

Ion solvation in aqueous–organic mixtures*

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Abstract: The importance of ion solvation in determining the properties of electrolyte solutions in aqueous–organic solvent mixtures is discussed. Solubility measurements are shown to be particularly useful for determining the Gibbs energies of transfer of ions between solvents, which reflect differences in the overall solvation of the ions in different solvent mixtures. Solubility measurements can also be used to determine the other thermodynamic parameters of transfer, but such quantities are usually better obtained by more direct methods. The inadequacy of current theories of ion solvation to quantitatively account for the thermodynamics of ion transfer is discussed by reference to measurements on some simple model systems. Although donor/acceptor interactions can explain many of the observed effects between pure solvents, the situation is more complex in aqueous–organic mixtures because selective solvation and even solvent–solvent interactions may become significant. This is illustrated by consideration of ion transfer from water to water + *t*-butanol solutions, where spectacular effects are observed in the enthalpies and entropies and especially in the heat capacities and volumes.

Keywords: ions; solvation; electrolytes; aqueous–organic; thermodynamics; solubility.

INTRODUCTION

The solvation of dissolved ions determines many of the properties of electrolyte solutions [1–3], including their redox, complexation, and kinetic behavior. Its particular importance to solubilities, the central topic of the International Symposium on Solubility Phenomena, is illustrated by the thermodynamic cycle in Fig. 1. As shown, the (standard) Gibbs energy of solution, $\Delta_{\text{sln}}G^\circ$, is seen to be the sum of (the negative of the) lattice energy of the salt, $\Delta_{\text{latt}}G^\circ$, and the solvation energies of the ions, $\Delta_{\text{solv}}G^\circ$. This cycle makes it clear that the only reason that salts dissolve in solvents is because the very large lattice energies that are lost upon dissolution are compensated by the even larger solvation energies of the ions.

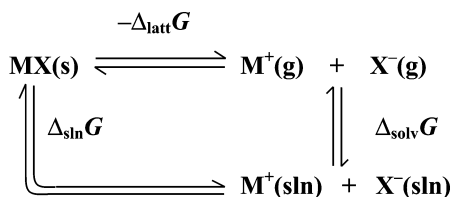


Fig. 1 Born–Haber cycle for dissolution of the salt MX.

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Because both $\Delta_{\text{latt}}G^\circ$ and $\Delta_{\text{solv}}G^\circ$ are very large (negative) quantities, typically of the order of -1000 kJ/mol, it follows that relatively small changes in *either*, for example, arising from minor changes in the nature of the solvent or the salt, can result in dramatic changes in solubility. Given that

$$\Delta_{\text{sln}}G^\circ = -RT \ln K_s^\circ = 5.706 \text{ p}K_s^\circ \quad (1)$$

(for a 1:1 electrolyte at 25 °C) where R and T have their usual meanings and K_s° is the (standard) solubility product of the salt:

$$K_s^\circ(\text{MX}) = a_{\text{M}} a_{\text{X}} = [\text{M}^+][\text{X}^-]\gamma_{\text{M}}\gamma_{\text{X}} = K_s\gamma_{\pm}^2 \quad (2)$$

it follows that a variation of just 10 kJ/mol (i.e., $\sim 1\%$) in $\Delta_{\text{latt}}G^\circ$ or $\Delta_{\text{solv}}G^\circ$ will change the solubility of a 1:1 salt by approximately one order of magnitude. Such small variations in either $\Delta_{\text{latt}}G^\circ$ or $\Delta_{\text{solv}}G^\circ$ are quite beyond the abilities of current theories to predict. It follows that the prediction of the solubilities of even relatively simple electrolytes is not possible at present. This situation is illustrated in Fig. 2, which summarizes the solubilities of the alkali metal halides in water at 25 °C. Clearly, no simple theory will be able to account for the diversity of behavior shown even in these “model” systems.

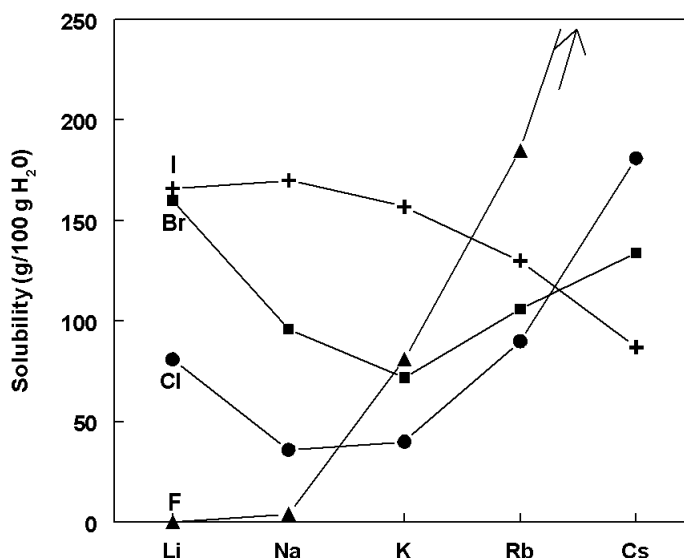


Fig. 2 Solubilities of the alkali metal halide salts in water at 25 °C.

On the other hand, the sensitivity to small changes in $\Delta_{\text{sln}}G$ makes solubility measurements an excellent method for the determination of such quantities [3–5]. Consider, for example, a 1:1 salt with an experimentally determined solubility of say $(5.0 \pm 0.5) \times 10^{-3}$ mol/l. The stated uncertainty of $\pm 10\%$ (relative), a precision that would usually require only modest experimental competence and equipment, gives $\Delta_{\text{sln}}G = (26.3 \pm 0.5)$ kJ/mol, ignoring activity coefficient effects. The uncertainty in $\Delta_{\text{sln}}G$ (or $\text{p}K_s$) of $\sim 2\%$ (relative) would be considered sufficiently accurate for all but the most exacting purposes.

