

Enthalpies and Entropies of Transfer of Electrolytes and Ions from Water to Mixed Aqueous Organic Solvents

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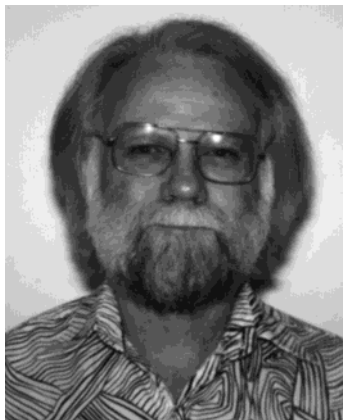
I. Introduction

A. Enthalpies and Entropies of Transfer

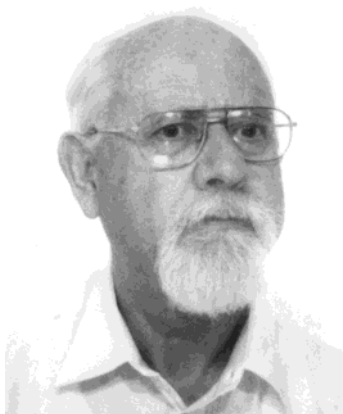
Many quantitative studies have been made of the standard molar enthalpies and, to a lesser extent, entropies of transfer of electrolytes from a reference solvent, usually water, to aqueous–organic solvent mixtures. Most results have been obtained at 25 °C, although some data have been reported at other, mostly near-ambient, temperatures. Values of these quantities have also been estimated for individual ions on many occasions by use of various extrathermodynamic assumptions. Despite this abundance, no systematic review or critical evaluation of these data has been undertaken before now.

The standard molar enthalpy of transfer, $\Delta_t H^\circ(\text{MX}, w \rightarrow w + s)$, of an electrolyte MX from water, *w*, to a mixed aqueous–organic solvent, *w* + *s*, is given by the difference between the standard molar solvation enthalpies of MX in the mixed solvent and in water. Note that here and throughout this review ‘MX’ will be used as a convenient shorthand for any strong electrolyte, without restriction as to its charge type or stoichiometry, and that “standard” refers to the electrolyte at infinite dilution in the solvent (mixture), where the ions of the electrolyte interact with the solvent molecules in their surroundings but not with each other. It is generally understood that $\Delta_t H^\circ(\text{MX}, w \rightarrow w + s)$ is largely a measure of the changes in the strength of the binding of the solvent molecules to the constituent ions of the electrolyte. Since these effects may be quite different (even of opposite sign) for cations and anions, it is of interest to have values for the individual ions: $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + s)$ and $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + s)$, although these cannot be obtained within the framework of thermodynamics. The ionic enthalpies of transfer are closely related to the preferential solvation of the ions in the mixed solvent, since it is, after all, the individual ions rather than the entire electrolyte that are surrounded by molecules of water and the cosolvent.

In the same manner, the standard molar entropy of transfer, $\Delta_t S^\circ(\text{MX}, w \rightarrow w + s)$, of the electrolyte MX from water to a mixed aqueous–organic solvent is a measure of the differences in the degree of organization or structure between the (mixed) solvent and water, occasioned by the electrolyte. Again, the effects of the individual ions are of particular interest.



Glenn Hefter received his B.Sc. (in 1969) and Ph.D. (in 1973) degrees from the University of Melbourne. He worked as a high school teacher and then at Stirling University in Scotland, the University of Malaya in Malaysia, and the Marine Science Laboratories in Victoria before joining Murdoch University in Perth in 1982, where he is currently Associate Professor in Chemistry. His main research interests are in solution chemistry including the thermodynamics of ion solvation, chemical speciation in hydrometallurgical and environmental solutions, and corrosion inhibitors. He also has interests in amorphous silicon solar cells and electrochemistry.



Yizhak Marcus, was born in Germany and having immigrated to Israel as a child, obtained his M.Sc. degree in 1952 and Ph.D. degree in 1956 from the Hebrew University of Jerusalem, where he has been Professor of inorganic and analytical chemistry since 1965. He has been a visiting professor in universities in several countries and has recently stayed at Murdoch University in Australia, where some of the present work was done. His research interests concern solution chemistry, as evidenced by the articles in *Chemical Reviews* that he has written as well as the titles of books he (co)authored: *Ion Exchange and Solvent Extraction of Metal Complexes* (1969), *Introduction to Liquid State Chemistry* (1977), *Ion Solvation* (1985), *Ion Properties* (1997), *Properties of Solvents* (1998), and *Solvent Mixtures. Properties and Preferential Solvation* (2002).

In purely aqueous solutions, some ions (usually either small and multiply charged or large hydrophobic ions) are known as “structure makers” while others (mainly medium-sized singly charged ions) are thought to be “structure breakers”. In aqueous–organic mixtures the structure of the water is already modified (enhanced, weakened, or completely destroyed) by the cosolvent; the effects of the ions come on top of such modifications, possibly even reversing them.

The present review follows on from a previous one¹ on the standard molar Gibbs energies of transfer of cations between water and mixed aqueous–organic solvents, $\Delta_t G^\circ(M^{n+}, w \rightarrow w + s)$. The general organization is along similar lines as are the representation of the data and the criteria used in their critical



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evaluation. The cosolvents included here differ only slightly from those considered previously, consistent with the data available in the literature. The present review also complements an earlier one on the standard molar enthalpies and entropies of transfer of ions from water into neat solvents.²

Thus, the major purpose of the present review is to provide a wide-ranging critically evaluated compilation of the standard molar enthalpies and entropies of transfer of electrolytes from water to mixed aqueous–organic solvents. For this compilation the original authors’ reported values were recalculated to obtain a consistent format that enabled comparisons to be made among the data. These whole-salt data were then split, where possible, into the transfer functions of the individual ions, using an appropriate extrathermodynamic assumption. The ion-to-solvent binding and solvent organization aspects of the various systems are then discussed, using these values, in the light of current views on ion solvation and solvent structuring. Another important feature of the data that is discussed is the compensation that sometimes occurs between the enthalpy and entropy changes, which results in values of ΔG° that are small in comparison with both ΔH° and $T\Delta S^\circ$.

B. Coverage

Data on the thermodynamics of transfer of electrolytes from water to aqueous–organic mixtures are widely scattered. The scope of the present review was limited mainly by the availability of data in the open literature. Although every effort was made to be exhaustive, some publications, mainly from the Russian literature, were difficult or, in some cases, impossible to obtain within the time available.

Although sporadic investigations almost certainly appeared earlier, the first *systematic* study of the thermodynamics of electrolyte solutions in mixed aqueous–organic solvents was that of Harned and co-workers. This group made extensive measurements with galvanic cells in aqueous–dioxane solutions in the years 1936–1939; their findings are

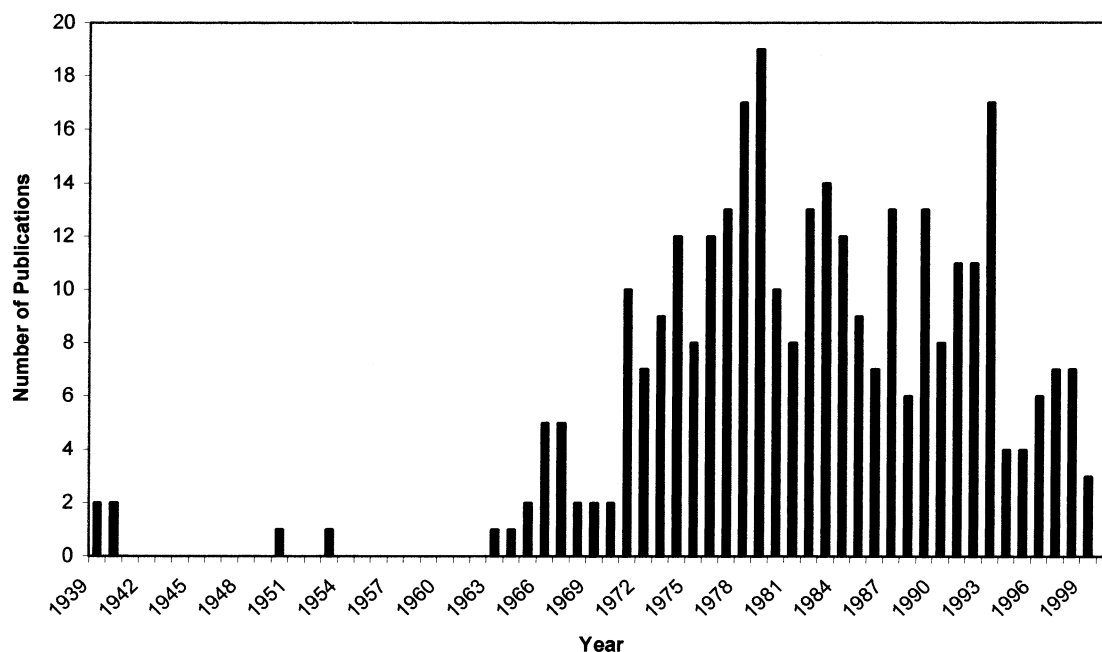


Figure 1. Publication of papers reporting experimental enthalpy (and/or entropy) of transfer data for electrolytes between water and aqueous–organic mixtures for the period 1939–2000.

summarized in the paper by Harned et al.³ The earliest useful *calorimetric* data, published at about the same time, appear to be those of Moss and Wolfenden⁴ and of Slansky,⁵ both reporting enthalpies of solution of salts in MeOH/H₂O mixtures. A hiatus in activity in this area then occurred, lasting until the almost simultaneous appearance of the studies by Feakins⁶ and Krestov⁷ and their respective co-workers. The frequency of publications reporting quantitative studies of enthalpies or entropies of transfer of electrolytes or ions from water to aqueous–organic mixtures is presented in Figure 1, derived from literature abstracted up to the end of the year 2000.

Data for enthalpies and entropies of transfer are mainly available for 1:1 electrolytes. Some information also exists for 1:2 and even 1:3 electrolytes, but virtually none has been reported for 2:1 and 3:1 salts. As in the previous paper,¹ the focus of the present review has been on electrolytes composed of simple (monatomic and symmetrical polyatomic) ions. Where data exist for more complex species, these are referenced in the text or in appropriate footnotes to the data tables. This review has been limited to $\Delta_t H^\circ$ and $\Delta_t S^\circ$ data reported for or interpolated over short intervals to 298.15 K, except for those in aqueous TMS (the abbreviation used for each solvent is given in the appropriate subheading in section IV), which are reported at 303.15 K. Where known, data at other temperatures are alluded to in footnotes to the data tables.

Wherever possible, data were included for the entire solvent composition range. However, for a number of solvents, notably *t*-BuOH, DX, AC, and THF, data are largely restricted to the water-rich region. Three cosolvents included in the review of $\Delta_t G^\circ(M^{n+})$ data,¹ propylene glycol, propylene carbonate, and pyridine, were excluded from the present study because little or no $\Delta_t H^\circ$ or $\Delta_t S^\circ$ data exist for

them. For convenience, all aqueous–organic solvent mixtures for which quantitative data were found but which were insufficient for the preparation of separate tables are listed in Table 1.

As in the previous review,¹ systems have been restricted to molecular cosolvents that are liquid at near-ambient conditions and in common use. A notable exception is urea (UR). Although a solid at room temperature (mp, 135 °C), a considerable amount of thermodynamic transfer data are available for this substance, presumably because of its purported effects on the structure of water and its well-known ability to promote the denaturation of proteins. Electrolyte transfers involving mixtures of nonaqueous solvents were excluded. This is partly a sensible limitation of the scope of the present review but is also because few systematic studies of such mixtures have been published and probably none has been confirmed by independent measurements, thus precluding any critical evaluation.

C. Thermodynamics

The essential thermodynamic relationship in the present context is the equation that relates the change in the Gibbs energy to those in enthalpy and entropy

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (1)$$

This fundamental equation of thermodynamics, relating ΔG , ΔH , and ΔS at constant temperature T and pressure P (and hereafter abbreviated as the GHSE), can be applied to any process, including the transfer of electrolytes (or ions) from one solvent to another (or to a mixture of solvents). In this case the symbol for the change in the thermodynamic quantities (Δ) is subscripted by *t*, as has already been used above. This equation has often been used to calculate one of the quantities from (known) values of the other

Table 1. Cosolvents for Which Insufficient Enthalpy of Transfer Data Existed To Justify Compilation

cosolvent	MX	composition (x_s)	ref	comments
acetamide	NaI	≤ 0.3	8	25–85 °C data
butane-1,2-diol	NaI	≤ 1	9	
	NaBPh ₄ , Ph ₄ PCl	≤ 1	10	
	NaCl	≤ 0.2	11	
butane-1,3-diol	NaCl	≤ 0.2	11	
butane-1,4-diol	NaCl	≤ 1	12	15–55 °C data KCl data ?
	LiCl, NaCl	≤ 0.5	13	
	NaI	≤ 1	9	
	NaCl	≤ 0.3	11	
butane-2,3-diol	NaCl	≤ 0.3	11	
2-butanol	NaI	≤ 1	14	
	NaI	≤ 0.04	15	308 K
	NaI	≤ 1	48	
diethyleneglycol	KCl, KBr, KI	?	16	25–55 °C data
	LiCl	≤ 0.3	17	
	NaClO ₄	≤ 0.3	18	
	CsClO ₄	≤ 0.0678	19	
1,2-dimethoxyethane	HBr	≤ 50 wt %	20	
	HI	≤ 50 wt %	21	
2-ethoxyethanol	NaCl	≤ 35 wt %	22	
	NaI	≤ 1	23	25–45 °C data
ethylenecarbonate ^a	Bu ₄ NBr	≤ 1	24, 25	
	HCl	≤ 80 wt %	26	
	KCl, KPi, KBPh ₄ , Ph ₄ AsPi	≤ 70 wt %	27	
ethylformamide	KI, NaI	≤ 0.8	28	
2-methoxyethanol	HCl, HBr	≤ 70 wt %	29	
	NaCl	≤ 20 wt %	22	
	NaI	≤ 1	23	25–45 °C data
2-methyl-1-propanol	NaI	≤ 1	49	
<i>N</i> -methylpyrrolidin-2-one	TMDABr, Bu ₄ NBr, Me ₄ NBr	≤ 0.353	30	
<i>N</i> -methylacetamide	HBr	≤ 0.5	31	
<i>N,N</i> -dimethylacetamide	NaI, CsI	≤ 1	32	
	NaCl, KCl	≤ 0.2	33	
	Bu ₄ NBr	≤ 1	25	
1,2-propandiol	MX	≤ 1	34	15–55 °C data
	NH ₄ NO ₃	≤ 1	35	
	LiCl, NaCl, KCl	≤ 0.3	13	
	CsClO ₄	≤ 1	36	
	CsBPh ₄	≤ 1	37	
	NaBPh ₄ , Bu ₄ NBr	≤ 1	35	
	NaCl, KCl, CsCl	≤ 0.5	38	
1,2,3-propantriol	NaI, RbI	≤ 1	40	
propanoic acid	NaBr, KBr	≤ 16 wt %	41	
propylene carbonate	CsI	≤ 1	42	miscibility gap
	LiCl, KCl	≤ 16 wt %	43	
	SrCl ₂ , BaCl ₂	≤ 16 wt %	44	
	PrCl ₃ , NdCl ₃	≤ 16 wt %	45	
	MgCl ₂ , CaCl ₂	≤ 16 wt %	46	
	CsClO ₄	≤ 1	47	
	CsClO ₄	≤ 0.0382	19	
tetraethyleneglycol	CsClO ₄	≤ 0.0489	19	273–318 K data PEG data also
triethyleneglycol	CsClO ₄	≤ 0.0489	19	

^a Ionic values were not derived because there were unresolvable uncertainties in the data.

two. Thus, enthalpy changes for the transfer process

$$\Delta_t H^\circ = \Delta_t G^\circ + T\Delta_t S^\circ \quad (2)$$

have been obtained from measurements on suitable electrochemical cells that yield $\Delta_t G^\circ$ and $\Delta_t S^\circ$ data (see section II.A.3). Similarly, entropies of transfer

$$\Delta_t S^\circ = (\Delta_t H^\circ - \Delta_t G^\circ)/T \quad (3)$$

have been determined from known values of $\Delta_t G^\circ$ and $\Delta_t H^\circ$ (see section II.B.3).

II. Measurement of the Thermodynamic Transfer Functions

A. Standard Molar Enthalpies of Transfer

1. Calorimetry

Calorimetry provides the most direct method for determining the enthalpies of transfer of an electrolyte from one solvent to another.⁵⁰ This is generally done by measuring the enthalpy of solution, $\Delta_{\text{sln}}H$, of the electrolyte in the reference and the target (mixed) solvents and taking the difference. In the case of electrolytes that are sufficiently soluble and

that dissolve relatively quickly, $\Delta_{\text{sln}}H$ can be measured using a calorimeter equipped with an appropriate mechanism for introducing the solid solute into the solution. The measured $\Delta_{\text{sln}}H$ are concentration-dependent because of the ion–ion interactions in the solution, and thus, the standard enthalpies of solution, $\Delta_{\text{sln}}H^\circ$, are best obtained from such values using an extended Debye–Hückel (or equivalent⁵¹) expression

$$\Delta_{\text{sln}}H^\circ = \Delta_{\text{sln}}H - [(2/3)A_{\text{H}}c^{1/2} + Bc + Cc^2] \quad (4)$$

In eq 4, B and C are empirical constants and A_{H} is the Debye–Hückel limiting law constant for enthalpies,⁵² which is given by the expression

$$A_{\text{H}} = \nu RT^2(3/2^{1/2})[T^{-1} + (\partial \ln \epsilon / \partial T)_P + (1/3\rho)(\partial \rho / \partial T)_P] \quad (5)$$

where ϵ and ρ are the relative permittivity and density of the solvent at the measurement temperature T and ν is the number of ions present in the formula of the electrolyte. At low concentrations the empirical coefficient C can be set equal to zero and, depending on the precision of the measurements, the term Bc may also be disregarded. Use of eq 4 necessitates measurements over a range of concentrations, preferably in time-consuming independent experiments, and thus, such extrapolations are possible (and justified) only in work of the highest precision. Where measurements have been made at just a few concentrations, $\Delta_{\text{sln}}H^\circ$ is often calculated using the Debye–Hückel limiting law

$$\Delta_{\text{sln}}H^\circ = \Delta_{\text{sln}}H - (2/3)A_{\text{H}}\sqrt{c} \quad (6)$$

In many mixed solvents, the information required for calculating A_{H} (eq 5) is not available. Under these circumstances a Masson-type equation,^{51,52} analogous to eq 6 but with A_{H} taken as an empirical parameter, A_{H}' , must be used. Values of $\Delta_{\text{sln}}H$ are plotted against \sqrt{c} , with $\Delta_{\text{sln}}H^\circ$ and A_{H}' being determined as the intercept and slope, respectively. Inevitably, the values of $\Delta_{\text{sln}}H^\circ$ so obtained are less accurate than those determined from the theory-based equations. For work of even lower precision, the concentration dependence of $\Delta_{\text{sln}}H$ is undetectable and the values are simply averaged and reported as $\Delta_{\text{sln}}H^\circ$.

The transfer enthalpy is calculated simply as

$$\Delta_{\text{t}}H^\circ = \Delta_{\text{sln}}H^\circ(\text{s}) - \Delta_{\text{sln}}H^\circ(\text{w}) \quad (7)$$

where $\Delta_{\text{sln}}H^\circ(\text{w})$ and $\Delta_{\text{sln}}H^\circ(\text{s})$ are the standard enthalpies of solution of the solute in water and the target (mixed) solvent, respectively.

High-precision calorimetry has a resolution of about 50 J mol⁻¹, but more realistically, the precision of routine measurements is probably 200 J mol⁻¹ or larger. Accuracy is of course worse, and in practice, the agreement between values from different laboratories is often poor.

Where the electrolyte forms a stable hydrate (MX· n H₂O), the value of $\Delta_{\text{t}}H^\circ$ for the anhydrous electrolyte can be determined from the enthalpies of solution of the hydrate and of water in the target

solvent as

$$\begin{aligned} \Delta_{\text{t}}H^\circ(\text{MX}, \text{w} \rightarrow \text{s}) = & \\ & \Delta_{\text{sln}}H^\circ(\text{MX} \cdot n\text{H}_2\text{O in s}) - \\ & \Delta_{\text{sln}}H^\circ(\text{MX} \cdot n\text{H}_2\text{O in w}) - n\Delta_{\text{sln}}H_{\text{w}} \quad (8) \end{aligned}$$

where $\Delta_{\text{sln}}H_{\text{w}}$ is the enthalpy of solution (partial molar excess enthalpy) of water in the target solvent and n is the hydration number of the crystalline hydrate.

Electrolytes that dissolve slowly present a particular problem. Although there are calorimeters available commercially that can handle such processes, most cannot. An alternative that circumvents this difficulty is to measure the enthalpies of dilution of a concentrated solution of the electrolyte in water and in the target solvent. This is analogous to measuring the enthalpies of solution of hydrated salts, and $\Delta_{\text{t}}H^\circ$ is calculated as

$$\begin{aligned} \Delta_{\text{t}}H^\circ(\text{MX}, \text{w} \rightarrow \text{s}) = & \Delta_{\text{dil}}H^\circ(\text{MX in s}) - \\ & \Delta_{\text{dil}}H^\circ(\text{MX in w}) - n\Delta_{\text{sln}}H_{\text{w}} \quad (9) \end{aligned}$$

where the first two terms on the RHS of eq 9 are the enthalpies of dilution of the solution in the target solvent and in water, respectively, and n is the number of moles of water associated with one mole of the solute in the concentrated solution.

When $\Delta_{\text{t}}H^\circ$ values are calculated from the solution enthalpies of the solid hydrates or from the enthalpies of dilution, it is usual to determine the infinite dilution value of the enthalpy change and then correct for the enthalpy of solution of water. Clearly, the accuracy of $\Delta_{\text{t}}H^\circ$ values determined in these ways depends on the uncertainties of the $\Delta_{\text{sln}}H_{\text{w}}$ values and so is lower than for data determined from dissolution of the anhydrous electrolyte. Generally, $\Delta_{\text{t}}H^\circ$ values become less precise as the concentration of the organic cosolvent increases since the $\Delta_{\text{sln}}H_{\text{w}}$ term becomes large and its error increasingly significant.

Where the electrolyte is sparingly soluble, the enthalpy of precipitation, $\Delta_{\text{ppt}}H$, can be measured. For example, adding a solution of KCl to one of AgNO₃ allows determination of the enthalpy of precipitation of AgCl. These measurements can be made using a conventional isoperibol or, more conveniently, a titration calorimeter. It should be noted that $\Delta_{\text{ppt}}H$ values have rarely been used for obtaining $\Delta_{\text{t}}H^\circ$. However, this technique could, at least in principle, be very useful for obtaining the $\Delta_{\text{t}}H^\circ$ values for the very sparingly soluble TATB or TPTB salts required for the estimation of the enthalpies of transfer of individual ions (see section III.A.5). Extrapolation to infinite dilution via eq 4 or 6 requires measurements using different concentrations of the solution in the calorimeter.

2. $(\partial \Delta_{\text{t}}G^\circ / \partial T)_P$ Measurements

If the standard molar Gibbs energy of transfer of an electrolyte or ion, $\Delta_{\text{t}}G^\circ$, is known at several temperatures, then in principle it is possible to obtain $\Delta_{\text{t}}H^\circ$ at a given temperature T from the temperature derivative of $\Delta_{\text{t}}G^\circ$

$$\Delta_t H^\circ = \Delta_t G^\circ + T\Delta_t S^\circ = \Delta_t G^\circ - T(\partial\Delta_t G^\circ/\partial T)_P \quad (10)$$

This procedure has no advantage over the calculation via the GHSE, that is, by explicit use of the entropy of transfer $\Delta_t S^\circ$, obtained as described in section II.B. Furthermore, the use of eq 10 suffers from the inaccuracies introduced by derivatization as well as the errors that are inherent in temperature-dependent measurements.^{56,57} Examples of the problems associated with such measurements will be found in some of the systems discussed in section IV. Use of this approach is strongly discouraged, especially with regard to solubility data (which constitute most of the information available),⁵⁸ and it was not employed in the present review to obtain otherwise unavailable data.

3. GHS Equation Calculations

While the GHSE can be used to calculate $\Delta_t H^\circ$ from the corresponding Gibbs energy and entropy (eq 2), in practice it has not often been done. This is because it is usually easier and more accurate to determine $\Delta_t H^\circ$ by calorimetry, as described above.

B. Standard Molar Entropies of Transfer

1. Temperature Derivatives of Cell EMFs

The most direct method for the determination of the standard molar entropy of transfer of an electrolyte is from electrochemical data. Consider the isothermal galvanic cell I, containing the electrolyte MX dissolved at ionic strength I in water (w) or the mixed aqueous organic solvent (s), at temperature T



with the M electrode responsive to the cation M^{n+} and the X electrode responsive to the anion X^- . The standard molar Gibbs energy change for the cell reaction, ΔG° , in any solvent is related to the standard electromotive force (emf) of this cell, E° , by

$$\Delta G^\circ = -nFE^\circ \quad (11)$$

where n is the number of electrons involved in the cell reaction and F is the Faraday constant. Entropy being the (negative) temperature derivative of the Gibbs energy, $\Delta S^\circ = -(\partial\Delta G^\circ/\partial T)_P$, it follows that

$$\Delta S^\circ = nF(\partial E^\circ/\partial T)_P \quad (12)$$

That is, the standard entropy change for the cell reaction is proportional to the temperature derivative of the standard emf of the cell at constant pressure. If the latter quantity is measured in the target mixed solvent (subscript s) and in the reference solvent (water, subscript w), the difference yields the desired $\Delta_t S^\circ$

$$\Delta_t S^\circ = nF(\partial[E_s^\circ - E_w^\circ]/\partial T)_P \quad (13)$$

The emf, E , of cell I at finite concentrations of MX can be measured with a precision of ± 0.01 mV, although the true uncertainties are usually considerably larger. The extrapolation of measured E values

to infinite dilution of the electrolyte to provide E° can be achieved with little deterioration in precision. This extrapolation can be conveniently done using the extended Debye–Hückel expression for the activity coefficient of MX. Usually, the Debye–Hückel term in $I^{1/2}$ is subtracted from the measured E values to permit a linear extrapolation to zero against I

$$E - (RT/nF)[A(T)I^{1/2}/(1 + Ba(T)I^{1/2})] = E^\circ(T) + (RT/nF)b(T)I \quad (14)$$

where all undefined symbols have their usual meanings.⁵³ The temperature- and solvent-dependent coefficients A and B are calculated from the properties of the solvent (the relative permittivity and the density if the molal scale is used for MX) and other fundamental constants. The so-called ion-size parameter a is usually assumed to be independent of the solvent and temperature. Any uncertainty associated with this assumption is compensated for by changes in the value of the empirical parameter, $b(T)$. This parameter and the desired value of $E^\circ(T)$ are obtained as the slope and intercept of a plot of the LHS of eq 14 against I .

A common practice is to express the measured differences $E_s^\circ(T) - E_w^\circ(T)$ as a second-degree polynomial in T (when measured for at least three temperatures, typically in the interval 15–45 °C)

$$E_s^\circ(T) - E_w^\circ(T) = a_s + b_s T + c_s T^2 \quad (15)$$

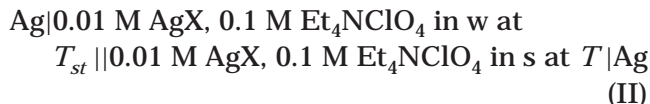
and to calculate the derivative in eq 15 numerically at the desired temperature (usually 298.15 K). This procedure permits $\Delta_t S^\circ(\text{MX})$ to be determined with a precision of $\pm 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$. In a few instances polarographic (or voltammetric) half-wave potentials, $E_{1/2}$, have been measured rather than galvanic cell emfs. These potentials are difficult to measure to better than ± 1 mV, and this uncertainty is reflected in the resulting entropies of transfer.

The major disadvantage of measuring $\Delta_t S^\circ$ via the temperature derivative of the emf of a galvanic or polarographic cell is that this procedure is applicable to relatively few electrolytes. Few electrodes (and hence cells) are sufficiently reversible for such purposes, the most widely employed undoubtedly being the hydrogen ($\text{Pt}|\text{H}_2, \text{H}^+$) and the $\text{Ag}|\text{AgX}, \text{X}^-$ electrodes, used to determine $\Delta_t S^\circ(\text{HX})$. Even electrodes that are useful in aqueous solutions often require special procedures to enable them to function properly in aqueous–organic solvent mixtures,⁵⁴ and then the results obtained are usually less accurate.^{50,55} Furthermore, it should be noted that all measurements made as a function of temperature are subject to temperature-dependent errors. These systematic but often unsuspected errors, even when small, can have significant effects on the temperature derivative and thus on the reliability of quantities obtained from it.^{50,56–58} On the whole, it is fair to say that the expected accuracy in $\Delta_t S^\circ$ arising from the apparent experimental precision and directness of this method has commonly not been realized.

2. Nonisothermal Cell EMF (NICE) Measurements

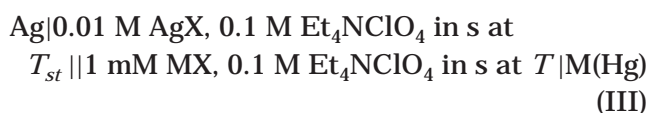
Entropies of transfer may also be determined from nonisothermal cell emf (NICE) measurements. In the

few instances where this approach has been employed, both polarography and potentiometry were used.^{59–61} Initially, galvanic cell II, at $283 \leq T/K \leq 323$, was used to obtain the dependence of the potential of the $\text{Ag}|\text{Ag}^+$ electrode on temperature



where M stands for mol L^{-1} and X^- for CF_3SO_3^- . The cell electrodes were of course ultimately in contact with copper terminals that were maintained at the standard temperature $T_{st} = 298.15 \text{ K}$. The thermocouple potential, E_{tc} , developed between the Ag electrode (at T) and the copper connector at T_{st} , was small enough to neglect ($dE_{tc}/dT < 20 \mu\text{V K}^{-1}$ ⁶²).

To determine $\Delta_t S^\circ(\text{M}^{n+})$, the right-hand compartment of cell II was replaced by a polarographic half-cell



The values of the half-wave potentials $E_{1/2}$ in cell III could be determined to within $\pm 4 \text{ mV}$, but the temperature dependences were claimed⁶¹ to be measurable to within $20 \mu\text{V K}^{-1}$. The authors estimated that this corresponded to an uncertainty of $\pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ in the cell reaction entropies. A similar determination was made with bis(biphenyl)chromium (BBCr) instead of MX in the right-hand compartment of cell III. The extrathermodynamic assumption that was applied was thus that there is a negligible thermal diffusion potential ($< 20 \mu\text{V K}^{-1}$)⁶² between the hot and cold compartments in the various nonisothermal cells.⁶³ Values of $\Delta_t S^\circ(\text{M}^{n+})$ obtained in this way were combined with the corresponding Gibbs energies of transfer, estimated by the BBCr assumption,¹ to yield the enthalpy of transfer.⁶¹

3. GHS Equation Calculations

Probably the most common method for obtaining $\Delta_t S^\circ$ values for electrolytes has been via the GHSE. This involves the combination, via eq 3, of $\Delta_t G^\circ$ obtained from the solubilities or other suitable measurements and the corresponding $\Delta_t H^\circ$, usually obtained by calorimetry. The values of $\Delta_t G^\circ$ and $\Delta_t H^\circ$ often come from different sources and typically have an uncertainty of at least $\pm 0.1 \text{ kJ mol}^{-1}$, so that the uncertainty in $\Delta_t S^\circ$ would probably be up to $\pm 0.5 \text{ J K}^{-1} \text{ mol}^{-1}$. This method, thus, appears to be at least as accurate for the determination of the standard molar entropies of transfer of electrolytes as the other methods mentioned above. It has the advantage of being more or less universally applicable, since both $\Delta_t G^\circ$ and $\Delta_t H^\circ$ can be determined with reasonable accuracy for almost any system of interest. This approach will be exploited in the present review mostly to obtain $\Delta_t S^\circ(\text{ion})$ values from the corresponding ionic enthalpies and Gibbs energies.

III. Data Treatment

A. Estimation of Single Ion Values

1. Background

Single-ion values of $\Delta_t H^\circ$ and $\Delta_t S^\circ$ (hereafter referred to collectively as $\Delta_t Y^\circ$) are invaluable for developing an understanding of the interactions between an ion and its surrounding solvent medium. Values of $\Delta_t Y^\circ(\text{ion})$ are also useful for the efficient recording of the corresponding thermodynamic functions of transfer of electrolytes, since the latter are easily reconstituted from the former, so that far fewer values need to be listed.

Single-ion values of $\Delta_t Y^\circ$ cannot, of course, be measured by direct experiment. To obtain such values it is necessary to use an appropriate extrathermodynamic assumption. The assumptions employed for this purpose resemble those used for calculating $\Delta_t G^\circ(\text{ion})$, which have been reviewed on numerous occasions (ref 1 and references therein). It should be emphasized that strictly it is only necessary to obtain a value of $\Delta_t Y^\circ$ for just one ion. Those for other ions can then be determined, without any further assumption, by application of the principle of additivity of standard state electrolyte (or ionic) values, because at infinite dilution the ions behave independently of other solute species. In practice, however, if possible, it is advisable to use $\Delta_t Y^\circ$ values of more than one ion so as to avoid artifacts that might arise from singular erroneous values of the chosen ion.

