 10 and 20 cm^3 syringes and the 10-speed gear boxes of the perfusor pumps, different mixing ratios were achieved. The flow rates were determined by pumping distilled water through the calorimeter, and weighing the amounts collected in specific time intervals. For each typical H^E measurement, different calibration constants were determined according to the flow rate, the amplification needed and the composition of the mixture. The H^E data per mole of the solute were evaluated from

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

where i is the electric current (amp), R is the resistance of the calorimeter heater (ohm), Δh_1 and Δh_2 are the baseline shifts (in the steady state) on mixing and in calibration, respectively, at the same sensitivity, and n_1 and n_2, etc., are the number of moles of the electrolytes in solution 1 and 2, respectively.

RESULTS

The H^E data of various binary solutions of the salts at 308.15 K (recorded in Table 1 and plotted in Fig. 1) were expressed as

$$\frac{H^E}{y_1(1-y_1)} = \sum h_n(1-y_1)^n \quad (2)$$

where h_n ($n = 0$–3) are parameters and y_1 is the solute mole fraction of solute 1. These parameters were evaluated by fitting eqn. (2) to the $H^E/y_1(1-y_1)$ data by the least-squares method and are recorded in Table 2 together with the standard deviation σ, defined by $\sigma^2 = [H^E(\text{exp}) - H^E(\text{cal})$ from eqn. $(1)]^2/(m-n)$, where m is the number of data points and n is the number of variables in eqn. (2). The choice of the parameters of eqn. (1) were dictated by the consideration that the maximum deviation, $\sigma_m(H^E)$, satisfied the relation $\sigma_m(H^E) \leq 2\sigma(H^E)$.

DISCUSSION

We are unaware of any H^E data at 308.15 K of the present $Na^+/K^+/Cl^-/Br^-/S$ systems with which to compare our results. Wu et al. [5] have measured H^E data at 298.15 K for 1 M aqueous solutions of the Cl^- and Br^- of Na^+ and K^+. The available H^E data [8] from 273.15 to 313.15 K of the 1 M aqueous solutions of HCl and NaCl, although positive, decrease with the rise in temperature. If this is assumed to be true for the H^E data of 1 M aqueous solutions of the Cl^- and Br^- of Na^+ and K^+, then although the

TABLE 1

Measured H^E data (J mol^{-1}) at 308.15 K of 6 pairs of 1 m solutions of some 1:1 electrolyes in water + 1,4-dioxane solvent system as a function of the solute mole fraction of the solute numbered (1)

y_2	H^E	y_1	H^E
NaCl(1) + KCl(2)			
0.1001	7.6	0.5029	39.6
0.2019	18.6	0.6028	36.4
0.2526	25.3	0.6692	32.0
0.3359	32.9	0.7522	23.6
0.4033	37.9	0.8018	17.5
0.4602	39.4	0.8800	8.8
NaCl(1) + KBr(2)			
0.1200	8.6	0.5045	20.2
0.2028	13.0	0.6043	20.0
0.2533	15.7	0.6701	18.4
0.3373	18.7	0.7533	15.1
0.4043	19.4	0.8028	12.6
0.4602	20.2	0.8902	17.0
NaCl(1) + NaBr(2)			
0.0798	−22.0	0.5016	−45.9
0.1399	−33.1	0.6015	−40.1
0.2011	−41.2	0.6680	−35.1
0.2512	−45.8	0.7512	−28.4
0.3347	−49.0	0.8010	−23.6
0.4015	−48.8	0.8801	−15.8
KCl(1) + NaBr(2)			
0.0790	−15.0	0.4986	23.0
0.1502	−16.1	0.5987	26.9
0.1991	−12.7	0.6654	27.6
0.2489	−7.2	0.7489	24.8
0.3002	1.5	0.7991	20.0
0.3321	4.6	0.9201	9.4
0.3987	13.4		
KBr(1) + KCl(2)			
0.0697	14.3	0.4984	−5.4
0.1302	20.8	0.5985	−16.8
0.1990	23.7	0.6653	−21.2
0.2488	23.0	0.7402	−22.1
0.2796	21.2	0.8497	−16.0
0.3319	16.5	0.9195	−9.0
0.3985	7.5		
KBr(1) + NaBr(2)			
0.0995	−7.0	0.4971	−23.2
0.1981	−13.5	0.5972	−21.2
0.2478	−16.3	0.6640	−19.2
0.3308	−20.5	0.7478	−15.8
0.3972	−21.8	0.7981	−12.6
0.4605	−22.8	0.8897	−13.6