Of course, *accurate* determination of solubility is not as straightforward as it may appear [4–6]. First, the solubility should be neither too high nor too low. Solubilities that are very low create analytical difficulties that can lead to a drastic loss of accuracy; solubilities that are too high require (inevitably uncertain) corrections for activity coefficients (cf. eq. 2). In addition, it will usually be necessary to make appropriate allowance for ion pairing. This effect may become critical when the solubility is very high, or the solvent permittivity (dielectric constant) is low, or the salt contains one or more highly charged ($z > 1$) ions. However, because solubility is a characteristic property of a given salt in a given solvent, at constant temperature and pressure, it may be difficult to find an appropriate salt.

Solubility measurements can also, at least in principle, be used to obtain other thermodynamic parameters associated with the dissolution process via standard relationships such as:

$$\left(\frac{\partial(\Delta_{\text{sln}}G/T)}{\partial(1/T)}\right)_p = \Delta_{\text{sln}}H; \left(\frac{\partial(\Delta_{\text{sln}}G)}{\partial T}\right)_p = -\Delta_{\text{sln}}S; \left(\frac{\partial\Delta_{\text{sln}}H}{\partial T}\right)_p = \Delta_{\text{sln}}C_p; \text{ and} \\ \left(\frac{\partial\Delta_{\text{sln}}G}{\partial p}\right)_T = \Delta_{\text{sln}}V$$

where all symbols have their usual thermodynamic meanings. In practice, however, such parameters are usually better measured by other means. For example, $\Delta_{\text{sln}}H$ and $\Delta_{\text{sln}}C_p$ are best determined by various types of calorimetry [7], whilst $\Delta_{\text{sln}}V$ is normally obtained from density or dilatometry measurements [8].

TRANSFER THERMODYNAMICS

As $\Delta_{\text{solv}}G^\circ$ and the other thermodynamic parameters associated with ion solvation are almost always very large, and the differences between them in different solvents correspondingly relatively small, it is usually more useful to discuss ion solvation in terms of thermodynamic transfer quantities, $\Delta_t Y^\circ$:

$$\Delta_t Y^\circ(\text{MX}, s1 \rightarrow s2) = \Delta_{\text{sln}} Y^\circ(\text{MX}, s2) - \Delta_{\text{sln}} Y^\circ(\text{MX}, s1) \quad (3)$$

with $Y = G, H, S, C_p, V, \dots$ where $s1$ is referred to as the “reference” solvent from which the salt is transferred into the target solvent $s2$ [1].

Clearly, the magnitude of $\Delta_t Y^\circ$ reflects the *differences* in the solvation of MX (i.e., of its component ions) in the two solvents $s1$ and $s2$, which may be neat or mixed. The choice of “reference” solvent, $s1$, from which the ions are transferred, is arbitrary but for aqueous–organic mixtures ($s2 = w + s$) the obvious choice is usually water ($s1 = w$) [5,7].

IONIC TRANSFER THERMODYNAMICS

For a fully dissociated electrolyte, the differences in the transfer thermodynamic properties are the sum of those properties for its constituent ions:

$$\Delta_t Y^\circ(\text{MX}, s1 \rightarrow s2) = \Delta_t Y^\circ(\text{M}^+, s1 \rightarrow s2) + \Delta_t Y^\circ(\text{X}^-, s1 \rightarrow s2) \quad (4)$$

Because the ions are the actual species present in solution, it makes sense to discuss solvation thermodynamics in terms of the ionic quantities $\Delta_t Y^\circ(\text{ion}, s1 \rightarrow s2)$. However, as is well known, such ionic quantities cannot be determined within the framework of thermodynamics: they can only be estimated using an appropriate extra-thermodynamic assumption (where “extra” is used in the sense “outside of”).

The various assumptions that have been used for estimating single ion thermodynamic properties have been reviewed on many occasions [1,5,9,10]. All can be objected to on some grounds, since they are *assumptions* whose ultimate validity cannot be established except by comparison with other assumptions or with *reliable* theoretical predictions. However, to borrow Marcus’s description, the “least objectionable” among those currently used is the so-called “reference electrolyte” approach. This involves the assumption that the measurable thermodynamic properties of a carefully selected salt, RR' , can be apportioned in a specified manner between its cation (R^+) and anion (R'^-). The salts commonly chosen for this purpose are tetraphenylarsonium tetraphenylborate ($\text{Ph}_4\text{AsBPh}_4$, TATB) or its phosphonium analog (Ph_4PBPh_4 , TPTB), usually with an equal split between the cation and anion:

$$\Delta_t Y^\circ(\text{Ph}_4\text{AsBPh}_4, s1 \rightarrow s2) = 2\Delta_t Y^\circ(\text{Ph}_4\text{As}^+, s1 \rightarrow s2) = 2\Delta_t Y^\circ(\text{BPh}_4^-, s1 \rightarrow s2) \quad (5)$$

An exception is for volumes ($Y = V$) where differences in the intrinsic sizes of the ions justify a slightly unequal split [8,10]. Note that it is only necessary to use the assumption, whatever it may be, to estimate the value of $\Delta_t Y^\circ$ for just one ion; all others can then be obtained in a thermodynamically valid manner by appropriate combinations of measurable whole salt quantities (cf. eq. 4). Thus, the fol-

lowing discussion is focused on the thermodynamic transfer parameters of ions between water and aqueous–organic mixtures.