In the following description of extrathermodynamic assumptions suitable for the calculation of $\Delta_t Y^\circ(\text{ion})$, only those employed reasonably widely are discussed. A fuller consideration of the numerous methods proposed over the years is presented by Marcus.⁶⁴ For convenience, assumptions used for enthalpies and entropies are discussed together.

2. Assumptions Involving the GHS Equation

The GHSE is as applicable to ions as it is to electrolytes, due to the additivity principle. Thus

$$\Delta_t G^\circ(\text{ion}) = \Delta_t H^\circ(\text{ion}) - T\Delta_t S^\circ(\text{ion}) \quad (16)$$

The calculation of either $\Delta_t H^\circ(\text{ion})$ or $\Delta_t S^\circ(\text{ion})$ therefore requires values of $\Delta_t G^\circ(\text{ion})$. The latter must also be obtained using a suitable extrathermodynamic assumption. Three assumptions have been widely employed for the calculation of $\Delta_t G^\circ(\text{ion})$. These are¹ the reference redox couple assumption, usually employing bis(biphenyl)chromium(0/I) (BBCr), the negligible liquid junction potential assumption (NLJP), and the reference electrolyte assumption, employing the salts tetraphenylarsonium tetraphenylborate ($\text{Ph}_4\text{AsBPh}_4$, TATB) or its phosphorus analogue (Ph_4PBPh_4 , TPTB). Combination of $\Delta_t G^\circ(\text{ion})$ so obtained with $\Delta_t H^\circ(\text{ion})$ or $\Delta_t S^\circ(\text{ion})$, derived by an appropriate assumption, yields the third quantity. This approach has been most commonly used for calculating $\Delta_t S^\circ(\text{ion})$. However, $\Delta_t H^\circ(\text{ion})$ values have also been obtained^{61,63} by combining $\Delta_t G^\circ(\text{ion})$ values

using the BBCr assumption with $\Delta_t S^\circ(\text{ion})$ determined from NICE measurements (see below).

3. Negligible Thermal Diffusion Potential Assumption

The assumption of negligible diffusion potential at the liquid–liquid junction between two halves of an electrochemical cell maintained at two constant but different temperatures was used by Weaver et al.⁶² to measure the entropy change of single-electrode processes. This assumption was adopted by Gritzner and Lewandowski⁶³ for the determination of $\Delta_t S^\circ$ for various ions between two (neat) solvents and later extended⁶¹ to include transfers between water and aqueous–organic mixtures. This method is loosely analogous to the negligible liquid junction potential method for the determination of $\Delta_t G^\circ(\text{ion})$ (ref 1 and references therein). Its validity depends on the small magnitude of most thermal diffusion potentials.

4. Reference Electrolyte Assumptions

This type of assumption has been by far the most popular among researchers. Almost all have taken electrolytes involving a large cation and anion of similar size and structure, the most common being Ph_4As^+ or Ph_4P^+ and BPh_4^- . It should be noted that whenever such effects have been investigated, no significant differences between the two cations have been observed. Accordingly, they will be treated as equivalent throughout this review. Occasionally salts with small ions have been selected as the reference electrolyte. For example, Booij and Somsen⁶⁵ employed the assumption

$$\Delta_t H^\circ(\text{Na}^+) = \Delta_t H^\circ(\text{Br}^-) = \frac{1}{2}\Delta_t H^\circ(\text{NaBr}) \quad (17)$$

to obtain $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{DMF})$. The reason given for this choice was that $\Delta_t H^\circ(\text{NaBr}, w \rightarrow w + \text{DMF})$ was nearly linear with respect to x_{DMF} whereas $\Delta_t H^\circ$ for electrolytes involving large ions showed pronounced extrema as functions of x_{DMF} . Whether this observation has any fundamental significance is not clear, and the use of small ions for obtaining ionic values has been criticized by Krestov et al.⁶⁶ Certainly, most researchers in this area consider that assumptions involving large, chemically similar ions, and in particular, those involving $\text{Ph}_4\text{As}(\text{or P})^+$ and BPh_4^- , can be used with some confidence for obtaining $\Delta_t Y^\circ(\text{ion})$. No strong evidence has been presented to suggest that $\Delta_{\text{solvn}} H^\circ(\text{Ph}_4\text{As}(\text{or P})^+)$ should differ significantly from $\Delta_{\text{solvn}} H^\circ(\text{BPh}_4^-)$. Such reservations have been discussed at length for neat solvents by Marcus,⁶⁴ and similar considerations should apply to aqueous–organic mixtures. Furthermore, if the TA(P)TB assumption is acceptable for $\Delta_t G^\circ(\text{ion})$ at 25 °C,¹ there does not seem to be any fundamental reason to cause it to be less satisfactory at other temperatures. This implies, via the usual thermodynamic relationships, that the TA(P)TB assumption should be equally satisfactory for $\Delta_t Y^\circ(\text{ion})$.²

5. Implementation of the Adopted Assumption

From the above considerations, the TA(P)TB assumption has been adopted throughout this review to calculate $\Delta_t Y^\circ(\text{ion})$. Unfortunately, both TATB and

TPTB are very sparingly soluble in virtually all aqueous–organic mixtures. This creates particular problems for the measurement of $\Delta_t G^\circ(\text{TA(P)TB})$ ^{1,67} but not necessarily for the corresponding values of $\Delta_t Y^\circ$. Thus, while measurement of $\Delta_{\text{sln}} H^\circ$ for TA(P)TB is impractical, calorimetric determination of its standard enthalpy of precipitation ($= -\Delta_{\text{sln}} H^\circ$) is possible, at least in principle. Somewhat surprisingly, this approach does not seem to have been used, although it has been employed to determine $\Delta_t H^\circ$ values for other sparingly soluble substances.⁶⁸

Instead, $\Delta_t H^\circ(\text{TA(P)TB})$ has been determined by application of the additivity principle. This requires accurate data for three electrolytes

$$\Delta_t H^\circ(\text{TA(P)TB}) = \Delta_t H^\circ(\text{TA(P)X}) + \Delta_t H^\circ(\text{MTB}) - \Delta_t H^\circ(\text{MX}) \quad (18)$$

According to the TA(P)TB assumption, the ionic values are then given by

$$\Delta_t H^\circ(\text{TA(P)}^+) = \Delta_t H^\circ(\text{TB}^-) = \frac{1}{2}\Delta_t H^\circ(\text{TA(P)TB}) \quad (19)$$

An identical approach is used for determining $\Delta_t S^\circ(\text{TA(P)TB})$ and hence $\Delta_t S^\circ(\text{ion})$. The need to calculate $\Delta_t Y^\circ(\text{TA(P)TB})$ by additivity increases the uncertainty in the ionic values derived from them. Of course, the overall reliability of the resulting ionic values depends mainly on the validity of the extra-thermodynamic assumption employed.

B. Solute Concentration and Solvent Composition Scales

1. Solute Concentrations

The standard molar enthalpy of transfer of a solute $\Delta_t H^\circ(\text{MX})$ is independent of the solute concentration scale.⁶⁹ On the other hand, $\Delta_t S^\circ(\text{MX})$ depends on the solute concentration scale in the same manner as $\Delta_t G^\circ(\text{MX})$. The latter dependence was discussed previously¹ and, for the same reasons as given then, the mol L⁻¹ scale was adopted for $\Delta_t S^\circ(\text{MX})$ in the present review. The relationships between the values of $\Delta_t S^\circ$ on the different solute concentration scales are

$$\Delta_t S^\circ_{(c)} = \Delta_t S^\circ_{(m)} + 2.303R \log(d_s/d_w) = \Delta_t S^\circ_{(x)} + 2.303R \log(M_w d_s / M_s d_w) \quad (20)$$

where the subscripts (c), (m), and (x) denote the mol L⁻¹, mol (kg solvent)⁻¹, and solute mole fraction scales, respectively. The unbracketed subscripts w and s, respectively, refer to water (as the reference solvent) and the mixed aqueous–organic solvent, including the neat (100%) organic component. The symbols *M* and *d* represent the molar mass and density.

Thus, knowledge of the mean molar mass ($M_s = x_w M_w + x_s M_{\text{org}}$) and density of the mixed solvent is required for interconversion of the transfer entropies among the various scales. Since the correction term involving densities is rather small, it is reasonable

to ignore the volume change on mixing and simply use the molar volumes V° of the neat solvents to calculate the density of the mixture. That is

$$d_s \approx [x_w M_w + x_s M_{\text{org}}] / [x_w V_w^\circ + x_s V_{\text{org}}^\circ] \quad (21)$$

where x here represents the solvent mole fraction composition and the subscript org denotes the neat (pure) organic solvent.

2. Solvent Composition

As discussed previously,¹ solvent compositions have been reported on a variety of scales, including mole, mass, and volume fractions or percentages. The relationships among these scales for aqueous–organic mixtures are as follows. When n_w mol of water of mass $n_w M_w$ are mixed with n_{org} mol of an organic cosolvent of mass $n_{\text{org}} M_{\text{org}}$, the mol fraction of the organic component is

$$x_s = n_{\text{org}} / (n_{\text{org}} + n_w) \quad (22)$$

and the mass (weight) fraction of the cosolvent is

$$w_s = n_{\text{org}} M_{\text{org}} / (n_{\text{org}} M_{\text{org}} + n_w M_w) \quad (23)$$

Some authors have used ideal volume fractions, $\phi_{s,\text{id}} = V_{\text{org}} / (V_{\text{org}} + V_w)$, to express solvent composition, where V_w and V_{org} represent known volumes of the neat components used to prepare the solvent mixture. This permits the ready calculation of the mole or mass fractions providing the densities of the neat components at the temperature of preparation of the mixture are known. However, if a volume V_{org} of the neat organic component is used in preparing a volume V_{mix} of the solvent mixture by adding the water to the mark in a volumetric flask, then its volume fraction is

$$\phi_s = V_{\text{org}} / V_{\text{mix}} \quad (24)$$

Because the volume of mixing may not be zero, this introduces uncertainties into the data without providing any significant advantage. Its use should be avoided.

For the reasons given previously,¹ the solvent composition scale adopted here is mol fraction x_s (or mol percent, $100x_s$). Conversions among the scales used in the original publications were made using eqs 22–24, and the data were interpolated numerically or graphically to evenly spaced values of $100x_s$. In contrast to the previous review, it was deemed useful to routinely include values at $100x_s = 5$, because $\Delta_t H^\circ$ and $\Delta_t S^\circ$ of the solutes, in contrast to the corresponding $\Delta_t G^\circ$ values, often exhibit extrema at low cosolvent concentrations. For some solvents, where complex behavior is known to occur, even more closely spaced data are presented.

C. Relevant Properties of the Solutes and Solvents

Explanation of the observed trends in $\Delta_t H^\circ$ and $\Delta_t S^\circ$ ultimately must be made in terms of the properties of the solutes (specifically, the component ions) and the solvents involved. The most relevant

properties of the ions are their size and tendency toward coordinative interactions with solvent molecules. For the cations, the latter can be expressed as the ‘softness’ parameter (which incorporates the favorable nature of hard/hard interactions).¹ For the anions, the relevant quantity is their H-bond acceptor ability as described in ref 70.

Relevant properties of the solvents have been given previously,¹ except for the hydrophilicity/hydrophobicity factor.^{71,72} In addition, there are four solvents GY, DMA, TMS, and UR for which reasonable amounts of $\Delta_t H^\circ / \Delta_t S^\circ$ data exist that were not included in the review of $\Delta_t G^\circ$ values. Properties of neat GY, DMA, and TMS are available,⁷¹ but those of their mixtures with water have not been compiled as yet.

D. Organization of the Data

1. Organization of the Data

Separate tables for the enthalpies of transfer, $\Delta_t H^\circ$ (in kJ mol⁻¹), and the entropies of transfer, $\Delta_t S^\circ$ (in J K⁻¹ mol⁻¹ on the mol L⁻¹ scale) of electrolytes, were included for all aqueous–organic mixtures for which sufficient data were available. Where necessary, the data were recalculated and interpolated from the original publications. Values of $\Delta_t H^\circ$ for electrolytes were listed to a maximum of two decimal places where so reported or as was consistent with the claimed accuracy. Values of $\Delta_t S^\circ$ for electrolytes were restricted to one decimal place. In many cases the quality of the data does not justify this many significant figures, since the uncertainties in $\Delta_t H^\circ$ are often ≥ 0.5 kJ mol⁻¹ and those in $\Delta_t S^\circ$ are often ≥ 3 J K⁻¹ mol⁻¹. In these cases, $\Delta_t H^\circ$ data were rounded to the nearest 0.1 kJ mol⁻¹, while integral values were used for $\Delta_t S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$.

Data for individual ions are presented in separate tables for both $\Delta_t H^\circ$ and $\Delta_t S^\circ$. Most of these values were derived as part of the present review, using the TATB/TPTB assumption (see section III.A.5). The tables of ionic values also include, where available, those reported by the original authors. So as not to lose possible information for whole salts (obtainable by applying additivity to appropriate cation and anion data), values of $\Delta_t H^\circ$ and $\Delta_t S^\circ$ for single ions are cited to one decimal place and integer values, respectively, while recognizing that the uncertainty of the extrathermodynamic assumption does not justify such precision.

The tables included in section IV were ordered with respect to the solvent along the lines used previously¹ with the additional solvents inserted in appropriate places. In the tables, cations are listed first (in the same order as used previously¹) followed by anions, commencing with the halide ions.

2. Selection Criteria

Critical assessment of $\Delta_t H^\circ$ and $\Delta_t S^\circ$ data has relied in general on the existence of independently determined values from the literature. Such data are much less common than for the corresponding Gibbs energies.¹ Where data were not available at the evenly spaced intervals required for tabulation, they

were interpolated graphically or numerically. Such data are enclosed in parentheses. In many cases only one set of data was available. In some instances, particular research groups reported significantly different values for some systems, often without comment, in separate publications. Such data are included in the tables and/or appropriate comments are made in the text in section IV.

Occasionally, values of $\Delta_t Y^\circ(\text{MX})$ available only from a single source were deemed unreliable, due to obvious flaws in the determination or calculations in the original report. Where reported data for whole electrolytes were considered unreliable, reasons are given in detail in the comments on the relevant system in section IV. Such values are often included in the tables for completeness but are enclosed in square brackets and were not used further.

Values deemed reliable, i.e., those differing among independent determinations by less than $\pm 2 \text{ kJ mol}^{-1}$ for $\Delta_t H^\circ$ or $\pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$ for $\Delta_t S^\circ$, were given equal weight and averaged. The averaged values are listed in the tables as "Recommended" and printed in **bold**. Note that authors working in the same laboratories, even if not necessarily publishing together, were not considered to be independent. If over part of the solvent composition range only one set of apparently reliable data was available, these were classified as "Tentative" over that range and are also printed in **bold** but placed in curly brackets. In a few cases Recommended or Tentative data were smoothed graphically to remove random (small) variations in trend. Such values are designated with an asterisk. Because of the greater uncertainties in the values of $\Delta_t H^\circ$ and $\Delta_t S^\circ$ (relative to those in $\Delta_t G^\circ$), data available from only one source were often not assessed, even if thought to be reliable by the present reviewers.

3. Enthalpy Data

In judging the likely reliability of widely divergent data, values obtained calorimetrically were preferred over those obtained by other methods. The reliability of the calorimetric data was assessed by consideration of the reported precision, the reasonableness of the procedures used, and comparisons with related data. Particular emphasis was placed on the agreement of the values of $\Delta_{\text{sln,w}} H^\circ$ reported by the authors with accepted values.⁷³ In addition, where $\Delta_t H^\circ(\text{MX}, \text{w} \rightarrow \text{s})$ data were available for transfer between the neat solvents, they were compared with those calculable from the ionic values given in the critical review of Marcus.⁶⁴ The Recommended/Tentative enthalpy values are rounded off to the nearest 0.1 kJ mol^{-1} , in view of the uncertainties in the data themselves and those associated with interpolation, averaging, and smoothing.

Accurate values of $\Delta_t Y^\circ$ must be additive. Thus, differences between sets of electrolytes having a common ion should be independent of the nature of the common ion. This approach was used wherever possible to assess the quality of doubtful data. The failure of additivity, to worse than ca. $\pm 2 \text{ kJ mol}^{-1}$ for $\Delta_t H^\circ$, is prima facie evidence that the data contain significant errors. A typical application of this ap-

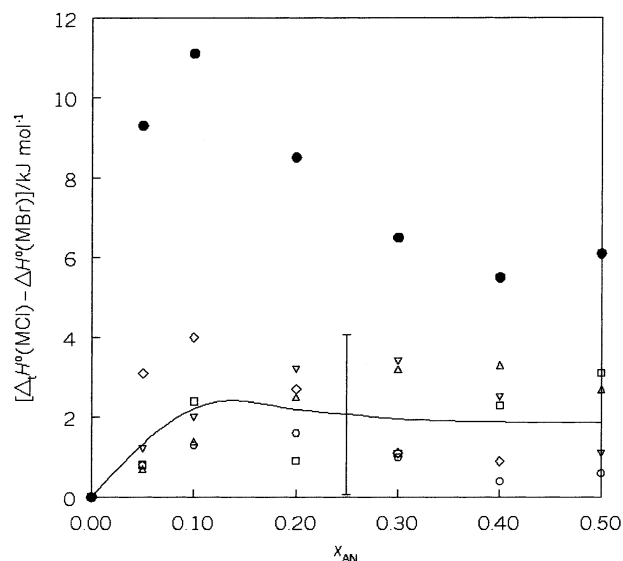


Figure 2. Differences between the standard molar enthalpies of transfer of chloride and bromide salts, $[\Delta_t H^\circ(\text{MCl}) - \Delta_t H^\circ(\text{MBr})]/\text{kJ mol}^{-1}$, from water to aqueous-AN mixtures at 25 °C, for various M^+ : $\circ \text{Na}^+$, $\triangle \text{K}^+$, ∇Ag^+ , $\diamond \text{Et}_4\text{N}^+$, $\square \text{Ph}_4\text{As}^+$ (ref 248), and $\bullet \text{Ph}_4\text{As}^+$ (ref 68). The line represents the average, and the error bar the maximum uncertainty, of the data deemed reliable.

proach is illustrated in Figure 2 for aqueous-acetonitrile mixtures. The data shown clearly indicate that the values for $\Delta_t H^\circ(\text{Ph}_4\text{AsBr}) - \Delta_t H^\circ(\text{Ph}_4\text{AsCl})$ are aberrant. In this particular case the error could be ascribed to the reported values of $\Delta_t H^\circ(\text{Ph}_4\text{AsCl})$.⁶⁸

Ionic values were estimated by the TATB/TPTB extrathermodynamic assumption as described in section III.A.5. Particular attention was paid to deriving the most reliable data for the salts required for calculating the TATB/TPTB values (eqs 18 and 19). This yielded the values of $\Delta_t H^\circ(\text{Ph}_4(\text{As}, \text{P})^+)$ and $\Delta_t H^\circ(\text{BPh}_4^-)$ which were then used to calculate values for other ions in the hierarchical manner illustrated in Table 2. In comparison with the body of data used in the assessment of $\Delta_t G^\circ$ values,¹ relatively fewer enthalpies of transfer of electrolytes have been sufficiently well studied to permit values to be Recommended.

4. Entropy Data

The situation with respect to entropies is much less satisfactory. Far fewer data are available for $\Delta_t S^\circ$ than for $\Delta_t H^\circ$, for all solvent mixtures. Even fewer values have been confirmed independently, and thus, assessment of the quality of these data was at best difficult and frequently impossible. As discussed earlier (section II.B), $\Delta_t S^\circ$ are obtained directly from the temperature derivatives of suitable cell potentials $(\partial E^\circ/\partial T)_P$, eq 13, or indirectly via the GHSE using $\Delta_t G^\circ$ and $\Delta_t H^\circ$ data (eq 3). Where comparisons were possible, the agreement was often extremely poor. Pending further investigations, almost all the available $\Delta_t S^\circ(\text{MX})$ data should be viewed sceptically.

In principle, many values of $\Delta_t S^\circ(\text{MX})$ could be obtained by combination of the present tabulations of $\Delta_t H^\circ(\text{MX})$ values with appropriate $\Delta_t G^\circ(\text{MX})$ data. However, no comprehensive critical evaluation of the latter is available for transfers to aqueous-organic

Table 2. Hierarchy Used in Deriving $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{EtOH})$ Values

ordinal number	MX used to derive value	ion	MX used to derive value	ion	MX used to derive value	ion
1	Ph ₄ PBPh ₄	Ph ₄ P ⁺ =BPh ₄ ⁻				
2	NaBPh ₄	Na ⁺	Ph ₄ PBr	Br ⁻	Pr ₄ NBPh ₄	Pr ₄ N ⁺
3	NaCl	Cl ⁻	KBr	K ⁺ ^a	NaClO ₄	ClO ₄ ^{-b}
4	HBr	H ⁺ ^c	NH ₄ ClO ₄	NH ₄ ⁺ ^c	Me ₄ NCl	Me ₄ N ⁺ ^d
5	NH ₄ NO ₃	NO ₃ ⁻	KPi	Pi ⁻	CsF	F ⁻
6	AgPi	Ag ⁺	LiNO ₃	Li ⁺		
7	AgMeCO ₂	MeCO ₂ ^{-e}				

^a KBr and KI were also used to obtain the average value, similarly for Rb⁺ (RbCl and RbI) and Cs⁺ (CsCl, CsBr, and CsI). ^b Further ions for this ordinal number are I⁻ (from NaI), OH⁻ (from NaOH), and Bu₄N⁺ (from Bu₄NBr). ^c HCl and HClO₄ were also used to obtain the average value, similarly for NH₄⁺ (NH₄I). ^d Further ions for this ordinal number are Ca²⁺, Sr²⁺, Ba²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Al³⁺, and Fe³⁺, from the corresponding chlorides. ^e Further ions for this ordinal number are EtCO₂⁻ and PrCO₂⁻, from the silver salts.

mixtures. Without such a corpus of data it would be necessary to make a personalized selection of values that would expand considerably the present review and introduce extra inconsistencies. On the other hand, relevant critically evaluated data are available for $\Delta_t G^\circ(M^{n+})$ values.¹ Combination of these with the $\Delta_t H^\circ(M^{n+})$ values reported here enabled estimation of a modest number of values for $\Delta_t S^\circ(M^{n+})$. Values of $\Delta_t S^\circ(X^-)$ were then obtained from $\Delta_t S^\circ(\text{MX})$ data using additivity. For the reasons discussed above in relation to $\Delta_t H^\circ(\text{ion})$ values, those for $\Delta_t S^\circ(\text{ion})$ are reported to the nearest 1 J K⁻¹ mol⁻¹. The true uncertainties will be much larger.

IV. Detailed Presentation of the Data

A. Transfers from Water to Water + Methanol (MeOH)

1. Enthalpy Data for Electrolytes

Enthalpy data for the transfer of electrolytes between water and water/MeOH mixtures are probably the best characterized of any aqueous–organic solvent system. Data are available for over thirty 1:1 electrolytes, more than ten 1:2 electrolytes, and La(NO₃)₃, mostly over the whole solvent composition range (Table 3). Many of the data have been well confirmed by independent studies, and it is possible to make additivity checks even for some of the 1:2 electrolytes. Data reported⁸⁰ for a number of salts at the single composition $x_{\text{MeOH}} = 0.568$ are not listed in Table 3 but are cited in its footnotes and in the text below. The potentiometric measurements reported by Dash and co-workers^{105–109} for a number of silver and mercury salts at low cosolvent concentrations contained too little useful information to justify their inclusion, as also did the paper by Krasnoperova.¹¹¹

In contrast to the wide availability of data for other salts, only one study⁸⁰ has been made of the key salts required for the application of the TPTB assumption: Ph₄PCl and NaBPh₄. Even though this calorimetric study is comprehensive and apparently reliable, independent confirmation is desirable in view of the large amount of information available for other electrolytes. Data for Ph₄AsPi are available from solubility studies at $x_{\text{MeOH}} \leq 0.6$, but values for an appropriate picrate salt are lacking, and so even a limited comparison with the TPTB results could not be made.

A reasonable body of data exists for the hydrohalic acids. In particular, three calorimetric studies have long been available for HCl.^{5,54,74} The data of Slansky⁵ and of Feakins et al.⁵⁴ are in excellent agreement, although the provenance of the numerical results in the latter is unclear (the references cited are unhelpful, and the values listed may have been recalculated from Slansky's work). On the other hand, the results of Bertrand et al.⁷⁴ appear to be up to 5 kJ/mol too negative. This is confirmed by additivity checks using values of $\Delta_t H^\circ(\text{HCl}) - \Delta_t H^\circ(\text{HBr})$. [Note that for convenience such quantities will be denoted throughout this review by the shorthand (HCl–HBr), (HCl–NaCl), etc.] Accordingly, even though the difference is not great, the data of Bertrand et al.⁷⁴ were rejected. For HBr only one report exists.⁵⁴ Additivity checks using (MCl–MBr) and (MI–MBr) suggest the results are reasonable. For HI, the calorimetric data of Feakins et al.⁵⁴ differ by up to 20 kJ/mol from the potentiometrically derived values of McIntyre and Amis.⁷⁵ Additivity checks indicate the latter are almost certainly in error, and they have therefore been rejected.

Abundant amounts of data exist for the alkali metal halides, mostly obtained by calorimetry. As usual,^{58,110} data for fluoride salts are scarce, with values available only for KF⁸⁸ and CsF.³⁵ Most of the alkali metal halide data are in good agreement, which means that for many of the salts their averaged values could be classified as Recommended over the whole solvent composition range. It also means that unusually strict criteria could be applied to data that deviated from the average. Thus, the pioneering results of Moss and Wolfenden⁴ for NaCl have been rejected even though they differ from the Recommended values by <1 kJ/mol (Table 3), which is much smaller than has been achieved for most salts in other solvent mixtures. This is tribute both to the accuracy of the original study of Moss and Wolfenden⁴ and to that attainable by good calorimetric practice. Almost all of the other published data have been accepted. An exception is the (graphical) data of Krestov and Klopov,⁷ which are more positive, by up to 11 kJ/mol, than all other studies and were therefore rejected. For LiCl, the earlier results reported by Feakins et al.,⁵⁴ which are in excellent agreement with those of Slansky,⁵ have been preferred over the later values from Feakins' group.⁷⁷ However, doubts about the provenance of the earlier data noted above must be kept in mind. Too few data

Table 3. $\Delta_t H^{\circ}(\text{MX}, \text{w} \rightarrow \text{w} + \text{MeOH})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{MeOH}}$

MX	$\Delta_{\text{sn}} H^{\circ}$	5	10	20	30	40	50	60	70	80	90	100	ref	
HCl	-74.81	1.26	2.11	2.77	2.43	1.47	0.18	-1.25	-2.72	-4.21	-5.79	-7.63	5	
HCl	-75.7	[2.4]	[3.3]	[2.7]	[0.6]	[-1.8]	[-4.1]	[-6.3]	[-8.3]	[-9.3]	[-7.1]	[-2.1]	74	
HCl		1.35	2.32	(3.33)	3.21	(2.26)	0.75	-1.07	(-2.99)	-4.80	-6.37	-7.56	54	
HCl		1.3	2.2	3.1	2.8	1.9	0.5	-1.1	-2.8	-4.5	-6.1	-7.6		
HBr		1.15	1.91	(2.68)	2.32	(0.89)	-1.40	-4.26	(-7.28)	-9.95	-11.64	-11.63	54	
HI		1.07	1.60	(2.18)	1.77	(0.17)	-2.58	-6.21	(-10.28)	-13.86	-16.17	-15.93	54	
HI		0.95	0.83	-2.65	-8.33	-14.72	-20.59	-24.94	-27.04	-26.40	-22.06	-16.11	75	
H ₂ CrO ₄		3.36	5.71	7.04	4.05	-3.03	-13.96	-28.50	-46.43	-67.52			76	
LiCl	-37.24	2.73	4.31	4.92	3.67	1.52	-0.81	-2.92	-4.69	-6.28	-8.14	-11.01	5	
LiCl		2.82	4.50	(5.09)	3.64	(1.29)	-1.20	-3.35	(-5.03)	-6.46	-8.16	-10.99	54	
LiCl		[0.68]	[1.24]	[1.79]	[1.53]	[0.28]	[-1.97]	[-5.08]	[-8.69]			[-16.59]	77	
LiCl		2.8	4.4	5.0	3.7	1.4	-1.0	-3.1	-4.8	-6.4	-8.2	-11.0		
LiNO ₃	-2.66	1.19	1.72	1.2	-0.64	-3.21	-6.09	-9.01	-11.88	-14.74	-17.81	-21.47	35	
NaCl	[4.52]	[1.49]	[2.42]	[3.03]	[2.51]	[1.40]	[0.01]	[-1.57]	[-3.44]	[-5.92]	[-9.54]	[-15.04]	4	
NaCl		3.85	1.62	2.69	3.56	3.35	2.50	1.30	-0.14	-1.90	-4.21	-7.47	-12.25 5, 78	
NaCl		3.7	[3.9]	[6.4]	[8.4]	[8.2]	[7.0]	[5.9]	[5.1]	[4.4]	[2.8]	[-1.0]	[-9.2]	7
NaCl		1.60	2.66	(3.45)	3.18	(2.31)	1.12	-0.28	(-1.97)	-4.21	-7.43	-12.26	54	
NaCl		3.79	[1.8]	[3.3]	[4.7]	[3.9]							79	
NaCl		1.62	2.72	3.65	3.40	2.39	0.89	-0.97	-3.24	(-6.12)	(-9.97)	-15.31	77	
NaCl		3.90	1.66	2.73	3.52	3.06	1.89	0.35	-1.37	-3.26	-5.45	-8.28	-12.20	80
NaCl		(1.65)	2.65	3.28	2.67	1.66	1.06						81	
NaCl		1.6	2.7	3.5	3.2	2.2	0.9	-0.7	-2.6	-5.0	-8.3	-13.0		
NaBr	-0.13	1.49	2.44	2.96	2.31	0.89	-0.99	-3.20	-5.69	-8.59	-12.12	-16.66	5	
NaBr		1.79	2.83	3.25	2.22	0.43	-1.67	-3.90	-6.29	(-9.15)	(-13.02)	-18.70	77	
NaBr		2.12	2.95	2.74	1.98	1.13	-1.50						82	
NaBr		1.8	2.7	3.0	2.2	0.8	-1.4	-3.6	-6.0	-8.9	-12.6	-17.7		
NaI	-7.61	1.69	2.70	2.92	1.76	-0.21	-2.65	-5.36	-8.36	-11.81	-16.10	-21.77	5	
NaI	(-7.60)					-1.04	-3.11						83	
NaI	-7.58	1.71	2.69	3.03	1.88	-0.11	-2.56	-5.31	-8.44	-12.27	-17.39	-24.60	15, 84 ^a	
NaI		1.93	2.97	2.98	1.10	-1.84	-5.26	-8.81	-12.37	-16.06	-20.22	-25.44	77	
NaI^b		1.7	2.7	3.0	1.8	-0.2	-2.6	-5.3	-8.4	-12.0	-16.7	-23.2		
NaNO ₃	20.0	2.1	3.4	4.0	3.1	1.6	-0.1	-1.8	-4.0	-7.3	-12.9	-22.2	85	
NaNO ₃	20.80	1.93	3.05	3.56	2.58	0.90	-0.98	-2.91	-5.01	-7.73	-11.82	-18.36	86	
NaNO₃		2.0	3.2	3.8	2.8	1.3	-0.5	-2.4	-4.5	-7.5	-11.4	-20.3		
NaNO ₂	14.11	1.31	2.25	2.38	1.30	-0.29	-2.00	-3.70	-5.56	-8.05	-11.92	-18.18	87	
NaBPh ₄	-20.00	14.07	23.37	31.14	29.78	24.24	17.30	10.13	2.86	-4.87	-13.29	-21.99	80	
KF	-16.19	(0.99)	(1.70)	2.49	(2.75)	2.72	(2.52)	2.12	(1.36)	(-0.04)	(-2.50)	-6.58	88	
KCl	17.24	1.12	1.81	2.1	1.41	0.03	-1.73	-3.68	-5.72	-7.83	-10.10	-12.72	5, 78	
KCl	17.4	[2.2]	[3.6]	[4.7]	[4.7]	[4.3]	[4.2]	[4.1]	[4.0]	[3.4]	[1.1]	[-4.1]	7	
KCl		1.15	1.85	(2.21)	1.58	(0.10)	-1.69	-3.67	(-5.74)	-7.87	-10.14	-12.71	54	
KCl	17.22	1.39	2.23	2.71	2.19	1.19	0.00	-1.30	-2.88	-5.11	-8.60	-14.19	89	
KCl	17.14	1.0	2.1	(3.6)	2.1								79	
KCl		1.38	2.24	2.79	2.36	1.39	0.17	-1.22	-2.90	(-5.18)	(-8.57)	-13.77	77	
KCl		1.2	2.0	2.5	1.9	0.7	-0.9	-2.5	-4.3	-6.5	-9.4	-13.3		
KBr	20.00	1.09	1.65	1.52	0.25	-1.66	-3.85	-6.10	-8.34	-10.64	-13.20	-16.38	5	
KBr	20.3	2.2	3.5	5.4	6.5	6.7	6.1	4.7	2.5	-0.6	-4.3	-8.9	7	
KI	20.38	1.10	1.65	1.45	0.11	-1.90	-4.22	-6.70	-9.29	-12.11	-15.43	-19.66	5, 78	
KI	[22.9]	[0.3]	[0.7]	[0.9]	[0.6]	[-0.3]	[-1.7]	[-3.5]	[-5.8]	[-8.5]	[-11.5]	[-14.8]	7	
KI		1.73	2.72	3.02	1.86	-0.13	-2.57	-5.31	-8.44	-12.28	-17.40	-24.60	84	
KI		1.4	2.2	2.2	1.0	-1.0	-3.4	-6.0	-8.9	-12.2	-16.4	-22.1		
KNO ₃	34.8	2.3	3.3	2.5	0.1	-2.4	-4.4	-6.7	-11.2				85	
KNO ₃	35.20	2.30	3.35	2.76	-0.18	-4.06	-7.88	-11.04	-13.35	-15.04	-16.74	-19.49	86	
KNO₃		2.3	3.3	2.6	0.0	-3.3	{-6.1}	{-8.9}	-12.3	{-15.0}	{-16.7}	{-19.5}		
KSCN	24.35	1.64	2.73	1.95	-0.49	-3.48	-6.33	-8.77	-10.94	-13.43	-17.22	-23.74	87	
RbCl	16.74	0.57	1.00	1.44	1.45	1.06	0.30	-0.86	-2.50	-4.70	-7.61	-11.40	5	
RbCl		0.54	1.02	(1.46)	1.45	(1.05)	0.26	-0.93	(-2.58)	-4.78	-7.66	-11.39	54	
RbCl	16.84	2.4	3.0	(2.8)	2.3								79	
RbCl		1.38	2.18	2.55	1.93	0.91	-0.16	-1.19	-2.27	(-3.76)	(-6.24)	-10.50	77	
RbCl		0.6	1.0	1.4	1.5	1.1	0.3	-0.9	-2.5	-4.7	-7.6	-11.4		
RbNO ₃	36.3	2.0	3.0	2.4	-0.3	-3.1	-4.5						85	
CsF	-36.33	1.21	1.93	2.57	2.63	2.58	2.66	2.89	3.11	2.95	1.81	-1.10	35	
CsCl	17.74	0.50	0.78	0.78	0.24	-0.68	-1.85	-3.20	-4.68	-6.29	-8.05	-10.02	5	
CsCl		0.77	0.85	(0.89)	0.36	(-0.59)	-1.81	-3.21	(-4.73)	-6.35	-8.09	-10.00	54	
CsCl	17.41	1.6	2.4	(2.3)	2.0								79	
CsCl		1.60	2.18	2.31	1.42	0.22	-0.84	-1.58	-2.08	(-2.72)	(-4.10)	-7.11	77	
CsCl		0.6	0.8	0.8	0.3	-0.6	-1.8	-3.2	-4.7	-6.3	-8.1	-10.0		
CsI	(31.8)	-2.7	3.5	1.8	-0.6								90	
AgCl	64.8	-4.1			-14.2								91	
NH ₄ I	13.70	1.03	1.24	(-0.09)	-2.74	-5.82	(-8.75)	(-11.29)	(-13.54)	(-15.91)	-19.18	-24.42	92	
NH ₄ I	13.72	1.06	1.26	0.09	-2.40	-5.45	-8.55	-11.44	-14.06	-16.59	-19.46	-23.32	35	
NH₄I		1.0	1.2	0.0	-2.6	-5.7	-8.7	-11.5	-14.0	-16.5	-19.5	-23.8		
NH ₄ NO ₃	25.49	1.30	1.68	0.91	-1.14	-3.72	-6.35	-8.78	-11.00	-13.27	-16.07	-20.12	35	
NH ₄ BF ₄	35.86	1.70	2.72	2.35	0.03	-3.27	-6.86	-10.28	-13.35	-16.14	-18.98	-22.46	87	
Pr ₄ NBr		1.6	3.4	7.0	5.1	3.8	3.2						93	
Bu ₄ NBr		8.1	15.1	25.5	30.3	30.5	28.0	25.2	23.9	24.9	27.3	27.6	94	
Bu ₄ NBr	-8.42	9.95	17.70	27.32	31.22	31.56	30.09	28.07	26.36	25.36	25.04	24.92	35	