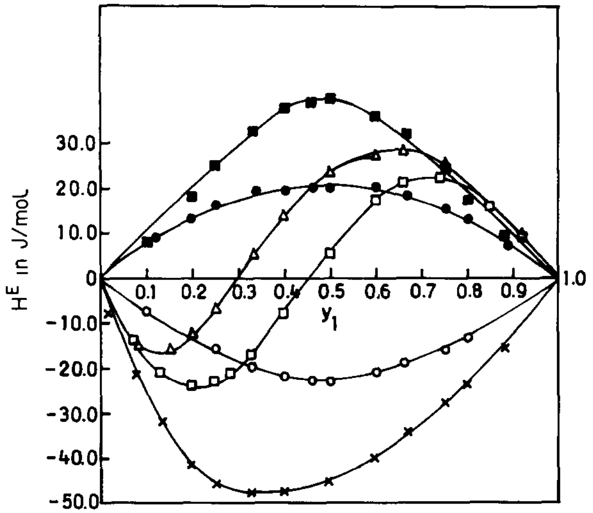

Fig. 1. Variation of H^E with solute mole fraction y_1 of solute 1 for: ○, KBr(1)–NaCl(2); □, KBr(1)–NaBr(2); △, KCl(1)–NaBr(2); ×, NaCl(1)–NaBr(2); ■, NaCl(1)–KCl(2); ●, NaCl(1)–KBr(2).

present data are of the right order of magnitude, they differ from the data of Wu et al. in some important aspects. Thus while the H^E data of the 1 M aqueous solution of Cl^- and Br^- of Na^+ and K^+ are always positive and independent of the common cation, the corresponding H^E data are negative when Na^+ is the common cation and change from positive to negative values when K^+ is the common cation in the present solvent system. Again, though the H^E data [5] of 1 M aqueous solutions of NaCl and KBr or of NaBr and KCl are always positive, the present data are positive only for the 1 M solutions of NaCl and KBr. For 1 M solutions of NaBr and KCl, the present H^E data change sign: they are negative for $y_{KCl} < 0.3$ with a minimum at $y_{KCl} = 0.5$ of -14 J mol^{-1}, and become positive thereafter, with a maximum of 28 J mol^{-1} at $y_{KCl} = 0.65$.

TABLE 2

Parameters of eqn. (1) and standard deviations

System	h_0	h_1	h_2	h_3	$\sigma/(\text{J mol}^{-1})$
NaCl(1)–KCl(2)	160.0	−5.9524	−122.02	0.0	0.4
NaCl(1)–KBr(2)	82.0	0.0	10.0	0.0	0.2
NaCl(1)–NaBr(2)	−184.0	89.29	−55.94	0.0	0.3
KCl(1)–NaBr(2)	92.0	142.9	−188.09	75.22	0.4
KBr(1)–KCl(2)	−24.0	250.02	101.4	100.00	0.5
KBr(1)NaBr(2)	−92.0	5.9524	24.4047	0.0	0.3

Friedman and Krishanan [9] have developed a model treatment for the interpretation of excess functions of mixing in terms of interactions between solvated ions, and have postulated that apart from the electrostatic contribution, the H^{E}, etc., values of such systems are modified by the overlap of ionic solvation shells. If the ion-ion potential between the solvated ions i and j are expressed [9] by

$$V_{ij}(r) = (\mathrm{ES})_{ij} + (\mathrm{CORE})_{ij} + (\mathrm{CAV})_{ij} + (\mathrm{Overlap})_{ij}$$

where all the terms have their usual significance [9], and because the interference between the solvated shells leads to an extrusion of the solvent overlap volume that relaxes to its normal bulk state, a detailed structure of the solvent in the vicinity of the ions thus requires close scrutiny.

The hydration of the ions suggests [10] that (i) the electric field of the central ion orients the water molecules in its close vicinity in such a way that their opposite ends face the central ion in the hydration shell, (ii) the water molecules in the first hydration shell exert their own orienting effect on the outer water molecules, and (iii) beyond the second hydration shell, the water molecules are indistinguishable in their behaviour from those in pure water.