GIBBS ENERGIES OF TRANSFER

The magnitude of $\Delta_t G^\circ(\text{ion}, w \rightarrow w + s)$ is a measure of the overall change in the solvation (energy) of an ion upon its transfer from water to an aqueous–organic mixture. Such quantities are usually “well behaved” in the sense that they vary smoothly as a function of solvent composition, even though they may show great diversity. A typical plot for the transfer of hydrogen ions from water to various aqueous–organic mixtures is shown in Fig. 3.

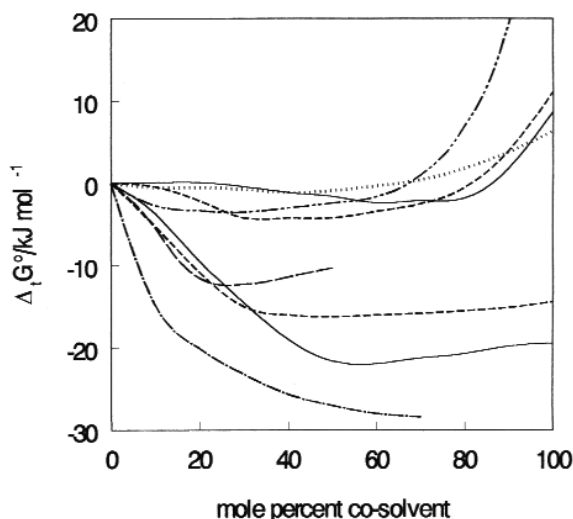


Fig. 3 Variation of $\Delta_t G^\circ(\text{H}^+, w \rightarrow w + s)$ with solvent composition in various water + co-solvent mixtures at 25 °C: (—) MeOH (upper), (---) EtOH (upper), (····) EG, (---) AC, (-·-·-) MeCN, (-·-·-) FA, (-·-·-) DMF (lower), (—) DMSO (lower); reproduced from [5]. Acronyms: EG, ethylene glycol; AC, acetone; FA, formamide, DMF, dimethylformamide; DMSO, dimethylsulfoxide.

There is as yet no general model that enables *prediction* of $\Delta_t G^\circ(\text{ion}, w \rightarrow w + s)$ although various theories have had limited successes. Statistical analysis suggests that short-range “chemical” forces dominate. As an illustration of the importance of such effects, consider the so-called “coordination model” of ion solvation [11,12]. Put in simple terms, this model focuses on the first coordination or solvation shell around an ion as the most critical in determining solvation parameters. The solvation of both cations and anions is regarded as being dominated by the short-range donor–acceptor interactions:



On this basis, it would be expected that $\Delta_t G^\circ(\text{M}^+, s1 \rightarrow s2)$ would correlate with the solvent donor strength (of $s2$, since $s1$ is constant) whilst $\Delta_t G^\circ(\text{X}^-, s1 \rightarrow s2)$ should correlate with the solvent acceptor (or H-bonding) strength. Typical correlations are shown in Figs. 4 and 5 for transfer between neat solvents. These data show that the solvent donor strength (here expressed as the Gutmann donor number [1,12]) accounts (Fig. 4) for about 71 % of the variation in $\Delta_t G^\circ(\text{M}^+, w \rightarrow s)$. For anions (Fig. 5), the correlation is even better, with solvent acceptor strength (expressed as the Dimroth–Reichardt E_T parameter [1,12]) accounting for ~96 % of the variation in $\Delta_t G^\circ(\text{X}^-, w \rightarrow s)$. Major departures from these correlations usually occur only when other short-range interactions are important. Typically, this

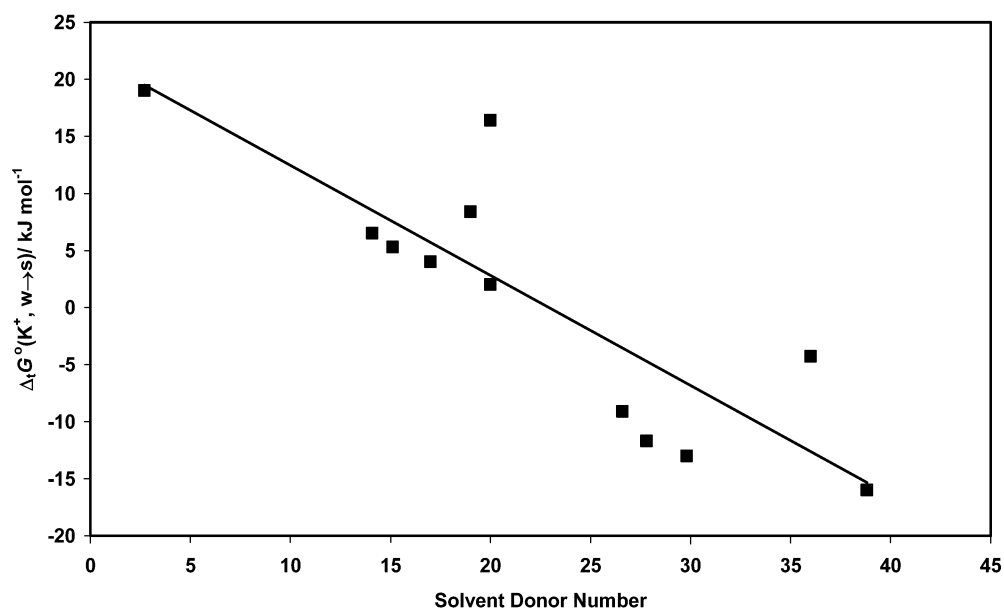


Fig. 4 Dependence of $\Delta_t G^\circ(\text{K}^+, w \rightarrow s)$ on solvent donor strength (data from [1]).

