Electrolytes in Binary Solvents: An Experimental Approach

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1 Introduction

Early investigations into electrolyte solutions focused on aqueous systems, because of the universal availability and importance of water. Later, electrolytes in single organic solvents were investigated, and more recently similar studies on mixed solvent systems have been carried out. The latter find application in various technologies, as they offer a wide choice of solutions with appropriate properties.

Although research on electrolyte solutions has received a great deal of attention, a general theory describing their properties and structure has yet to be formulated and, to the best of the author's knowledge, no theoretical attempt has even been made to describe ternary solutions containing electrolytes.

Most investigations have focused on experimental methods affording the possibility of drawing conclusions about the properties of the systems under discussion. Information on electrolyte solutions in binary mixed solvents has so far come mainly from the use of thermodynamic, viscosimetric, electrochemical, and other macroscopic methods. Few spectroscopic investigations of these systems have been carried out.

Thermodynamic methods are important because changes in properties caused by variations of temperature, composition, and pressure can be studied without any reference to assumptions, models, or hypotheses.

This review will consider the properties of alkali metal halides and $NaBPh_4$, as an example of salts with organic ions, in binary mixed solvents. Such a selection simplifies the task of interpretation, because the chosen electrolytes do not form complexes or enter into reactions with solvents.

2 Thermochemical Features

Thermodynamic functions have shed some light on the energetics of solvation of ions in the chosen mixed solvents, the effects of ions upon the properties of mixed solvents (*e.g.* interactions and structure), and on the role of the solvents themselves, *i.e.* their bulk properties and their electron donor and acceptor abilities. Of the thermodynamic functions describing solvation or solution processes, entropy is significantly connected with the solvent structure perturbations brought about by the dissolved ions. Unfortunately, only limited entropy data for electrolytes in mixed solvents are available. Enthalpy values are more widely available which is the reason why these are more frequently analysed. As is known, plots of entropy changes *vs.* salt concentrations or mixed solvent compositions are analogous to corresponding enthalpy plots. In order to concentrate attention on the properties of electrolyte solutions in binary mixed solvents, enthalpies of various salt solutions are discussed in this article. It is worth remembering that the solvation of a salt in any solvent proceeds as the transfer of individual ions constituting an electrolyte from the ideal gas standard state into their standard state in solution. This process reflects the sum of all interactions occurring between dissolved ions and solvent. In such a solution the ion–ion interactions are absent, thereby simplifying the discussion of standard enthalpy data.

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2.1 Solutions of Inorganic Electrolytes in Water–Organic Mixtures

In order to study the character of plots of the enthalpies of electrolyte solvation in water–organic mixtures it is necessary to know the standard enthalpies of solution over the whole range of mixed-solvent compositions. To facilitate the analysis the entire range of $\Delta H_{\mathrm{s}}^{\circ} = f$(co-solvent content) is frequently divided into three areas, *i.e.* water-rich, intermediate, and co-solvent-rich regions.

2.1.1 Water-rich Region

The properties of mixed solvents in this region show distinctive changes due to the effects of ions and, especially, of organic co-solvents on the three-dimensional structure of water.

Figure 1 presents the standard enthalpies of NaI solution in various mixed solvents as a function of binary solvent compositions. Sodium iodide has been predominantly employed from the inorganic salts because of its relatively high solubility in organic solvents. Moreover, extensive data on its heats of solution have been reported in the literature.[1–3]

It is known that curves of $\Delta H_{\mathrm{s}}^{\circ}$(NaI) *vs.* alcohol content pass through their maxima in the water-rich region (Figure 1a), as with the enthalpies of solution of other electrolytes and non-electrolytes. Plots of several properties (spectral, NMR, viscosity, kinetics parameters of reactions, thermodynamic functions of complex formation processes, *etc.*) also show variations in the range of compositions corresponding to the $\Delta H_{\mathrm{s}}^{\circ}$ maxima.[4]

It is relevant to mention here that there are differing views about the meaning of the extrema (positions, heights, depths) of curves that illustrate the properties of multi-component systems *versus* their compositions. Some authors[5,6] consider extrema of $\Delta H_{\mathrm{s}}^{\circ}$ not to be significant, resulting only from the slopes of both ends of these curves (*e.g.* the McMillan–Mayer interaction coefficients). Other authors[3,7–9] are of the opinion that the observed extrema reflect solution structure and intermolecular interactions. The presence of $\Delta H_{\mathrm{s}}^{\circ}$ maxima in the water-rich region has been attributed to 'iceberg' formation, structure making or breaking effects, higher-order microphase transitions, the appearance of clathrate-like aggregates, and to hydrophobic effects. Possibly these terms are simply different names for the same phenomena, but it has not been easy to demonstrate this supposition so far. In this article the assumption is made