Table 3. (Continued)

MX	$\Delta_{\text{sln}}H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
Bu₄NBr		9.3	16.8	26.6	30.8	31.1	29.3	27.1	25.5	25.1	25.7	25.8	
Hx ₄ NBr	14.56	16.07	27.39	39.36	41.95	39.29	34.47	29.61	25.94	23.86	23.00	22.30	95
Ph ₄ PCl	-8.91	14.74	23.12	26.51	21.79	15.63	11.05	8.58	7.41	6.47	5.64	6.82	80
Ph ₄ AsPi		7.1	13.3	22.8	26.8	24.3	14.3	-4.7					96
MgCl ₂		2.51	3.65	3.50	1.36	(-0.99)	(-2.60)	-3.52	-4.45	-6.07	-7.93	-6.93	97
CaCl ₂	-80.8	0.3	(0.7)	-0.5	-4.7	-11.2	-13.4	(-17.7)	-22.7	-26.6	-31.7	-27.1	98
Ca(NO ₃) ₂	-14.3	1.8	2.6	1.2	-2.5	-7.1	-11.5	-15.2	-17.9	-20.0	-21.9	-24.7	85
Ca(NO ₃) ₂	-17.60	1.62	2.26	1.25	-1.98	-6.48	-11.45	-16.30	-20.58	-24.04	-26.57	-28.26	86
Ca(NO₃)₂		1.7	2.4	1.2	-2.3	-6.8	-11.5	-15.8	-19.3	-22.0	-24.2	-26.5	
SrCl ₂	-50.74	3.5	3.5	(2.1)	1.7								79
SrCl ₂	-51.13	2.25	3.16	3.19	-0.28								99
SrCl₂		2.9	3.3	2.7									
Sr(NO ₃) ₂	18.3	3.1	4.3	2.2	-3.3	-8.9	-11.5						85
BaCl ₂	-12.61	2.8	3.1	(1.4)	0.1								79
BaCl ₂	-13.50	2.15	2.80	1.95	-3.38								99
BaCl₂		2.5	3.0	1.7									
Co(ClO ₄) ₂	7.00	4.23	4.87	-0.30	-9.10	-17.97	-25.84	-33.20	-41.24	-50.96	-62.27	-73.09	100
NiCl ₂	-83.43	2.91	4.84	5.66	3.10								101
CuCl ₂	-51.83	0.94	1.38	0.79	-0.89	-2.81	-4.34	-5.08	-4.87	-3.78	-2.08	-0.31	101
ZnCl ₂		1.34	2.29	3.07	2.61	1.26	-0.52	-2.12					102
ZnCl ₂	-69.87	2.03	2.96	2.17	-0.90	-4.68	-7.65	-8.48	-6.14	0.02	10.15	23.77	103
CdCl ₂	-18.20	2.65	3.69	3.18	1.48	-0.26	-2.06	-4.50	-8.02	-12.24	-15.27	-13.08	103
La(NO ₃) ₃	-62.05	3.34	3.60	-0.79	-7.29	-11.06	-13.84	-16.70	-20.04	-23.63	-26.57	-27.28	86

^a Mean of data at 288.15 and 308.15 K, agreeing with those of same author,⁸⁴ at 298.15 K. ^b Data also available at 233.15 ≤ *T*/K ≤ 293.1

are available for other lithium salts to enable meaningful additivity checks to be made.

There is a surprising absence of data for the enthalpies of transfer of the tetraalkylammonium salts. Thus, apart from some measurements of $\Delta_{\text{t}}H^\circ$ (R₄NI) at $x_{\text{MeOH}} = 0.568$,⁸⁰ almost no data exist for salts containing the smaller R₄N⁺ ions. The only exception is Bu₄NBr, for which two independent calorimetric data sets are available and are in good agreement over the entire solvent composition range. By analogy with the Bu₄NBr data, the calorimetric results of Manin et al.⁹⁵ for Hx₄NBr appear to be reasonable but those of Sinha and Kundu⁹³ for Pr₄NBr, derived from the temperature dependence of solubilities, do not. The trend in Sinha and Kundu's data (Table 3) is also at odds with the value of $\Delta_{\text{t}}H^\circ$ (Pr₄NBr) = 15 ± 2 kJ/mol at $x_{\text{MeOH}} = 0.568$ that can be derived by additivity from the calorimetric study of Abraham et al.⁸⁰

Reasonable amounts of data have been reported for 1:2 electrolytes in H₂O/MeOH mixtures, and a number of salts have been independently investigated by calorimetry, albeit mainly in water-rich mixtures (Table 3). In general, agreement is good, and a number of averaged values have been recommended. Additivity checks using $([M(\text{NO}_3)_n - \text{MCl}_n]/n)$, where $n = 1$ or 2, indicated that the data for the alkaline earth metal salts were in reasonable agreement with the better-established values for the alkali metal salts, except perhaps at $x_{\text{MeOH}} \geq 0.8$. The data for the MCl₂ salts and, possibly to a lesser extent, the M(NO₃)₂ salts must nevertheless be viewed with caution. All of these salts show some degree of association even in water. This association would be expected to increase with increasing amounts of MeOH due to the decreasing relative permittivity of the solvent mixtures. Although the data in Table 3 refer to standard state conditions (infinite dilution of the solute), it is not a trivial matter to truly remove the effects of ion association from the observed (finite

concentration) data. Clearly, it would be desirable for calorimetric studies to be made with divalent salts containing anions such as perchlorate (ClO₄⁻) and 'triflate' (CF₃SO₃⁻) that have a considerably lower tendency to associate. Ideally, such studies should be performed in conjunction with another technique, such as conductivity, that can characterize the level of ion association in dilute solutions.

2. Ionic Enthalpies of Transfer

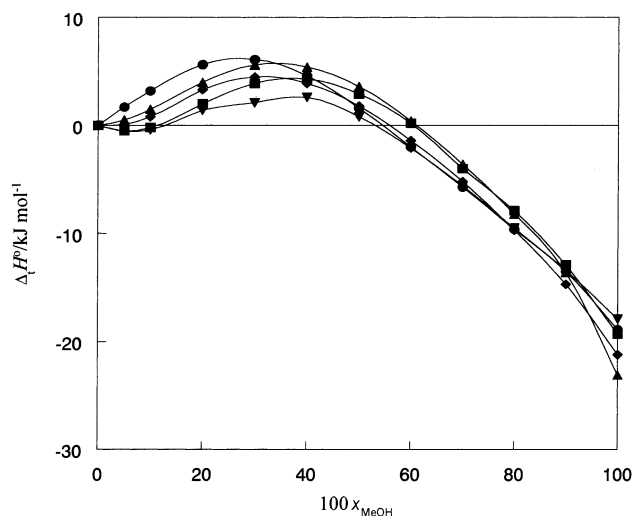
Standard enthalpies of transfer of single ions from water to aqueous–methanol solutions were obtained via the TPTB assumption using the data of Abraham et al.⁸⁰ and the procedures outlined in section III.A.5. The results for 1 trivalent, 7 divalent, and 12 monovalent cations and for 8 monovalent anions are summarized in Table 4. Because the TPTB data are unconfirmed (see above), all values of $\Delta_{\text{t}}H^\circ$ (ion) must be regarded with some degree of caution.

The values of $\Delta_{\text{t}}H^\circ$ (M⁺, w → w + MeOH) for the alkali metal ions are plotted in Figure 3 as a function of solvent composition. There is a strong similarity among the curves. Thus, at low x_{MeOH} the curves are concave upward. For Rb⁺ and Cs⁺ there is even a very small minimum at $x_{\text{MeOH}} \approx 0.05$, although its magnitude is well within the uncertainty of the TPTB assumption and so may not be significant. As x_{MeOH} increases so too do $\Delta_{\text{t}}H^\circ$ (M⁺, w → w + MeOH) until they reach a maximum at $x_{\text{MeOH}} \approx 0.3$. The height, but not the position, of this maximum varies systematically with cation size: Li⁺ > Na⁺ > K⁺ ≈ Rb⁺ > Cs⁺. At higher x_{MeOH} the values of $\Delta_{\text{t}}H^\circ$ (M⁺) become increasingly negative. However, there are a number of 'crossovers' in the curves such that $\Delta_{\text{t}}H^\circ$ (M⁺, w → MeOH), i.e., for transfer to neat MeOH, are in the order (noting the sign) Cs⁺ > Rb⁺ > K⁺ > Na⁺. The position of the difficult-to-study Li⁺ is anomalous.

The corresponding values of $\Delta_{\text{t}}H^\circ$ for the halide ions (Table 4, data not plotted) show similar but

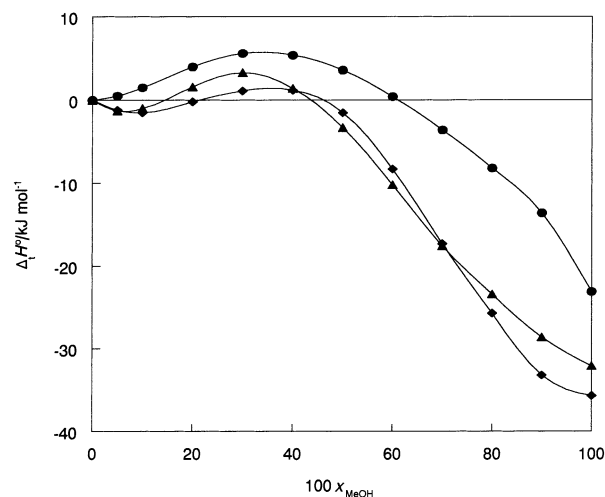
Table 4. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{MeOH})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{MeOH}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
H ⁺	HCl	0.2	1.0	3.6	5.2	5.1	3.1	0.0	-3.7	-7.7	-11.4	-15.5
Li ⁺	LiCl	1.7	3.2	5.6	6.1	4.6	1.6	-2.0	-5.7	-9.6	-13.5	-18.9
Na ⁺	NaBPh ₄	0.5	1.5	4.0	5.6	5.4	3.6	0.4	-3.6	-8.2	-13.6	-23.1
K ⁺	KCl	0.1	0.8	3.3	4.5	3.9	1.8	-1.4	-5.2	-9.7	-14.7	-21.2
Rb ⁺	RbCl	-0.5	-0.2	2.0	3.9	4.3	2.9	0.2	-4.0*	-7.9	-12.9	-19.3
Cs ⁺	CsCl	-0.5	-0.4	1.4	2.1	2.6	0.8	-2.1	-5.6	-9.5	-13.4	-17.9
Ag ⁺	AgCl	-5.2			-11.8							
NH ₄ ⁺	NH ₄ I	-0.2	0.0	1.0	1.2	-0.1	-2.5	-5.8	-9.2	-12.7	-16.4	-23.7
Pr ₄ N ⁺	Pr ₄ NBr	0.3	2.2	8.0	8.4	8.4	8.2					
Bu ₄ N ⁺	Bu ₄ NBr	8.0	15.6	27.6	34.2	35.7	34.3	31.1	27.9	25.8	24.7	20.4
Hx ₄ N ⁺	Hx ₄ NBr	14.8	26.2	20.4	45.4	43.9	39.5	33.6	28.3	24.6	22.0	16.6
Ph ₄ P ⁺	Ph ₄ PBPh ₄	13.6	21.9	27.1	24.2	18.8	13.7	9.7	6.5	3.3	0.3	-1.1
Mg ²⁺	MgCl ₂	0.3	1.3	4.7	6.2	5.4	2.6	-1.3	-2.7	-12.4	-18.5	-22.7
Ca ²⁺	Ca(NO ₃) ₂	-1.3	-1.0	1.6	3.3	1.4	-3.3	-10.2	-17.5	-23.4	-28.6	-32.1
Sr ²⁺	SrCl ₂	0.3	0.6	2.9	3.2							
Ba ²⁺	BaCl ₂	0.7	0.9	3.2	5.5							
Ni ²⁺	NiCl ₂	0.7	2.4	6.9	7.9							
Cu ²⁺	CuCl ₂	-1.3	-1.0	2.0	3.9	3.6	0.9	-2.9	-6.7	-10.2	-12.7	-15.1
Zn ²⁺	ZnCl ₂	-0.2	0.6	3.4	3.9	1.7	-2.5	-6.3	-7.9	-6.4	-0.4	8.0
Cd ²⁺	CdCl ₂	0.5	1.3	4.4	6.3	6.1	3.1	-2.3				
La ³⁺	La(NO ₃) ₃	-1.2	-1.5	-0.2	1.1	1.2	-1.5	-8.3	-17.3	-25.7	-33.2	-35.7
F ⁻	(K,Cs)F	1.3	1.6	0.2	-0.6	-0.4	1.2	4.3	7.7	11.1	13.7	15.7
Cl ⁻	Ph ₄ Cl	1.1	1.2	-0.6	-2.4	-3.2	-2.6	-1.1	0.9	3.2	5.3	7.9
Br ⁻	NaBr	1.3	1.2	-1.0	-3.4	-4.6	-5.0	-4.0	-2.4	-0.7	1.0	5.4
I ⁻	NaI	1.2	1.2	-1.0	-3.8	-5.6	-6.2	-5.7	-4.8	-3.8	-3.1	-0.1
SCN ⁻	KSCN	1.5	1.9	-1.3	-5.0	-7.4	-8.1	-7.4	-5.7	-3.7	-2.5	-2.5
NO ₃ ⁻	NaNO ₃	1.5	1.7	-0.2	-2.8	-4.1	-4.1	-2.8	-0.9	0.7	2.2	2.8
BF ₄ ⁻	NH ₄ BF ₄	1.9	2.7	1.4	-1.2	-3.2	-4.4	-4.5	-4.2	-3.4	-2.6	1.2
BPh ₄ ⁻	Ph ₄ PBPh ₄	13.6	21.9	27.1	24.2	18.8	13.7	9.7	6.5	3.3	0.3	-1.1

**Figure 3.** Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, from water into aqueous–MeOH mixtures at 25 °C of the alkali metal ions: ● Li⁺, ▲ Na⁺, ◆ K⁺, ■ Rb⁺, ▼ Cs⁺.

broadly opposite effects⁸⁸ to the cations. That is, there is (some) compensation between cations and anions in the values of $\Delta_t H^\circ(\text{ion})$ in these solvent mixtures. Thus, the $\Delta_t H^\circ$ values for all the halides (including F⁻) show a small maximum at $x_{\text{MeOH}} \approx 0.07$ followed by a broad minimum, the depth and position of which, in contrast to the behavior of the cations (Figure 3), depend markedly on the anion size. At higher MeOH concentrations the values $\Delta_t H^\circ(X^-)$ become more positive (less negative). The differences are systematic, with $F^- \gg Cl^- > Br^- > I^-$, and diverge with increasing MeOH content.⁸⁸

Figure 4 shows the effects of charge (at approximately constant ionic size) on $\Delta_t H^\circ(M^{n+})$. The differ-

**Figure 4.** Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, from water into aqueous–MeOH mixtures at 25 °C of cations of similar size but varying charge: ● Na⁺, ▲ Ca²⁺, ◆ La³⁺.

ences between Na⁺ and Ca²⁺ are large, but those between Ca²⁺ and La³⁺ are not, and all three ions show a broadly similar pattern. Nevertheless, $\Delta_t H^\circ(M^{n+}, w \rightarrow w + \text{MeOH})$ becomes more negative with increasing charge, as has previously been recognized³⁶² for transfers from water to neat MeOH. As a corollary, the small minimum at $x_{\text{MeOH}} \approx 0.07$ becomes more pronounced with increasing charge, although its size remains within the likely uncertainty of the TPTB assumption. The crossovers observed for Ca²⁺ and La³⁺ might be artifacts given the difficulties of accurate determination of $\Delta_{\text{sln}} H^\circ$ for high-valent electrolytes.

Table 5. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{MeOH})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{MeOH}}$

MX	5	10	20	30	40	50	60	70	80	90	100	ref
HCl	1.7	3.1	4.0	1.9	-4.0	-13.6	-27.1	-43.9	-63.2	-84.0	-104.8	54
HBr	2.7	4.3	4.4	0.7	-6.2	-15.8	-27.9	-42.9	-60.9	-82.6	-108.9	54
HI	2.3	4.2	6.1	5.1	-0.2	-10.4	-25.2	-43.6	-63.7	-83.1	-98.3	54
HI	3.9	3.2	-8.7	-28.2	-50.0	-70.1	-86.1	-96.6	-101.7	-103.1	-103.4	75
H ₂ CrO ₄	6.6	9.8	6.3	-10.3	-39.9	-82.3	-137.2	-204.5	-283.9			76
LiCl	5.9	7.8	2.9	-8.7	-23.2	-33.2	-52.0	-64.2	-75.3	-86.8	-101.5	54
LiCl	-0.1	-1.4	-6.8	-15.8	-27.3	-40.8	-55.3	-70.2	(-84.9)	(-98.7)	-111.1	77
LiCl	3	3	-2	-12	-25	-37	-54	-67	-80	-93	-106	
NaCl	0	-1.4	-7.2	-16.0	-26.7	-38.6	-51.4	-65.3	-80.5	-98.0	-118.9	78
NaCl	0.8	-0.7	-8.4	-19.4	-31.2	-42.5	-53.0	-63.5	-76.1	-93.8	-121.0	54
NaCl	0.4	-0.5	-5.5	-14.2	-25.3	-38.1	-52.2	-67.6	(-84.3)	(-102.9)	124.3	77
NaCl	0.7	-0.4	-6.9	-16.8	-27.5	-36.4						81
NaCl	1	-1	-7	-17	-28	-39	-52	-65	-80	-98	-121	
NaBr	1.4	0.8	-4.8	-14.8	-27.5	-41.5	-56.1	-71.3	(-87.5)	(-105.8)	-127.8	77
NaBr	2.6	1.1	-7.1	-15.9	-24.9	-41.8						82
NaBr	2	1	-6	-15	-26	-42	{-56}	{-71}	{-88}	{-106}	{-128}	
NaI	2.9	3.2	-2.1	-13.3	-28.1	-44.8	-62.3	-80.1	(-98.1)	(-117.0)	-137.9	77
KCl	-1.0	-3.1	-10.3	-21.2	-35.3	-51.8	-70.3	-89.7	-109.3	-128.1	-145.0	78
KCl	-3.0	-6.5	-14.7	-25.5	-39.4	-56.4	-75.7	-95.8	-114.6	-129.0	-135.4	54
KCl	2.9	2.1	-1.7	-10.0	-25.8	-44.8	-65.1	-86.9	-108.6	-127.8	-144.3	112
KCl	-0.3	-2.0	-8.4	-17.9	-29.3	-41.8	-55.2	-69.4	(-85.0)	(-102.9)	-124.6	77
KCl	0	-2	-9	-16	-32	-49	-67	-85	-111	-128	-142	
KBr	-1.0	-3.1	-10.3	-21.2	-35.3	-51.8	-70.3	-89.7	-108.8	-127.0	-143.2	78
RbCl	-0.2	-2.0	-8.8	-18.7	-30.2	-42.2	-54.5	-67.1	(-80.6)	(-96.3)	-115.9	77
CsCl	-0.7	-2.1	-7.7	-17.3	-30.5	-45.2	-57.9	-63.6				77
AgCl	-14.8			-68.5								91
Pr ₄ NBr	0.5	5	19	14	9	6						93
Ph ₄ AsPi	9.4	17.9	32.7	42.0	44.1	37.3	20.0					96
ZnCl ₂	-1.7	-5.7	-18.5	-35.0	-53.1	-72.6	-94.4					102

Little can be said about the other ionic values except to note that $\Delta_t H^\circ(\text{Pr}_4\text{N}^+)$ are almost certainly unreliable because of problems for the Pr_4NBr data on which they are based (see above).

3. Entropy Data for Electrolytes

As for all mixed solvent systems, the amount of entropy data available for the transfer of electrolytes from water to aqueous–methanol mixtures is very limited (Table 5). Most of these data were obtained from $\Delta_t G^\circ$ and $\Delta_t H^\circ$ values via the GHSE. With the exception of some of the alkali metal halides, few of the data have been independently confirmed and then usually only over a limited range of solvent compositions. Where comparisons are possible, the agreement is not always as good as might be desired. To take the best-characterized salt, KCl, as an example, the averaged Recommended value at $x_{\text{MeOH}} = 0.2$ is $(-8.8 \pm 4.7) \text{ J K}^{-1} \text{ mol}^{-1}$ from four independent studies.^{54,77,78,112} The uncertainty corresponds to $\pm 1\sigma$. Rejection of the outlier¹¹² gives a value of $(-11.1 \pm 2.6) \text{ J K}^{-1} \text{ mol}^{-1}$. However, inspection of the overall trends in the data (Table 5) and the relatively small decrease in σ upon removal of the outlier indicate that rejection is not appropriate. Thus, the Recommended value is given as $-9 \text{ J K}^{-1} \text{ mol}^{-1}$. The uncertainty ($\pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$) in this value increases at higher MeOH concentrations ($\sigma \approx 10 \text{ J K}^{-1} \text{ mol}^{-1}$). For the latter, the near perfect agreement among the remaining data provided justification for rejecting two outliers. Despite these reservations, it must be recognized that even an uncertainty of $\pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$ corresponds to an uncertainty of only $\pm 3 \text{ kJ mol}^{-1}$ in $T\Delta_t S^\circ$ at 25 °C. Although this is rather worse than has often been achieved for $\Delta_t H^\circ(\text{MX})$, it is not much different from the criterion used to judge the

enthalpies. As the measurement of $\Delta_t S^\circ(\text{KCl}, w \rightarrow w + \text{MeOH})$ would appear to be reasonably straightforward in all respects, this level of uncertainty may be seen as a benchmark for what can routinely be expected in the determination of entropies of transfer of electrolytes between water and aqueous–organic mixtures.

A few other comments on the data in Table 5 are possible. For HI, two data sets in very poor agreement exist: one due to Feakins et al.,⁵⁴ who used the GHSE with calorimetric $\Delta_t H^\circ$ values, and the other from McIntyre and Amis,⁷⁵ using direct potentiometric (dE°/dT) measurements. Additivity checks employing $(\text{HX} - \text{NaX})$ indicate that, as for the $\Delta_t H^\circ$ values derived from these data (see above), the $\Delta_t S^\circ$ results of McIntyre and Amis⁷⁵ are almost certainly incorrect and are therefore rejected.

Two data sets are available for LiCl from Feakins et al.;^{54,77} both publications used the same values of $\Delta_t G^\circ$ along with the GHSE to calculate $\Delta_t S^\circ$. The earlier work⁵⁴ employed $\Delta_{\text{sln}} H^\circ$, while the later study⁷⁷ used $\Delta_{\text{dil}} H^\circ$ measurements. Pending independent verification, the averaged values are listed as Tentative.

Two independent data sets are available for NaBr. DeValera et al.⁷⁷ used $\Delta_{\text{dil}} H^\circ$ measurements and the GHSE, whereas Kozłowski et al.⁸² determined $\Delta_t S^\circ$ via dE°/dT data at $x_{\text{MeOH}} \leq 0.5$. Where comparisons are possible, the two sets of results are in excellent agreement and their average has been Recommended. The potentiometric work of the Łódź group is commended to anyone wishing to perform accurate measurements of this type and shows that, with due attention to detail, reliable results can be obtained from the temperature dependence of emfs.

Table 6. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{MeOH})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, TPTB Assumption, mol/L Scale, as a Function of $100x_{\text{MeOH}}$

ion	5	10	20	30	40	50	60	70	80	90	100	ref
H ⁺	-0.9	1.9	13.6	20.9	20.6	14.5	4.7	-8.3	-26.5	-52.9	-88.3	80
H⁺	1	3	12	19	21	16	8	-5	-20	-44	-81	
Li ⁺	-4.9	-6.0	1.0	1.8	-5.4	-16.1	-27.1	-39.5	-56.5	-77.4	-86.6	80
Li⁺	3	6	11	11	5	-5	-17	-30	-73	-56	-73	
Na ⁺	-3.9	-4.7	3.1	2.9	-5.1	-15.2	-24.3	-35.5	-54.9	-82.5	-97.9	80
Na⁺	-3	-3	0	3	-1	-8	-21	-36	-52	-70	-101	
K ⁺	-7.4	-6.8	-0.5	-0.2	-7.2	-17.1	-27.1	-39.0	-56.9	-80.9	-96.2	80
K⁺	-4	-4	-1	0	-5	-15	-28	-45	-61	-78	-99	
Rb ⁺	-7.8	-6.8	-0.8	-0.9	-8.0	-17.5	-26.5	-36.9	-52.9	-74.8	-86.6	80
Rb⁺	-10	-9	-7	-4	-6	-14	-25	-40	-59	-79	-103	
Cs ⁺	-6.8	-5.8	0.0	-1.3	-9.2	-18.2	-25.6	-34.1	-49.0	-70.2	-78.2	80
Cs⁺	-10	-9	-8	-9	-9	-18	-30	-45	-60	-74	-89	
Ag ⁺	12	19	24	19	13	10	17					127
NH ₄ ⁺	-4	-6	-4	-5	-12	-22	-35	-48	-63	-82	-100	
Pr ₄ N ⁺	4	12	38	45	48	50						
Bu₄N⁺	31	61	110	140	154	157	153	152	151	150	146	
Ph ₄ P ⁺	51.1	85.4	119.8	122.6	112.9	103.6	98.5	94.0	84.3	70.2	72.0	80
Ph₄P⁺	45	87	119	122	114	106	99	93	85	77	75	
Mg ²⁺	-6	-10	-4	-4	-12	-26	-42	-60	-79	-99	-114	
Ca²⁺	-3	-3	5	11	5	-11	-34	-59	-78	-96	-108	
Sr ²⁺		-48.8	-3.0									80
Ba ²⁺		-16.7	-7.9	-12.6							-262.3	80
Zn ²⁺	-19.2	-15.0	0.7	-1.3	-12.5	-12.5	-25.6	-41.9			-249.4	80
F ⁻	6.7	3.7	-16.3	(-24.0)	-28.0	(-28.6)	-27.1	-25.4	-24.4	-23.7	-20.0	88
Cl ⁻	6.8	3.7	-10.3	-20.0	-23.8	-26.1	-29.2	-30.6	-24.9	-13.2	-15.9	80
Cl⁻	3	0	-9	-20	-28	-32	-36	-35	-33	-33	-27	
Br ⁻	9.1	6.2	-10.0	-21.8	-26.4	-28.9	-32.7	-35.3	-31.1	-19.9	-21.3	80
Br⁻	2	1	-7	-18	-26	-33	-36	-37	-39	-38	-28	
I ⁻	10.4	8.0	-8.9	-22.2	-28.5	-33.1	-39.4	-45.2	-44.2	-33.8	-29.3	80
I⁻	4	3	-4	-15	-24	-31	-37	-42	-45	-43	-27	
MeCO ₂ ⁻	-20	-31	-34	-24	-14	-17	-48					127
EtCO ₂ ⁻	-17	-26	-28	-18	-9	-12	-38					127
PrCO ₂ ⁻	-14	-21	-21	-12	-4	-6	-29					127
Pi ⁻	36	69	86	80	70	69	79					
BPh ₄ ⁻	51.1	85.4	119.8	122.6	112.9	103.6	98.5	94.0	84.3	70.2	72.0	80
BPh₄⁻	45	87	119	122	114	106	99	93	85	77	75	

Finally, it is noted that further dE°/dT data for NaCl in $w + \text{MeOH}$ are available¹¹³ but were not processed because of the abundance of alternative good quality data for this salt.

4. Ionic Entropies of Transfer

The standard ionic entropies of transfer, $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{MeOH})$, that can be obtained from the available data are summarized in Table 6. Values given in **bold** font were obtained by the present reviewers in the following ways. For cations, $\Delta_t S^\circ(M^{n+})$ were calculated via the GHSE using the values of $\Delta_t H^\circ(M^{n+})$ in Table 4 and $\Delta_t G^\circ(M^{n+})$ from the critically evaluated data tabulated elsewhere.¹ Anionic entropies were then derived by subtracting the cation values so obtained from the $\Delta_t S^\circ(\text{MX}_n)$ listed in Table 5

$$\Delta_t S^\circ(X^-) = [\Delta_t S^\circ(\text{MX}_n) - \Delta_t S^\circ(M^{n+})]/n$$

Where more than one possible route to $\Delta_t S^\circ(X^-)$ was available, all values were obtained and then averaged. The data were subsequently plotted and, if necessary, smoothed to remove obvious inconsistencies. Smoothed data are designated by an asterisk. Also included in Table 6, in normal font, are literature values of $\Delta_t S^\circ(\text{ion})$. It is gratifying to note the agreement between the present values and those derived in the very thorough review made of this

system by Abraham et al.⁸⁰ Of course, both sets of data are ultimately based on the TPTB values determined by these authors, but the present values include much information that was not available to them.

Plots (not shown) of $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{MeOH})$ against x_{MeOH} show remarkable similarities, with respect to shape and magnitude, to the corresponding enthalpy plots (e.g., Figures 3 and 4) for the alkali metal, alkaline earth, and halide anions. That is, for the $w + \text{MeOH}$ system, in addition to the cation/anion compensation already noted, there is considerable enthalpy/entropy compensation (bearing in mind the opposite signs of favorable enthalpy and entropy changes). Thus, the rather complex plots of $\Delta_t H^\circ$ or $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{MeOH})$ result in relatively featureless plots of $\Delta_t G^\circ(\text{ion}, w \rightarrow w + \text{MeOH})$.