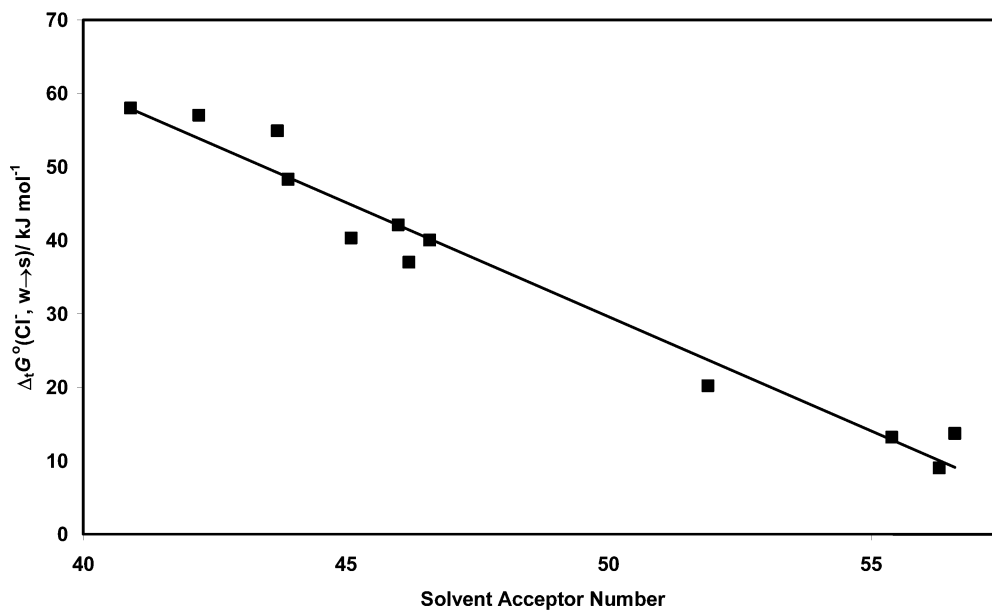


Fig. 5 Dependence of $\Delta_t G^\circ(\text{Cl}^-, w \rightarrow s)$ on solvent acceptor strength (data from [1]).

happens when there are specific (covalent) bonding interactions, often described under the rubric of “soft–soft” interactions [1,5].

Note, however, that for *mixed* solvents, such simple correlations may not always be observed. This is due to the possibility of selective solvation of ions by one of the components of the mixture and/or interactions between the solvent molecules themselves [1,13]. This is born out by the data in Figs. 3 and 6, which show typical results for $\Delta_t G^\circ(\text{ion}, w \rightarrow w + s)$ for H^+ and for F^- into various aqueous–organic mixtures as a function of solvent composition [5]. As indicated by the sharp decrease at

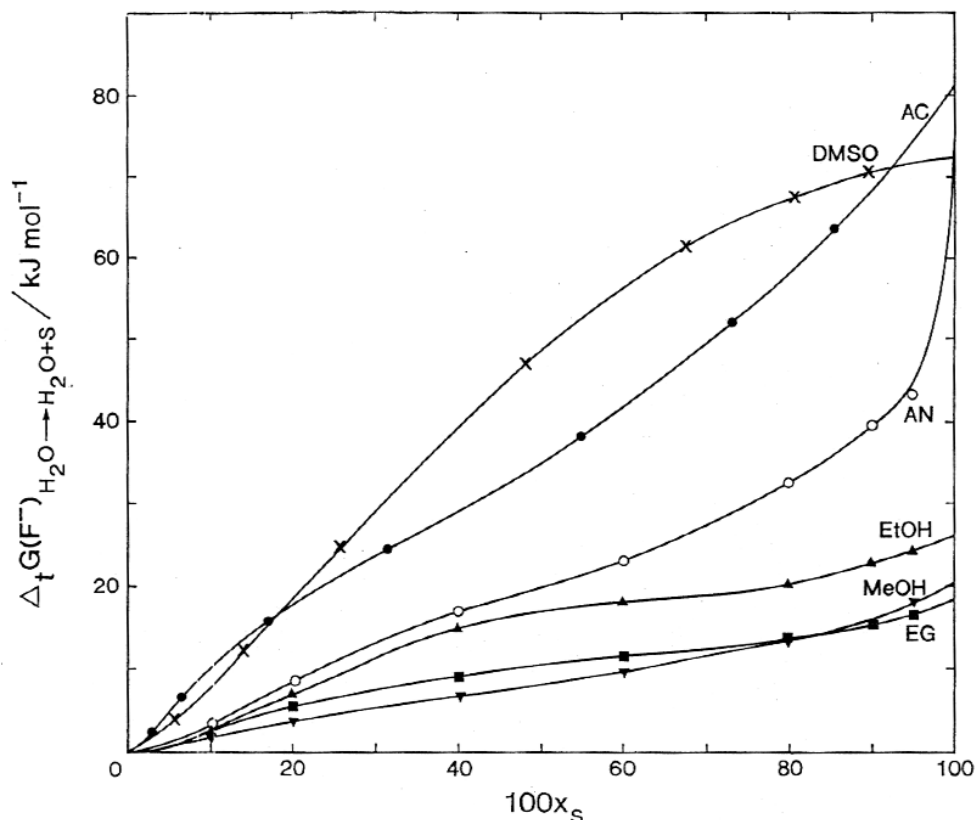


Fig. 6 Variation of $\Delta_t G^\circ(\text{F}^-, w \rightarrow w + s)$ with solvent composition in various water + cosolvent mixtures at 25 °C: [reproduced from G. T. Hefter. *Pure Appl. Chem.* **63**, 1749 (1991)]. For solvent abbreviations, see Fig. 3 legend; AN = MeCN.