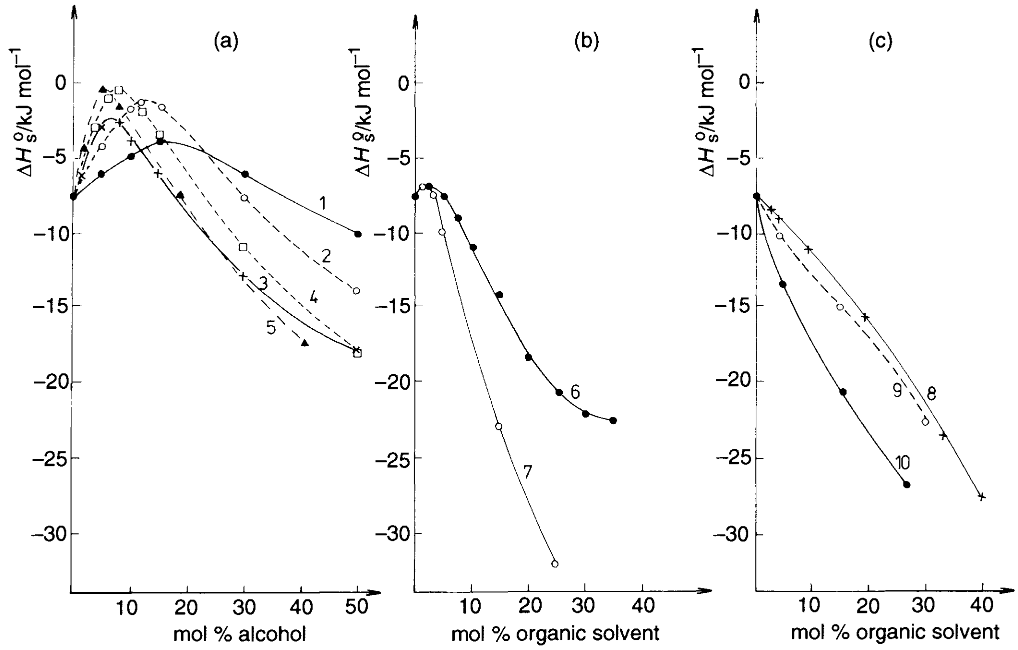

Figure 1 Standard enthalpies of solution of NaI in water–organic mixtures as a function of organic solvent content at 25 °C. (a): (1) methanol; (2) ethanol; (3) propan-1-ol; (4) propan-2-ol; (5) t-butyl alcohol. (b): (6) tetrahydrofuran; (7) hexamethylphosphoramide, ref. 3. (c): (8) dimethylsulfoxide, ref. 2; (9) dimethylformamide, ref. 3; (10) dioxane, ref. 2.

that the extrema originate from the hydrophobic hydration of the organic components, and that hydrogen bonds play only a minor role.

In some aqueous non-electrolyte solutions the apparent molar volume V_Φ of the organic component passes through a minimum. According to Franks[10] the position and depth of V_Φ minimum depend on the size and shape of the apolar (*i.e.* hydrophobic) groups of solute molecules. Therefore, positions of V_Φ minima can be treated as measures of the hydrophobic effect. In Table 1 the positions of the minima of the apparent molar volume of alcohols in water ($V_\Phi$min)[11] are juxtaposed with those for the maxima of standard enthalpies of solution of NaI in these mixtures (ΔH_s°max) and with the minima of mixing enthalpies of water with co-solvents (H^E min).[12] The positions of all three extrema are close to each other. This observation could be treated as evidence for the importance of hydrophobic interactions in the enthalpy of mixing (except for solutions containing methanol).

The proximity of the positions of ΔH_s°(NaI) maxima and of H^E minima suggests that NaI does not affect the solvent structure. It can also be postulated that this absence of a NaI effect is the result of equalization of the interactions of cations and anions with the solvent.

The enthalpy maxima of NaI solutions are probably connected with particular difficulties in the formation of solvation shells in the region of the hydrophobically ordered structure of the solution. The latter leads to the maxima of enthalpy, ΔH_s°.

On the other hand, the positions of ΔH_s° maxima for NaCl (Table 1), KBr, *etc.* in water–alcohol mixtures are somewhat different – as was observed for the enthalpy maxima of NaI and the NaCl in solutions containing propanols and t-butyl alcohol.[3] In the cases of methanol and ethanol, however, the shifts of the positions of maxima, if any, are within the limits of error. The differences in behaviour of NaCl and NaI probably result from a stronger relative affinity to water in the case of Cl^- due to the smaller size of the chloride anion, its larger electric surface density, and lower polarizability. The displacement of the ΔH_s°(NaCl) maxima positions in relation to the minima of mixing enthalpy for water and alcohol suggests a change in the structure of the binary solvent caused by sodium chloride. This view is supported by Franks' and Desnoyers'[9] opinion that NaCl causes 'the shift in the equilibrium between different states of the alcohol–water mixtures'. Unlike the case for anions, the positions of the maxima do not seem to depend on the character of the cations.[13]

The pattern for NaI is particularly interesting. Feakins' old rule 'When in doubt, leave the iodide out' can be replaced, at least for the solvents in question, by 'When in doubt, watch the iodide'. It is possible that I^- ion is hydrated in the region from pure water to the H^E minima (ΔH_s°maxima), at which point the alcohol molecules invade the solvation shells. The Na^+ cation is

Table 1 Minima positions of the apparent molar volume, V_Φ, heat of mixing, H^E for water–organic mixtures and maxima positions of the standard enthalpies of NaI and NaCl solution in these mixtures*

Organic solvent	V_Φ (min)[11]	ΔH_s°(NaI) (max)[3]	H^E (min)[12,16,17]	ΔH_s°(NaCl) (max)[2,3]
Methanol	17	17	30	17
Ethanol	11	12	15	12
Propan-1-ol	5	6	5	7.5
Propan-2-ol	7	9	10	12
t-Butyl alcohol	5	6	6	9
Tetrahydrofuran	5	2.5	15	25
Hexamethylphosphoramide	5	1.5	20	10

* The accuracy with which the extrema positions were determined tends to differ, and is dependent on the data available for the above analysis.

probably hydrated in a wide range of solvent compositions. In the case of chlorides, bromides, and other small anions the courses of these curves are different, thus showing a perturbation effect of such anions on the structure of mixed solvents. That the preferential solvation of ions plays some role here cannot be ruled out.

Significant conclusions concerning the preferential solvation of both inorganic and organic ions in binary aqueous mixtures containing four alcohols (from methanol to t-butyl alcohol), acetone, and dimethylsulfoxide (DMSO) can be found in a series of important papers by Blandamer *et al.*[14] The authors analysed the transfer chemical potentials of simple and complex ions as the basis for a further analysis of kinetic data in systems involving ions in the chosen mixtures.