B. Transfers from Water to Water + Ethanol (EtOH)

1. Enthalpy Data for Electrolytes

The aqueous-ethanol system has been extensively studied, and enthalpy of transfer data from water have been reported for around forty 1:1 electrolytes (Table 7), with multiple data sets in most cases making comparison and additivity checks possible. Data also exist for a far smaller number of 1:2, 2:1, and 1:3 electrolytes, but they have not been inde-

Table 7. $\Delta_t H^\circ(\text{MX}, \text{w} \rightarrow \text{w} + \text{EtOH})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{EtOH}}$

MX	$\Delta_{\text{sln}} H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
HCl	-75.14	3.5	4.3	0.7	-3.7	-6.8	-9.0	-12.9	-18.3	-20.1	-19.1	-11.8	74
HCl		5.3	3.3	0.0	-2.4								114
HCl		[22.8]											108
HCl		4.4	3.8	0.4	-3.0	{-7}	{-9}	{-13}	{-18}	{-20}	{-19}	{-12}	
HBr		2.3	3.0	-0.2	-5.6								114
HBr		3.8	3.2	0.1	-5.7								114
HBr		-1.6	-2.6	-3.3	-2.1	-4.3	-9.5	-16.7	-22.6	-23.6	-19.6	20.1	116
HBr		{1.5}	{1.2}	{-1.1}	{-4.5}	{-4}	{-10}	{-17}	{-23}	{-24}	{-20}	{20}	
HI		4.7	3.5	-1.4	-9.5								114
HClO ₄	-88.95	5.9	8.3	0.0	-8.3	-13.2	-17.3	-21.0	-23.9	-24.9			117
H ₂ C ₂ O ₄	37.70	3.9	5.7	1.6	-1.7	-3.8	-5.1	-5.9	-6.5	-7.1			118
H ₂ SO ₄		[0.3]											107
H ₂ SO ₄	-66.27	7.3	12.7	10.7	7.8	5.1	3.2	2.4	2.3	2.5			118
LiNO ₃	-2.66	2.8	3.8	1.3	-1.8	-5.6	-7.0	-9.4	-11.5	-13.6	-16.5	-20.6	35
NaCl	3.81	3.3	5.6	7.2	6.4	4.5	2.7	1.4	0.7	0.1	-1.2		74
NaCl	3.88	2.7	6.2	7.1	5.7	3.6	1.7	0.4	-0.6	-1.8	-4.5		119
NaCl		3.0	5.9	7.2	6.1	4.1	2.2	0.9	0.0	-0.9	-2.9		
NaBr	-0.71	2.9	6.6	5.8	2.7	0.5	-2.0	-3.5	-4.4	-4.9			117
NaBr	-0.64	3.2	5.7	5.5	3.4	0.8	-1.5	-3.2	-4.3	-5.5	-7.8		119
NaBr		3.1	6.2	5.7	3.1	0.7	-1.8	-3.3	-4.4	-5.2	{-8}		
NaI	-7.37	3.8	5.9	3.7	0.7	-2.3	-4.7	-6.2	-7.0	-8.1	-10.7		120
NaI	-7.58	3.7	5.7	3.4	0.0	-3.3	-5.9	-7.8	-9.1	-10.7	-13.8		119
NaI	-7.58	3.3	5.8	3.3	-0.2	-3.7	-6.4	-7.9	-8.8	-10.3	-13.0	-20.2	84
NaI^a		3.6	5.8	3.5	0.2	-3.1	-5.7	-7.3	-8.3	-9.7	-12.5	{-20.2}	
NaOH	-41.84	[2.1]	[4.1]	[5.5]	[3.5]	[1.6]	[1.1]			[-2.4]			118
NaOH	-42.68	1.3	2.5	2.4	0.2	-2.9	-6.2	-9.3	-11.9	-14.5	-17.4	-23.8	74
NaClO ₄	14.52	5.0	8.5	4.1	-0.1	-4.1	-6.4	-8.0	-8.8	-9.4			117
NaBPh ₄	-21.92	29.60	43.72	37.32	20.61								121
NaBPh ₄	-20.79	22.34	45.43	33.51	21.08	12.92	9.24	6.56	4.77	1.42			117
NaBPh₄		{26}	44.6	35.4	20.9	{12.9}	{9.2}	{6.6}	{4.8}	{1.4}			
KCl	17.28	2.7	5.4	4.8	3.7	1.1							121
KCl	17.57	2.2	6.7	[10.6]	[10.0]	[9.0]	[6.9]	[4.0]	[-0.8]	[-5.2]	[-10.5]	[-15.5]	122
KCl	17.16	3.0	5.4	6.6	5.4	3.3	1.4	-0.2					123
KCl	17.41	2.8	5.2	6.3	4.0	1.9							124
KCl	17.19	2.6	5.3	5.6	3.9	1.6	-0.4	-1.8	-2.6	-2.3	-4.8		119
KCl		2.7	5.6	5.8	4.3	2.0	0.5	1.0	{-3}	{-2}	{-5}		
KBr	18.79	2.0	3.7	4.1	0.5	-3.1							121
KBr	20.01	2.1	3.4	3.6	1.1	-2.7	-5.7						125
KBr	20.01	3.2	5.0	4.3	2.0	-0.3	-2.4	-4.0	-4.8				124
KBr	19.81	3.0	4.8	4.1	1.5	-1.4	-3.7	-5.2	-5.9	-6.2	-7.0		119
KBr		2.6	4.2	4.0	1.3	-1.2	-3.9	-4.6	-5.3	{-6}	{-7}		
KI	21.13	3.7	4.9	2.6	-1.6	-4.6	-5.8	-6.7					118
KI	20.04	2.9	4.1	0.9	-3.1	-5.2							121
KI	20.45	3.7	5.2	2.6	-1.6	-4.5	-6.8	-8.0	-8.3	-8.5	-9.5		124
KI		3.4	4.7	2.0	-2.1	-4.8	-6.3	-7.3	{-8}	{-9}	{-10}		
KPi		0.7	4.2	5.9	3.8	0.2	-4.8						96
KBPh ₄		34.5	50.1	45.4	21.6	8.0	28.9						96
RbCl	17.24	2.8	5.1	5.0	3.3	1.2	-0.5	-1.5	-1.9				120
RbCl	17.03	2.7	4.7	4.8	2.7	0.2	-1.8	-2.9	-3.0	-2.7	-3.1		119
RbCl		2.8	4.9	4.9	3.0	0.7	-1.2	-2.2	-2.5	{-3}	{-3}		
RbBr	22.14	3.1	4.4	3.2	0.4	-2.6	-5.1	-6.4	-6.8	-6.3	-6.5		119
RbI	25.78							-9.7	-9.6	-9.9	-10.3		120
RbI	25.59	3.6	4.5	1.1	-2.9	-6.7	-9.5	-10.9	-11.8	-11.4	-13.0		119
RbI		{4}	{5}	{1}	{-3}	{-7}	{-10}	{-10.3}	{-10.7}	{-10.7}	{-11.7}		
CsF	-36.33	3.3	5.3	7.4	6.2	4.8	3.5	3.2	4.0	6.0	7.8	7.0	35
CsCl	17.53						-2.0	-2.7	-2.4	-2.1			126
CsCl	17.34	2.2	4.4	3.8	1.5	-1.1	-3.2	-4.2	-4.8	-3.8	-3.8		119
CsCl		{2}	{4}	{4}	{2}	{-1}	{-2.6}	{-3.5}	{-3.6}	{-3.0}	{-4}		
CsBr	26.18	2.8	4.3	2.7	-0.3	-3.0	-4.9	-6.2	-6.0	-6.1			126
CsBr	26.02	2.6	4.0	2.2	-0.8	-3.9	-6.4	-7.6	-8.4	-7.7	-7.0		119
CsBr		{2.7}	{4.2}	{2.5}	{-0.6}	{-3.5}	{-5.7}	{-6.9}	{-7.2}	{-6.9}	{-7}		
CsI	33.34	3.2	4.5	0.7	-3.9	-7.2	-9.4	-11.0	-11.5	-10.7	-11.3		126
CsI	34.71	0.8	2.0	-2.3									90
CsI	33.18	3.3	4.0	0.2	-4.1	-8.0	-11.0	-12.6	-13.1	-12.8	-12.7		119
CsI		{2.4}	{2.8}	{-0.5}	{-4.0}	{-7.6}	{-10.2}	{-11.8}	{-12.3}	{-11.8}	{-12.0}		
AgPi		7.0	10.6	6.9	3.1	-0.8	-4.8						127
AgO ₂ CMe		3.3	4.7	4.6	4.0	3.5							127
AgO ₂ CET		4.4	7.6	6.2	5.1	3.8							127
AgO ₂ CPr		5.5	10.3	7.7	6.0	4.7							127
NH ₄ I	13.72	1.6	2.1	-2.2	-6.7	-10.5	-13.4	-15.9	-18.0	-20.2	-22.9	-26.2	35
NH ₄ NO ₃	25.49	2.7	3.1	-0.6	-4.3	-8.3	-10.1	-12.5	-14.6	-16.5	-20.0	-25.5	35
NH ₄ ClO ₄	32.68	5.8	7.8	0.9	-5.6	-8.9	-13.3	-15.9	-18.5	-20.8			117
Me ₄ NCl	3.97	3.9	6.2	7.1	5.5	4.3							121

Table 7. (Continued)

MX	$\Delta_{\text{sln}}H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
Pr ₄ NBPh ₄		36.0	53.5	46.0	32.0	27.0	28.0						93
Bu ₄ NBr		14.5	28.4	36.7	37.0	36.3	35.0	33.4	31.8	30.3	29.5	29.5	94
Bu ₄ NBr	-8.42	15.4	31.4	41.9	40.5	37.8	35.0	32.3	29.8	27.7	26.5	26.1	35
Bu₄NBr		15.0	29.9	39.3	38.8	37.1	35.0	32.9	30.8	29.0	28.0	27.8	
Bu ₄ NI	14.77	17.4	31.2	39.6	37.8	35.3							121
Ph ₄ AsCl	-10.88	22.3	35.1	28.7									121
Ph ₄ AsI		23.1	34.6	36.4	26.0	17.8	21.6						96
Ph ₄ AsPi		28.9	39.5	37.4	32.8								96
Ph ₄ PCl	-8.79	25.3	34.2	26.8									128
Ph ₄ PBr	8.24	22.9	33.7	25.0	19.0	13.8	11.3	9.0	7.5	5.7			117
CaCl ₂	-80.80	2.8	6.2	3.6	-1.3	-6.8	-10.6	-16.7	-21.9	-24.2	-23.4	-20.2	98
SrCl ₂	-51.13	4.1	7.2	5.1	-0.8	-4.7	-10.7	-15.9					99
BaCl ₂	-13.50	4.0	6.0	3.6	-0.2								99
FeCl ₂	-130.96	7.2	11.2	13.9	14.1	14.3	14.6	19.4	27.4	38.5	50.3	58.2	118
CoCl ₂		4.1	7.2	8.2	5.8	3.0	0.8	-1.6	-1.7	1.8			118
Co(ClO ₄) ₂		7.7	7.9	-2.1	-14.6	-23.8	-29.2	-32.6	-35.9	-39.8	-44.1	-47.5	100
NiCl ₂		4.0	7.5	9.2	6.3	3.7	1.6	-0.9	-1.8	-0.2			118
CuCl ₂		5.4	9.6	13.3	12.6	12.7	13.7	14.9	16.9	19.8			118
Cu(ClO ₄) ₂			(0.5)	5.2	15.1	21.6	25.6	(30.0)	32.2	(28.5)	39.6	(15.0)	129
FeCl ₃		7.8	13.6	18.8	17.3	15.9	17.4	21.4	28.8	37.8	43.6		118
AlCl ₃		6.8	12.0	16.0	13.0	9.9	7.5	5.0	4.5	7.3			118

^a Data also available at $233.15 \leq T/K \leq 293.15$ in ref 104.

pendently duplicated. The potentiometric data reported by Klyueva et al.¹³⁰ contain internal inconsistencies and so were excluded from further consideration, as was the paper by Krasnoperova.¹¹¹ Potentiometric data for NaI¹³¹ and calorimetric data (at $283.15 \leq T/K \leq 328.15$) for KBr¹³² were not available for consideration.

There is reasonable agreement between the HCl data of Bose et al.,¹¹⁴ determined from the temperature dependence of electrochemical cell potentials, and those determined calorimetrically by Bertrand et al.⁷⁴ The data of Dash and Samanta¹⁰⁸ are wildly different and have been disregarded. In the case of HBr there is poor agreement between the values of Das et al.¹¹⁵ and those of Robinette and Amis.¹¹⁶ In this case additivities (HCl–HBr, MCl–MBr) indicate that the latter are seriously in error at the higher ethanol compositions.

There is good agreement between independent sets of data for the sodium halides, and their averages have been Recommended. Agreement between the two data sets for NaOH^{74,118} is so poor that no values are Recommended; the data of Bertrand et al.⁷⁴ are probably more realistic. It should be noted that there is a general problem with the data of Bobtelsky and Larisch¹¹⁸ in that the signs of the solution enthalpies appear to be misreported in several cases; the reviewers have attempted to correct these in Table 7. There is passable agreement between the two sets of data for NaBPh₄ up to 30 mol % ethanol, and the averages have been Recommended; above this the results of Nevskii et al.¹¹⁷ have been classified as Tentative.

For KCl the data of Krestov et al.¹²² differ markedly from the other available values and have been disregarded. The remaining data for KCl are in reasonable agreement, and their averages have been Recommended. There is reasonable agreement between the various data sets available for both KBr^{119,121,124,125} and KI,^{118,121,124} and the averaged values are Recommended wherever possible. There

is also good agreement between two sets of data from Perelygin et al.^{119,126} for the rubidium and cesium halides; however, pending independent confirmation, the averaged values must be classified Tentative. A (partial) exception is for CsI at $x_{\text{EtOH}} \leq 0.2$, where the data of Korolev et al.⁹⁰ are in fair agreement with those of Perelygin et al.

The two independent studies of Bu₄NBr are in excellent agreement, enabling the averaged values to be Recommended at all solvent compositions. No critical evaluation of the data for the salts with more highly charged ions is possible, but it may be noted that most involve chloride electrolytes for which ion pairing will be a problem, especially at higher x_{EtOH} .

2. Ionic Enthalpies of Transfer

Data exist for several electrolytes that can be used to apply the TATB or TPTB assumption (Table 7), providing a number of routes to the ionic values. Additivity checks (NaX–KX) show that either the enthalpies of transfer of KBPh₄, determined from the temperature dependence of solubility,⁹⁶ are too endothermic or those of NaBPh₄ not sufficiently so. Since there are independent calorimetric data sets for NaBPh₄,^{117,121} which are in broad agreement, the single-ion values have been based on the NaBPh₄ data. Similarly, using the (MCl–MI) additivities, the values for Ph₄AsI appear to be too large and values based on Ph₄AsCl or the Ph₄P⁺ salts have been preferred. It should be noted that there is poorer agreement among the data at 50 mol % EtOH and only one set of values can be derived above this concentration and must therefore be taken as Tentative.

The application of the TA(P)TB assumption leads to ionic transfer enthalpies for 12 monovalent cations and 13 monovalent anions (Table 8). In addition, there are values for 7 divalent and 2 trivalent cations; for the usual reasons, these data should be treated with caution. As with the aqueous methanol system

Table 8. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{EtOH})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{EtOH}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
H ⁺	H(Cl,Br,ClO ₄)	3.3	4.6	2.0	-5.8	-10.2	-13.2	-16.8	-20.6	-22.6		
Li ⁺	LiNO ₃	3.3	4.6	2.3	-0.6	-4.2	-5.8	-8.4	-10.8	-13.1		
Na ⁺	NaBPh ₄	2.9	8.0	7.6	2.5	-0.1	-2.1	-4.7	-3.5	-5.0		-19.4 ^a
K ⁺	K(Cl,Br,I)	2.7	7.2	6.4	0.5	-2.0	-3.2	-5.1	-5.0	-5.0		-19.6 ^a
Rb ⁺	Rb(Cl,I)	3.0	7.1	5.2	-0.7	-3.8	-6.0	-7.8	-6.0	-6.5		
Cs ⁺	Cs(Cl,Br,I)	1.4	6.1	4.4	-1.5	-4.7	-6.5	-7.5	-7.1	-6.9		
Ag ⁺	AgPi	7.2	13.6	7.4	-0.2	-3.0	-3.2					
NH ₄ ⁺	NH ₄ ClO ₄	3.7	3.3	4.4	-3.0	-4.9	-9.0	-12.6	-13.2	-16.4		-26.5 ^a
Me ₄ N ⁺	Me ₄ NCl	3.8	8.3	7.5	1.9	0.1						0.2 ^a
Pr ₄ N ⁺	Pr ₄ NBPh ₄	12.9	16.9	18.2	13.6	13.9	16.9					
Bu ₄ N ⁺	Bu ₄ NBr	14.7	31.3	39.5	36.4	35.6	34.8	36.1	32.8	30.6		21.8 ^a
Ph ₄ P ⁺	Ph ₄ PBPh ₄	23.1	36.6	27.8	18.4	13.1	11.1	11.7	8.5	5.0	(3.0)	0.0 ^a
Ca ²⁺	CaCl ₂	2.6	10.3	4.4	-8.6	-15.2	-19.2	-27.9	-28.9	-32.2		-21.3 ^a
Sr ²⁺	SrCl ₂	3.9	11.3	5.9	-8.0	-13.1	-19.3	-27.1				-19.2 ^a
Ba ²⁺	BaCl ₂	3.8	10.1	4.4	-7.4							-21.7 ^a
Fe ²⁺	FeCl ₂ ^b	7.0	15.4	14.7	6.9	5.9	6.0	7.2	20.4	30.5		
Co ²⁺	CoCl ₂ ^b	3.9	11.4	9.0	-1.4	-5.4	-7.8	-12.8	-8.7	-6.2		
Ni ²⁺	NiCl ₂ ^b	3.8	11.7	10.0	-0.9	-4.7	-7.0	-12.1	-8.8	-8.2		
Cu ²⁺	CuCl ₂ ^{b,c}	5.2	13.8	14.1	5.4	4.3	5.1	3.7	9.9	11.8		
Fe ³⁺	FeCl ₃ ^b	7.5	19.9	20.0	6.5	3.3	4.5	4.6	18.3	25.8		
Al ³⁺	AlCl ₃ ^b	6.5	18.3	17.2	1.2	-2.7	-5.4	-11.8	-6.0	-4.7		
F ⁻	CsF	1.9	-0.8	3.0	7.5	9.5	10.0	10.7	11.1	12.9		
Cl ⁻	NaCl	0.1	-2.1	-0.4	3.6	4.2	4.3	5.6	3.5	4.0		10.2 ^a
Br ⁻	Ph ₄ PBr	-0.2	-2.9	-2.8	0.6	0.7	0.2	-2.7	-1.0	-0.3		5.4 ^a
I ⁻	NaI	0.7	-2.2	-4.1	-2.3	-3.0	-3.6	-2.6	-4.8	-4.7		-0.4 ^a
OH ⁻	NaOH	-1.6	-5.5	-5.2	-2.3	-2.8	-4.1	-4.6	-8.4	-9.5		
NO ₃ ⁻	NH ₄ NO ₃	-0.5	-0.7	-1.0	-1.2	-1.4	-1.2	-1.0	-0.7	-0.5		
ClO ₄ ⁻	NaClO ₄	2.1	4.5	-3.5	-2.6	-4.0	-4.3	-3.3	-5.3	-4.4		-2.6 ^a
MeCO ₂ ⁻	AgO ₂ CMe	-3.9	-8.9	-2.8	4.2	6.5						
EtCO ₂ ⁻	AgO ₂ CEt	-2.8	-6.0	-1.0	5.3	6.8						
PrCO ₂ ⁻	AgO ₂ CPr	-1.7	-3.3	0.5	6.2	7.7						
HSO ₄ ⁻	H ₂ SO ₄	4.0	8.1	8.7	13.6	15.3	16.4	19.2	22.9	25.1		
Pi ⁻	KPi	-0.2	-3.0	-0.5	3.3	2.2	-1.6					
BPh ₄ ⁻	Ph ₄ PBPh ₄	23.1	36.6	27.8	18.4	13.1	11.1	11.7	8.5	5.0	(3.0)	0.0 ^a

^a From the review by Marcus.² ^b Values for Cu²⁺ and Co²⁺ calculated from the chlorides disagree strongly with those calculated from the perchlorates; hence, the values for all these MX from ref 118 may be incorrect. ^c Mikheev et al.¹²⁹ presented graphical values for $\Delta_t H^\circ(\text{Cu}^{2+}, w \rightarrow w + \text{EtOH})$.

Table 9. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{EtOH})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol L⁻¹ Scale, as a Function of $100x_{\text{EtOH}}$

MX	$\Delta_{\text{sln}} S^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
HCl		4.8	7.3	-8.6	-18.3								114
HBr		5.9	9.2	-3.3	-24.1								115
HBr		-8.8	-13.1	-15.1	-16.5	-24.2	-41.2	-66.9	-96.6	-122.4	-4.1	-22.9	116
HI		8.2	12.3	-2.8	-30.2								114
KCl	17.8	1.2	2.3	1.4	-2.5	-7.4	-13.3	-19.2	-25.0	-30.6	-36.3	-41.9	122
KCl		1.4	1.8	0.4	-2.5	-6.2	-9.9						130
KCl		1	2	1	-3	-7	-12						
KPi	134.0	9.8	17.4	-0.7	-18.0	-32.1	-37.6						96
KBPh ₄	-68.5	125.7	169.5	160.5	117.4	103.5	118.8						96
AgPi		24.8	37.2	26.6	22.4	10.3	-1.7						127
AgO ₂ CMe		5.7	7.0	0.0	-6.7	-13.5	-20.2						127
AgO ₂ CEt		9.4	14.7	6.8	0.0	-6.1	-11.3						127
AgO ₂ CPr		13.7	27.1	14.2	7.4	1.9	-2.1						127
Ph ₄ AsI	15.3	94.4	119.1	148.8	132.0	119.4	111.1						96
Ph ₄ AsPi	-22.1	102.5	157.6	175.4	168.2	154.4	134.1						96

there are maxima in the cation values, which are sufficiently large to indicate that they are probably real, and much smaller minima in those for the anions.

3. Entropy Data for Electrolytes

There are entropy of transfer data for only 12 electrolytes and independent data sets for just HBr and KCl (Table 9). There is good agreement for the latter,^{122,130} and it is possible to recommend values up to 50 mol % EtOH. For HBr the values are too

disparate to justify averaging. Little can be said of the other data.

4. Ionic Entropies of Transfer

Only one set of values is available for $\Delta_t S^\circ(\text{BPh}_4^-, w \rightarrow w + \text{EtOH})$,⁹⁶ but two sets of values exist for Ph₄As⁺ salts, providing two-half-independent routes to single-ion values. There is good agreement between the values so obtained. An alternative route to the ionic values is to use the GHSE, combining the single-ion enthalpies in Table 8 and those re-

Table 10. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{EtOH})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TPTB Assumption, as a Function of $100x_{\text{EtOH}}$

ion	5	10	20	30	40	50	60	70	80	90	100
H ⁺	12	17	0	-5	-20	-30	-45	-61	-74		
Na ⁺	5	17	15	-3	-14	-24	-37	-38	-50	-108 ^a	
K ⁺	6	19	14	-8	-19	-28	-41	-49	-56	-113 ^a	
Rb ⁺	7	18	9	-14	-28	-40	-53	-54	-63	-103 ^a	
Cs ⁺	3	17	6	-14	-30	-40	-51	-56	-62	-92 ^a	
Ag ⁺	26	50	33	12	-2	-3					
Me ₄ N ⁺	16	33	30	8	-4						-36 ^a
Bu ₄ N ⁺	57	119	154	144	143	143	150	141	137		
Ph ₄ As ⁺ ^b	109	155	168	152	145	145					
Ph ₄ P ⁺	95	152	142	121	111	108	111	103	96	87	75
Cu ²⁺ ^c	15	42	41	10	5	4	-3	11	6		
Cu ²⁺ ^d	18	24	21	13	7	5	2	-3	-8	-8	
Cl ⁻	0	-16	-12	9	7	-22					
Br ⁻	-17	-27	-15	-11	-3	-16	-29	-39	-40		
I ⁻	-15	-36	-20	-20	-26	-34					
Pi ⁻	9	6	28	39	37	26					
MeCO ₂ ⁻	-10	-25	2	10	13	7					
EtCO ₂ ⁻	-7	-17	8	17	20	16					
PrCO ₂ ⁻	-2	-5	16	24	28	25					
BPh ₄ ⁻ ^b	109	155	168	152	145	145					
BPh ₄ ⁻	95	152	142	121	111	108	111	103	96	87	75

^a From the review by Marcus.² ^b Calculated from the data for Ph₄AsPi, KBPh₄, and KPi in Table 9; TATB assumption. ^c Calculated from CuCl₂ data.¹¹⁸ ^d Calculated from Cu(ClO₄)₂ data.¹²⁹

ported previously for $\Delta_t G^\circ$ for cations.¹ The values of $\Delta_t S^\circ(\text{Ph}_4\text{As}^+/\text{BPh}_4^-)$ obtained in these alternative ways are generally in good agreement ($\pm 10 \text{ J K}^{-1} \text{mol}^{-1}$). Since the $\Delta_t G^\circ(\text{Ph}_4\text{As}^+; \text{BPh}_4^-)$ and $\Delta_t H^\circ(\text{Ph}_4\text{As}^+; \text{BPh}_4^-)$ values are obtained from a wider set of data, they are preferred.

Using this approach provides $\Delta_t S^\circ(\text{ion})$ values for 10 monovalent cations, while combination of these values with the data in Table 9 provides $\Delta_t S^\circ(\text{ion})$ values for 9 monovalent anions (Table 10). As with the $\Delta_t H^\circ$ values, there are opposite trends in the anion and cation data with $\Delta_t S^\circ$ for the cations passing through maxima and those for the anions through minima. Given the large values (around $100 \text{ J K}^{-1} \text{mol}^{-1}$) of $\Delta_t S^\circ(\text{Ph}_4\text{As}^+; \text{BPh}_4^-)$ and the scale of their uncertainties, some caution must be exercised in interpreting these apparent trends.

C. Transfers from Water to Water + 1-Propanol (1-PrOH)

1. Enthalpy Data for Electrolytes

Interestingly, there are more enthalpy data available for electrolytes in these mixtures than there are values for the corresponding Gibbs energies of transfer. Indeed, there were insufficient data to warrant compilation of the latter for cations.¹ Table 11 summarizes the data that exist for the transfer enthalpies of electrolytes from water to aqueous mixtures of 1-PrOH. Values are available for 15 1:1 and two 1:2 electrolytes and NdCl₃. Less than one-half of these have been confirmed by independent measurements. Potentiometric measurements reported by Dash and co-workers¹⁰⁵⁻¹⁰⁹ for a number of silver and mercury salts at low cosolvent concentrations contained too little useful information to justify their inclusion.

For HCl two independent emf studies^{133,134} are in reasonable agreement at $x_{1-\text{PrOH}} \leq 0.4$ but diverge strongly thereafter. In the absence of calorimetric

confirmation, it is prudent to classify the averaged results as Tentative.

Data exist for $\Delta_t H^\circ(\text{NaCl}, w \rightarrow w + 1\text{-PrOH})$ only at $x_{1-\text{PrOH}} \leq 0.6$, presumably as a result of solubility problems at higher cosolvent concentrations. At $x_{1-\text{PrOH}} \leq 0.2$, the values, from three independent studies (two calorimetric^{136,137} and one emf¹³⁸), are in reasonable agreement. At higher $x_{1-\text{PrOH}}$ the data of Gregorowicz et al.¹³⁸ are significantly more negative than the calorimetric data and have been rejected. The values for NaCl listed at $x_{1-\text{PrOH}} > 0.6$, required for calculation of the TPTB values, were obtained by additivity (for neat 1-PrOH) followed by interpolation.

There are two sets of calorimetric data available for NaI from the Łódź group.^{15,84,137} The values are in reasonable agreement where comparison is possible ($x_{1-\text{PrOH}} \leq 0.4$), but in the absence of independent confirmation, their averages have been classified as Tentative. A similar situation exists for the two KCl data sets from the Ivanovo group.^{140,141} In contrast, for CsI there are two independent calorimetric data sets^{90,137} that are in excellent agreement, where comparison is possible (at $x_{1-\text{PrOH}} \leq 0.3$), enabling their averaged values to be Recommended. Similarly, for Bu₄NBr the two independent calorimetric data sets, one obtained³⁰ from $\Delta_{\text{sln}} H^\circ$ and the other from $\Delta_{\text{dil}} H^\circ$ measurements,^{142,143} are in good agreement at $x_{1-\text{PrOH}} \leq 0.15$. At higher 1-PrOH concentrations only the data of Carthy et al.^{142,143} are available and are therefore classified as Tentative.

None of the other data have been confirmed, so little can be said of them. Fortunately, the data available for NaBPh₄ and Ph₄PCl¹³⁹ appear reasonable (by comparison with other cosolvent mixtures). The derived values of Ph₄PBPh₄ differ slightly ($< 3 \text{ kJ mol}^{-1}$) from those reported by the original authors^{137,139} because of the use of different values for NaCl.

2. Ionic Enthalpies of Transfer

The values of $\Delta_t H^\circ(\text{ion}, w \rightarrow w + 1\text{-PrOH})$ that can be derived via the TPTB assumption are listed in Table 12. As the TPTB values have not been confirmed, the ionic values should be viewed with caution.

As in $w + \text{MeOH}$ mixtures (see Figure 3), the values of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + 1\text{-PrOH})$ for the alkali metals (data not plotted) are remarkably similar to each other over the whole solvent composition range. The waviness in these curves is almost certainly a reflection of the uncertainties in the single-ion quantities rather than a real effect. There is also a similar but somewhat larger charge effect (cf. Figure 4), with values of $\Delta_t H^\circ(\text{Ca}^{2+})$ being up to 20 kJ mol^{-1} more negative than $\Delta_t H^\circ(\text{Na}^+)$ in 1-PrOH-rich solutions.

The R₄N⁺ ions from Me₄N⁺ to Bu₄N⁺ show a fairly regular pattern with $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + 1\text{-PrOH})$ becoming more positive with increasing chain length. Further discussion of these data is deferred to section V.B.5 below.

The enthalpies of transfer of the halide ions are similar but opposite to those of the alkali metal ions. That is, there is cation/anion compensation. The plots

Table 11. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + 1\text{-PrOH})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{1-\text{PrOH}}$

MX	$\Delta_{\text{sin}} H^\circ$	5	10	15	20	30	40	50	60	70	80	90	100	ref
HCl		2.57	4.60	4.54	3.76	(2.08)	-1.06			-4.22		-27.59		133
HCl		0.11	0.31	0.09	-0.04	-0.63	-1.05	-1.16	-1.07	-1.15	-2.04	-4.63	-10.11	134
NaF	0.88	5.42	8.42	8.45	7.00	1.91	-1.65							135
NaCl	(0.35)	7.72	9.98	8.69	6.44	2.11	-1.93	-3.92	-4.60					136
NaCl		3.92	5.64	5.20	4.00	1.53	-2.53							137
NaCl		4.45	6.01	5.47	3.60	-1.74	-6.27	-8.01						138
NaCl		5.4	7.2	6.5	4.7	0.6	-3.6	{-6.0}	{-4.6}					
NaI	-7.58	3.97	3.86	-0.97	-1.12	-6.14	-8.95	-10.37	-11.71	-13.49	-15.14	-16.02	-17.44	15 ^a ,84
NaI		4.21	4.14	1.61	1.46	-5.46	-8.81							137
NaI		4.1	4.0	0.3	-0.2	-5.8	-8.9	{-10.4}	{-11.7}	{-13.5}	{-15.1}	{-16.0}	{-17.4}	
NaBPh ₄	-20.00	23.86	27.27	20.85	12.07	(5.44)	3.15	(2.17)	0.59	(-2.34)	-6.22	(-9.49)	-9.45	139
KCl	17.22	4.19	6.25	4.98	3.32	.51	-2.3	-5.11						140 ^b
KCl		6.5	8.9	8.7	7.0	2.7	0.1							141
KCl		5.3	7.6	6.9	5.7	1.6	-1.1	{-5.1}						
CsI	36.2	[0.0]	[-1.6]	[-4.2]	[-7.0]	[-10.7]								90
CsI	33.13	3.25	1.38	-0.66	-3.28	-8.06	-12.85							137
CsI		{3.3}	{1.4}	{-0.7}	{-3.3}	{-8.1}	{-12.9}							
Me ₄ NBr		1.95	2.90	3.05	2.38	0.35	-2.22	-4.51	(-5.86)	-5.82	(-4.06)	(-0.46)	4.95	142
Et ₄ NCl		4.85	8.23	10.46	11.35	11.23	9.24	6.63	(4.53)	3.91	(5.62)	(10.39)	18.79	142
Et ₄ NBr		4.44	7.31	9.04	9.29	8.25	5.76	3.17	(1.54)	1.72	(4.27)	(9.50)	17.47	142
Et ₄ NI		4.88	6.61	6.11	3.88	0.21	-1.48	-1.73	(-2.58)	-5.53	(-9.57)	(-9.14)	7.83	142
Pr ₄ NBr		9.49	15.52	18.87	19.73	18.41	15.07	12.19	(11.20)	12.46	(15.29)	(17.97)	17.69	142
Bu ₄ NBr		25.40	35.53	43.39	45.24	42.38	34.71	27.64	(24.19)	25.09	(28.67)	(30.94)	25.55	142
Bu ₄ NBr		23.05	32.94	40.71	42.85	41.34	35.10	28.86	(25.39)	25.49	(28.02)	(29.86)	25.93	143
Bu ₄ NBr	-8.6	27.5	38.2	35.9									30	
Bu₄NBr		25.3	35.6	40.0	44.0	41.9	34.9	28.3	{24.8}	25.3	{28.3}	{30.4}	25.7	
Me ₃ DcNBr	32.0	32.0	22.8	-8.8										30
Ph ₄ PCl	-8.37	24.19	31.69	30.46	26.18	(22.63)	20.25	(18.43)	16.79	(15.15)	13.55	(12.24)	11.67	139
Ph ₄ PBPh ₄		80.9	54.4		32.1	(21.6)	28.0							137
CaCl ₂	-80.8	6.2	5.6	3.6	-0.6	-6.3	-12.7	-18.1	-22.9	-26.9	-31.6	-18.0	-5.5	98
Co(ClO ₄) ₂	7.00	6.5	6.0	1.6	-4.4	-16.0	-23.5	-27.2	-29.1	-30.8	-32.1	-29.7	-17.6	100
NdCl ₃	-153.6	6.1	8.2	7.3	4.3	-5.2	-15.1	-21.6	-22.3	-17.7	-8.3			144

^a Mean of data at 288.15 and 308.15 K, agreeing with those of same author at 298.15 K.⁸⁴ ^b Interpolated by the reviewers from data given at $283.15 \leq T/\text{K} \leq 333.15$.