low cosolvent concentrations, $\Delta_t G^\circ(\text{H}^+, w \rightarrow w + s)$ reflects preferential solvation of the proton by the strong donor solvents FA, DMSO, and DMF (solvent abbreviations are listed in the legend of Figs. 3 and 6). The opposite effect (i.e., preferential solvation by water) is indicated for $w + \text{AN}$ mixtures and, somewhat surprisingly but much more weakly, $w + \text{ROH}$ mixtures. For $\Delta_t G^\circ(\text{F}^-, w \rightarrow w + s)$ the preferential solvation by water (a very strong acceptor solvent) is apparent in the very sharp increases, of up to 80 kJ/mol, in $\Delta_t G^\circ$ at very low water concentrations in the weak acceptor dipolar aprotic solvents AC and AN (with DMSO exhibiting a less-usual variation). Again, there is a significant difference between the mixtures of water with aprotic solvents and those with the reasonably strong acceptor alcohols.

SOLUBILITIES OF ALKALI METAL FLUORIDES IN WATER-ALCOHOL MIXTURES: A CAUTIONARY TALE

To give some idea of the difficulties in explaining $\Delta_t G^\circ$ values in mixed solvents (without resort to adjustable parameters!) consider the case of what might be seen as a model electrostatic system: the alkali metal fluoride salts in aqueous-alcohol mixtures [14]. If electrostatic interactions are dominant, it would be expected that the variation of the Gibbs energies of transfer should be reasonably well described by the Born model [15,16]. This simple electrostatic model calculates ion solvation energies by

taking the ion to be a hard sphere of radius r_i and charge $z_i e$, and the solvent as a dielectric continuum of relative permittivity ϵ_s , thus giving:

$$\Delta_{\text{solv}} G^\circ(\text{ion}) = -(N_A z_i^2 e^2 / 8\pi \epsilon_0 r_i) (1 - \epsilon_s^{-1}) \quad (6)$$

where N_A is Avogadro's constant and ϵ_0 is the permittivity of free space. Combination of eqs. 4 and 6 predicts at 25 °C, assuming ionic radii to be constant:

$$\Delta_t G^\circ(\text{MF}, w \rightarrow s) = 69.25(\epsilon_s^{-1} - \epsilon_w^{-1})(r_M^{-1} + r_F^{-1}) \quad (7)$$

with $\Delta_t G^\circ$ in kJ/mol when the radii are in nm. (Note that current values of the fundamental constants in eq. 6 give a slightly different constant term in eq. 7). Figure 7 compares the values of $\Delta_t G^\circ(\text{NaF}, w \rightarrow w + \text{ROH})$ predicted (thick line) by eq. 7 with the experimental results for mixtures of water with six alcohols. The agreement is excellent, even up to values of ~50 kJ/mol, with the exception of some of the *t*-BuOH-rich mixtures. Note that because the transfer of the whole salt is being calculated, the results do not require any single ion assumption and the values of ϵ_s for the $w + \text{ROH}$ mixtures were experimental data taken from the literature [14].

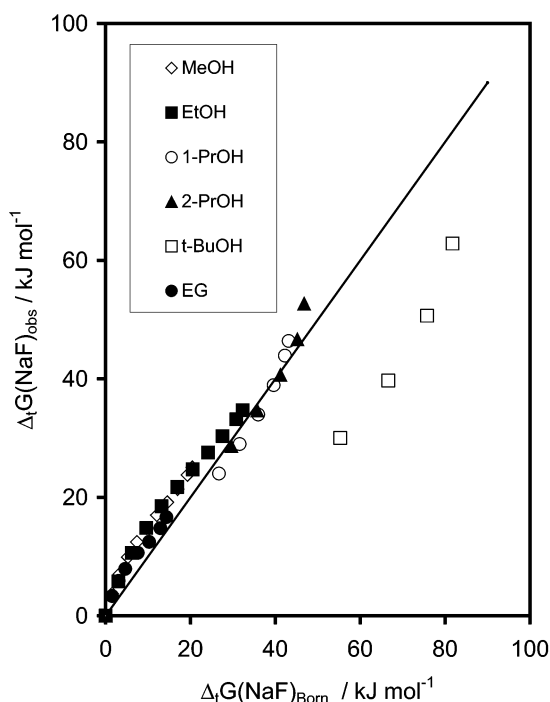


Fig. 7 Comparison of observed Gibbs energies of transfer of NaF from $w \rightarrow w + \text{ROH}$ for various alcohols with those calculated from the Born model (heavy line) at 25 °C (reproduced from [14]).

Unfortunately, this agreement is illusory. As shown in detail elsewhere [14], it arises from a fortuitous relationship between the donor and acceptor strengths for this closely related set of solvents, which in turn results in a cancellation of effects. This is readily demonstrated by consideration of an unrelated solvent. Figure 8 plots the experimental and predicted (thick line) values of $\Delta_t G^\circ(\text{NaF}, w \rightarrow w + \text{MeCN})$. It is clear that even at very low MeCN concentrations, the simple Born model does not reliably predict the experimental results (nor can the deviations between experiment and theory be easily explained away by invoking “soft–soft” interactions). Similar poor-quality predictions are found for most other systems.