Hawlicka,[15] applying the self-diffusion method to the constituents of electrolyte solutions in water with methanol, propan-1-ol, and acetonitrile also expressed views on the preferential solvation of ions. Unfortunately, the conclusions drawn by various authors, using different experimental methods, are not always identical.

Feakins *et al.*,[5] on the basis that the mixing enthalpy of water with methanol, H^E, passes through a minimum at a mole fraction of methanol $x_{MeOH} = 0.3$, while the enthalpies of transfer of alkali metal halides ΔH_{tr}° have their minima in the region $x_{MeOH} = 0.1$—0.2, have developed a general relationship $H^E/x_{alc} = f(\Delta H_{tr}^\circ/x_{alc})$. They applied the relationship to the alkali metal chlorides in water–methanol, and obtained a linear relation for a large part of the range of solvent composition. They concluded that neither the absence of a maximum in ΔH_{tr}°, nor its exact position are of any significance for the structure of a mixed solvent. However, these authors did not take into account the fact that ΔH_{tr}° curves of MeI, $MeClO_4$, *etc.*, pass through the extrema at the same positions, like those for H^E of water with alcohols (with the exception of methanol). Therefore, the above relationship seems to be more appropriate for solutions other than those used by Feakins *et al.*

As well as alcohol-containing systems, there are also electrolyte solutions in mixtures of water with aprotic solvents, *viz.* tetrahydrofuran and hexamethylphosphoramide (Figure 1b) in which the curves of $\Delta H_s^\circ(\text{salt}) = f(\text{organic solvent content})$ also exhibit maxima.[3] The maxima are shifted by anions (Table 1) in a manner similar to systems containing alcohols. However, the positions of the solution enthalpy maxima for alkali metal iodides are not close to those for the mixing enthalpy minima of these binaries,[16,17] as is observed in the case of the methanol–water mixed solvent (Table 1).

It can be postulated that the specific behaviour of methanol, tetrahydrofuran, and hexamethylphosphoramide as the components of electrolyte solutions involves equalizing, at least to some extent, the effects of the hydrophilic and hydrophobic groups in the solvent molecules.

Solutions in binaries composed mainly of non-self-associating aprotic solvents do not display the ΔH_s° maxima for NaI and other inorganic electrolytes (Figure 1c). In these systems the interaction of the electron-donor groups of the solvent with water is a more important factor than the hydrocarbon–water interaction. Therefore, the ability to interact in a hydrophobic way, revealed by the V_Φ minima measure, is not a sufficient criterion for a comprehensive description of these solutions.

The solution enthalpy maxima of NaI do not occur in water mixtures with hydrophilic co-solvents (formamide, urea),[3] whose interactions with water consist mainly in hydrogen-bond formation. Numerous association equilibria occur in these systems, varying with changes in composition of the mixed solvent.

Electrolyte solutions in water–polyol mixed solvents have been investigated only to a limited extent. The curves of enthalpy of KI solution in water with ethane-1,2-diol or glycerol over the considered range of mixed solvent composition appear to be monotonic,[2] pointing to similar properties for these co-solvents (Figure 2). These solvents exhibit a strong tendency to form intermolecular hydrogen bonds. The weak hydrophobicity of ethane-1,2-diol and glycerol displayed, for example, by the shallow V_Φ minima in mixtures with a high water content cannot be observed in electrolyte solutions involving these mixtures.

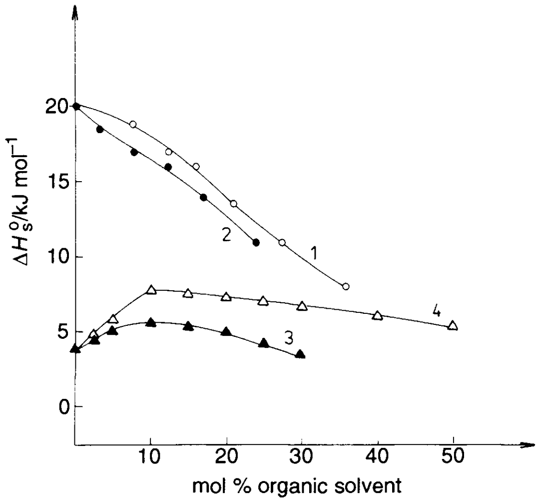

Figure 2 Standard enthalpies of solution of inorganic salts in water–polyol mixtures as a function of organic solvent content at 25 °C. (1) KI–water–ethane-1,2-diol; (2) KI–water–glycerol, ref. 2; (3) NaCl–water–propane-1,2-diol; (4) NaCl–water–butane-1,4-diol, ref. 18.

Unlike the above mentioned solutions, the enthalpies of inorganic salt solutions in water with propane-1,2-diol or butane-1,4-diol[18] exhibit their maxima in the water-rich region. The stronger hydrophobic effect of butane-1,4-diol, with its ethyl group unsubstituted by –OH groups, is demonstrated by the higher maximum.

2.1.2 *Enthalpic Pair-interaction Coefficients*

Standard enthalpies of electrolyte solutions provide some information about the interactions between the solute and the bulk solvent. In order to analyse the interactions between solute and organic co-solvent molecules in water, the pair interaction coefficients derived from the McMillan–Mayer theory were applied to the transfer enthalpy by Desnoyers *et al.*[19] The enthalpic pair-interaction coefficients were evaluated for several electrolyte solutions in water–organic binary solvents (h_{ES}).

The standard enthalpy of electrolyte solution in the mixture of water with a small amount of organic co-solvent can be presented as follows:

$$\begin{aligned}\Delta H_s^\circ(\text{E in S + W}) - \Delta H_s^\circ(\text{E in W}) &= \Delta H_{tr}^\circ(\text{E}) \\ &= 2m_s h_{ES} + 3m_s h_{ESS} + \ldots\end{aligned} \tag{1}$$

hence

$$(\partial \Delta H_{tr}^\circ/\partial m_s) = 2h_{ES} + 3m_s h_{ESS} + \ldots \tag{2}$$

where ΔH_s° is the standard enthalpy of electrolyte solution, ΔH_{tr}° is the transfer enthalpy of electrolyte from water to solvent S, and m_s is molality of solvent S.