Table 12. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + 1\text{-PrOH})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{1-\text{PrOH}}$

ion	MX data	5	10	15	20	30	40	50	60	70	80	90	100
H ⁺	HCl	-0.9	-3.3	-5.9	-7.6	-8.7	-9.0	-8.4	-8.3	-9.0	-10.3	-13.0	-17.4
Na ⁺	NaBPh ₄	2.3	1.2	-1.5	-4.5	-7.9	-9.7	-9.9	-10.4	-11.2	-12.6	-13.9	-13.9
K ⁺	KCl	2.8	2.0	-1.3	-3.9	-7.7	-9.1	-11.4					
Cs ⁺	CsI	1.5	-1.4	-4.4	-7.6	-10.2	-13.7						
Me ₄ N ⁺	Me ₄ NBr	-0.7*	-1.8	-3.6	-5.1	-6.0	-6.8	-7.4	-8.7	-9.9	-9.9	-7.4	-0.9
Et ₄ N ⁺	Et ₄ NCl	2.4	2.6	2.3	2.1*	1.9	1.2	0.3	-1.3	-2.4	-1.5	2.6	11.6
Pr ₄ N ⁺	Pr ₄ NBr	7.5	10.8	12.2	12.2	12.0	10.5	9.3	8.4	8.3	9.8	11.1*	11.8
Bu ₄ N ⁺	Bu ₄ NBr	23.3	30.9	34.3*	36.5	37.5	30.3	25.4	22.0	21.2	22.5	23.5*	19.8
Ph ₄ P ⁺	Ph ₄ PBPh ₄	21.6	26.1	22.3	16.6	13.3	12.8	12.1	11.0	8.9	6.4	4.4	4.4
Ca ²⁺	CaCl ₂	1.2	-5.6	-12.8	-19.8	-24.9	-28.7	-30.7	-34.5	-39.5	-45.8	-33.6	-20.1
Nd ³⁺	NdCl ₃	-1.4	-8.6	-17.3	-24.5	-33.1	-39.1	-40.5	-39.7	-36.6	-29.6		
F ⁻	NaF	3.2	7.3	9.9	11.5	9.8	8.0						
Cl ⁻	Ph ₄ PCl	2.5	5.6	8.2	9.6	9.3	8.0	6.3	5.8	6.3	7.1	7.8	7.3
Br ⁻	Et ₄ NBr	2.0	4.7	6.7	7.2	6.4	4.6	2.9	2.8	4.1	5.8	6.9	5.9
I ⁻	NaI	1.8	2.8	3.7*	4.3	2.1	0.8	-0.5	-1.3	-2.3	-2.5	-2.9*	-3.6
BPh ₄ ⁻	Ph ₄ PBPh ₄	21.6	26.1	22.3	16.6	13.3	12.8	12.1	11.0	8.9	6.4	4.4	4.4

of $\Delta_t H^\circ(X^-)$ against $x_{1-\text{PrOH}}$ are roughly parallel, with $F^- > Cl^- > Br^- > I^-$ over the whole composition range. However, I^- exhibits a marked crossover at higher cosolvent concentrations, ultimately becoming more positive than Cl^- (there are no F^- data at $x_{1-\text{PrOH}} > 0.5$). As in aqueous–MeOH mixtures, there are much greater differences between the halides than there are for the alkali metal ions.

3. Entropies of Transfer

There are very few entropy data for the transfer of electrolytes from $w \rightarrow w + 1\text{-PrOH}$ (Table 13). The two independent sets of data derived for HCl from dE°/dT measurements^{133,134} are in fair agreement at $x_{1-\text{PrOH}} \leq 0.4$, and the averaged values are Recom-

mended. However, at higher $x_{1-\text{PrOH}}$ the trends are rather different; the datum of Roy et al.¹³³ at $x_{1-\text{PrOH}} = 0.7$ appears too negative and has been rejected.

No estimation of ionic entropies via the GHSE was possible because of the absence of critically evaluated $\Delta_t G^\circ$ data for electrolytes or ions in these mixtures,¹ and none has been reported in the literature.

D. Transfers from Water to Water + 2-Propanol (2-PrOH)

1. Enthalpy Data for Electrolytes

The results for $\Delta_t H^\circ(\text{MX}, w \rightarrow w + 2\text{-PrOH})$ reported in the literature are summarized in Table 14. Numerical data are available for more than 20

Table 13. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + 1\text{-PrOH})/\text{J K}^{-1} \text{ mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{1\text{-PrOH}}$

MX	5	10	20	30	40	50	60	70	80	90	100	ref
HCl	11	3	-17	(-22)	-30			[-120]				133
HCl	-3	-7	-13	-20	-29	(-37)	(-45)	-53	(-61)	(-69)	-77	134
HCl	4	-2	-15	-21	-30							
NaCl	3.6	4.7	-17.8	-45.3	-75.8	-93.2						138
KCl	-13.9	-15.3	1.9	26.1	47.3							141

Table 14. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + 2\text{-PrOH})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{2\text{-PrOH}}$

MX	$\Delta_{\text{sin}} H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
HCl		0.9	0.7	-2.7	-6.1	-10.0	-14.5	-19.4	-25.0				145, 146
HCl		3.2	2.3	-1.8									114
HCl		2.1	1.5	-2.3	{-6}	{-10}	{-15}	{-19}	{-25}				
HBr		3.4	1.0	5.9									114, 147
HBr		2.1	0.3	5.1									148
HBr		2.8	0.7	5.5									
HI		3.6	-0.4	-9.2									114
NaCl		[6.6]	[9.4]	[7.2]		[5.0]							188
NaCl	3.90	4.5	7.1										22
NaCl		4.5	7.2										149
NaCl		4.5	7.2										
NaBr		1.4	1.1	2.0									148
NaBr		3.5	3.5	3.2									150
NaBr^a		2.5	2.3	2.6									
NaI		5.5	6.4	1.4	-3.3	-7.0	-10.7	-13.8	-16.1	-18.1	-19.1	-18.0	84, 157
NaI			6.8	2.6	-0.1	-6.2	-11.0	-14.2	-15.5	[-13.9]	[-12.8]	-22.9	151
NaI		5.3	6.0	1.4	-3.3	-7.8	-11.7	-14.8	-17.1	-18.7	-19.8	-20.9	152
NaI		5.4	6.4	1.8	-2.2	-7.0	-11.1	-14.3	-16.2	-18.4	-19.5	-20.6	
NaBPh ₄	-19.91	35.1	45.6	21.6	11.7	9.1	6.6	4.5	4.5	2.2	1.6	1.7	153
KCl	17.16	4.9	7.8	6.3	3.1	-0.5							123
KBr ^a	20.01	4.4	6.4	2.8	-1.1								125
KI	20.30	5.1	5.0	-0.6	-3.7	-9.6	-13.5	-15.6	-15.9				154
KPi ^b		7.9	7.0	-9.8	-13.8	-14.4							96
KBPh ₄ ^b		43.0	54.0	38.8	27.1	17.4							96
NH ₄ I		4.7	3.8	-8.4	-12.8	-14.7	-19.3						155
NH ₄ I		8.6	1.4	-7.8	-10.1								156
NH ₄ I	13.70		2.3										92
NH₄I		{6.7}	{2.5}	{-8.1}	{-11.5}	{-15}	{-19}						
AgPi		12.7	10.2	-1.8	-12.1	-7.1							127
AgO ₂ CMe		3.8	5.0	4.6	3.6	6.0							127
AgO ₂ CEt		7.6	7.2	5.3	6.7	8.2							127
AgO ₂ CPr		11.2	9.8	6.0	8.5	11.1							127
Me ₄ NBPh ₄		39.0	52.0	50.0	45.0	42.0							93
Et ₄ NBPh ₄ ^d		45.5	56.0	51.5	47.0	45.0							93
Pr ₄ NBPh ₄ ^d		50.0	60.5	51.0	45.0	43.0							93
Bu ₄ NBPh ₄ ^d		55.5	68.5	57.0	56.0	42.0							93
Ph ₄ AsI ^b		25.3	39.0	40.4	35.7	30.7							96
Ph ₄ AsPi ^b		29.4	43.9	38.6	36.8	37.5							96
Ph ₄ PCl	-8.79	36.8	32.3	25.6	20.6	17.7	14.7	12.7	11.6	11.2	10.3	10.8	153
NiCl ₂	-83.43	(5.4) ^c											101

^a Data derived from potentiometry are also available,³³⁷ but the reported heats of solution are unreasonable, and hence, the resulting $\Delta_t H^\circ$ values are rejected. ^b Data probably not reliable, see text. ^c $\Delta_t H^\circ = 2.3$ and 6.7 kJ mol^{-1} for $x_{2\text{-PrOH}} = 0.019$ and 0.065 , respectively. ^d Data also available¹⁵⁹ for unsymmetrical RNH₃BPh₄ salts (R = Et, Pr, Bu).

1:1 electrolytes and also NiCl₂. Potentiometric measurements reported by Dash and co-workers¹⁰⁵⁻¹⁰⁹ for a number of silver and mercury salts at low cosolvent concentrations contained too little useful information to justify their inclusion. Potentiometric data for KBr¹⁵⁸ were unavailable for consideration.

Values of $\Delta_t H^\circ$ have been independently confirmed for only six of the 1:1 electrolytes. Thus, for HCl, two independent sets of results derived from potentiometric (dE°/dT) data are available.^{114,145,146} Where comparison is possible ($x_{2\text{-PrOH}} \leq 0.1$), the data are in reasonable agreement and the averaged values are recommended. At higher cosolvent concentrations only the data of Roy et al.^{145,146} are available and so have been classified as Tentative. A similar situation exists for HBr^{114,147,148} and NaBr^{148,150} with indepen-

dent potentiometrically derived values in good agreement over the narrow range of solvent compositions investigated.

For NaCl^{22,149} and NaI^{84,151,152} independent calorimetric and potentiometric data, albeit mainly from the Lodz group, are in excellent agreement at $x_{2\text{-PrOH}} \leq 0.2$ (for NaCl) or over the whole solvent composition range (for NaI). The potentiometrically derived data for NaCl reported by Parfenyuk et al.¹⁸⁸ appear less reliable than the other available data^{22,149} and have been rejected. The Kharkov group reported one calorimetric⁹² and two potentiometric^{155,156} sets of data for $\Delta_t H^\circ(\text{NH}_4\text{I}, w \rightarrow w + 2\text{-PrOH})$ at various cosolvent compositions. The results are in good agreement, but again, lacking independent confirmation, their averaged values are classified as Tenta-

Table 15. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + 2\text{-PrOH})/\text{kJ mol}^{-1}$, 298.15K, TATB/TPTB Assumption, as a Function of $100x_{2\text{-PrOH}}$

ion	MX data	5	10	20	30	40
H ⁺	HCl	9.5	-1.1	-20.0	-25.1	-29.2
Na ⁺	NaBPh ₄	12.7	6.6	-9.0	-14.4	-17.1
K ⁺	KCl	12.3	5.2	-11.4	-15.9	-19.6
NH ₄ ⁺	NH ₄ I	13.9	2.7	-18.9	-23.6	-24.8
Me ₄ N ⁺	Me ₄ NBPh ₄	10.1	12.8	19.1	21.8	21.4
Et ₄ N ⁺	Et ₄ NBPh ₄	16.8	15.6	21.2	24.0	24.5
Pr ₄ N ⁺	Pr ₄ NBPh ₄	21.0	18.8	21.0	21.9	22.2
Bu ₄ N ⁺	Bu ₄ NBPh ₄	25.2	27.3	28.2	29.2	31.0
Ph ₄ As ⁺ /Ph ₄ P ⁺	Ph ₄ P(As)BPh ₄	32.5	39.2	29.6	23.6	20.6
Cl ⁻	Ph ₄ PCl	-7.4	2.6	17.7	18.9	19.1
Br ⁻	NaBr	-7.4	2.6	17.7		
I ⁻	NaI	-7.2	-0.2	10.8	12.2	10.1
BPh ₄ ⁻	Ph ₄ P(As)BPh ₄	32.5	39.2	29.6	23.6	20.6

tive. As none of the other data has been confirmed, no further critical evaluation is possible at present.

2. Ionic Enthalpies of Transfer

Reasonable amounts of data exist for salts required for the TATB/TPTB assumption. At $0.1 \leq x_{2\text{-PrOH}} \leq 0.4$ there is good agreement between the TATB/TPTB values obtained using the combinations (NaBPh₄ + Ph₄AsI - NaI) and (KBPh₄ + Ph₄PCl - KCl) based mainly on the data of Sinha and Kundu.⁹⁶ At $x_{2\text{-PrOH}} = 0.05$, these two routes are in rather poor agreement but their average agrees well with that obtained from (NaBPh₄ + Ph₄PCl - NaCl) based on the calorimetric data of Taniewska-Osinska et al.¹⁵³ and the averaged NaCl data in Table 14 and thus can be used with some confidence. Unfortunately, the NaCl data are available only at low 2-PrOH concentrations, presumably because of solubility limitations. On the other hand, the values calculated from (KBPh₄ + Ph₄AsPi - KPi)⁹⁶ differ markedly, implying that the values for either or both Ph₄AsPi and KPi are in error. These data were therefore not considered

further, and the ionic values were based on averages of the first two combinations.

The ionic transfer enthalpies (for nine monovalent cations and four monovalent anions) from water to aqueous-2-PrOH mixtures so obtained are summarized in Table 15. It should be noted that because of the uncertainty in the data for the picrate salts, no values have been derived for $\Delta_t H^\circ(\text{Ag}^+)$ and hence for the various carboxylate anions.

3. Entropy Data for Electrolytes

Data have been reported for the entropies of transfer of approximately twenty 1:1 electrolytes from water to aqueous-2-PrOH mixtures (Table 16) but there are independent sets only for HCl^{114,145} and HBr^{147,148} at low cosolvent concentrations and NaI^{151,152} over the whole composition range. For HCl the values become increasingly divergent with increasing 2-PrOH content, so only values at $x_{2\text{-PrOH}} \leq 0.3$ are recommended. There is good agreement between the two sets of data for HBr and reasonable agreement for the NaI data. No further assessment of the data is possible at this stage.

4. Ionic Entropies of Transfer

Ionic values for nine cations and five anions (all monovalent) are reported in Table 17 based on the single-ion enthalpies reported in Table 15 and previously reported single-ion Gibbs energies¹ along with relevant electrolyte entropy data from Table 16. Values of $\Delta_t S^\circ$ for Ph₄As⁺ (= BPh₄⁻) can be calculated from the corresponding $\Delta_t H^\circ$ and $\Delta_t G^\circ$ data for 10 and 20 mol % 2-PrOH. These are in reasonable agreement with those calculated from the $\Delta_t S^\circ$ data for Ph₄AsI and the ionic values for I⁻ or from the corresponding picrate data. In contrast, the values calculated from the KBPh₄ and K⁺ values are some

Table 16. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + 2\text{-PrOH})/\text{kJ mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{2\text{-PrOH}}$

MX	5	10	20	30	40	50	60	70	80	90	100	ref
HCl	7.2	0.5	-19.0	-37.1								114
HCl	-2.2	-4.7	-9.6	-14.7	-20.3	-26.2	-32.7	-39.8				145
HCl	3	-2	-14									
HBr	9.1	-0.1	-26.7	-51.4								147
HBr	4.9	-2.5	-24.3									148
HBr	7	1	25									
HI	11.4	-0.8	-30.5	-49.7								114
NaCl	3.7	2.8										149
NaBr	4.3	12.5	-22.7									148
NaI	15.0	13.6	-14.7	-37.4	-76.0	-100.0	-123.5	-140.5	-150.8	-152.6	-220.7	151
NaI	10.8	8.0	-16.3	-43.2	-69.6	-93.6	-114.6	-133.2	-151.3	-172.0	-199.5	152
NaI	13	11	-15	-40	-73	-97	-119	-137	-151	-172*	-210	
KPi	23.3	22.9	-19.8	-47.5	-55.6							96
KBPh ₄	158	213	173	136	108							96
AgPi	52.1	48.5	17.2	6.9	18.5							127
AgO ₂ CMe	10.6	12.0	8.0	8.6	14.1							127
AgO ₂ CET	23.0	22.4	15.5	17.1	27.5							127
AgO ₂ CPr	36.3	34.1	23.3	25.5	40.8							127
NH ₄ I	9.0	1.3	-47.6	-68.5	-90.4	-109.8						155
Me ₄ NBPh ₄	145.3	202.9	211.2	215.8	208.5							93
Et ₄ NBPh ₄ ^a	163.7	212.1	216.0	214.0	210.2							93
Pr ₄ NBPh ₄ ^a	180.2	241.0	224.4	219.0	215.9							93
Bu ₄ NBPh ₄ ^a	203.6	264.3	236.0	230.1	229.8							93
Ph ₄ AsI	93	160	173	160	142							96
Ph ₄ AsPi	109	185	192	188	200							96

^a Data also available for unsymmetrical RNH₃BPh₄ salts (R = Et, Pr, Bu).¹⁵⁹

Table 17. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + 2\text{PrOH})/\text{kJ mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{2-\text{PrOH}}$

ion	5	10	20	30
H ⁺	28.1	2.2	-56.7	-71.7
Na ⁺	35.6	22.9	-11.6	
K ⁺	31.7	13.3	-43.7	-61.0
NH ₄ ⁺	40.9	11.6	-61.8	
Me ₄ N ⁺	28.8	29.4	38.5	41.4
Et ₄ N ⁺	172.1	202.5	192.1	200.5
Pr ₄ N ⁺	180.2	241.0	224.4	219.0
Bu ₄ N ⁺	203.6	264.3	236.0	230.1
Ph ₄ As ⁺	116.5	173.5	172.7	174.4
Cl ⁻	-31.9	-20.1		
Br ⁻	-23.2	-4.7	32.4	
I ⁻	-22.7	-12.0	-3.9	
Pi ⁻	-8.4	9.6	23.9	13.5
BPh ₄ ⁻	116.5	173.5	172.7	174.4

20–30 J K⁻¹ mol⁻¹ more positive. Thus, Table 17 reports values calculated via the iodide and picrate data.

E. Transfers from Water to Water + *tert*-Butyl Alcohol (*t*-BuOH)

1. Enthalpy Data for Electrolytes

A plethora of data are available for the enthalpies of transfer from water to aqueous *t*-BuOH mixtures, including 25 1:1 and four 1:2 electrolytes, but only at low cosolvent concentrations (Table 18). Because of the very large changes in the thermodynamic transfer functions for electrolytes that occur with solvent composition in water-rich mixtures of this system,^{168,169} the $\Delta_t H^\circ$ data in Table 18 are presented at closely spaced intervals for $x_{t\text{-BuOH}} < 0.2$. Potentiometric measurements reported by Dash and Samanta¹⁷⁹ for a number of silver salts at low cosolvent concentrations contained too little useful information to justify their inclusion. Data have also been reported for the enthalpies of dissociation of water¹⁸⁰ and various carboxylic acids.³⁶⁸

For HCl there appear to be only two original data sets: one derived from the temperature dependence of galvanic cell potentials¹⁴⁶ and the other from the calorimetric ($\Delta_{\text{sln}}H^\circ$) measurements.¹⁶⁰ In addition, Bose et al.¹⁶¹ recalculated the values of Roy et al.¹⁴⁶ All three data sets show the same general trend, with the exception of the datum of Bose et al. at $x_{t\text{-BuOH}} = 0.14$, which is rejected. Nevertheless, the agreement is only fair, and the averaged values should be regarded as Tentative pending further studies.

Two independent sets of potentiometrically derived values exist for $\Delta_t H^\circ(\text{HBr})$: from Bose et al.^{114,161} and from Robinette and Amis¹¹⁶ along with the calorimetric results of Pointud et al.¹⁶⁰ The data show the same broad trends with solvent composition, but the values of Bose et al.^{114,161} vary unreasonably and are therefore rejected. The averaged values of the remaining data^{116,160} are classified as Tentative at $x_{t\text{-BuOH}} \leq 0.14$. At higher $x_{t\text{-BuOH}}$ only the data of Robinette and Amis are available, so no critical evaluation is possible. The situation for HI is similar, except that the calorimetric¹⁶⁰ and potentiometric^{114,161} results are in excellent agreement over the whole composition range studied. The averaged values are therefore Recommended.

For NaCl, independently measured values of $\Delta_t H^\circ$ from calorimetry¹⁶² and potentiometry¹⁶⁵ are in good agreement except at $x_{t\text{-BuOH}} = 0.2$. Averaged values for all other compositions are Recommended. Values of $\Delta_t H^\circ(\text{NaI}, w \rightarrow w + t\text{-BuOH})$ have been reported in four publications from the Lodz group,^{14,84,164,165} the first three using $\Delta_{\text{sln}}H^\circ$ measurements and the last potentiometry. The data of Taniewska-Osinska et al.¹⁴ differ markedly from the other studies and are rejected; their value of $\Delta_{\text{sln},w}H^\circ$ is also aberrant.⁷³ The remaining data are in excellent agreement at $x_{t\text{-BuOH}} \leq 0.5$, and the averaged values are Recommended. At higher cosolvent compositions the differences are too great for a critical evaluation to be made.

Three sets of calorimetric data have been reported for $\Delta_t H^\circ(\text{NaBPh}_4, w \rightarrow w + t\text{-BuOH})$: two due to Arnett and McKelvey^{168,169} and one by Juillard.¹⁷⁴ Ignoring the earlier graphically presented values,¹⁶⁸ the results reported by the two groups are in excellent agreement, and their averages have been Recommended wherever comparison is possible. The variation of $\Delta_t H^\circ$ for this salt with even quite small changes in solvent composition is notable and warrants further study. For KCl at $x_{t\text{-BuOH}} \leq 0.14$, the two available independent calorimetric studies^{162,168} are in excellent agreement and are therefore Recommended. At $x_{t\text{-BuOH}} = 0.2$, the two reported values differ significantly; the lower value¹⁶⁸ seems more reasonable.

Two independent calorimetrically determined sets of values for $\Delta_t H^\circ(\text{R}_4\text{NBr}, w \rightarrow w + t\text{-BuOH})$ exist for R = Me, Bu, and Pe (Table 18) and are in excellent agreement wherever comparison is possible. The averaged values are accordingly classified as Recommended or, when unconfirmed, Tentative, throughout. A similar situation exists for Ph₄AsCl, where the values of Arnett and McKelvey¹⁶⁸ are in good agreement with those reported by Juillard.¹⁷¹ As the former were calculated by the reviewers by graphical interpolation, the values of Juillard are Recommended.

2. Ionic Enthalpies of Transfer

As noted above, good quality data are available for the enthalpies of transfer of Ph₄AsCl, NaBPh₄, and NaCl from water to aqueous solutions of *t*-BuOH up to $x_{t\text{-BuOH}} = 0.2$ (Table 18). The single-ion enthalpies of transfer derived from these data via the TATB assumption are given in Table 19.

The most notable features of the values of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + t\text{-BuOH})$ are the pronounced extrema at very low cosolvent concentrations. As in aqueous MeOH solutions, the position and, to some degree, the size of these extrema are almost independent of the size of the alkali metal ion (Figure 5). The small differences are largely systematic, in the order Na⁺ > K⁺ > Rb⁺ > Cs⁺; however, the position of Li⁺ is anomalous. Again, as in aqueous MeOH, increasing the charge on the cation (compare Na⁺ and Ca²⁺ in Table 19) has a significant effect on the magnitude but not the position of the extrema.

The values of $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + t\text{-BuOH})$ also exhibit two extrema at low cosolvent concentrations (Table 19, data not plotted), but they are generally

Table 18. $\Delta_t H^\circ(\text{MX}, \text{w} \rightarrow \text{w} + t\text{-BuOH})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{t\text{-BuOH}}$

MX	$\Delta_{\text{sin}} H^\circ$	2	4	6	8	10	12	14	20	30	50	70	90	100	ref
HCl		[2.5]	[4.4]	[5.6]	[6.0]	[5.4]	[3.7]	[0.9]	[-0.2]	[-2.3]					146
HCl		2.3	3.3	3.1	2.0	0.3	-1.2	-1.9							160
HCl		[6.0]	[7.9]	[7.1]	[5.0]	[2.9]	[2.2]	[4.3]							114, 161
HCl		{ 2.3 }	{ 3.3 }	{ 3.1 }	{ 2.0 }	{ 0.3 }	{ -1.2 }	{ -1.9 }							
HBr		2.5	3.1	2.2	0.4	-1.6	-3.3	-4.2							160
HBr		(2.9)	(4.3)	(4.4)	(3.9)	(2.5)	(0.7)	(-1.4)	-7.6			-34.7	-75.8	-41.9	116
HBr		[6.3]	[7.6]	[5.7]	[1.7]	[-3.3]	[-8.4]	[-12.4]	[-8.6]						161, 114
HBr		2.7	3.7	{ 3.3 }	{ 2.2 }	{ -0.6 }	{ -1.3 }	{ -2.8 }							
HI		3.2	3.5	1.8	-1.0	-4.1	-6.5	-7.5							160
HI		3.9	4.6	3.0	-0.2	-4.2	-8.4	-11.9	-11.3						114, 161
HI		3.6	4.1	2.4	-0.6	-4.2	-7.5	-9.9	{ -11.3 }						
LiCl		1.3	3.3	5.0	5.9	5.9	5.4	5.0							160
NaCl	+3.87	2.4	5.5	8.2	9.9	10.3	9.6	8.5							162
NaCl		2.59	5.70	8.42	10.25	10.95	10.54	9.26	6.74						163
NaCl		2.5	5.6	8.3	10.1	10.6	10.1	8.9	{ 6.7 }						
NaI	-6.52	2.9	4.6	5.2	5.2	4.6	3.7	2.6	-1.3	-6.7	-15.2	-19.4	-18.3		164
NaI	[-9.5]	[-4.2]	[-1.5]	[-0.7]	[-1.5]	[-2.4]	[-3.5]	[-4.5]	[-7.6]	[-12.4]	[-20.2]	[-23.7]	[-20.7]		14
NaI	-7.58	3.12	6.00												84
NaI		3.4	5.4	6.3	6.4	5.9	5.0	3.8	-0.2	-5.9	-14.5	(-28.4)	(-36.3)		165
NaI		3.1	5.3	5.7	5.8	5.3	4.4	3.2	-0.8	-6.5	-14.9				
NaO ₂ CH	0.74	2.51	5.99	9.19	(9.8)	10.34	(11.1)	(11.0)	7.91						166
NaO ₂ CMe	-17.46	2.98	7.87	12.34	(14.1)	15.82	(17.7)	(18.4)	14.71						166
NaO ₂ CEt	-12.76	3.15	8.83	15.25	(16.6)	18.37	(20.9)	(21.7)	17.57						166
NaO ₂ CPr	-14.09	3.52	11.65	18.65	(20.0)	21.86	(24.6)	(25.4)	20.66						166
NaBz		5.80	14.44	19.31	19.70	18.00	16.74	15.73							167
NaBPh ₄	[-22.0]	[22.5]	[74.5]	[60.0]	[48.3]	[38.9]	[31.6]	[26.1]	[17.5]	[12.2]					168
NaBPh ₄	-19.96	17.5	55.8	62.0	45.6	33.4	24.8	19.3	14.7	11.3					169
NaBPh ₄	-20.10			[70]											170
NaBPh ₄	[-18.59]	19.4	56.0	63.1	48.2	32.2	25.6	23.6							171
NaBPh₄		18.5	55.9	62.6	46.9	32.8	25.2	{ 21.4 }	{ 14.7 }	{ 11.3 }					
KCl	17.7	1.9	4.8	7.3	8.6	8.8	8.3	7.5	6.7						168
KCl	17.18	2.3	5.1	7.4	8.8	9.0	8.3	7.2	(13.5)						162
KCl		2.1	5.0	7.4	8.7	8.9	8.3	7.4	{ 6.7 }						
KBr	19.9	2.1	4.7	6.6	7.3	6.8	5.7	5.2							172
KI	20.2	3.0	5.3	6.2	5.8	4.4	2.7	2.0							172
KBz		5.62	13.98	18.57	18.72	16.83	15.46	14.31							167
RbCl	16.9	2.1	4.8	7.0	8.2	8.4	7.6	6.5	(11.7)						162
CsCl	17.1	2.2	4.6	6.4	7.4	7.4	6.7	5.7	(9.4)						162
NH ₄ Cl	14.9	1.3	2.8	3.8	4.1	3.7	2.9	2.5							174
Me ₄ NCl	4.5	1.7	3.9	5.9	7.1	7.5	7.1	6.2	4.5	5.0					168
Me ₄ NBr	24.48	[0.2]	[0.3]	[0.2]	[0]	[-0.3]	[4.5]	[4.3]							175
Me ₄ NBr	24.4	2.3	4.0	4.9	5.2	4.9									171
Et ₄ NBr	6.1	3.9	7.2	9.4	10.4	10.5	10.4	10.8							171
Pr ₄ NBr	-4.5	7.7	15.5	21.2	24.2	24.8	24.6	26.3							171
Bu ₄ NBr	-8.5	15.5	27.9	36.9	42.9	45.8	45.9	43.3							171
Bu ₄ NBr	-8.58	11.4	28.7	40.0	42.8	44.2	44.0	43.9	43.2	41.9	38.7	34.6	29.7	26.9	170
Bu₄NBr	-8.5	11.5	28.3	38.5	42.9	45.0	45.0	43.6	{ 43.2 }	{ 41.9 }	{ 38.7 }	{ 34.6 }	{ 29.7 }	{ 26.9 }	
Bu ₄ NBPh ₄	24.10	92.05													176
Pe ₄ NBr		18.9	47.4	65.3	69.0	61.9	(57.0)	(53.9)	51.8	49.1					177
Pe ₄ NBr	3.8	19.6	46.4	64.0	66.1	55.6	44.9	55.9							171
Pe₄NBr		19.3	46.9	64.7	67.6	{ 59 }	{ 51 }	54.9	{ 51.8 }	{ 49.1 }					
Ph ₄ AsCl		25.4	35.2	35.5	31.6	27.1	23.7	22.1	22.9	20.2					168
Ph ₄ AsCl	8.8	25.1	36.8	38.6	34.3	28.0	23.7	25.2							171
Ph₄AsCl		25.3	36.0	37.0	33.0	27.6	23.7	23.7	{ 22.9 }	{ 20.2 }					
Ph ₄ AsPi		11.3	32.4	43.9	38.7	21.1	(7.5)	25.9							96
Ph ₄ AsBPh ₄	31.55	[105.4]													176
MgCl ₂		1.3	5.0	8.2	9.6	9.2	(8.2)								178
CaCl ₂		2.6	6.7	10.3	12.4	12.6	11.6	11.1							178
SrCl ₂		4.0	9.0	13.3	15.7	16.2	15.3	14.6							178
BaCl ₂		4.0	9.2	13.6	16.0	16.3	15.3	14.7							178

mutated, cf. the alkali metal ions. The values of $\Delta_t H^\circ(\text{R}_4\text{N}^+)$ increase systematically with increasing ion size, although the curve for Pe_4N^+ differs somewhat from the smaller R_4N^+ ions at $x_{t\text{-BuOH}} > 0.08$. In particular, the upturn at $x_{t\text{-BuOH}} = 0.14$ may be an artifact, but more detailed studies are required.

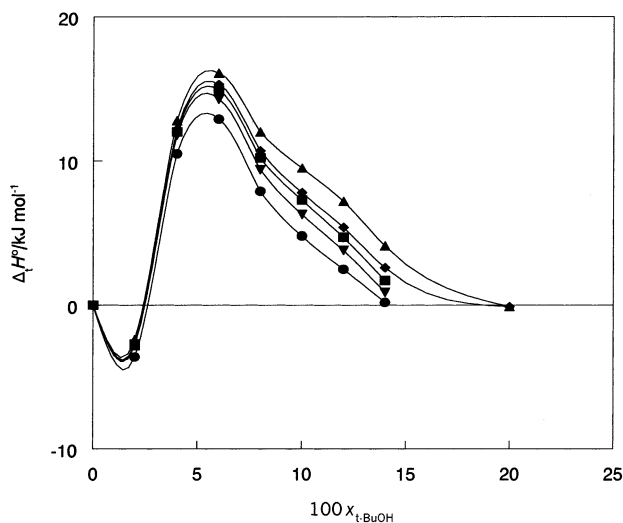
The variation of $\Delta_t H^\circ(\text{X}^-, \text{w} \rightarrow \text{w} + t\text{-BuOH})$ for the halide ions with solvent composition (not plotted) is similar, but opposite in sign, to those of the alkali metal ions, as also found for aqueous MeOH mixtures. That is, at least to some extent, there is cation/anion compensation in aqueous *t*-BuOH solutions.