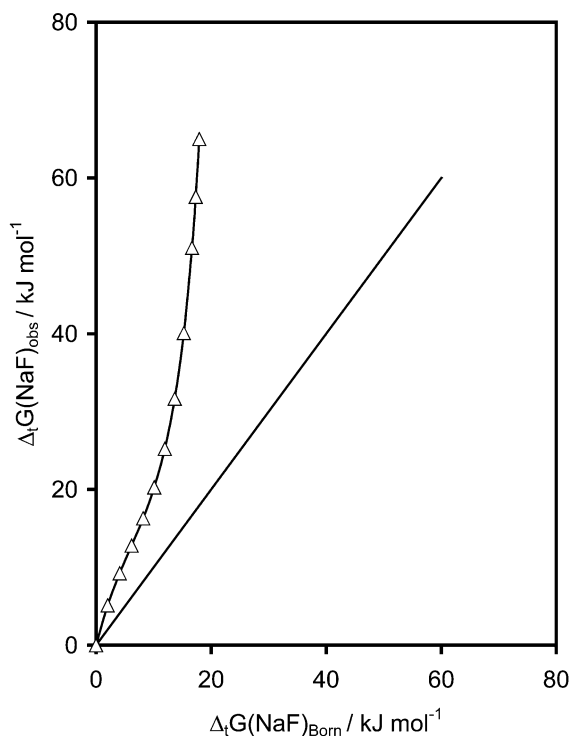


Fig. 8 Comparison of observed Gibbs energies of transfer of NaF from $w \rightarrow w + \text{MeCN}$ with those calculated from the Born model (heavy line) at 25 °C (reproduced from [14]).

The conclusion to be drawn from these data is that even when conditions are favorable, simple models cannot reliably predict transfer energies of salts or ions from water to aqueous–organic mixtures. Unfortunately, more theoretically realistic models seem to be a long way off. In this context, it should be noted that transfer energies provide a much sterner test of model capabilities than do solvation energies. Approximately correct values of the latter can be obtained from widely different models because of the very large numbers involved. Addition of an adjustable parameter or two can make the agreement look even more impressive, but not more meaningful.

OTHER THERMODYNAMIC QUANTITIES

More detailed insights into the nature of ion solvation can be obtained by breaking up the overall changes in solvation upon transfer into their enthalpy and entropy components (recalling that $\Delta_t G^\circ = \Delta_t H^\circ - T\Delta_t S^\circ$). The former reflect the changes in bond making and bond breaking, whilst the latter are associated with changes in order and disorder upon transfer. A qualitative consideration [7] of the transfer of an ion i from $w \rightarrow w + s$ indicates that the enthalpy change will be affected by five essentially independent terms:

$$\Delta_t H^\circ(\text{ion}, w \rightarrow w + s) = \Delta_{b,i-w} H + \Delta_{m,i-s} H + \Delta_{m,w-w} H + \Delta_{b,s-s} H + \Delta_{af,w-s} H \quad (8)$$

where terms with subscript b and subscript m refer to bond breaking and making, respectively, and the subscript af refers to possible effects of the ion on the interactions of neighboring solvent molecules. A similar expression can be obtained for the corresponding entropies. Qualitatively, the terms in eq. 8 have +ve, -ve, -ve, +ve, and unknown signs, respectively, and it is expected that the sum of the first two terms will often be negative. However, the value of this sum relative to that of the remaining three terms

may make $\Delta_t H^\circ$ either +ve or –ve, depending on the ion i and the solvent s . A quantitative account from first principles of such complex changes is beyond the reach of current theories.

For the other thermodynamic parameters of transfer such as heat capacities and volumes, even qualitative interpretation becomes difficult. This is because they are composite quantities whose magnitudes are determined by more than one effect. For example, Marcus and Hefter [8] have proposed four distinct contributions to the molar volumes of ions in solution and hence to $\Delta_t V^\circ(\text{ion}, w \rightarrow s)$: intrinsic size, electrostriction, short-range covalent (coordination) effects and solvent-structural effects. Similar, and equally complex, schemes have been proposed for heat capacities [17].

ION SOLVATION IN AQUEOUS *t*-BuOH SOLUTIONS: A CASE STUDY IN COMPLEXITY

Mixtures of water and *t*-BuOH are one of the few mixed-solvent systems for which virtually all of the thermodynamic parameters of transfer for ions have been determined [5,7,18], albeit mostly only at low *t*-BuOH concentrations. Such mixtures are of particular interest because they can be used as models for studying the counterbalancing effects of hydrophobicity and hydrophilicity. For convenience, most of the following discussion is given in terms of cations, but similar conclusions can be drawn from anion data.

Typical Gibbs energies of transfer of cations from water to (water + *t*-BuOH) mixtures, obtained via the TATB reference electrolyte assumption [5], are shown in Fig. 9. For the monovalent ions, the curves are almost featureless, showing a possible small, flat maximum at mole fraction $x_{t\text{-BuOH}} \approx 0.05$. This maximum is accentuated for the divalent ions, but is still very small: ≤ 5 kJ/mol, which is not much more than the probable uncertainty associated with the TATB assumption.