In Table 2 a number of h_{ES} values for NaI and NaCl with several co-solvents in water are presented.[20] Different h_{ES} values are observed for chlorides and iodides in all binaries. Observed higher h_{ES} coefficients, in their absolute values, for NaI in comparison with those for NaCl seem to indicate a greater affinity of NaI for organic solvent polar groups, probably as a result of the higher polarization I^- ion.

It has been also found that in aqueous systems the enthalpic pair interaction coefficients h_{ES} of NaCl or NaI with different non-electrolytes are linearly correlated with some properties of the non-electrolytes, such as molecular polarizability (α_p), electric permittivity (ϵ), or Kosower acidity parameter (Z). However, these correlations are not general and hold only for groups

Table 2 Enthalpic pair-interaction coefficients, h_{ES} for NaI–non-electrolyte and NaCl–non-electrolyte in water[20]

	h_{ES}/J.kg.mol^{-2})	
Non-electrolyte	NaI	NaCl
Methanol	314	300
Ethanol	596	580
Propan-1-ol	780	740
Propan-2-ol	1018	900
t-Butyl alcohol	1140	980
Tetrahydrofuran	344	404
Hexamethylphosphoramide	564	842
Acetone	−92	20
Dimethyl sulfoxide	629	−202
Formamide	−696	−452
Dimethylformamide	−350	−79
Acetonitrile	−494	−286

of related compounds. For instance, a graph of h_{ES} as a function of the Kosower acidity parameter consists of two straight line segments: one for the pairs containing alcohols and the other for those with aprotic solvents. The best linear correlation, which encompasses almost all systems investigated so far, was obtained between the h_{ES}(NaCl/NaI–non-electrolyte) values and the heat capacities of transfer of the non-electrolytes from the gas phase to high dilution in water ($\bar{C}p^{\circ}_{s} - Cp_{g}$), or, better still, of the heat capacities of interaction Cp(int) between a non-electrolyte and water (Figure 3). The possible reasons for the observed h_{ES} behaviour were discussed in detail in reference 20.

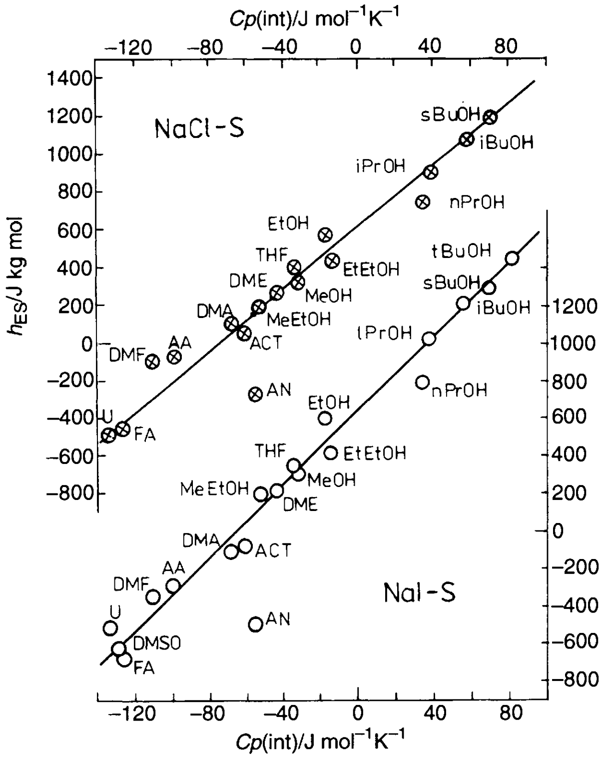

Figure 3 Enthalpic pair interaction coefficients, h_{ES} for electrolyte–non-electrolyte as a function of the heat capacity of interaction, C_p(int) of the non-electrolyte. MeEtOH = 2-methoxyethanol, EtEtOH = 2-ethoxyethanol, FA = formamide, DMF = *N,N*-dimethylformamide, AA = acetamide, DMA = *N,N*-dimethylacetamide, DME = 1,2-dimethoxythane, THF = tetrahydrofuran, DMSO = dimethyl sulfoxide, ACT = acetone, AN = acetonitrile, U = urea; data from ref. 20.

2.1.3 Intermediate Region

Having passed the region of composition at which solution enthalpy maxima occur, the ΔH°_{s} curves usually become smooth in the system containing alcohols *etc.* In the middle range of organic co-solvent contents, in all cases so far investigated, hydrophobic effects are already absent and changes in the equilibria of aggregates formed by hydrogen bonds occur continuously. According to Naberukhin,[21] water molecules form 'globules' in this region, *i.e.* small ice-like aggregates, and the co-solvent molecules probably form self-associates. Alternatively, entities containing molecules from both substances, linked by hydrogen bonds, may also form. By this hypothesis, the middle range of compositions would be microheterogeneous. This view is supported by the observation that for some mixtures, demixing occurs below critical solution temperature in this region. For example, a mixture of water with acetonitrile (approximately 3:2 molar ratio) separates into two phases at − 1 °C.