3. Entropy Data for Electrolytes

The entropy of transfer data for electrolytes from water to $\text{w} + t\text{-BuOH}$ are given in Table 20. Very few values are available, and few comparisons can be made. The hydrohalic acids are an (partial) exception. Thus, for HCl, there are apparently two sets of data^{146,161} derived from cell emfs, which are in good agreement. However, as it is not clear whether the values given by Bose et al.¹⁶¹ are original or were recalculated from the data of Roy et al.,¹⁴⁶

Table 19. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + t\text{-BuOH})/\text{kJ mol}^{-1}$, 298.15K, TATB Assumption, as a Function of $100x_{t\text{-BuOH}}$

ion	MX data	2	4	6	8	10	12	14	20
H ⁺	HCl	-2.3	10.5	11.8	3.9	-2.4	-5.5	-7.9	
Li ⁺	LiCl	-3.3	10.5	13.7	7.8	3.2	1.1	-1.0	
Na ⁺	NaBPh ₄	-2.2	12.8	16.9	12.0	7.9	5.8	3.3	-0.8
K ⁺	KCl	-2.5	12.2	16.1	10.6	6.2	4.0	1.4	-0.7
Rb ⁺	RbCl	-2.5	12.0	15.7	10.1	5.7	3.3	0.5	4.3
Cs ⁺	CsCl	-2.4	11.8	15.1	9.3	4.7	2.4	-0.3	
NH ₄ ⁺	NH ₄ Cl	-3.3	10.2	12.5	6.0	1.0	-1.4	-3.5	
Me ₄ N ⁺	Me ₄ NCl	-2.9	11.2	14.6	9.0	4.8	2.8	0.2	-2.9
Et ₄ N ⁺	Et ₄ NBr	-1.3	14.6	19.0	13.9	10.0	8.4	7.0	
Pr ₄ N ⁺	Pr ₄ NBr	2.5	22.9	30.9	27.7	24.3	22.6	22.5	
Bu ₄ N ⁺	Bu ₄ NBr	6.3	35.7	48.1	46.4	44.5	43.0	39.8	
Pe ₄ N ⁺	Pe ₄ NBr	14.1	54.3	74.3	71.1	58.5	49.0	51.1	
Mg ²⁺	MgCl ₂	-7.9	19.4	25.6	13.4	3.8	-0.4		
Ca ²⁺	CaCl ₂	-6.6	21.1	27.7	16.2	7.2	3.0	-0.9	
Sr ²⁺	SrCl ₂	-5.2	23.4	30.7	19.6	10.8	6.7	2.6	
Ba ²⁺	BaCl ₂	-5.2	23.6	31.0	19.8	10.9	6.7	2.7	
Ph ₄ As ⁺	Ph ₄ AsBPh ₄	20.7	43.2	45.7	34.9	24.9	19.4	18.1	15.5
Cl ⁻	Ph ₄ AsCl	4.6	-7.2	-8.7	-1.9	2.7	4.3	5.6	7.4
Br ⁻	(H,K,Me ₄ N)Br	5.2	-7.4	-9.6	-3.5	0.5	2.0	3.8	
I ⁻	(H,Na,K)I	5.5	-6.9	-10.2	-5.1	-2.1	-1.6	0.4	0.5
HCO ₂ ⁻	NaO ₂ CH	5.5	-6.7	-8.6	-2.1	2.8	4.3	8.1	8.6
MeCO ₂ ⁻	NaO ₂ CMe	6.2	-4.9	-5.2	2.2	8.4	11.9	15.5	15.4
EtCO ₂ ⁻	NaO ₂ CEt	7.0	-3.5	-3.7	4.7	11.2	15.1	18.8	18.2
PrCO ₂ ⁻	NaO ₂ CPr	8.3	-1.1	-0.6	8.1	14.9	18.8	22.5	21.3
Bz ⁻	(Na,K)Bz	8.0	1.7	2.5	8.0	10.4	11.2	12.9	
BPh ₄ ⁻	Ph ₄ AsBPh ₄	20.7	43.2	45.7	34.9	24.9	19.4	18.1	15.5

**Figure 5.** Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, from water into aqueous-*t*-BuOH mixtures at 25 °C for the alkali metal ions: ● Li⁺, ▲ Na⁺, ◆ K⁺, ■ Rb⁺, ▼ Cs⁺.

the averaged values have been classified as Tentative.

For HBr, on the other hand, there are two independent sets of potentiometrically derived values.^{116,161} Those reported by Robinette and Amis¹¹⁶ cover the whole solvent composition range but at very wide intervals. Those of Bose et al. are better spaced but extend only to $x_{t\text{-BuOH}} = 0.2$. Nevertheless, where comparison is possible, the data are in good agreement and thus the averaged values are Recommended. At higher *t*-BuOH concentrations the values of Robinette and Amis¹¹⁶ become very negative and should be viewed with caution. Little comment is possible on the remaining data in Table 20.

4. Ionic Entropies of Transfer

Despite the dearth of entropy data for electrolytes, the extensive information available at low $x_{t\text{-BuOH}}$ for $\Delta_t H^\circ(M^{n+})$ in Table 19 and for $\Delta_t G^\circ(M^{n+})$ from our previous review¹ enabled the estimation of $\Delta_t S^\circ(\text{ion}, w \rightarrow w + t\text{-BuOH})$ for 13 monovalent and 4 divalent cations and 6 monovalent anions via the GHSE (Table 21).

Plots of $\Delta_t S^\circ(\text{ion}, w \rightarrow w + t\text{-BuOH})$ exhibit a marked similarity to the corresponding enthalpies, including the size, sign, position, and independence from ionic size of the two extrema at low cosolvent concentrations. That is, there is strong enthalpy/entropy compensation in this system.

F. Transfers from Water to Water + Ethylene Glycol (EG)

1. Enthalpy Data for Electrolytes

Enthalpy of transfer data between water and aqueous EG are available for more than 20 electrolytes (Table 22) including several 1:2 salts and La(NO₃)₃. Data for some of the salts are restricted to relatively low cosolvent compositions ($x_{\text{EG}} \leq 0.3$), and very few have been independently confirmed. Potentiometric data for KCl¹⁸⁵ and HCl¹⁸⁶ were unavailable for consideration.

Two data sets exist for $\Delta_t H^\circ(\text{LiCl}, w \rightarrow w + \text{EG})$: one is restricted to $x_{\text{EG}} \leq 0.4$ ¹⁷ but the other¹⁸² covers the whole solvent composition range. These reports are in reasonable agreement where comparison is possible but, as they originate from the same laboratory, their averaged values are classified as Tentative. A similar situation applies to NaCl where values of $\Delta_t H^\circ$ obtained by calorimetry are reported at $x_{\text{EG}} < 0.2$ ¹⁸³ and over the whole composition range from emf measurements.¹⁸²

Table 20. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + t\text{-BuOH})/\text{J K}^{-1} \text{ mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{t\text{-BuOH}}$

MX	2	4	6	8	10	12	14	20	30	50	70	90	100	ref
HCl	(5)	(10)	12	11	7	3	-3	-11	-23					146
HCl	16	21	19	16	14	11	-10							161 ^a
HCl	11	16	16	14	11	7	-7	{-11}	{-23}					
HBr			(5)		3			-34	-70		-190	-310	-265	116
HBr	29	22	9	1	-6	-13	-20	-40						161
HBr	{29}	{22}	7	{1}	-2	{-13}	{-20}	-37	{-70}		{-190}	{-310}	{-265}	
HI	13.6	16.9	12.3	2.3	-10.7	-24.3	-36.1	-36.4						161
NaCl	3.0	8.2	13.0	15.6	15.1	10.9	3.4	-27.0						163
NaI	7.7	11.0	11.0	8.5	4.2	-1.4	-7.8	-28.6	-59.3	-112	-198			165

^a Origin of the data is unclear; they may have been recalculated from earlier results,¹⁴⁶ although the recorded solvent compositions differ.

Table 21. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + t\text{-BuOH})/\text{J K}^{-1} \text{ mol}^{-1}$, 298.15 K, mol/L Scale, TATB Assumption, as a Function of $100x_{t\text{-BuOH}}$

MX	2	4	6	8	10	12	14	20	ref
H⁺	-8	-30	44	22	9				
Li⁺	-13	35	44	27	17				
Na⁺	-11	39	50	37	29			-2	
K⁺	-12	39	50	35	25			-3	
Rb⁺	-11	38	48	33	24			15	
Cs⁺	-11	38	47	31	21				
NH₄⁺	-13	34	41	22	11				
Ag ⁺	44	65	67	55	35	12	-7		127
Me ₄ N ⁺	-14.5		49.9		4.8		5.9		261
Me₄N⁺	-14	34	43	28	19				
Et ₄ N ⁺	-14.5		57.4		14.9		20.6		261
Et₄N⁺	-14	37	48	35	28				
Pr ₄ N ⁺	-0.7		102.1		65.1		80.6		261
Pr₄N⁺	2	68	92	85	80				
Bu ₄ N ⁺	10.0		152.7		111.5		119.7		261
Bu₄N⁺	10	101	136	132	132				
Ph₄As⁺	77	165	182	158	136			110	
Mg²⁺	-38	58	80	51	34				
Ca²⁺	-34	61	85	56	37				
Sr²⁺	-33	63	86	58	42				
Ba²⁺	-33	63	86	58	42				
Cl⁻	14	-31	-37	-21	-14				
Br⁻	37	52	-35	-15					
I⁻	19	-28	-39	-28	-25				
MeCO ₂ ⁻	-42	-56	-50	-31	-8	11	17		127
EtCO ₂ ⁻	-32	-41	-35	-18	3	21	30		127
PrCO ₂ ⁻	-21	-26	-19	-5	14	31	43		127

For NaBPh₄, the datum of Mohanty et al.¹⁷⁰ at $x_{\text{EG}} = 0.035$ is rejected because their value for $\Delta_{\text{sln},w}H^\circ$ differs by ~ 7 kJ mol⁻¹ from the well-established value.^{73,80} The remaining two independently measured data sets are in excellent agreement over the entire solvent composition range, and their average is therefore Recommended. Of the three reported studies of $\Delta_t H^\circ(\text{Bu}_4\text{NBr}, w \rightarrow w + \text{EG})$, two are from the Ivanovo group^{35,187} and cover the whole solvent composition range while the data of Mohanty et al.¹⁷⁰ extend only to $x_{\text{EG}} \leq 0.3$. Up to this cosolvent concentration the agreement is good, enabling the averaged values to be Recommended. Over the range $0.3 < x_{\text{EG}} \leq 0.8$ the data from Markov et al.¹⁸⁷ and Manin et al.³⁵ are also in good agreement, but coming from the same group, the averaged values are regarded as Tentative. At $x_{\text{EG}} > 0.8$, in the absence of further information it is not possible to choose between the increasingly divergent values.^{35,187} None of the remaining salts has been studied independently, so little can be said about them. Additivities for the whole salt combinations (LiNO₃-NaNO₃) and

(LiCl-NaCl) are in good agreement (better than ± 0.4 kJ mol⁻¹) over the limited composition range available for comparison ($x_{\text{EG}} \leq 0.2$), but the differences themselves are very small.

2. Ionic Enthalpies of Transfer

Application of the TPTB assumption using the Recommended values (Table 22) for NaCl ($x_{\text{EG}} \leq 0.4$) and NaBPh₄ and the data of Emelin et al.¹⁸² for NaCl at higher x_{EG} and of Pietrzak et al.¹⁰ for Ph₄PCl enables calculation of values for $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{EG})$ for eight monovalent and four divalent cations and seven monovalent anions (Table 23).

Plots (not shown) of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + \text{EG})$ against x_{EG} are similar to those observed for aqueous-MeOH mixtures (Figure 3). Thus, there is a very small maximum at low cosolvent concentrations ($x_{\text{EG}} \approx 0.15$, cf. $x_{\text{MeOH}} \approx 0.3$), followed by a steady decrease, with only slight differences among the cations. Also, as observed for $w + \text{MeOH}$ solutions, increasing the cation charge, at approximately constant ionic size, appears to have a significant impact on the enthalpies of transfer, although the data are rather limited. The corresponding plots (not shown) for the rather sparse halide data are roughly similar but of opposite sign. That is, there is at least partial cation/anion compensation for the enthalpies in EG/water mixtures.

3. Entropy Data for Electrolytes

In contrast to the extensive data available for the enthalpies, there are very few reports of the corresponding entropies of transfer of electrolytes from water to aqueous-EG mixtures. All the available values (Table 24) were obtained by potentiometry.^{181,182} None has been replicated, so they should be regarded with caution.

4. Ionic Entropies of Transfer

It is ironic that the extensive calorimetric database for enthalpies of transfer in $w + \text{EG}$ mixtures is not matched by equivalent data for the Gibbs energies.¹ Thus, only a limited set of values of $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{EG})$ can be derived for this system via the GHSE (Table 25).

The only comparison that can be made is for Cl⁻, for which the agreement between the two available

Table 22. $\Delta_t H^{\circ}(\text{MX}, w \rightarrow w + \text{EG})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{EG}}$

MX	$\Delta_{\text{sin}} H^{\circ}$	5	10	20	30	40	50	60	70	80	90	100	ref
HCl		0.48	0.58	-0.32	(-2.02)	-3.89	(-5.35)	(-5.98)	-5.48	(-3.64)	(-0.39)	4.20	181
LiCl	-37.10	1.01	1.50	1.36	0.16	-1.57							17
LiCl		0.37	0.47	0.24	(-0.20)	-0.60	(-0.91)	-1.16	(-1.44)	-1.79	(-2.18)	-2.36	182
LiCl		{ 0.7 }	{ 1.0 }	{ 0.8 }	{ 0.0 }	{ -1.2 }							
LiNO ₃	-2.66	0.05	-0.29	-1.75	-3.68	-5.62	-7.26	-8.42	-9.10	-9.42	-9.67	-10.29	35
NaCl	3.85	-0.22	-0.46	-0.96									183
NaCl		-0.03	-0.15	-0.57	(-1.14)	-1.76	(-2.35)	-2.85	(-3.22)	-3.46	(-3.59)	-3.64	182
NaCl		{ -0.1 }	{ -0.3 }	{ -0.8 }	{ -1.1 }	{ -1.8 }							
NaI	-7.55	-0.10	-1.21	-4.43	-7.48	-11.06	-12.96	(-15.66)	-18.07	-19.47			184 ^a
NaNO ₃	20.29	-0.21	-1.01	-3.73									363
NaClO ₄	13.96	2.51	2.25	-1.91	-6.10	-10.11							18
NaClO ₄		2.5	2.3	-1.7	-5.9	-9.6							184 ^a
NaClO₄		2.5	2.3	-1.8	-6.0	-9.9							
NaBPh ₄	[-26.69]		<i>b</i>										170
NaBPh ₄	-19.75	11.63	17.41	18.19	12.39	5.41	-0.76	-6.22	-11.96	-18.61	-25.13	-27.63	35
NaBPh ₄	-19.91	10.47	16.97	17.65	12.71	5.02	-0.96	-7.62	-12.14	-17.60	-22.11	-27.67	10
NaBPh₄		11.1	17.2	17.9	12.5	5.2	-0.9	-6.9	-12.1	-18.1	-23.6	-27.6	
KCl	17.24	-0.56	-1.08	-2.56	-4.86								183
KCl		-0.14	-0.33	-0.80	(-1.36)	-1.97	(-2.58)	-3.14	(-3.61)	-3.94	(-4.09)	-4.00	182
KCl		-0.4	-0.7	-1.7	-3.1								
KBr	20.21	-0.47	-1.61	-4.79	-7.12								183
KI	20.54	-0.97	-2.44	-6.23	-10.26	-13.49							183
KNO ₃	34.92	-0.54	-1.54	-5.28									363
CsF	-36.33	-0.14	-0.39	-1.04	-1.67	-2.08	-2.15	-1.88	-1.32	-0.64	-0.09	0.00	35
CsNO ₃	39.61	-1.21	-3.15										363
CsClO ₄	55.22		-0.58 ^c										19
NH ₄ NO ₃	25.49	-0.67	-1.63	-3.96	-6.57	-9.18	-11.59	-13.67	-15.37	-16.70	-17.79	-18.80	35
Bu ₄ NBr	-8.58	10.21	18.04	28.24	33.61								170
Bu ₄ NBr	-8.42	10.46	18.37	28.01	32.66	35.17	37.14	38.93	39.68	37.29	28.43	8.53	35
Bu₄NBr		10.3	18.2	28.1	33.1	{ 35.2 }	{ 37.1 }	{ 38.9 }	{ 39.7 }	{ 37.3 }	{ 28.4 }	{ 8.5 }	
Ph ₄ PCl	-8.79	12.45	17.76	18.82	16.90	15.34	14.31	13.68		13.32	12.13	11.67	10
Ca(NO ₃) ₂	-17.08	-2.52	-6.27										363
Sr(NO ₃) ₂	-18.02	-2.82											363
Co(ClO ₄) ₂	7.00	0.16	-1.81	-9.29	-18.30	-26.71	-33.78	-39.56	-44.33	-48.18	-50.61	-50.29	100
NiCl ₂	-83.43	-1.05	-2.01	-3.93	-5.73	-7.26	-8.38						101
La(NO ₃) ₃	-52.29	-2.72	-6.11	-12.42									363

^a Read from graph. ^b A single value, 15.10 kJ/mol, at $100x_{\text{EG}} = 3.5$. ^c Data also available at lower concentrations.

Table 23. $\Delta_t H^{\circ}(\text{ion}, w \rightarrow w + \text{EG})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{EG}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
H ⁺	HCl	-0.2	0.4	-0.3	-3.6	-8.0	-11.8	-14.9	-16.7	-17.7	-16.5	-22.0
Li ⁺	LiCl	0.0	0.8	0.8	-1.6	-5.3						
Na ⁺	NaBPh ₄	-0.7	-0.4	-0.9	-2.8	-6.0	-8.8	-11.7	-14.4	-17.3	-19.6	-21.5
K ⁺	KI	-1.6	-1.6	-2.7	-5.6	-8.1						
Cs ⁺	CsNO ₃	-2.3	-3.3									
NH ₄ ⁺	NH ₄ NO ₃	-1.8	-1.7	-1.4								
Bu ₄ N ⁺	Bu ₄ NBr	9.2	18.3	30.2	34.7							
Ph ₄ P ⁺	Ph ₄ PBPh ₄	11.8	17.6	18.8	15.3	11.2	7.9	4.8	2.3	-0.8	-4.0	-6.1
Ca ²⁺	Ca(NO ₃) ₂	-4.7	-6.5									
Sr ²⁺	Sr(NO ₃) ₂	-5.0										
Co ²⁺	Co(ClO ₄) ₂	-6.2	-7.2	-7.5	-11.9	-18.9						
Ni ²⁺	NiCl ₂	-2.5	-2.4	-3.9	-8.9	-15.5						
La ³⁺	La(NO ₃) ₃	-6.0	-6.4	-4.6								
F ⁻	CsF	2.2	2.9									
Cl ⁻	Ph ₄ PCl	0.7	0.2	0.0	1.6	4.1	6.4	8.9	11.2	14.1	16.1	17.8
Br ⁻	KBr	1.1	-0.1	-2.1	-1.6							
I ⁻	NaI	0.6	-0.8	-3.5	-4.7	-5.1	-4.2	-4.0	-3.7	-2.2		
NO ₃ ⁻	KNO ₃	1.1	0.1	-2.6								
ClO ₄ ⁻	NaClO ₄	3.2	2.7	-0.9	-3.2	-3.9						
BPh ₄ ⁻	Ph ₄ PBPh ₄	11.8	17.6	18.8	15.3	11.2	7.9	4.8	2.3	-0.8	-4.0	-6.1

data sets is poor, with differences of up to 80 J K⁻¹ mol⁻¹ (~24 kJ/mol for 298 $\Delta_t S^{\circ}$). Taking the values for Na⁺ and Cl⁻ at face value, there appears to be considerable cation/anion compensation for the ionic entropies in this system in addition to the extensive enthalpy/entropy compensation (see later, Figures 12 and 13).

G. Transfers from Water to Water + Glycerol (GY)

1. Enthalpy Data for Electrolytes

Enthalpy of transfer data from water to aqueous-GY mixtures have been reported for one 1:3, two 1:2, and 15 1:1 electrolytes (Table 26). As most of the data

Table 24. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{EG})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{EG}}$

MX	5	10	20	30	40	50	60	70	80	90	100	ref
HCl	0.0	-0.2	-1.4	(-2.6)	-4.7	(-6.8)	(-8.8)	-10.2	(-10.7)	(-10.0)	-7.9	181
LiCl	0	2	10	(21)	31	(42)	53	(63)	70	(75)	76	182
NaCl	4	9	20	(32)	43	(54)	64	(72)	77	(80)	80	182
KCl	5	11	23	(36)	48	(60)	70	(78)	85	(89)	89	182

Table 25. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{EG})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, TATB/TPTB Assumption, mol/L Scale, as a Function of $100x_{\text{EG}}$

ion	5	10	20	30	40	50	60	70	80	90	100
H ⁺	0	3	1	-9	-22	-36	-48	-56	-64	-77	-87
Li ⁺	0	2	-1	-12	-26						
Na ⁺	-1	-2	-4	-12	-24	-34	-44	-53	-63	-70	-75
K ⁺	-3	-6	-14	-24	-33						
Ph ₄ (P,As) ⁺	40	75	90	88	83	79	75	71	64	56	50
Cl ⁻ (from HCl)	0	-3	-2	8	19	30	40	47	54	57	80
Cl ⁻ (from NaCl)	5	11	24	35	68	89	122	127	130	129	128
BPh ₄ ⁻	40	75	90	88	83	79	75	71	64	56	50

Table 26. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{GY})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{GY}}$

MX	$\Delta_{\text{sln}} H^\circ$	5	10	15	20	30	40	50	60	70	80	90	100	ref
HCl		0.81	1.15	0.91										191
HCl		0.62												192
HBr		1.04	0.96	0.09	-1.13	-2.85								191
HI		0.88	0.05	-1.95	-4.38	-7.43								191
NaCl		-1.10	-2.26	-3.20	-3.98	-5.17	-6.03	-6.71	-7.28	-7.69	-7.83	-7.51	-6.45	193
NaCl	3.85	-0.49	-1.19											183
NaI	(6.99)	(-0.9)	(-1.8)	(-2.8)	(-3.9)	(-5.9)	(-8.1)	(-10.9)	(-12.9)	(-13.7)	(-14.6)	(-15.6)	(-16.8)	196 ^a
NaNO ₃	20.29	-1.37	-2.56	-3.72	-4.90									189
KCl	17.24	-1.27	-2.38											183
KCl		-2.15	-3.09	-4.78	-6.04	-7.78	-7.85	-8.01	-8.00	-8.09	-8.09	-10.17	-12.33	141
KBr	20.21	-1.47	-2.84	-4.28	-5.81									183
KI	20.54	-1.43	-3.13	-5.01	-7.07									183
KNO ₃	34.92	-1.89	-3.64											189
KNO ₃	35.31	-1.71	-3.15	-4.33										190 ^b
KPi		-3.76	-4.52	-5.91										194
KBPh ₄		-3.14	-5.24	-6.55										194
RbNO ₃	36.25	-2.41	-4.58											189
CsNO ₃	39.61	-1.73	-4.20											189
Bu ₄ NBr	2.60	6.28	14.49	18.22	21.74	28.74	28.40	27.77	27.15	26.73	26.31	25.98	25.68	195
Ph ₄ AsPi		1.08	2.49	4.13										194
Ca(NO ₃) ₂	-17.08	-4.78												189
Ca(NO ₃) ₂	-17.22	-4.76	-9.27	-13.64										190 ^b
Sr(NO ₃) ₂	18.02	-4.62												189
La(NO ₃) ₃	-59.27	-4.54	-8.42	-11.77										189

^a Extrapolated to 298.15 K by the reviewers from data reported at $313.15 \leq T/\text{K} \leq 353.15$ assuming constant $\Delta_{\text{sln}} C_p$. ^b Data from ref 190 extrapolated to infinite dilution by the reviewers.

were measured at low GY concentrations, an additional composition, 15 mol % GY, has been included in the table.

Although there are duplicate data sets for a number of salts that are in good agreement over limited ranges of solvent concentration, almost all have emanated from the Ivanovo group and thus cannot be considered as independent. The relationship between some of the data reported by Krestov and co-workers^{189,190} is also unclear, and thus, pending independent confirmation, no data have been recommended. Additivity checks are relatively unhelpful since the $\Delta_t H^\circ(\text{MX})$ values are small over the composition range where additivity can be tested. Potentiometric data reported by Dash and co-workers for a number of exotic acids and silver salts^{106,197,198,199} contained too little data to warrant inclusion.

2. Ionic Enthalpies of Transfer

Combination of the appropriate data from Table 26 enables the calculation of $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{GY})$

Table 27. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{GY})/\text{kJ mol}^{-1}$, 298.15 K, TATB Assumption, as a Function of $100x_{\text{GY}}$

ion	MX data	5	10	15
H ⁺	H(Cl,Br,I)	-0.5	-0.8	-1.3
Na ⁺	Na(Cl,NO ₃)	-3.3	-5.2	-7.2
K ⁺	KBPh ₄	-4.0	-6.1	-8.3
Rb ⁺	RbNO ₃	-4.6	-7.3	
Cs ⁺	CsNO ₃	-3.9	-6.9	
Bu ₄ N ⁺	Bu ₄ NBr	3.8	11.2	14.2
Ph ₄ As ⁺	Ph ₄ AsBPh ₄	0.8	0.9	1.7
Ca ²⁺	Ca(NO ₃) ₂	-9.2	-14.7	-21.6
Sr ²⁺	Sr(NO ₃) ₂	-9.0		
La ³⁺	La(NO ₃) ₃	-11.1	-16.6	-23.7
Cl ⁻	KCl	2.3	3.4	3.5
Br ⁻	KBr	2.5	3.3	4.0
I ⁻	KI	2.6	3.0	3.3
NO ₃ ⁻	KNO ₃	2.2	2.7	4.0
Pi ⁻	KPi	0.2	1.6	2.4
BPh ₄ ⁻	Ph ₄ AsBPh ₄	0.8	0.9	1.7

values for 16 ions via the TATB assumption for solutions containing up to 15 mol % GY (Table 27).

Table 28. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{GY})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{GY}}$

MX	5	10	15	20	30	40	50	60	70	80	90	100	ref
HCl	-10.1	-15.8	-24.8	-31.4	-39.6	-45.8	-48.8	-50.5	-53.0	-55.8		-73.7	192
HCl	-2.3												191
HBr	-8.7	-16.9	-23.7	-29.3	-38.0	-44.3	-49.1	-53.0	-56.1	-58.1	-58.5	-56.1	191
HI	-7.0	-12.5	-18.2										191
NaCl	-12.8	-18.8	-21.1										193
KCl	12.4	23.0	32.4										141
KBPh ₄	-0.1	-1.4	-4.6										194
KPi	0.6	0.0	-4.8	-13.4	-23.4								194
Ph ₄ AsPi	1.3	0.1	-7.9	-21.6	-34.3								194

Table 29. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{GY})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TATB Assumption, as a Function of $100x_{\text{GY}}$

ion	5	10	15	ion	5	10	15
H ⁺	-6	-13	-16	Br ⁻	7	13	11
Na ⁺	-15	-28	-35	I ⁻	7	13	8
K ⁺	-16	-27	-36	Pi ⁻	3	8	15
Ph ₄ As ⁺	9	15	18	BPh ₄ ⁻	9	15	18
Cl ⁻	6	11	11				

Unfortunately there is no way of assessing these values.

Interestingly, $\Delta_t H^\circ(\text{ion})$ vary monotonically with solvent composition, those of the anions and of the large hydrophobic ions (Bu₄N⁺ and Ph₄As⁺ and BPh₄⁻) being endothermic while those of the small cations are exothermic.

3. Entropy Data for Electrolytes

Entropy of transfer data between water and aqueous-GY mixtures have been reported for eight electrolytes (Table 28). Only for HCl at 5 mol % GY is there any independent determination but the agreement is poor. No assessment of the data is possible at present.

4. Ionic Entropies of Transfer

Ionic entropies of transfer from water to aqueous solutions containing up to 15 mol % GY can be calculated via the TATB assumption using the data of Talukdar et al.¹⁹⁴ Values so obtained are reported for eight ions in Table 29. These values cannot be assessed in the absence of reliable independent data. Again, it can be noted that, as with $\Delta_t H^\circ(\text{ion})$, the ionic $\Delta_t S^\circ$ vary monotonically, with the anion and

large organic ion values being positive and those for the simple cations being negative.

H. Transfers from Water to Water + Tetrahydrofuran (THF)

1. Enthalpy Data for Electrolytes

Transfer enthalpies between water and aqueous-THF mixtures have been reported for nine 1:1 electrolytes (Table 30); no data for higher valent salts are available. Strictly speaking, comparisons between independent data sets can be made only for two electrolytes. For HCl there is moderate agreement at $x_{\text{THF}} \leq 0.2$ between two potentiometrically derived data sets,^{77,146} but at higher cosolvent compositions only the data of Roy et al.¹⁴⁶ are available. For NaCl there is reasonable agreement among four sets of data, but most of these are from the Łódź group, albeit using both calorimetry^{201,202} and potentiometry.²⁰³ The additivity (MCl-MI) shows generally poor agreement, so even these data must be treated with caution. Multiple data sets apparently exist also for NaI and NaClO₄, but as they have all been determined by the same group they must be considered Tentative.

2. Ionic Enthalpies of Transfer

There are sufficient data to allow application of the TPTB assumption, but no checks for consistency are possible. Values for four cations and five anions (including BPh₄⁻ = Ph₄P⁺) are reported in Table 31 but only up to 30 mol % THF.