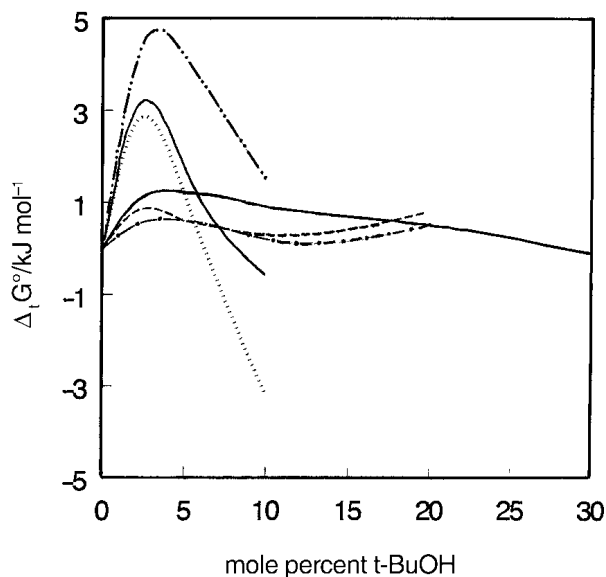


Fig. 9 Variation of $\Delta_t G^\circ(M^{n+}, w \rightarrow w + t\text{-BuOH})$ for various cations with solvent composition at 25 °C: (—) Na^+ (extending to 30 %), (---) K^+ , (-·-·) Rb^+ , (····) Mg^{2+} , (—) Ca^{2+} (with sharp peak), (-·-·) Sr^{2+} (reproduced from [5]).

The corresponding enthalpies of transfer for the monovalent cations are shown in Fig. 10 [7]. The values of $\Delta_t H^\circ(M^+, w \rightarrow w + t\text{-BuOH})$ show much larger effects, with a clearly defined maximum of ~ 15 kJ/mol at $x_{t\text{-BuOH}} \approx 0.05$ and a possible small minimum (≤ 4 kJ/mol) at $x_{t\text{-BuOH}} \approx 0.02$. The shapes of the curves are remarkably similar to each other, i.e., the cation size has little influence on the

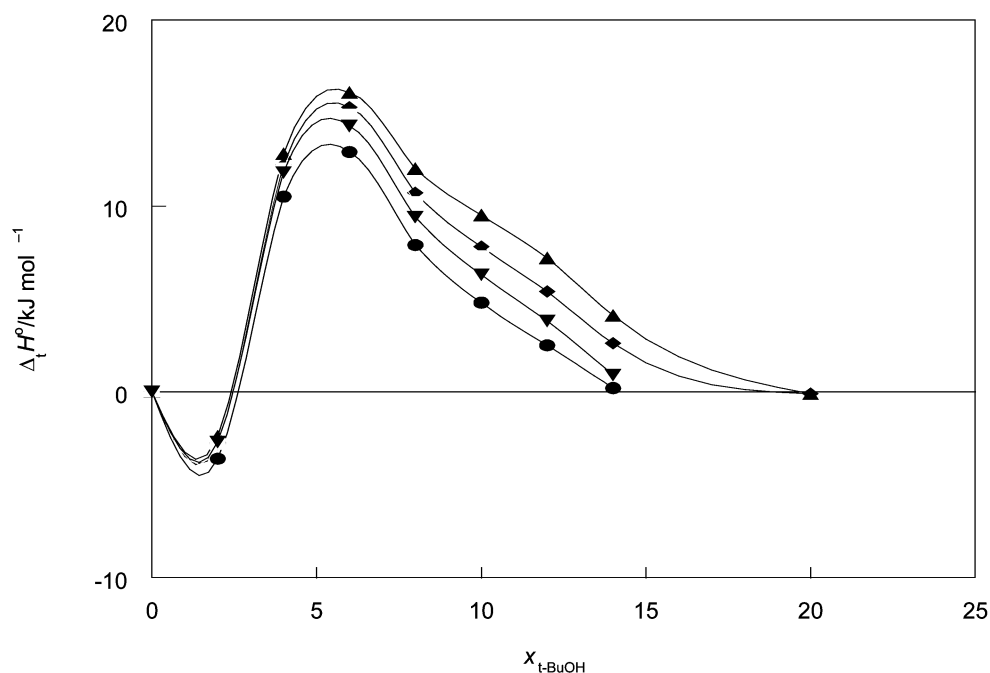


Fig. 10 Variation of $\Delta_t H^\circ(M^+, w \rightarrow w + t\text{-BuOH})$ for the alkali metal ions with solvent composition at 25 °C: ● Li^+ , ▲ Na^+ , ◆ K^+ , ■ Rb^+ , ▼ Cs^+ (reproduced from [7]).

magnitude and position of the extrema. Similar but thermodynamically opposing effects are observed for the entropies of transfer [7]. This compensation of enthalpy and entropy effects results in the relatively featureless plots of $\Delta_t G^\circ$ in Fig. 9.

The significant features observed for $\Delta_t H^\circ$ and $\Delta_t S^\circ$ as a function of solvent composition become truly dramatic for the plots (Fig. 11) of the corresponding heat capacities of transfer, $\Delta_t C_{p\phi}(\text{ion}, w \rightarrow w + t\text{-BuOH})$ [18]. Now, the presence of two extrema, one at $x_{t\text{-BuOH}} \approx 0.026$ (~10 mass % $t\text{-BuOH}$) and a second much larger one at $x_{t\text{-BuOH}} \approx 0.075$ (~25 mass % $t\text{-BuOH}$) is clearcut, with their magnitude being much greater than the likely uncertainty in the TATB assumption. Interestingly, there is (partial) compensation between the cations and anions. Virtually identical effects, including the cation/anion compensation, are observed [18] for the corresponding molar volumes of transfer, $\Delta_t V_\phi(\text{ion}, w \rightarrow w + t\text{-BuOH})$, Fig. 12.