2.1.4 Co-solvent-rich Region

Enthalpy plots in the non-aqueous region are often featureless. However, in alcohol-rich regions the solution enthalpies of salts exhibit minima within the 70—90 mol% alcohol range. These minima were first observed for ΔH°_{s}(NaI) in water with butanols,[3] and then for $CaCl_2$ in water–alcohol mixtures from methanol to propanol.[22] Since the minima of the electric permittivity and viscosity[23] of the water–butanol mixtures, without an electrolyte, correspond to the same alcohol content region as in the case of ΔH°_{s}(salts) (Figure 4), it was concluded that such minima are due to solvent structure. This conclusion is in accordance with ideas about the formation of Brown–Ives 'centrosymmetric' associates, composed of one water and four alcohol molecules.[7]

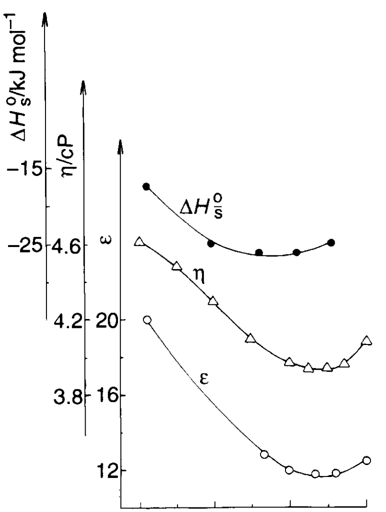

Figure 4 Viscosities, η, and electric permittivities, ϵ, of water–t-butyl alcohol mixtures and standard enthalpies of solution of NaI in these mixtures, ΔH°_{s}, at 26 °C (t-butyl alcohol-rich region), data from refs. 3, 7, and 23.

The analogous minimum of enthalpy of $NaClO_4$ solution was noticed in the 90 mol% tetrahydrofuran-rich region.[24] (In this range NaI is almost insoluble.) It should also be added that the mixing enthalpy of water with propanols, and butanols, as well as with tetrahydrofuran, exhibits a maximum in the same organic-rich area as the minimum in the case of the solution enthalpy of electrolyte.

The evident minima of solution enthalpy are also observed for all solutes so far investigated in the acetonitrile–water system in the region of 80—90 mol% acetonitrile.[1] Some authors attribute this minimum to the preferential hydration of ions, whereas others refer to the formation of complexes from molecules of acetonitrile and water, with a cation or even with both ions. It is noteworthy that the heat of mixing for water–acetonitrile mixtures exhibits a minimum at 70 mol% organic solvent, and the azeotrope ($t = 76\,^\circ$C) contains about 69 mol% acetonitrile. These extrema in properties suggest that acetonitrile molecules form mixed associates with water which affect the solution enthalpies of electrolytes.

2.2 Solutions of Salts with Organic Ions

That organic ions devoid of groups specifically interacting with solvent exhibit special properties when dissolved in water is well-known. In spite of their large size, in comparison with alkali metal and halide ions, they probably do not destroy the three-dimensional structure of water, but rather enhance it. That view can be supported by the large and positive heat capacities of electrolytes containing these ions in water, positive viscosity **B** coefficients from the Jones–Dole equation, and negative structural entropies of hydration $\Delta S^0_{1\,\mathrm{str}}$, *etc.* These somewhat unexpected values display some similarity to the behaviour of organic ions and non-polar solutes, in contrast to that of inorganic ions. The strange properties of the ions studied were attributed by many authors to the hydrophobic hydration and were also observed in water–organic binary solvents.

In the water-rich range, curves illustrating the $\Delta H^0_s = f$(organic solvent content) of electrolytes containing ions with aryl groups exhibit maxima in all systems so far investigated.[2,25–27] Figure 5 shows plots of the standard solution enthalpies of the chosen electrolyte, NaBPh$_4$.The appearance of high enthalpy extrema for electrolytes with organic ions can probably be attributed to competition between an organic co-solvent and organic ions for the water molecules needed to form hydration shells, quasi-clathrates, or other such structures. This phenomenon could possibly be due to hydrophobic effects.

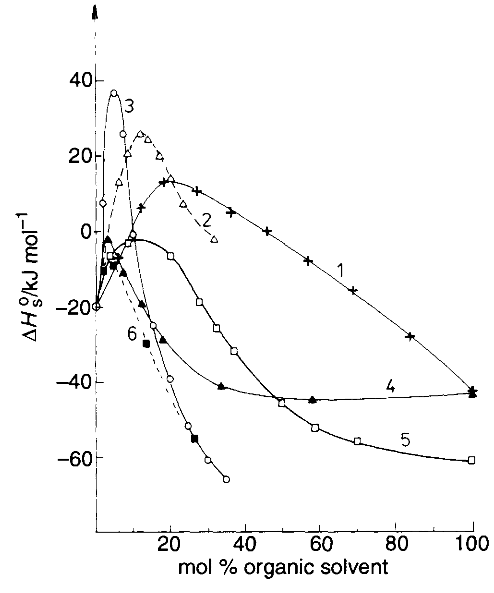

Figure 5 Standard enthalpies of solution of NaBPh$_4$ in water–organic mixtures as a function of organic solvent content at 25 °C. (1) methanol, ref. 25; (2) ethanol, ref. 26; (3) tetrahydrofuran, ref. 27; (4) acetonitrile; (5) dimethyl sulfoxide; (6) dioxane, ref. 2.

In systems containing NaBPh$_4$, or other salts with organic ions dissolved in binary organic solvents, the solution enthalpy maxima are absent. This observation supports the hypothesis regarding an hydrophobic origin for the maxima in water-containing systems. In solutions of one common salt, a significant effect for the hydrophobic hydration of co-solvents on the shape and position of maxima could be confirmed by determining the degree of hydrophobicity of the organic co-solvent and comparing it to the characteristics of the ΔH^0_{tr} maxima.

A comprehensive theory of liquids or hydration that could be utilized to determine hydrophobic effects has yet to be postulated. Kessler,[28] using the McMillan–Mayer theory, recently proposed the semi-empirical parameter $(\partial B_{22}/\partial p)_T$ as a reasonable measure of the hydrophobic interactions of two dissolved molecules. B_{22} is the second virial coefficient of the power series of the osmotic pressure as a function of solution density.

$$2\left(\frac{\partial B_{22}}{\partial p}\right)_T = V^0_1\frac{\partial a^*_{22}}{\partial p} + a^*_{22}\frac{\partial V^0_1}{\partial p} + 2\frac{\partial V^0_2}{\partial p} - RT\frac{\partial \chi^0_1}{\partial p} \qquad (3)$$

where χ^0_1 denotes isothermic compressibility and a^*_{22} the Lewis–Randall virial coefficient.