However, the present solvent (S) contains 6.59% (w/w) of 1,4-dioxane (D), and because the presence of two lone pairs of electrons on each of the two oxygen atoms of D means that it undergoes hydrogen-bonded interactions with the hydrogen atoms of the water molecules, the solvent S may be perceived as an equilibrium mixture of $(H_2O)_m$ ($m = 1$–3) and the $(H_2O)_nD$ ($n = 1, 2$) molecular entities; the $(H_2O)_nD$ molecular entities may further exist as an equilibrium mixture of the aprotic boat form of D and the protic chair form of D. Furthermore, because the Gutman donor number ($\mathrm{DN} = 75.3\ \mathrm{kJ\ mol^{-1}}$) of water is more than that of D ($\mathrm{DN} = 61.9\ \mathrm{kJ\ mol^{-1}}$), the hydration of the ions of 1:1 electrolytes in S would not be of the same nature as that in pure water. Again, because Na^+ is a water-structure maker and the water-structure breaking ability [11] of K^+, Br^- and Cl^- ions vary as $Cl^- < K^+ < Br^-$, it may be reasonable to assume [12] that while the Na^+ ions in S would contain water molecules in the first hydration shell and an aprotic form of D in the second shell, K^+ ions in S may contain both water and the protic and aprotic forms of D in their hydration shells; the Cl^- and Br^- ions may contain appropriately oriented water molecules in their hydration shells. The presence of D molecules in the hydration shells of Na^+ and K^+ in S would evidently require (because the solvent overlap volume in the interference between the hydration shells of these ions does not relax in the same manner as that in pure water) that the H^E data of the present systems be dependent on the nature of the common ion (unlike that in water); as has indeed been observed in the present case.

Moreover, following Young et al. [13], if the four salts are arranged at

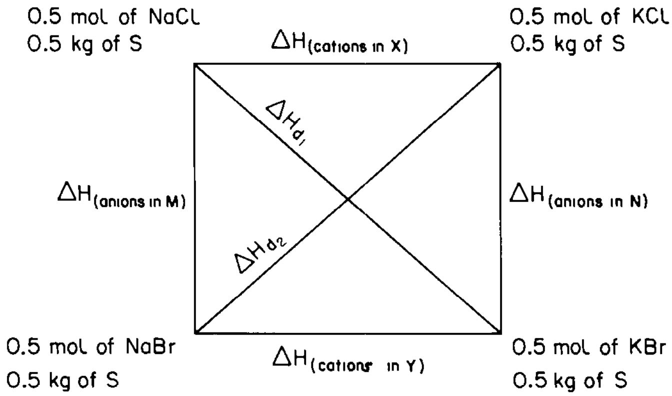

Fig. 2. Quinary mixture, following Young et al. [13].

the corners of a square (Fig. 2), then a quinary mixture of ternary solutions containing 0.5 mol of each of the electrolytes and 2 kg of S can be made in the following three ways:

(i) [0.5 mol NaCl + 0.5 mol NaBr]
+ [0.5 mol KCl + 0.5 mol KBr] + 2 kg S

(ii) [0.5 mol NaCl + 0.5 mol KCl]
+ [0.5 mol KBr + 0.5 mol NaBr] + 2 kg S

(iii) [0.5 mol NaCl + 0.5 mol KBr]
+ [0.5 mol KCl + 0.5 mol KBr] + 2 kg S

The corresponding enthalpy changes accompanying the formation of the quinary mixture of ternary solution may then be represented, following Bottcher [14], in Fig. 3. Because $\sum \square$ (-35.0 J mol^{-1}) $\neq \sum$ X (45.2 J mol^{-1}), the present H^E data suggest that Bottcher's asumptions that

ΔH cations (X) $\approx \Delta H$ cations (Y) $\approx \Delta H$ cations (X + Y)

and

ΔH anions (M) $\approx \Delta H$ anions (N) $\approx \Delta H$ anions (M + N)

are not valid in the present solvent S. This would then require that interactions between the solvated cations (or anions) in S in the presence of a common anion (or cation), or between cations and anions in hetero systems in S, should be dictated not only by coulombic interactions but also by appreciable asymmetric effects.

An examination of the h_n parameters of Table 2 has further revealed that while $h_0 > h_1$ or h_2 or h_3 for NaCl + KCl (or KBr) systems, $h_0 < h_1$ or h_2 or h_3 for NaCl (or KCl) + NaBr and KBr + KCl (or NaBr) systems. Furthermore, while h_0 is positive and varies as h_0 (NaCl + KCl) > h_0