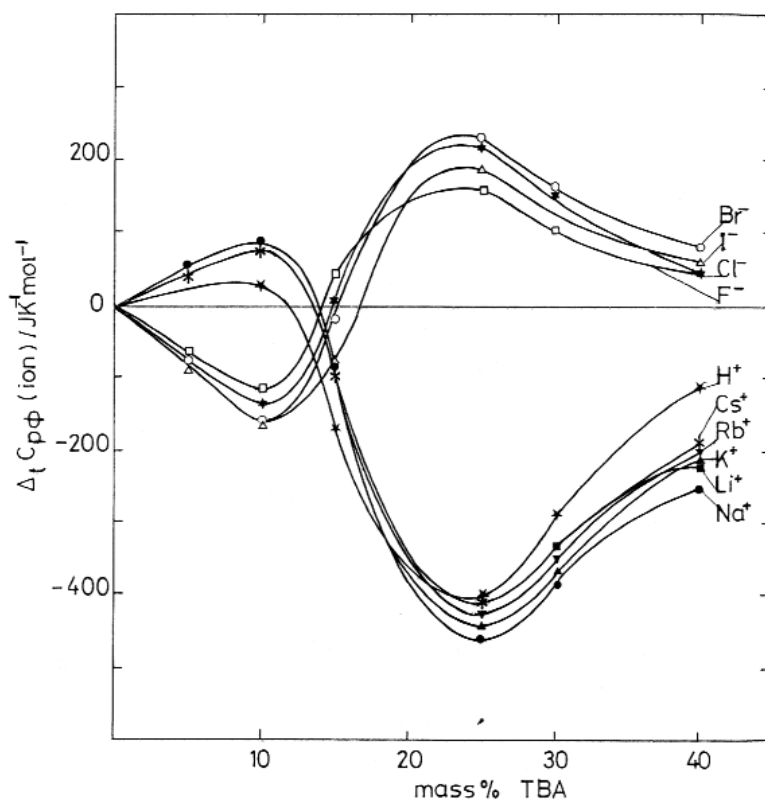


Fig. 11 Variation of $\Delta_{f}C_{p\phi}(\text{ion}, w \rightarrow w + t\text{-BuOH})$ for the alkali metal and halide ions with solvent composition at 25 °C: (reproduced from [18]).

As noted above, both heat capacities and volumes are composite quantities. However, the transfer quantities do not include any “intrinsic” component (since this is effectively constant for a given ion) and thus are especially sensitive to solvent–solvent interactions. Indeed, the most probable explanation of the thermodynamic effects observed for the transfer of ions from water to (w + *t*-BuOH) mixtures is that they reflect the influence of the ions on incipient or actual nanoheterogeneity in these mixtures [18]. It may be concluded from the size of these changes (Figs. 11 and 12) that transfer thermodynamic quantities are sensitive probes for studying such effects, in addition to their usefulness in characterizing variations in solubility, redox potentials, and equilibrium constants in nonaqueous and mixed solvents [1,13,19].

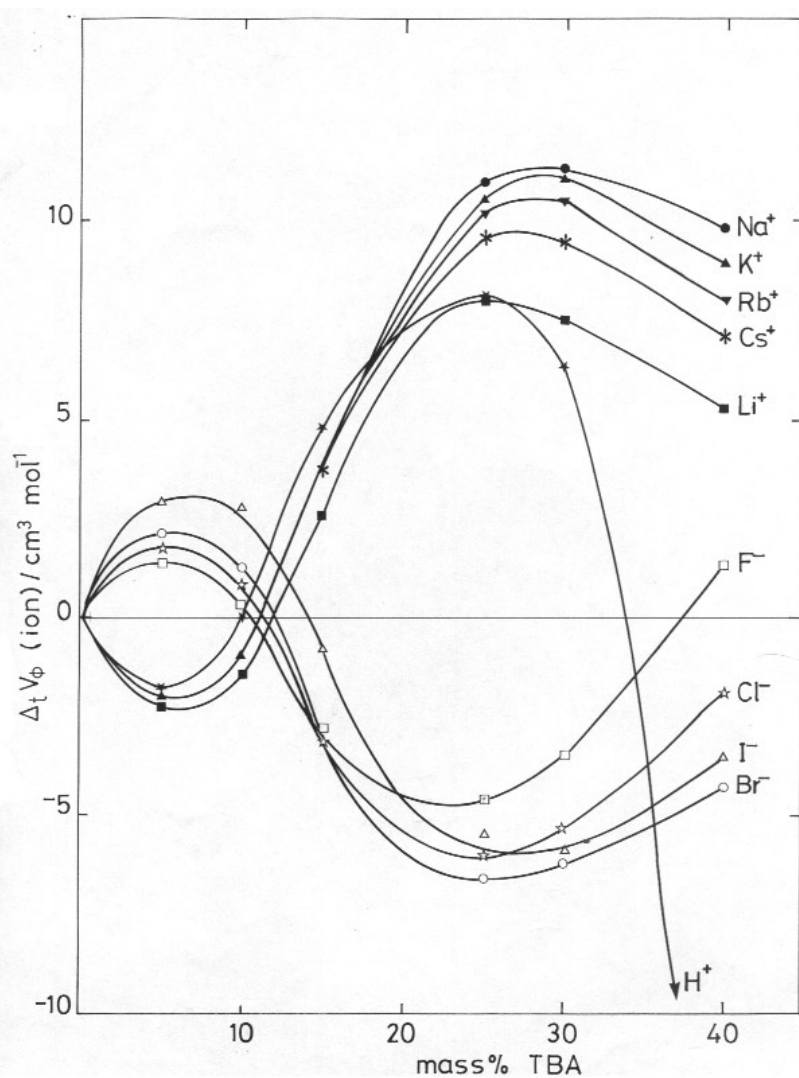


Fig. 12 Variation of $\Delta_t V_\phi(\text{ion}, w \rightarrow w + t\text{-BuOH})$ for the alkali metal and halide ions with solvent composition at 25 °C: (reproduced from [18]).

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