The chosen parameter is positive for hydrophobic solutes in water and negative for hydrophilic ones.

It was pointed out by Desnoyers[29] that the partial molal heat capacities of solutes in water $\bar{C}p^0_2$ are associated with the hydrophobic hydration. As is known, the hydrophobic hydration and hydrophobic interactions are of a common origin. The correlation between $(\partial B_{22}/\partial p)_T$ and $\bar{C}^0_{p_2}$ (Figure 6) shows that $\bar{C}^0_{p_2}$ can also quantitatively describe the hydrophobic effects. Knowing the parameters for hydrophobic effects, it is possible to compare them with the heights of the ΔH^0_{tr}(NaBPh$_4$) maxima in plots of water–organic mixtures. The Na$^+$ ion in the NaBPh$_4$ does not seem to have a significant influence on the heights of enthalpy maxima.

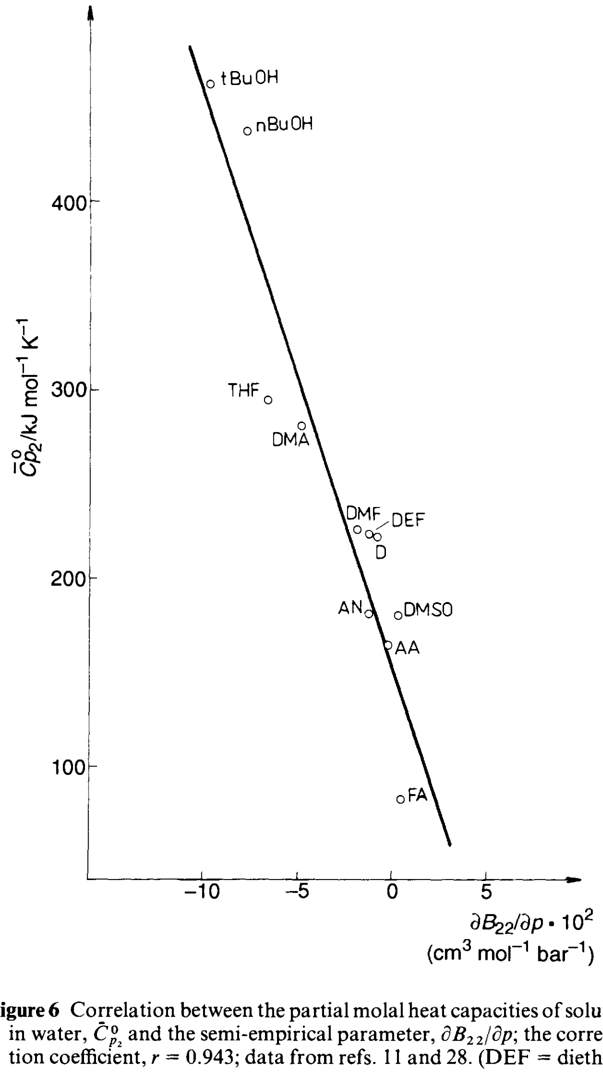

Figure 6 Correlation between the partial molal heat capacities of solutes in water, $\bar{C}^0_{p_2}$ and the semi-empirical parameter, $\partial B_{22}/\partial p$; the correlation coefficient, $r = 0.943$; data from refs. 11 and 28. (DEF = diethylformamide, D = dioxane, other symbols are the same as for Figure 3.)

In Figure 7 $\Delta H^{\circ}_{tr}(NaBPh_4)$ maxima are presented as a function of $\bar{C}^{\circ}_{p_2}$ of the organic co-solvents. The reference function $\bar{C}^{\circ}_{p_2}$ was chosen because it is known for a larger number of solvents than the Kesler coefficient. Two straight lines are produced: one corresponds to systems containing alcohols and the other to mostly aprotic solvents. The distance between these two lines is approximately equal to the hydrogen bond enthalpy. This pattern can be explained by the ability of alcohols to form more hydrogen bonds than is the case for the aprotic solvents.

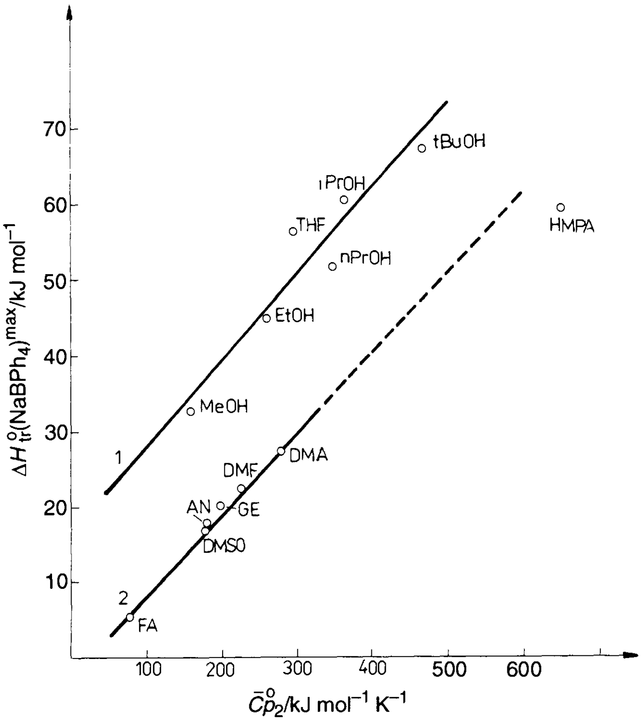

Figure 7 Correlation between the transfer enthalpies of $NaBPh_4$ from water to water–organic mixtures, corresponding to H°_{s}max and the partial molal heat capacities of organic solvent in water, $\bar{C}^{\circ}_{p_2}$; correlation coefficients, $r_1 = 0.948$ and $r_2 = 0.995$; data from refs. 2, 11, and 25—27. (HMPA = hexamethylphosphoramide, GE = ethane-1,2-diol, other symbols are the same as for Figure 3.)