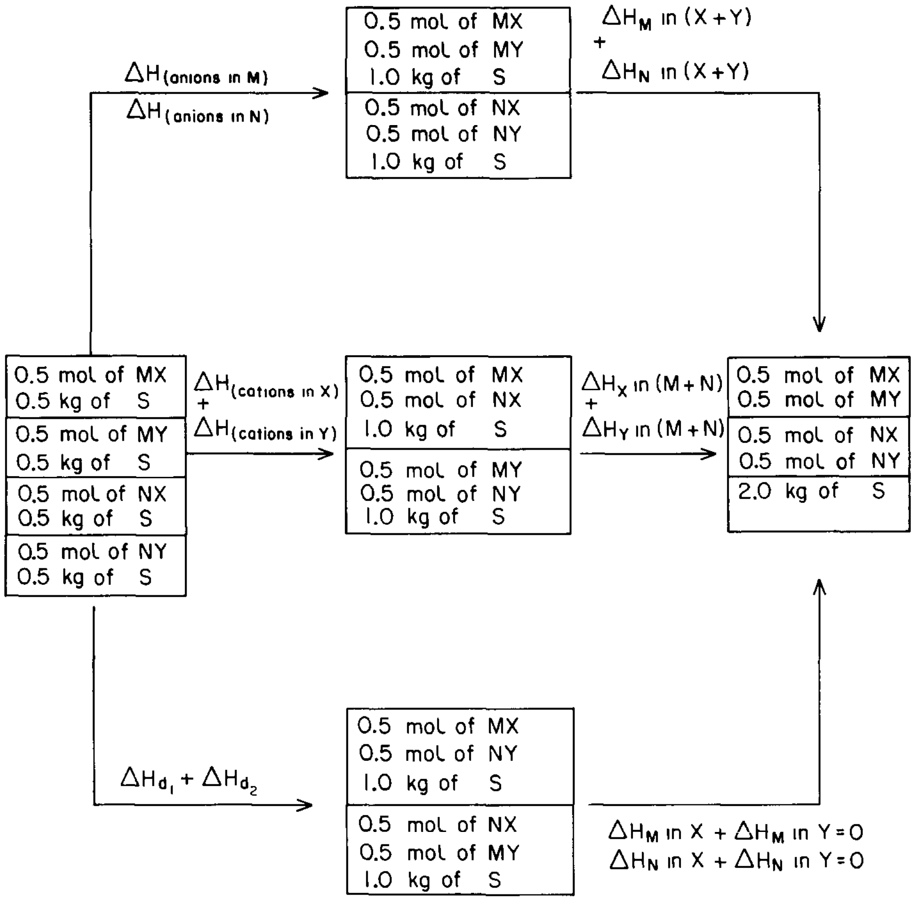

Fig. 3. Quinary mixture, following Bottcher [14]. M is Na^+, N is K^+, X is Cl^-, Y is Br^-.

(KCl + NaBr) > h_0 (NaCl + KBr), it is negative for the remaining systems and varies as h_0 (KBr + KCl) > h_0 (KBr + NaBr) > h_0 (NaCl + NaBr). If the activity coefficients of the components of these systems are related to their activity coefficients in the pure stock solution by Harned's rule [15] i.e.

$$\log \gamma_1 = \log \gamma_{1(S)} - \alpha_{12} m_2 - \beta_{12} m_2^2 \tag{3}$$

$$\log \gamma_2 = \log \gamma_{2(S)} - \alpha_{21} m_2 - \beta_{21} m_1^2 \tag{4}$$

then the H^E of these systems at constant ionic strength $I = m$ can be expressed by

$$H^E = 2.303RT^2 y_1(1 - y_1) m^2 \frac{\delta}{dT} \times \left[(\alpha_{12} + \alpha_{21}) + \frac{2m}{3} \beta_{12} + \frac{2m}{3} (\beta_{12} - \beta_{21})(1 - y_1) \right] \tag{5}$$

Because $(\alpha_{12} + \alpha_{21})$ is a measure [16] of the interactions that characterize these mixtures and $(\beta_{12} - \beta_{21})$ reflects [16] the difference in the properties of the stock solutions, a comparison of eqns. (2) and (5), coupled with the h_0 parameters of Table 2 for the various systems, shows that while the NaCl + NaBr and KBr + KCl (or NaBr) systems in the present solvent S are characterized by specific interactions between their components, NaCl + KCl (or KBr) systems are marked by repulsive interactions between their components.

Alternatively if the properties of electrolyte solutions are taken to be dictated [17] by an electrostatic term plus a virial coefficient series (that depend on the ionic strength of the solution), then G^E of a solution containing n_w kg of S and n_i, n_j, ... moles of solute species i, j, ... would be expressed [17] as a combination of long-range electrostatic forces and short-range forces between the ionic species. The MX–NY mixtures in S then differ [17] from the solutions of MX and NY in S by (i) not only the difference between the MN, MM and NN interactions but also by the effect of the ionic strength of the medium on these interactions and (ii) the difference in the MNY, MMX and NNX interactions; the MX–NY systems in S differ from the corresponding NY and MX system in S by the complex influence of the mixing ratio of the pure solutions on these interactions. A favourable cancellation of these interactions may yield $h_0 > h_1$ or h_2, or $h_0 < h_1$ or h_2, etc., as has indeed been observed in the present case.

The present study thus provides a deeper insight into the role of 1,4-dioxane consolvent in the process of hydration of the ions of individual electrolytes in the binary mixture of 1:1 electrolytes in the (1,4-dioxane + water) solvent system.

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