Table 30. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{THF})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{THF}}$

MX	$\Delta_{\text{sln}} H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
HCl		2.62	0.15			-20.47	-26.25		-36.18				146
HCl		0.50	-1.86	-8.31									21
HCl		1.6	-0.9	{-8.3}		{-20}	{-26}		{-36}				
HBr		-1.67	-6.69	-15.21									21
HI		-3.01	-11.41	-26.61									21
NaCl	3.88	2.06											200
NaCl	3.79	2.11	3.41										201
NaCl	3.90			5.78	6.20								202, 218
NaCl		2.24	4.03	6.48	6.60								203
NaCl		2.1	3.7	6.1	6.4								
NaI	-7.54	-0.13	3.64										201
NaI	-7.55			-10.91	-14.29								202, 218
NaI		{-0.1}	{3.6}	{-10.9}	{-14.3}								
NaClO ₄	14.57	2.81	-5.88	-18.34	(-24.1)	-30.18	(-33.1)	-38.34	-42.12	-47.09	-50.33	-42.96	201, 202, 204, 218
NaClO₄		{2.8}	{-5.9}	{-18.3}	{-24.1}	{-30.2}	{-33.1}	{-38.3}	{-42.1}	{-47.1}	{-50.3}	{-43.0}	
NaBPh ₄	-19.91	56.57	19.37	-18.97	-41.33	(-19.9)							202
KCl	17.20	1.66	2.90	5.04	5.30	(17.2)							202
Ph ₄ PCl	-8.79	27.23	23.11	18.12	15.48	(-8.8)							202

Table 34. $\Delta_t H^{\circ}(\text{MX}, \text{w} \rightarrow \text{w} + \text{DX})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{DX}}^a$

MX	$\Delta_{\text{sln}} H^{\circ}$	5	10	15	20	30	40	50	60	70	80	90	100	ref
HCl		-1.80	-5.41	-9.34	-12.66	-13.53	-20.53	-36.96						3
HCl		-1.61												3, 54 ^b
HCl		-0.73	-5.54	-12.61	-19.93	(-27.4)								205
HCl		-1.55	-4.59	-9.11										3, 21, 173
HCl		-0.7	-5.5	-11.3	-17.9	-26.3	-26.3	-21.5	-23.1	-50.2				206
HCl		-1.3	-5.3	-10.6	{-16.8}	{-22}	{-23}							
HBr		-3.39												54 ^c
HBr		-0.64	-1.75	-2.75	-3.01									207
HBr		-4.34	-8.67	-13.02										21, 208
HI		-5.10												54 ^c
HI		-7.80	-14.01	-18.62										21
HClO ₄	-88.70	-5.74	-15.24	-15.64	-36.43									209
LiCl		-2.45												54 ^b
LiCl		(-1.3)	(-3.4)	(-5.8)	(-7.3)	(-10.1)								210, 229
LiCl		-1.63	-3.56	-5.64	-7.56	-9.72								211
LiCl		-1.5	-3.5	-5.7	-7.4	-9.9								
NaCl		-1.38												54 ^b
NaCl		(-1.4)	(-2.5)	(-3.3)	(-4.1)	(-5.3)								210, 229
NaCl		-1.41	-2.48	-3.32	-4.04	-5.54								211
NaCl		-1.8	-3.1	-4.2	-5.4	-9.0	-14.9	-22.9	(-31.3)					212
NaCl					-4.2									213
NaCl		-1.5	-2.7	-3.6	-4.4	{-6.6}	{-15}	{-23}	{-31}					
NaBr		-3.12												54 ^b
NaBr		(-3.1)	(-4.0)	(-5.0)	(-7.0)	(-11)								229
NaBr	-0.59	-2.88	-4.76	-6.14	-8.77									209
NaBr		-3.0	-4.4	-5.6	-7.7									
NaI		(-6.0)	(-10.2)	(-13.8)	(-16.4)	(-19.2)								229, 369 ^c
NaI		-4.87												54 ^b
NaI		-5.4	{-10}	{-14}	{-16}	{-19}								
NaClO ₃	22.09	0.80	-0.38	-2.85	-5.93	-11.13								214
NaClO ₄	14.06	-3.83	-9.89	-16.33	-22.97									209
NaClO ₄					-24.4									213
NaClO₄		{-3.8}	{-9.9}	{-16.3}	{-23.7}									
NaBPh ₄		(9.4)	(-1.2)	(-10.7)										211, 226
NaBPh ₄		[18.54]												170
NaBPh ₄		(10.9)	(0.0)	(-12.5)	(-23.0)									229
NaBPh ₄	-20.13	9.77	0.90	-13.44	-16.43									209
NaBPh ₄					-19.4									213
NaBPh₄		10.0	-0.1	-12.2	-19.6									
KCl		-1.23												54 ^b
KCl	17.22	-1.68	-3.26	-4.60	-5.73	-7.62								215
KCl		-2.2	-4.3	-5.7	(-5.8)									212
KCl		-1.7	-3.8	-5.2	-5.8	{-7.6}								
KBr		-3.05												54 ^b
KBr	20.04	-3.28	-6.13	-8.44	-10.32	-13.33								215
KBr		(-3.0)	(-7.0)	(-10.5)	(-12.6)	(-16.8)								229
KBr		-3.1	-6.6	-9.5	-11.5	{-15}								
KI		-4.75												54 ^b
KI	20.52	-5.06	-9.51	-13.16	-16.16	-20.87								215
KI		-4.9	{-9.5}	{-13.2}	{-16.2}	{-20.9}								
RbCl		-1.40												54 ^b
CsCl		-2.45												54 ^b
CsNO ₃	40.11	-12.50	-20.21	-25.09	-28.83									216
AgI	111.71	-7.61												176
AgClO ₄					-26.5									213
NH ₄ Br	16.82	-2.66	-5.14	-7.47	-9.62	-13.27	-15.87	(-17.2)						216
NH ₄ NO ₃	25.57	-1.17	-5.19	-11.62	-19.57	(-36.4)								216
Me ₄ NBr		0.90	1.31	1.01	0.00	-4.16								210, 229
Me ₄ NBr	24.04	0.50	1.12	1.35	0.71	-5.23								211
Me₄NBr		0.7	1.2	1.2	1.4	-4.7								
Et ₄ NCl					11.0									213
Et ₄ NBr		1.39	2.33	3.06	3.58	4.02								210, 229
Et ₄ NBr	5.98	1.87	2.56	2.66	2.75	5.30								211
Et ₄ NBr	5.73	1.19	3.05	3.57	2.39	-2.02	-3.08	-4.47						216
Et₄NBr		1.5	2.6	3.1	2.9	{2.4}	{-3.1}	{-4.5}						
Et ₄ NClO ₄					-9.0									213

Ohtaki²¹³ at $x_{\text{DX}} = 0.2$ but not with that of Mohanty et al.¹⁷⁰ at $x_{\text{DX}} = 0.05$. The latter appears to be too positive and has been rejected. The remaining data are classified as Tentative pending further studies. For Ph₄PBr, only one report is available but the values appear reasonable through comparisons with other solvents.

2. Ionic Enthalpies of Transfer

Ionic enthalpies of transfer that can be derived from the data in Table 34 via the TPTB assumption at $x_{\text{DX}} \leq 0.2$ are given in Table 35 for 1 divalent and 15 monovalent cations and 7 monovalent anions. The values of $\Delta_t H^{\circ}(\text{M}^+, \text{w} \rightarrow \text{w} + \text{DX})$ for the alkali metal

Table 34. (Continued)

MX	$\Delta_{\text{sln}}H^\circ$	5	10	15	20	30	40	50	60	70	80	90	100	ref
Pr ₄ NBr		7.40	12.65	16.22	18.10	16.83								210, 229
Pr ₄ NBr	-4.41	8.36	13.06	15.75	18.08	28.28								211
Pr₄NBr		7.9	12.9	16.0	18.1									
Bu ₄ NBr		12.95	22.56	28.98	32.23	29.17								210, 229
Bu ₄ NBr	-8.58	13.40	22.94	29.02	32.03	30.33								211
Bu ₄ NBr			24.4		30.0	29.4	28.2	27.4	25.9	22.8	19.8	23.5	47.6	94
Bu ₄ NBr	-8.58	16.2	25.3	29.3	30.2	31.0								170
Bu₄NBr		14.2	23.8	29.1	31.1	30.0	{ 28.2 }	{ 27.4 }	{ 25.9 }	{ 22.8 }	{ 19.8 }	{ 23.5 }	{ 47.6 }	
Bu ₄ NNO ₃		16.7	25.9	28.9	29.7	29.7	28.5	26.8	25.1	23.4	22.2	21.3	27.2	
Bu ₄ NBPh ₄	24.10	29.16	31.92	27.91										176
Pe ₄ NBr	3.33	(25.2)	(32.5)	(36.5)	(40)									370, 371 ^c
Hx ₄ NBr	15.84	29.94	51.85	41.85	23.94	19.17	(16.3)	13.49						216
Bu ₄ PBr	-13.22	(17.4)	(27.5)	(32.0)	(33.0)	(33.4)								229
Ph ₄ PBr		(13.2)	(11.5)	(9.2)	(7.3)	(4.5)								229
Ph ₄ PBr	7.95	13.40	11.23	9.77	3.91									209
Ph₄PBr		13.3	11.4	9.5	{ 5.6 }	{ 5 }								
Ph ₄ AsCl					15.9									213
NiCl ₂					-10.1									213
Ni(ClO ₄) ₂	-164.14	-8.49	-21.17	-36.47	-45.51									209
CuCl ₂					-4.7									213

^a Data also available²¹⁷ for the single concentration of $x_{\text{DX}} = 0.0222$ for LiCl, NaCl, KCl, RbCl, CsCl, LiBr, NaBr, KBr, RbBr, CsBr, LiI, NaI, KI, RbI, and CsI, ranging from $\Delta_{\text{t}}H^\circ/\text{kJ mol}^{-1} = -0.55$ for LiCl to -2.77 for CsI along this series of MX. ^b At $x_{\text{DX}} = 0.0486$ (20 mass % DX). ^c Cited in ref 229.

Table 35. $\Delta_{\text{t}}H^\circ(\text{ion}, w \rightarrow w + \text{DX})/\text{kJ mol}^{-1}$, 298.15K, TPTB Assumption, as a Function of $100x_{\text{DX}}$

ion	MX data	5	10	15	20
H ⁺	HCl	-3.0	-10.6	-20.7	-28.9
Li ⁺	LiCl	-3.2	-8.8	-15.8	-19.5
Na ⁺	NaBPh ₄	-3.2	-8.0	-13.7	-16.5
K ⁺	KCl	-3.4	-9.1	-15.3	-17.9
Rb ⁺	RbCl	-3.1			
Cs ⁺	CsNO ₃	-14.1	-23.7	-29.0	-27.6
Ag ⁺	AgI	-6.1			
NH ₄ ⁺	NH ₄ Br	-2.8	-8.7	-15.5	-18.4
Me ₄ N ⁺	Me ₄ NBr	0.6	-2.4	-6.9	-7.4
Et ₄ N ⁺	Et ₄ NBr	1.4	-1.0	-5.0	-5.9
Pr ₄ N ⁺	Pr ₄ NBr	7.8	9.4	8.0	9.4
Bu ₄ N ⁺	Bu ₄ NBr	14.1	20.3	21.1	22.4
Hx ₄ N ⁺	Hx ₄ NBr	15.7	26.4	43.8	33.1
Ph ₄ P ⁺	Ph ₄ PBPh ₄	13.15	7.85	1.45	-3.15
Ph ₄ As ⁺	Ph ₄ AsCl				3.9
Ni ²⁺	Ni(ClO ₄) ₂	-7.2	-17.3	-31.2	-31.0
Cu ²⁺	CuCl ₂				-28.8
Cl ⁻	NaCl	1.7	5.3	10.1	12.1
Br ⁻	NaBr	0.2	3.6	8.1	8.8
I ⁻	KI	-1.6	-0.4	2.1	1.7
NO ₃ ⁻	NH ₄ NO ₃	1.6	3.5	3.9	-1.2
ClO ₃ ⁻	NaClO ₃	4.0	7.6	10.8	10.5
ClO ₄ ⁻	NaClO ₄	-0.6	-2.0	-2.7	-7.3
BPh ₄ ⁻	Ph ₄ PBPh ₄	13.15	7.85	1.45	-3.15

ions (not plotted) are unremarkable, becoming steadily more negative although with some evidence of a broad minimum at $x_{\text{DX}} \approx 0.2$. The corresponding values for the halides (not plotted) on the other hand exhibit a shallow minimum (at least for Br⁻ and I⁻; the Cl⁻ curve is merely concave downward) at $x_{\text{DX}} \leq 0.05$ followed by a maximum at $x_{\text{DX}} \approx 0.17$. The magnitudes of these extrema vary strongly with the anion size, their positions rather less so.

Interestingly, $\Delta_{\text{t}}H^\circ$ values for the R₄N⁺ ions in aqueous-dioxane mixtures show similar but opposite features to the halides, especially for Me₄N⁺ and Et₄N⁺ (Table 35; not plotted). As for all aqueous-organic mixtures, the $\Delta_{\text{t}}H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + \text{DX})$ vs x_{DX} curves become systematically more positive while largely retaining a similar (complex) shape.

3. Entropy Data for Electrolytes

Values of $\Delta_{\text{t}}S^\circ(\text{MX}, w \rightarrow w + \text{DX})$ are available for three of the hydrohalic acids (Table 36). For HCl, the various potentiometric studies^{3,21,54,205,206} are in good agreement at $x_{\text{DX}} \leq 0.5$ and their averaged values are Recommended. At higher cosolvent concentrations only the data of Elsemomy et al.²⁰⁶ are available. A similar situation exists for HBr, although rather fewer data are available. The reservations expressed above with respect to the $\Delta_{\text{t}}H^\circ(\text{MX})$ values should also be noted. For HI, the values of Feakins et al.⁵⁴ and of Datta and Kundu²¹ are in reasonable agreement at $x_{\text{DX}} \approx 0.05$ (strictly, 0.0486), the only composition where comparison is possible.

4. Ionic Entropies of Transfer

Ionic entropies of transfer from water to aqueous-dioxane mixtures are summarized in Table 37 for $x_{\text{DX}} \leq 0.2$. All values were calculated via the GHSE using the $\Delta_{\text{t}}H^\circ(\text{ion})$ estimates in Table 35 and those of $\Delta_{\text{t}}G^\circ(\text{ion})$ from Kalidas et al.¹ The values of $\Delta_{\text{t}}S^\circ(\text{ion}, w \rightarrow w + \text{DX})$ are largely featureless. For all cations they are negative (unfavorable) and decrease regularly with increasing x_{DX} . There is relatively little variation with cation size, and the order is unsystematic with crossovers occurring. The $\Delta_{\text{t}}S^\circ(\text{ion})$ values for the halide ions are mostly negative: there is no cation/anion compensation in the entropies for these mixtures. Other estimates of ionic entropies have been reported,²³⁹ but because of uncertainty about the definitions of the terms used, they have not been included in Table 37.

J. Transfers from Water to Water + Acetone (AC)

1. Enthalpy Data for Electrolytes

There is relatively little information available for transfers of electrolytes from water into aqueous-AC mixtures (Table 38). The only salt for which duplicate data are available is NaCl, for which the

Table 36. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{DX})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{DX}}$

MX	5	10	15	20	30	40	50	60	70	ref
HCl	-14.7	-31.0	-47.8	-64.9	-100.2	-136.6	-173.5			3
HCl	-11.4									54 ^a
HCl	-8.6	-31.4	-62.3	-94.2	(-132.9)					205
HCl	-8.7	-23.0	-42.9							21
HCl	-12.0	-30.6	-51.8	-73.3	-111.6	-139.9	-162.1	-191.3	-250.1	206
HCl	-11	-29	-51	-77	-115	-138	-168	{-191}	{-250}	
HBr	-14.7									54 ^a
HBr	-4.7	-13.7	-25.0	-26.4						207
HBr	-15.2	-31.4	-48.6							21
HBr	{-12}	{-23}	{-37}							
HI	-16.6									54 ^a
HI	-22.6	-41.6	-57.5							21
HI	{-20}	{-42}	{-58}							
NaClO ₃	0.7	0.5	-0.5	-2.3	-8.3					214

^a At $x_{\text{DX}} = 0.0486$ (20 mass% DX).

Table 37. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{DX})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TPTB Assumption, as a Function of $100x_{\text{DX}}$

ion	5	10	15	20
H ⁺	-0.3	-21.1	-57.0	-82.6
Li ⁺	-2.0	-20.1	-46.0	
Na ⁺	-7.4	-22.8	-43.3	-48.3
K ⁺	-6.4	-23.2	-50.0	
Cs ⁺	-41.3	-71.8	-95.6	
Ag ⁺	-27.2			
Me ₄ N ⁺	10.1	2.3	-19.5	
Pr ₄ N ⁺	40.9	55.4	49.7	50.7
Ph ₄ P ⁺	82.4	93.1	91.1	85.7
Cl ⁻	-10.7	-7.9	6.0	5.6
Br ⁻	-10.0	-2.9	9.0	
I ⁻	-12.6	-19.2	-14.7	
BPh ₄ ⁻	82.4	93.1	91.1	85.7

values of Piekarski²² and Lu et al.^{221,222} are in good agreement over the limited range of solvent compositions at which they have been reported. As there are no other duplicate values or data for salts that would enable additivity checks to be made, the data must be presented without assessment. The emf measurements reported by Dash et al.²⁴⁰ for mercury(I) sulfate at low cosolvent compositions contained too little information to justify their inclusion. Graphical data for NaI, obtained by potentiometry²⁴¹ over the entire solvent composition range at $283.15 \leq T/\text{K} \leq$

313.15, and for CsI, CsClO₄, and Ni(ClO₄)₂ at 298.15 K and $x_{\text{AC}} \leq 0.5$, obtained by calorimetry,²⁴² are available. Data are also available for a few complex salts,²²⁵ as is the enthalpy of dissociation of water.¹⁸⁰

There are insufficient data for the electrolytes necessary for their division into single-ion values via the TA(P)TB assumption. However, values for ΔH° (Cu²⁺) can be read from a graph of $\Delta_{\text{dil}}H$ data for Cu(ClO₄)₂.¹²⁹ These results were apparently based on the TPTB assumption, but the original data²⁴³ were unavailable to the reviewers.

2. Entropy Data for Electrolytes

There are too few entropy of transfer data for simple electrolytes from water to aqueous-AC mixtures to justify compilation of a table. All the available data, for four (mostly) complex salts, are to be found in the paper of Bury and Treiner.²²⁵

K. Transfers from Water to Water + Acetonitrile (AN)

1. Enthalpy Data for Electrolytes

A considerable amount of data exists for the enthalpies of transfer of electrolytes from water to aqueous-acetonitrile (AN, MeCN) mixtures. However, while there are data for almost 50 1:1 electro-

Table 38. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{AC})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{AC}}$

MX	$\Delta_{\text{sln}}H^\circ$	5	10	20	30	40	50	60	70	100	ref
HClO ₄	-88.90	-2.35	-24.15	-36.03	-44.02	-46.99					220
NaCl	3.90	0.04	0.09								22
NaCl		0.27	0.55								221, 222
NaCl		0.2	0.3								
KCl		-0.64	-1.06								221, 222
KI		-2.01	-6.04								221, 222
CsNO ₃	40.11	-11.43	-15.35	-22.41	-27.05	-27.37	-28.80				216
AgCl		-1.18	-7.19								223
AgBr		-2.02	-5.20								223
AgI		0.53	-0.48								223
NH ₄ Br	16.82	-3.42	-5.58	-9.44	-11.00	-14.59	-18.65	-21.99	-22.19		216
NH ₄ I	13.70	-1.96	-6.07	-12.89	-18.85						92, 255
NH ₄ NO ₃	25.57	-2.81	-12.03	-28.03	-34.97	-36.88	-38.57	-40.04	-41.30		216
NH ₄ ClO ₄	33.39	-0.50	-4.98	-12.68	-25.27	-31.46					224
Me ₄ NBr	24.48	0.37	0.11	-1.16	-2.76	-4.12	-4.87			-4.60	225
Et ₄ NBr	5.73	1.12	4.01	4.17	4.09	4.06	3.98	3.78	3.36		216
Bu ₄ NBr	-2.05	4.47	7.08	8.90	8.70						170
Hx ₄ NBr	15.84	19.99	47.91	42.40	24.19	22.60	20.27	17.19	13.37		216
Ph ₄ PCl	-8.79	19.21	22.34	18.77							128

Table 39. $\Delta_t H^{\circ}(\text{MX}, w \rightarrow w + \text{AN})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{AN}}$

MX	$\Delta_{\text{sln}} H^{\circ}$	5	10	20	30	40	50	60	70	80	90	100	ref	
HClO ₄	(-88.32)	-4.30	-8.34	-14.30	-18.83	-23.21	-28.22	-34.19	-40.98	-47.97	-54.06	-57.72	244	
LiCl	37.0	-0.8	-2.2	-3.8	-6.5	-8.6	-9.7	-12.0	-18.5	-27.9	-27.0	20.5	68	
LiBr	-49.0	-1.1	-2.2	-4.9	-8.2	-11.5	-14.8	-19.2	-23.0	-25.8	-24.1	8.8	25	
LiClO ₄	26.57	1.9	5.2	12.9	19.5	24.1	27.6	31.1	35.4	39.7	40.4	30.3	245, 256	
NaCl	[-0.59]	-1.7	-2.7	-4.0	-5.3	-7.7	-11.3	-15.3	-18.4	(-18.0)	(-11.0)	6.7 ^c	68	
NaCl	3.89	-1.6	-2.8	-5.0	-7.7	-11.0	-14.2	-15.6					246	
NaCl	4.07	-1.3	-2.5	-4.6	-7.6	-10.6	-13.4	-15.7	(-16.4)	(-14.5)	(-8.5)	7.2 ^d	247, 248	
NaCl		-1.5	-2.7	-5.0	-6.9	-9.8	-13.0	-15.5	{-17.4}	{-16.3}	{-9.8}	{7.0}		
NaBr	-0.59	-2.2	-3.8	-6.0	-8.0	-10.6	-14.3	-18.6	-22.1	-22.8	-18.0	-4.0 ^c	68	
NaBr	-0.63	-2.3	-4.2	-7.1	-9.4	-11.8	-14.4	-17.1	-19.5	-20.6	-19.4		246	
NaBr		-2.3	-4.0	-6.6	-8.7	-11.2	-14.4	-17.9	-20.8	-21.7	-18.7	3.8		
NaI	-7.8	-2.1	-5.0	-9.6	-14.6	-17.2	-20.1	-23.0	-25.5	-28.5	-31.8	-21.3	249	
NaI	-7.49	-2.7	-5.3	-10.3	-13.8	-16.0	-17.8	-20.3	-23.8	-27.5	-28.3	-20.7	246	
NaI		-2.4	-5.2	-10.0	-14.2	-16.6	-19.0	-21.7	-24.7	-28.0	-30.0	-21.0		
NaSCN	6.74	-4.5	-7.1	-11.5	-15.5	-19.1	-21.7	-23.7	-26.3	-29.7	-30.5	-18.0	246	
NaN ₃	12.5	-3.6	-5.8	-8.1	-10.1	-13.2	-16.6	-17.7					250	
NaNO ₂	13.9	-2.5	-4.1	-5.9	-7.8	-10.6	-13.7	-14.8					250	
NaClO ₃	21.5	-1.1	-2.5	-5.8	-8.9	-11.4	-13.1	-14.4					250	
NaBrO ₃	26.8	-1.2	-2.5	-5.1	-7.6	-9.8	(-11.3)						250	
NaClO ₄	13.89	-4.05	-7.37	-12.62	-17.74	-23.21	-27.65	-27.84	-18.70	6.69			244	
NaClO ₄	14.02	-3.0	-6.4	-13.0	(-18.6)	(-22.8)	(-26.5)	(-29.3)	-31.0	(-31.7)	(-31.6)	-30.4	247, 248	
NaClO₄		-3.5	-6.9	-12.8	-18.2	{-23.0}	{-27.1}	-28.6						
NaBF ₄	27.4	-3.3	-6.3	-12.2	-17.0	-20.5	-22.9	-24.8	-27.1	-31.0			250	
NaHCO ₂	0.7	-0.2	-0.7	-2.4	-4.9	-7.7	-10.4	-12.1					250	
NaCH ₃ CO ₂	-16.5	1.4	2.1	1.7	-0.4	-2.4							250	
NaCF ₃ CO ₂	-8.7	0.9	1.4	1.4	0.5	-1.3	-3.8	-6.3	-8.2	-8.3	-5.4	1.9	250	
NaBPh ₄	-20.1	13.9	7.5	[-8.0]	[-17.8]	[-23.2]	[-25.2]	[-24.9]	[-23.5]				-23.4	68
NaBPh ₄	-19.8	12.9	5.2	-23.8	-31.1	-32.0	-31.4	-30.3	-30.0	-31.7	-33.6	-23.7	246	
NaBPh ₄	-20.08	18.91	7.87	-21.13	-27.77	-28.79	-28.85	-27.40	-26.12	-27.32			244	
NaBPh ₄	-18.56		7.5	-24.4	-29.3	-28.5	-27.2	-26.4	-26.6	-28.4	-30.4	-23.3	248	
NaBPh₄		{16.3}	6.9	-23.1	-29.4	-29.7	-29.0	-28.0	-27.7	-29.0	-32.1	{-23.5}		
KCl	17.4	-2.4	-4.3	-7.2	-9.7	-12.4	-15.5	-18.4	-20.3	-19.7	-14.7	-2.9	68	
KBr	19.9	-3.1	-5.7	-9.7	-12.9	-15.7	-18.2	-20.5	-22.1	-22.3	-20.1	-14.2	68	
KI	20.3	-3.8	-6.9	-11.8	-15.5	-18.9	-22.3	-25.9	-29.3	-31.7	-32.4	-29.7	68	
KI	20.3	-4.8	-8.5	-13.5	-16.7	-19.4	-22.3	-25.6	-29.5	-32.3	-33.6	-31.3	246	
KI	21.09	-4.5	-8.3	-13.8	-17.1	-20.0	-22.9	-25.9	-28.9	-32.7	-35.2	-36.4	317	
KI		-4.4	-7.9	-13.0	-16.4	-19.4	-22.5	-25.8	-29.2	-32.2	-33.7	-32.4		
KNO ₃	34.7	-3.0	-5.5	-8.7	-11.0	-13.2	-15.8	-18.8	-21.7	-23.7	-23.4	-19.0	246	
RbCl	17.3	-3.1	-5.3	-7.7	-9.8	-12.6	-16.4	-20.0	-22.4	-21.7	-16.7	-6.2	68	
RbI	25.6	-5.0	-8.9	-14.2	-17.6	-20.3	-23.0	-26.2	-29.7	-32.9	-34.8	-33.7	246	
CsCl	17.8	-3.0	-5.1	-8.2	-10.6	-13.7	-18.0	-22.8	-26.8	-27.5	-21.8	-5.5	68	
CsI	32.3	-4.8	-8.7	-14.4	-18.3	-21.1	-23.6	-26.1	-28.8	-31.5	-33.9	-35.5	246	
AgCl	65.7	-25.0	-33.9	-34.8	-36.3	-41.7	-45.5	-47.7	-47.3	-56.5			-33.1	68
AgBr	84.5	-26.2	-35.9	-38.0	-39.7	-44.2	-46.6	-46.2	-49.2	-62.5			-45.6	68
AgI	112.5	-29.6	-38.8	-38.7	-41.3	-48.2	-51.9	-51.4	-56.4	-77.1			-61.1	68
AgNO ₃	22.7	-25.2	-36.9	-41.4	-43.6	-44.8	-46.3	-48.2	-50.3	-51.7	-50.8	-45.5	246	
TlNO ₃	40.7	-2.3	-4.7	-9.2	-12.8	-14.4							246	
Me ₄ NBr	24.5	-1.7	-2.9	-4.3	-5.4	-6.6	-8.4	-10.6	-12.4	-13.1	-11.0	-4.4	246	
Me ₄ NI	43.1	-1.8	-3.7	-7.2	-10.2	-12.5	-13.9	-14.9	-16.0	-17.9	-21.7	-28.8	246	
Et ₄ NCl	-12.9	-0.7	-1.1	-0.8	3.2	4.6	4.4	2.7	0.7	0.5	5.1	18.5	246	
Et ₄ NCl	-12.09	3.9	5.6	5.9	5.0	4.5	4.3	3.5	1.8	0.5	3.5	18.6	248	
Et₄NCl					4.1	4.6	4.4	3.1	1.3	0.5	4.3	18.6		
Et ₄ NBr	5.65	0.8	1.6	3.2	3.9	3.6	2.1	0.0	-2.1	-2.9	-1.0	5.5	246	
Et ₄ NI	27.3	-0.4	-0.4	-0.1	0.1	-0.3	-1.7	-3.8	-6.5	-8.9	-10.2	-9.0	246	
Et ₄ NClO ₄	31.0	1.8	2.1	-3.5	-6.2	-7.6	-8.7	-10.2	-12.2	-14.8	-17.2	-18.5	246	
Et ₄ NClO ₄	31.59	2.6	1.8	-3.2	-7.1	-8.5	-9.0	-10.2	-12.6	-15.4	-17.4	-18.8	248	
Et₄NClO₄		2.2	2.0	-3.4	-6.7	-8.1	-8.9	-10.2	-12.4	-15.1	-17.3	-18.7		
Et ₄ NPi	33.5	7.9	7.1	1.1	-1.8	-2.9	-1.8	-2.9	-3.1	-3.2	-3.4	-3.7	246	
Pr ₄ NBr	-4.82	9.45	15.09	17.89	17.24	16.40	15.68	14.40	12.31	10.43	11.18	18.11	335	
Pr ₄ NI	11.0	10.9	13.6	12.9	12.6	11.8	10.4	8.2	5.7	3.3	1.9	2.9	246	
Bu ₄ NBr	-9.20	21.1	27.3	26.8	25.6	24.6	24.4	25.2	26.7	[(28.2)]	[(28.7)]	26.8	68	
Bu ₄ NBr	-9.29	20.0	26.3	25.8	23.9	22.6	21.8	21.1	19.8	18.3	18.5	25.2	246	
Bu ₄ NBr	-8.42	19.24	26.80	26.80	25.08	24.53	23.66	22.12	20.62	18.96	18.47	25.54	24, 25, 335	
Bu₄NBr^g		20.1^h	26.8	26.5	24.9	23.9	23.3	22.8	22.4	18.7	18.5	25.8		
Bu ₄ NI	16.7	19.6	24.7	22.8	20.7	18.8	17.1	15.7	14.3	13.0	11.6	10.5	246	
Pe ₄ NBr	1.60	27.86	36.00	29.78	25.65	25.80	25.37	24.87	23.75	22.06	21.80	28.31	335	
Pe ₄ NBr	1.7	25.9	34.7	30.7	27.3	26.0	26.0	24.7	24.0	22.7	24.0	29.0	25	
Hp ₄ NBr	46.0 ^a	29.1	61.9	36.5	32.2	35.4	39.6	41.2	41.3	40.1	40.0	46.0	25, 335	
Me ₃ DcNBr	32.0	15.3	16.1	8.4									30	
Ph ₄ AsCl	-10.9	[21.6]	[23.1]	[12.4]	[6.4]	[3.7]	[3.1]	[3.8]	[5.1]	[(6.3)]	[(7.3)]	[7.9]	68	
Ph ₄ AsCl	-10.38	13.1	14.4	4.8	1.0	0.5	0.1	-1.7	-4.5	-6.5	-4.0	8.2	248	
Ph ₄ AsBr	7.70	12.3	12.0	3.9	-0.1	-1.8	-3.0	-4.5	-6.6	-8.5	-7.9	-1.6	246	
Ph ₄ AsI	34.7	12.5	10.2	-1.3	-5.8	-7.3	-8.3	-10.1	-13.2	-16.7	-19.3	-18.5	246	
Mg(ClO ₄) ₂		(-5.3)	-10.4	-26.4	(-35.1)	-45.3	(-55.9)	-64.7	(-74.6)	-83.5	(-93.0)	-28	251	
Ni(ClO ₄) ₂		(-6.7)	-12.7	-31.1	-39.4	-50.2	-61.0	-68.9	-79.4	-87.3	-95.1	-100.7 ^e	251	

Table 39. (Continued)

MX	$\Delta_{\text{sln}}H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
Ni(ClO ₄) ₂	8.73	-7.96	-15.98	-30.79	-42.61	-51.61	-58.34	-63.73	-69.08	-73.83	-56.62	-40 ^f	252
Ni(ClO₄)₂		-6.3	-14.3	-31.0	-41.0	-51.0	-59.7	{-66}	{-74}	{-81}			
Cu(ClO ₄) ₂	18.08	-3.88	-12.60	-30.97	-41.29	-47.90	-56.08	-64.94	-64.78	-71.53	-65.33	-25 ^f	252

^a At 288.15 K; $\Delta_{\text{sln}}H^\circ$ in water obtained from the extrapolation of Δ_tH° of Me₄NBr, Et₄NBr, Bu₄NBr, and Pe₄NBr from water to AN vs n_C to $n_C = 28$ with a third-degree polynomial and subtracting the result (assuming negligible temperature effect) from $\Delta_{\text{sln}}H^\circ$ in AN. ^b Misprint in original paper. ^c Value from ref 253. ^d From summation of reported ionic values. ^e Value from ref 254. ^f Original authors' graphically extrapolated value. ^g Data also available at $283.15 \leq T/K \leq 323.15$.²⁵⁷ ^h Graphical data at this composition also available.²⁵⁸

lytes, only three 1:2 (and no other highly charged) salts appear to have been studied (Table 39). It is also notable that most of the data have been reported in relatively few publications;^{68,82,246,250,82} this improves the self-consistency but not necessarily the accuracy of the data. Almost all of the data reported were obtained by calorimetry, mostly by $\Delta_{\text{sln}}H^\circ$ measurements, although $\Delta_{\text{dil}}H^\circ$ ^{245,251} and $\Delta_{\text{ppt}}H^\circ$ ⁶⁸ have also been used occasionally. Interestingly, there are no data for the hydrohalic acids, presumably because the popular Harned cell approach is not readily applied to w + AN mixtures due to the increased solubility of AgX(s), especially in the presence of excess X⁻. Potentiometric measurements reported by Dash and Pattanaik³⁵⁰ for a number of silver salts at low cosolvent compositions contained too little useful information to justify their inclusion. Data for Bu₄NBr at $283.15 \leq T/K \leq 323.15$ ²⁵⁹ were unavailable for consideration. Calorimetric data for sodium ion complexes are available²⁶⁰ but have not been included.

Extensive data are available for the alkali metal halides (except the fluorides), although many have not been independently confirmed. Of those that have, there is good agreement for NaCl,^{68,246-248} NaBr,^{68,246} and KI,^{68,246,317} enabling their averaged values to be Recommended. Independent data for NaClO₄^{244,247,248} are also in good agreement at $x_{\text{AN}} \leq 0.6$ but diverge rapidly at higher AN concentrations to the extent that no critical evaluation could be made. Data from independent studies of a number of tetraalkylammonium salts (Et₄NCl, Et₄NClO₄, Bu₄NBr, and Pe₄NBr) are likewise generally in good agreement, and their averaged values are listed as Recommended.

There have been numerous investigations of the salts required for the implementation of the TATB/TPTB assumption. For NaBPh₄, three independent calorimetric studies^{244,246,248} are in excellent agreement over the whole solvent composition range. A fourth⁶⁸ agrees at $x_{\text{AN}} \leq 0.1$ but deviates markedly at higher cosolvent concentrations. The latter have therefore been rejected. Calorimetric values of Δ_tH° have been reported for Ph₄AsCl,^{68,248} Ph₄AsBr,²⁴⁶ and Ph₄AsI.²⁴⁶ The data of Cox et al.⁶⁸ are again aberrant and have been rejected.

Because of the plethora of salts studied, numerous additivity checks are possible. One of these checks, using (MCl-MBr), was illustrated in Figure 2 and showed that the values of (Ph₄AsCl-Ph₄AsBr) are inconsistent with other data. Since the data for (Ph₄AsBr-Ph₄AsI) are consistent with other (MBr-MI) results, it may be concluded that it is the values of

$\Delta_tH^\circ(\text{Ph}_4\text{AsCl}, w \rightarrow w + \text{AN})$ reported by Cox et al.⁶⁸ that are in error, as already noted. Additivities also indicate that (AgCl-AgBr) values are consistent with other data but that (AgBr-AgI) and thus AgI differ *slightly* at $x_{\text{AN}} \leq 0.4$. For example, at $x_{\text{AN}} \leq 0.3$, seven combinations of (MBr-MI) have an average of 4.6 ± 0.7 kJ/mol whereas (AgBr-AgI) = 1.6 kJ/mol (all data from Table 39). Only for such a well-characterized system would this level of disagreement be significant.