2.3 Solutions of Salts in Organic–organic Solvents

Solutions of electrolytes in binary non-aqueous organic solvents are often used in Chemistry and Technology. Results from the studies of salt solutions in organic–organic binaries conducted by various experimental methods can be found in the literature. However, data obtained by thermochemical studies are quite scarce. Krestov,[30] Taniewska-Osińska,[31] and their co-workers have performed calorimetric measurements dealing with thermochemical properties of the discussed three-component system. A question considered in some papers concerned differences in the behaviour of salt solutions in both aqueous and non-aqueous mixed solvents. Taking into consideration the similar molecular structure and dipole moments of water and methanol, the standard enthalpies of the chosen electrolyte (NaI) were measured in mixtures of methanol with three other alcohols, of diminishing electric permittivities.[31] In the methanol-rich range, no maxima in $\Delta H^{\circ}_{s}(NaI)$ were observed (Figure 8), which shows the absence of an ordering structure effect or of a phenomenon analogous to the hydrophobic hydration (solvophobic solvation). This observation could be attributed to the difference in bulk structure between water and methanol.

In some systems, such as NaI–methanol containing propan-1-ol and propan-2-ol, the curves of $\Delta H^{\circ}_{s}(NaI)$ *vs.* solvent composition exhibit small maxima in the low methanol composition range. In these solutions, spatial associations presumably arise. Correcting for ionic association does not lead to the loss of these maxima.[32]

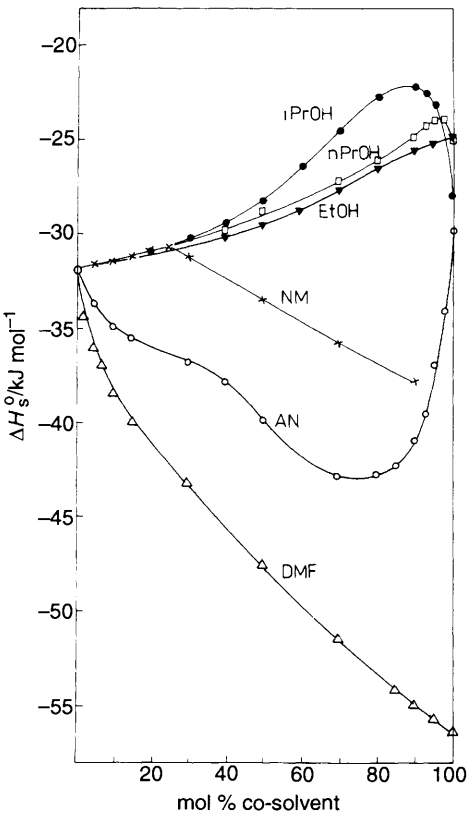

Figure 8 Standard enthalpies of solution of NaI in methanol–organic solvent mixtures as a function of cosolvent content at 25 °C; data from ref. 31 (NM = nitromethane, other symbols are the same as for Figure 3).

The enthalpy of solution for NaI in methanol with three aprotic solvents, of similar electric permittivities as that of methanol (Figure 8), was determined.[31] It follows from the analysis of the plots of $\Delta H^{\circ}_{s}(NaI) = f$(co-solvent content) in isodielectric mixtures that specific ion–solvent interactions are more important than the electric permittivity of the solvents.

In the systems containing NaI, AgCl, or AgBr *etc.* in methanol with acetonitrile, enthalpy minima were observed in the acetonitrile-rich region (approximately 80 mol %).[31,33] This observation is analogous to that made for the electrolyte–water–acetonitrile solutions.[33] Consideration of this minimum, together with the results of spectroscopic investigations,[1] supports the view that acetonitrile forms complexes with water, and possibly with methanol. The cations are probably attached to the oxygen atoms of water, or methanol, thus increasing the solvation energy in the region under consideration.

Glycerol is a solvent considered to be water-like because of its three-dimensional network of hydrogen bonds in the crystal and, probably, in the liquid state. Evidence supporting such a comparison is found in the monotonic plots of $\Delta H^{\circ}_{s}(NaI)$ *vs.* organic solvent content for the entire range of water–glycerol mixture compositions (Figure 2). As a comparison of these two liquids as components of ternary systems, Figure 9 shows the standard enthalpies of a solution of NaI in glycerol with three monohydroxyalcohols.[34] In the glycerol-rich range the ΔH°_{s} maxima are observed, as is the case for all salt solutions in water–alcohol mixtures. This could indicate the appearance of a structure ordering effect, analogous to the systems containing small amounts of alcohols in water. The minima of enthalpy in solutions with small amounts of glycerol may suggest the existence of some kind of associates.

Unlike the character of $\Delta H^{\circ}_{s}(NaI)$ curves for glycerol with alcohols, the analogous functions for NaI solutions in glycerol with five diols (Figure 9) are monotonic, without distinct extrema.[34] Based on the observation mentioned above it can be

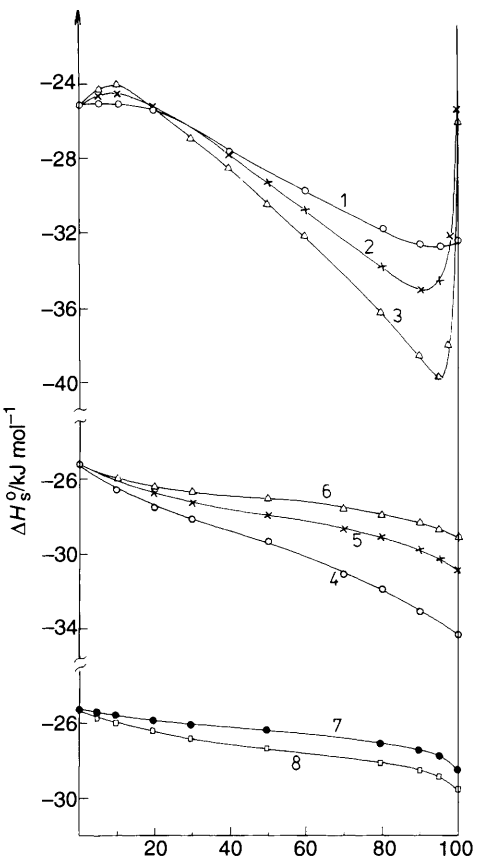

Figure 9 Standard enthalpies of solution of NaI in glycerol–organic mixtures as a function of cosolvent content at 40 °C, data from ref 34 (1) methanol, (2) ethanol, (3) propan-1-ol, (4) ethane-1,2-diol, (5) propane-1,3-diol, (6) propane-1,2-diol, (7) butane-1,2-diol, (8) butane-1,4-diol

supposed that glycerol is capable of solvophobic solvation, but to a lesser degree than water The enthalpic pair electrolyte – non-electrolyte interaction coefficients for all the systems mentioned above vary linearly with the reciprocal electric permittivities of the co-solvents

The character of enthalpy plots may reflect not only the change in structure of one solvent affected by another or by a dissolved electrolyte, but also the change in composition of solvation shells, the variation of solvation numbers, or the selective solvation Unfortunately, the methods for the analysis of the latter phenomenon concern chiefly ΔG°_{s} and not ΔH°_{s} Some of the attempts to determine selective solvation from enthalpy seem to be based on such simplifications, and they should not be applied to different systems without hesitation

3 Some Remarks on the Splitting of Enthalpy of Electrolytes into Ionic Contributions

The enthalpies of solvation, or transfer of electrolytes, depend on the properties of the ions constituting the salts, as well as on the physicochemical properties of the solvents In order to establish the relationship between ion–solvent interactions and the charge sign, the character of the ion, and the properties of the solvent, it is necessary to divide enthalpies of solvation into their individual ionic contributions Ionic enthalpies cannot be obtained theoretically, but only by using extra-thermodynamic assumptions Methods of division have been described and critically analysed by Conway,[35] who considered methods based on splitting thermodynamic values for salts containing cations and anions of similar radii as being unsatisfactory for the case of small ions In his view, ionic size affects the properties of cations and anions in differing ways, and the existing values of ionic radii are discrepant Conway prefers a method which uses the assumption $\Delta H_{\rm solv}({\rm BPh_4^-}) = \Delta H_{\rm solv}({\rm Ph_4P^+}$ or ${\rm Ph_4As^+})$ based on the spherical shape of these organic ions, on their large size and thus small surface density of charge, and on the lack of specific interactions of these ions with all solvents These organic ions were the object of numerous investigations, and the results led some authors (Krishnan and Friedman[36] and others[37]) to conclude that there was a marked difference in behaviour between $\rm BPh_4^-$ anion and $\rm Ph_4P^+$ or $\rm Ph_4AS^+$ cations The different properties of these ions are probably the result of the more hindered rotation of phenyl groups in the $\rm BPh_4^-$ anion compared with the $\rm Ph_4P^+$ cation, and from a difference in charge distribution on the surfaces of these ions This could be an explanation for why the application of known methods to the splitting of solvation or transfer enthalpies in simple solvents produces somewhat different ionic enthalpy values

The situation is more complicated with respect to electrolyte solutions in water–organic solvents The TATB (or TPTB) splitting method leads to different $\Delta H^{\circ}_{\rm tr}$ curves for cations and anions as a function of water–organic solvent compositions[6 25 27] In the water-rich region the curves exhibit cationic maxima and anionic minima that correspond to the same organic component contents The reason for the strange shape of plots of $\Delta H^{\circ}_{\rm tr}$(ion) obtained by the TPTB method, according to Taniewska-Osinska and Nowicka,[27] seems to be the different interactions of organic ions with binary solvents, leading to a difference in hydrophobic hydration This observation supports the suggestion that the TPTB method is not generally applicable to solutions in water–organic mixtures

On the other hand, adoption of the $\Delta H^{\circ}_{\rm tr}({\rm Cs^+}) = \Delta H^{\circ}_{\rm tr}({\rm I^-})$ method, or others based on the equality of enthalpy of inorganic ions, does not cause extrema for enthalpies of individual ions in binary solvents where the ΔH°_{s} of whole salts do not exhibit them, *e g* in water with most aprotic solvents In the case of water–alcohol mixtures, the ΔH°_{s} curves of inorganic salts pass through maxima similar to those of the ionic enthalpies

The suggestion regarding the preponderance of the splitting method of $\Delta H^{\circ}_{\rm tr}({\rm Cs^+}) = \Delta H^{\circ}_{\rm tr}({\rm I^-})$ over $\Delta H^{\circ}_{\rm tr}({\rm Ph_4P^+}) = \Delta H^{\circ}_{\rm tr}({\rm BPh_4})$ is in accordance with the view of Friedman *et al*[36] and Somsen *et al*,[6] and is also supported by the author of this article

4 Conclusion

The significant progress made in the study of electrolytes in binary solvents has been summarized in this review, the analysis having shown the increased understanding of the nature of the complex interactions between components of this kind of system It is reasonable to suppose that future studies will bring forth valuable ideas and results concerning, in particular, new systems, techniques, and methods of interpretation

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