Other additivity checks can be employed to assess the quality of the information available. In general, the values of $\Delta_tH^\circ(\text{salt}, w \rightarrow w + \text{AN})$ are additive to within ± 2 kJ/mol over the whole solvent composition range. This indicates that even when data have not been independently confirmed, they are likely to be reliable within this limit. The same should be true of the many more values of $\Delta_tH^\circ(\text{salt}, w \rightarrow w + \text{AN})$ that can be calculated by additivity from the data in Table 39. The major need for this system is for the investigation of salts containing ions for which there are no data currently available.

2. Ionic Enthalpies of Transfer

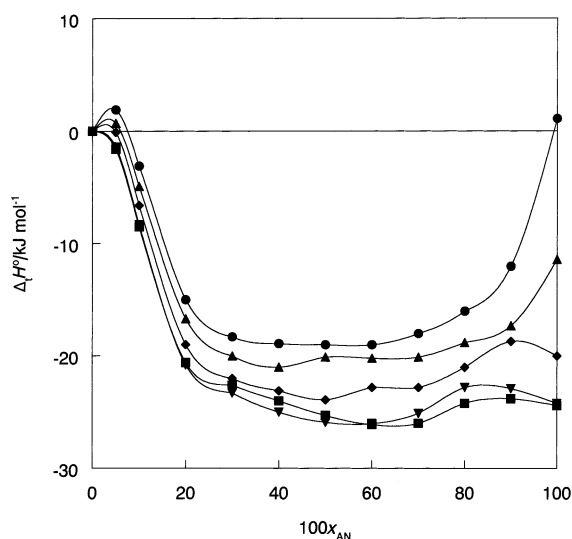
The values of $\Delta_tH^\circ(\text{ion}, w \rightarrow w + \text{AN})$ that can be derived from Table 39 via the TATB assumption are listed in Table 40. Because the additivities of the whole salt data are good and the TATB values are well established (see above), the values listed in Table 40 for the 15 monovalent cations (except H⁺) and most of the 17 monovalent anions should be reliable to within the limits of uncertainty of the assumption itself. The usual uncertainties exist with regard to the divalent cations.

Aqueous-AN mixtures are of special interest because they have a tendency toward microheterogeneity. The addition of electrolytes to such mixtures can have a significant impact on their behavior. The broad characteristics of these effects will be discussed below (section V.B.3); only the more specific details will be discussed in this section.

Figure 6 plots the enthalpies of transfer, $w \rightarrow w + \text{MeCN}$, for the alkali metal ions. These data may be compared with those for $w \rightarrow w + \text{MeOH}$ shown in Figure 3. In aqueous MeCN there is an initial small maximum in $\Delta_tH^\circ(\text{M}^+)$ followed by a general decrease: more or less opposite to what is observed in aqueous MeOH mixtures. Over the approximate range $0.2 \leq x_{\text{AN}} \leq 0.7$ the values of $\Delta_tH^\circ(\text{M}^+, w \rightarrow w + \text{AN})$ are virtually constant. This more or less flat 'trough' in the data (the small fluctuations are probably artifacts) appears to be associated with solvent microheterogeneity, although other explana-

Table 40. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{AN})/\text{kJ mol}^{-1}$, 298.15 K, TATB Assumption, as a Function of $100x_{\text{AN}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
H ⁺	HClO ₄	(-4.5)	-9.6	(-16)	-18.3	-18.9	-22.0	(-25)	(29)	-32.9	-36.4	-41.1
Li ⁺	LiBr	1.9	-3.1	-15.0	-18.3	-18.9	-20.5	(-19)	(-18)	(-16)	(-12)	1.1
Na ⁺	NaBPh ₄	0.7	-4.9	-16.7	(-20)	(-21)	-20.1	-20.2	-20.1	-18.8	-17.3	-11.4
K ⁺	KBr	-0.1	-6.6	-19.0	-23.0	-23.1	-23.9	-22.8	-22.8	(-21)	-18.7	(-20)
Rb ⁺	RbI	-1.6	-8.5	-20.6	-22.6	(-24)	-25.3	-26.1	-26.0	-24.2	-23.8	-24.4
Cs ⁺	CsI	-1.4	-8.3	-20.8	-23.3	(-25)	-25.9	-26.0	-25.1	-22.8	-22.9	-24.2
Ag ⁺	AgBr	-26.2	-36.8	(-45)	-49.8	-51.6	-54.3	(-57)	(-59)	-59.6		-53.2
Tl ⁺	TlNO ₃	0.6	-5.8	-20.3	-24.8	-24.3						
Me ₄ N ⁺	Me ₄ NBr	1.3	-3.8	-14.4	-15.5	-14.0	-14.1	-12.9	-13.1	-10.2	-9.6	-12.0
Et ₄ N ⁺	Et ₄ NBr	3.8	0.7	-6.9	-6.2	-3.8	-3.6	-2.3	-1.4	0.0	0.4	-2.1
Pr ₄ N ⁺	Pr ₄ NBr	12.5	14.2	7.8	7.1	9.0	10.0	12.1	13.0	13.3	12.6	10.5
Bu ₄ N ⁺	Bu ₄ NBr	23.1	25.9	16.4	14.8	16.5	17.6	20.5	23.1	21.6	19.9	18.2
Pe ₄ N ⁺	Pe ₄ NBr	29.9	34.5	20.2	16.4	18.5	20.0	22.5	24.6	25.3	24.3	21.1
Hp ₄ N ⁺	Hp ₄ NBr	32.1		26.4	22.1	28.0	33.9	38.9	42.0	43.0	41.4	38.4
Ph ₄ As ⁺	Ph ₄ AsBPh ₄	15.6	11.8	-6.4	-10.6	-11.1	-8.9	-7.8	-7.6	-10.2	-11.8	-12.1
Mg ²⁺	Mg(ClO ₄) ₂	-2.1	-13.0	-33.4	-34.1	-36.7	-45.3	-48.5	-52.6	-53.3	-57.6	5.2
Ni ²⁺	Ni(ClO ₄) ₂	-4.2	-11.8	-24.0	-40.0	-42.3	-49.1	-50.1				
Cu ²⁺	Cu(ClO ₄) ₂	-0.7	-15.2	-38.0	-40.3	-39.3	-45.5	-48.7	-42.8	-41.3	-29.9	8
Cl ⁻	NaCl	-2.2	2.2	11.7	11.9	8.8	7.1	4.7	2.7	2.5	7.5	18.4
Br ⁻	NaBr	-3.0	0.9	10.1	10.1	7.4	5.7	2.3	-0.7	-2.9	-1.4	7.6
I ⁻	NaI	-3.4	-0.4	6.4	5.0	(4)	2.3	-0.1	-3.7	-8.7	-11.0	-9.3
SCN ⁻	NaSCN	-5.2	-2.2	5.2	3.3	(1)	-1.6	-3.5	-6.2	-10.9	-13.2	-6.6
NO ₃ ⁻	KNO ₃	-2.9	1.1	11.1	12.0	9.9	8.1	4.0	1.1	-4.3	-4.7	2.8
ClO ₄ ⁻	Et ₄ NClO ₄	-1.6	1.3	3.5	0.5	(-3)	-5.3	-8.1	-11.0	-15.1	-17.7	-16.6
N ₃ ⁻	NaN ₃	-4.3	-0.9	8.6	8.7	5.4	3.5	2.5				
NO ₂ ⁻	NaNO ₂	-3.2	0.8	10.8	10.0	8.0	6.4	5.4				
ClO ₃ ⁻	NaClO ₃	-1.8	2.4	10.9	9.9	(8.5)	7.0	5.8				
BrO ₃ ⁻	NaBrO ₃	-1.9	2.4	(10)	11.2	8.8	8					
BF ₄ ⁻	NaBF ₄	-4.0	-1.4	(3)	1.8	-1.9	-3.5	-4.6	-7.0	-12.2		
HCO ₂ ⁻	NaO ₂ CH	-0.9	4.2	14.3	13.9	(12)	9.7	8.1				
MeCO ₂ ⁻	NaO ₂ CMe	0.7	2.4	15.0	14.4	(13)						
CF ₃ CO ₂ ⁻	NaO ₂ CCF ₃	0.2	6.3	18.1	19.3	18.0	16.3	13.9	10.9	10.5	11.9	13.3
Pi ⁻	Et ₄ NPi	4.1	6.4	8.0	4.4	(3)	1.8	-0.6	-1.7	-3.2	-3.8	-5.8
BPh ₄ ⁻	Ph ₄ AsBPh ₄	15.6	11.8	-6.4	-10.6	-11.1	-8.9	-7.8	-7.6	-10.2	-11.8	-12.1

**Figure 6.** Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, from water into aqueous-AN mixtures at 25 °C of the alkali metal ions: ● Li⁺, ▲ Na⁺, ◆ K⁺, ■ Rb⁺, ▼ Cs⁺.

tions have been proposed (see, for example, ref 250). At $x_{\text{AN}} > 0.7$ the $\Delta_t H^\circ(\text{M}^+)$ values become less negative, with some evidence of a maximum at $x_{\text{AN}} \approx 0.85$ for K⁺, Rb⁺ and Cs⁺. Unlike in $w + \text{MeOH}$ mixtures, the magnitude of the changes in $\Delta_t H^\circ(\text{M}^+)$, $w \rightarrow w + \text{AN}$ are rather dependent on the nature of the cation with differences of up to 13 kJ/mol, cf. ≤ 5 kJ/mol in $w + \text{MeOH}$ (Figure 3). The effects are

reasonably systematic, being in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ \approx \text{Cs}^+$ over the whole solvent composition range. This difference presumably arises from the differences in the liquid structures of these two cosolvents. The highly structured MeOH should be affected by cations in a manner similar to water. On the other hand, the effect of cations on the relatively weak dipole-based structure of MeCN should be quite different from that of water. The generally negative values of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + \text{AN})$ are somewhat surprising given that the donor number for (bulk) water (DN = 33) is very much greater than that of MeCN (DN = 14). The respective Kamlet-Taft β -parameters exhibit a similar relationship.

An unusually comprehensive set of results is available for $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + \text{AN})$, with R = Me-Pe, Hp. Plots against x_{AN} (Figure 7) show very systematic behavior, with $\Delta_t H^\circ$ becoming, as usual, more positive with increasing cation size. The most striking feature of these data is their virtual constancy at $0.2 \leq x_{\text{AN}} \leq 0.8$, although there is evidence for shallow extrema at $x_{\text{AN}} \approx 0.25$ and 0.85.

The values of $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + \text{AN})$ for the halide ions are plotted in Figure 8. The trends are systematic, with $\text{Cl}^- > \text{Br}^- > \text{I}^-$, but quite different from those of the alkali metal ions (Figure 6). At low x_{AN} , cation/anion compensation occurs: there is a small minimum in $\Delta_t H^\circ(\text{X}^-)$ followed by a maximum at $x_{\text{AN}} \approx 0.2$. The positions but not the magnitudes of these extrema are independent of the nature of the anion.

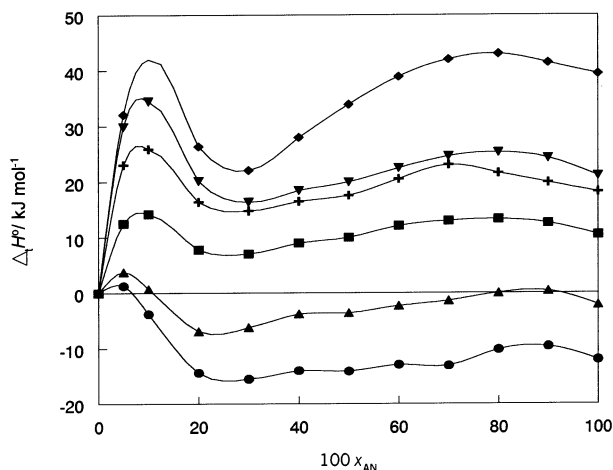


Figure 7. Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, from water into aqueous-AN mixtures at 25 °C for R_4N^+ ions: R = ● Me, ▲ Et, ■ Pr, + Bu, ▼ Pe, ◆ Hp.

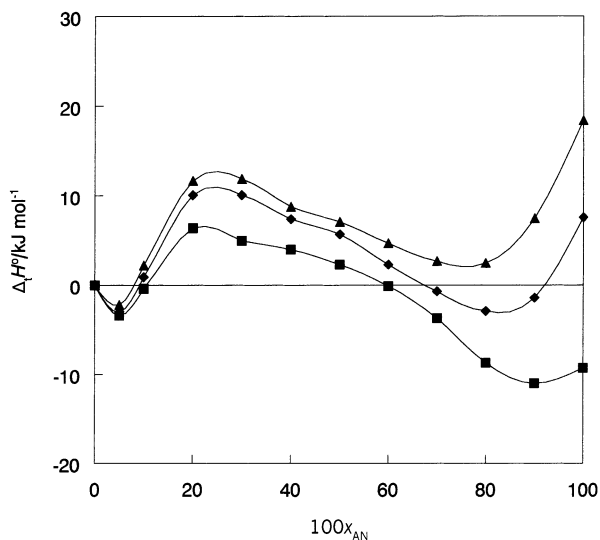


Figure 8. Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, from water into aqueous-AN mixtures at 25 °C for the halide ions: ▲ Cl^- , ◆ Br^- , ■ I^- .

At higher cosolvent concentrations, $\Delta_t H^\circ(X^-)$ shows a steady decrease of ~ 10 kJ/mol before eventually increasing. In other words, the values of $\Delta_t H^\circ(X^-)$ parallel those of $\Delta_t H^\circ(M^+)$ and there is a loss of cation/anion compensation at higher x_{AN} values. As for the cations (Figure 6), the position and size of this third extremum depend on the nature of the ion but the effects are rather larger for the anions. The generally positive values of $\Delta_t H^\circ(X^-)$ and their trend ($\text{Cl}^- > \text{Br}^- > \text{I}^-$) are related to the loss of H-bonding as the anion is transferred from water to the mixtures. Acetonitrile is a much weaker H-bond donor than water (their Kamlet-Taft α -parameters are 0.2 and 1.1, respectively⁷¹). For I^- , there may also be some favorable 'soft-soft' interactions with the 'soft' AN.³²⁰

The significant difference in the transfer thermodynamics of anions and cations in aqueous-AN mixtures is almost certainly a reflection of the importance of H-bonding interactions between X^- and H_2O . Indeed, Miyaji and Morinaga²⁵⁰ showed that a good correlation exists between $\Delta_t H^\circ(X^-, w \rightarrow w + \text{AN})$ at $x_{\text{AN}} = 0.3$ (corresponding to the maximum in

$\Delta_t H^\circ(X^-)$, Figure 8) and the enthalpies of hydration of the anions (in neat water). These authors also suggested a role for H-bond interactions beyond the primary solvation sheath of the anions, although they did not consider the implications of microheterogeneity.

3. Entropy Data for Electrolytes

The available numerical information for the entropies of transfer of electrolytes from water to aqueous-AN mixtures is given in Table 41. As usual, relatively few data are available; most were obtained by Cox et al.⁶⁸ via the GHSE using (mainly) their own $\Delta_t G^\circ$ and $\Delta_t H^\circ$ data. The exception is the data for $\Delta_t S^\circ(\text{KCl}, w \rightarrow w + \text{AN})$ reported by Efremov et al.⁵⁹ from NICE measurements. Their results differ markedly from those of Cox et al.,⁶⁸ but in the absence of further independent studies, no definite conclusions can be drawn from this difference.

4. Ionic Entropies of Transfer

A number of publications^{59,61,127,261} have estimated values of $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{AN})$ using various data and assumptions. All of these data are listed in Table 42, along with the values derived by the present reviewers (in **bold**) using the $\Delta_t H^\circ(M^{n+})$ data from Table 40 and the $\Delta_t G^\circ(M^{n+})$ from Kalidas et al.,¹ supplemented where appropriate with values of $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{AN})$ from Table 41. Where comparisons are possible, the agreement is generally good. For example, the values of $\Delta_t S^\circ(\text{Na}^+, w \rightarrow w + \text{AN})$ reported by Stellenberger et al.⁶¹ using NICE (see section II.B.2) data agree well with the present estimates via the GHSE, at least at $x_{\text{AN}} \leq 0.6$. At higher AN concentrations there is an increasing divergence: the present values are probably more reliable. For Ag^+ the situation is even better. At $x_{\text{AN}} \leq 0.4$ the NICE measurements⁶¹ are in excellent agreement with the GHSE values derived here by the reviewers and those of Sinha and Kundu¹²⁷ using their own $\Delta_t G^\circ$ values (from solubility measurements), literature $\Delta_t H^\circ$ data, and the TATB assumption. At $x_{\text{AN}} > 0.4$, the agreement persists between the present values and those of Stellenberger et al.⁶¹ with little deterioration up to neat AN. On the other hand, for Tl^+ the agreement at $x_{\text{AN}} \leq 0.4$, the only region where comparison is possible, is rather worse, with differences of up to $27 \text{ J K}^{-1} \text{ mol}^{-1}$.

For the R_4N^+ ions (R = Me-Bu) reasonable agreement also exists between the present GHSE estimates and those of Talukder and Kundu²⁶¹ at $x_{\text{AN}} \leq 0.4$. Surprisingly, the biggest differences are at $x_{\text{AN}} \leq 0.1$. The present values based on a wider cross-section of the literature are preferred. For $\Delta_t S^\circ(\text{Cl}^-, w \rightarrow w + \text{AN})$, the concordance between the NICE data of Efremov et al.⁵⁹ and the present GHSE estimates is good at $x_{\text{AN}} \leq 0.5$. At higher x_{AN} the results diverge sharply, with the present values being preferred. Little can be said about the reliability of the remaining (unconfirmed) data.

The shapes of the plots (not shown) of $\Delta_t S^\circ(M^+, w \rightarrow w + \text{AN})$ from Table 42 against x_{AN} are almost identical to those of the corresponding $\Delta_t H^\circ$ data (Figure 6). Thus, they exhibit the same small maxi-

Table 41. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{AN})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{AN}}$

MX	5	10	20	30	40	50	60	70	80	90	100	ref
LiCl	-6	-14	-33	-51	-68	-90	-124	-171	-218	-237	-173	68
NaCl	-8	-15	-32	-46	-62	-84	-116	-158	-199	-215	-166	68
NaBr	-6	-15	-35	-54	-70	-88	-113	-146	-181	-200	-167	68
KCl	-9	-19	-41	-60	-77	-96	-122	-155	-189	-207	-178	68
KBr	6	9	9	3	-8	-29	-41	-49				59
KBr	-12	-23	-45	-63	-79	-97	-120	-149	-178	-195	-177	68
KI	-14	-25	-44	-61	-79	-98	-119	-142	-163	-181	-191	68
RbCl	-12	-23	-42	-60	-79	-103	-131	-161	-188	-200	-185	68
CsCl	-11	-21	-39	-56	-75	-100	-133	-171	-206	-219	-181	68
AgCl	-51	-80	-91	-94	-110	-139	-169	-185	-182	-168	-181	68
AgBr	-53	-83	-97	-100	-111	-133	-157	-166	-162	-155	-186	68
AgI	-55	-87	-100	-99	-107	-125	-148	-162	-164	-160	-178	68
Bu ₄ NBr	60	99	122	131	139	137	123	121				68

Table 42. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{AN})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TPTB Assumption, as a Function of $100x_{\text{AN}}$

ion	5	10	20	30	40	50	60	70	80	90	100	ref
H⁺	-10	-23	-43	-50	-53	-66	-77	-93	-133	-187	-288	
Li⁺	8	-7	-47	-58	-64	-73	-74	-80	-90	-105	-99	
Na ⁺	-8	-22	-53	-72	-77	-76	-79	-91	-111	-130	-130	61
Na⁺	4	-13	-50	-62	-66	-67	-73	-76	-79	-79	-78	
K⁺	5	-14	-56	-71	-75	-78	-77	-83	-79	-75	-89	
Rb⁺	-1	-22	-62	-69	-77	-85	-91	-91	-87	-92	-100	
Cs⁺	0	-20	-60	-68	-76	-82	-87	-88	-82	-79	-96	
Ag ⁺	-55	-86	-110	-117	-120	-121	-121	-118	-115	-113	-108	61
Ag ⁺	-62	-95	-102	-84	-103							127
Ag⁺	-65	-85	-92	-101	-104	-112	-117	-123	-122		-98	
Tl ⁺	-17	-30	-49	-65	-77	-84	-88	-93	-102	-117	-123	61
Tl⁺	-2	-20	-72	-92	-92							
Me ₄ N ⁺	-16	-25	-30	-30	-41							261
Me₄N⁺		4	-13	-38	-38	-36						
Et ₄ N ⁺	5	3	-12	-23	-9							261
Et₄N⁺		13	-3	-24	-16	-5						
Pr ₄ N ⁺	31	46	45	33	44							261
Pr₄N⁺		42	48	31	35	46						
Bu ₄ N ⁺	52	72	55	23	54							261
Bu₄N⁺		67	72	42	45	60						
Ph₄P⁺		78	85	47	54	67	75	79	73	73	74	
Cu²⁺		-7	-62	-144	-161	-162	-187	-199	-224	-234	-197	
Cl ⁻	3	5	6	2	-4	-164	-24	-29				59
Cl⁻		-2	19	12	-2	-18	-44	-77	-114	-129	-87	
Br⁻		-6	13	8	-4	-20	-42	-68	-100	-120	-89	
I⁻		2	-5	1	-7	-21	-40	-43	-40		-88	
MeCO ₂ ⁻	70	107	111	82	93							127
EtCO ₂ ⁻	69	106	113	91	109							127
PrCO ₂ ⁻	67	104	114	97	123							127

imum at $x_{\text{AN}} \approx 0.05$, followed by a sharp decrease until $x_{\text{AN}} \approx 0.2$ from which point they are more or less constant up to neat AN. There is also some evidence of a small maximum at $x_{\text{AN}} \approx 0.9$, but as with the enthalpies (Figure 6), this may be an artifact. The coincidence of the entropies and enthalpies indicates there is a high degree of enthalpy/entropy compensation for the all the alkali metal ions in these mixtures. This is further discussed in section V.B.3 below. It is noteworthy that the values of $\Delta_t S^\circ(\text{M}^+, w \rightarrow w + \text{AN})$ show even less dependence on the nature of the cation than the corresponding enthalpies, with a total spread of $298\Delta_t S^\circ < 6 \text{ kJ/mol}$. There are also numerous crossovers, at least some of which are likely to be artifacts.

The available data for $\Delta_t S^\circ(\text{R}_4\text{N}^+, w \rightarrow w + \text{AN})$ are plotted in Figure 9. Unfortunately, because of the absence of the requisite $\Delta_t G^\circ$ values,¹ they are restricted to $x_{\text{AN}} \leq 0.4$. This means that it is not possible at present to establish the existence, or otherwise, of the plateau region at $x_{\text{AN}} > 0.2$ (Figures 6-8). Over the available range of solvent composi-

tions, $\Delta_t S^\circ(\text{R}_4\text{N}^+, w \rightarrow w + \text{AN})$ show a maximum at $x_{\text{AN}} \approx 0.1$, followed by a clear-cut minimum at $x_{\text{AN}} \approx 0.3$. The magnitude and position of the first extremum is dependent on the size of the cation but the second is less so. Comparison of Figures 7 and 9 indicates there is significant $\Delta_t H^\circ/\Delta_t S^\circ$ compensation, as for the alkali metal ions.

The values of $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{AN})$ for the halides are not as well established as those of the alkali metals. As usual,^{58,110} there are no data for F⁻ but more importantly the curve for I⁻ as a function of x_{AN} is erratic and rather different from those of Br⁻ and Cl⁻. This is probably a consequence of the present averaging process since the data of Miyaji and Morinaga,²⁵⁰ which are more self-consistent (if not necessarily more accurate) than the present values, show a more consistent pattern. Even keeping these limitations in mind, it is apparent that the values of $\Delta_t S^\circ(\text{X}^-, w \rightarrow w + \text{AN})$ show, like the corresponding enthalpies (Figure 8), much more complex behavior than those of the alkali metal ions as a function of solvent composition. Furthermore,

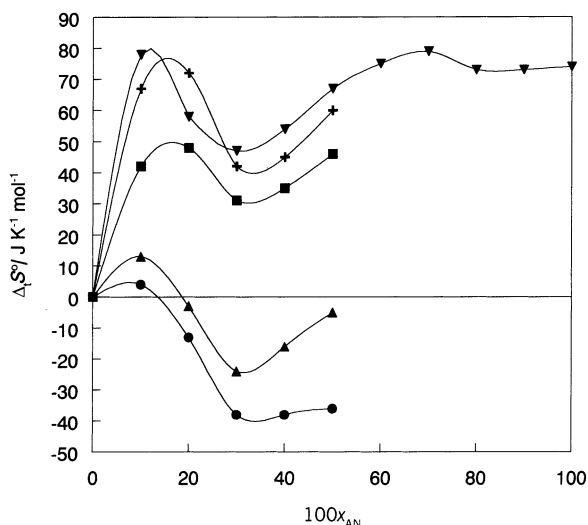


Figure 9. Standard molar entropy of transfer, $\Delta_t S^\circ/\text{J K}^{-1} \text{mol}^{-1}$, from water into aqueous-AN mixtures at 25 °C for R_4N^+ ions: R = ● Me, ▲ Et, ■ Pr, ⊕ Bu, ▼ Ph_4P^+ .

there is almost no $\Delta_t H^\circ/\Delta_t S^\circ$ compensation for Br^- and Cl^- (see below) nor is there much cation/anion compensation for $\Delta_t S^\circ$.

L. Transfers from Water to Water + Formamide (FA)

1. Enthalpy Data for Electrolytes

Data have been reported for the enthalpies of transfer of about twenty 1:1 electrolytes from water to w + FA mixtures (Table 43), but some of the

reported values were obtained by additivity. Surprisingly, data have been reported for six 1:3 electrolytes^{270,271} but none for any other charge types. With one exception, none of the data has been independently confirmed, although results for several salts have been published on more than one occasion by some groups. For NaI, reports by three independent groups^{263,265–267} are in excellent agreement enabling their averages to be classified as Recommended over the whole solvent composition range.

2. Ionic Enthalpies of Transfer

A comprehensive set of enthalpies of transfer for Ph_4PBr , NaBPh_4 , and KBr ^{263,268} permit estimation of $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{FA})$ via the TPTB assumption (Table 44). As the whole-salt data for this system are mostly unconfirmed, little can be said about the reliability of the single-ion values.

The trend of the values of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + \text{FA})$ for the alkali metal ions as a function of solvent composition (not plotted) is almost identical to that observed in aqueous mixtures of 1-PrOH. Thus, there is a small maximum ($\leq 2 \text{ kJ mol}^{-1}$) at $x_{\text{FA}} \approx 0.05$ followed by a steady decrease until $\Delta_t H^\circ(\text{M}^+, w \rightarrow \text{FA}) \approx -17 \text{ kJ mol}^{-1}$. As in aqueous 1-PrOH mixtures, there is almost no variation among the cations, except for Li^+ but this may be an artifact.

The values of $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + \text{FA})$ for the halide ions are plotted in Figure 10. There is some evidence of a small minimum at $x_{\text{FA}} \approx 0.1$, but it is poorly defined for F^- and Br^- . At higher x_{FA} there is little variation in $\Delta_t H^\circ(\text{X}^-)$, although for Cl^- and I^- there are signs of a broad, low maximum at $x_{\text{FA}} \approx 0.45$. The

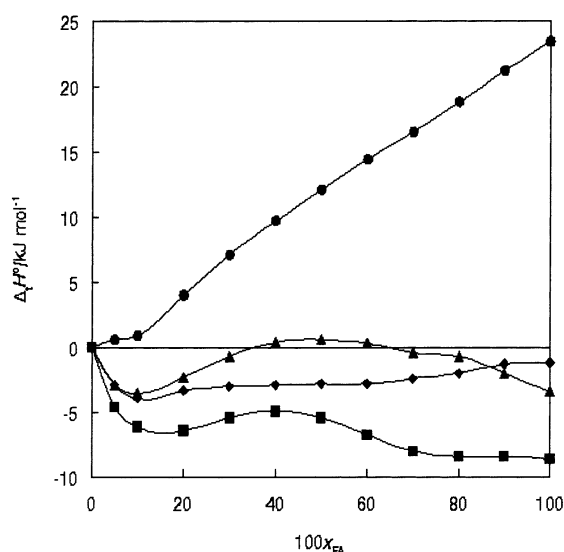
Table 43. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{FA})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{FA}}$

MX	$\Delta_{\text{sln}} H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
LiCl	-37.19	-1.22	-2.29	-3.86	(-4.84)	(-5.43)	-5.74	(-5.82)	(-5.63)	-5.10	(-4.05)	-2.25	262
LiBr	-49.08	-1.77	-3.27	-5.49	(-6.99)	(-8.06)	-8.85	(-9.44)	(-9.77)	-9.66	(-8.83)	-6.90	262
LiNO ₃	-2.49	-2.07	-3.94	-6.90	-9.12	-10.68	-11.62	-12.03	-11.97	-11.49	-10.68	-9.38	263
NaCl	3.85	(-1.50)	-2.95	-5.29	(-7.02)	(-8.29)	-9.27	(-10.12)	(-10.99)	-12.05			264
NaBr	-0.60	-1.87	-3.60	-6.64	-9.18	-11.25	-12.89	-14.13	-14.99	-15.50	-15.71	-15.64	263
NaI		-2.7	-5.0	-8.8	(-11.9)	-14.2	-16.3	-18.4	-19.7	-20.9	-22.2		265
NaI	-8.67	-2.01	-3.90	-7.38	-10.45	-13.13	-15.44	-17.41	-19.06	-20.40	-21.46	-22.27	266
NaI	-7.53	-3.10	-5.69	-9.50	-12.34	-14.60	-16.69	-18.74	-20.71	-22.47	-23.72	-23.97	267 ^a
NaI	-7.67	-2.63	-5.03	-9.09	-12.39	-15.02	(-17.1)	(-18.8)	(-20.1)	-21.28	-22.34	-23.43	263
NaI		-2.6	-4.9	-8.7	-11.8	-14.2	-16.4	-18.3	-19.9	-21.3	-22.4	-23.2	
NaNO ₃	20.19	-2.51	-4.79	-8.56	-11.52	-13.81	-15.55	-16.84	-17.82	-18.60	-19.29	-19.83	263, 268
NaBPh ₄	-19.36	4.01	4.98	1.09	-4.61	-8.76	-10.61	-11.02	-11.46	-13.00	-15.28	-15.56	263
NaBPh ₄	(-19.36)	4.99	5.15	0.69	-4.43	-8.22	-10.26	-11.16	-11.88	-13.18	-14.94	-15.63	268 ^b
KCl	17.20	(2.26)	4.00	6.40	(7.97)	(9.22)	10.44	(11.66)	(12.65)	12.98			264
KI		-2.9	-5.4	-9.6	-13.0	-15.5	-17.6	-19.2	-20.5	-22.2	-23.4	-24.7	265
KNO ₃	34.94	-2.36	-4.55	-8.27	-11.38	-13.95	-16.04	-17.71	-19.03	-20.06	-20.85	-21.35	263
RbCl	17.02	(2.28)	4.06	6.54	(8.14)	(9.36)	10.49	(11.64)	(12.69)	13.36			264
RbBr	21.66	-2.44	-4.61	-8.07	-10.66	-12.57	-13.94	-14.94	-15.74	-16.51	-17.40	-18.57	263
CsF	6.04	-0.08	(-0.1)	0.04	0.40	0.94	1.63	2.43	3.31	4.23	5.15	6.04	263
CsCl	17.26	(2.16)	3.94	6.58	(8.33)	(9.52)	10.38	(11.06)	(11.63)	12.05			264
CsNO ₃	39.60	-2.79	-5.28	-9.18	-12.12	-14.28	-15.86	-17.06	-18.07	-19.09	-20.32	-21.95	263
CsNO ₃	(39.60)	-4.52	-6.22	-9.25	-11.76	-13.82	-15.54	-16.99	-18.24	-19.40	-20.54	-21.75	268 ^b
NH ₄ NO ₃	25.68	-2.43	-4.60	-8.09	-10.76	-12.74	-14.19	-15.26	-16.09	-16.82	-17.61	-18.40	263
Me ₄ NBr	24.57	-1.15	-2.02	-3.04	-3.38	-3.28	-2.94	-2.51	-2.09	-1.71	-1.38	-1.01	269
Ph ₄ PBr	8.56	0.09	0.09	-0.33	-0.98	-1.63	-2.13	-2.40	-2.44	-2.33	-2.24	-2.39	263
YI ₃	-272.8		16.5	12.8			-8.1			-3.6			270
GdCl ₃	-183.1		23.0	25.1			19.0			21.0			271
GdBr ₃	-221.1		19.7	20.8			9.5			7.4			271
HoI ₃	-257.0		8.3	-5.0			-20.7			-19.1			270
ErCl ₃	-214.8		33.8	32.5			28.3			38.2			271
ErBr ₃	-231.8		30.5	28.2			18.8			24.6			271

^a Data also available at 278.15 and 288.15 K. ^b Authors in ref 268 are the same as ref 263, but the data were presented at fewer x_{FA} , so interpolations values led to somewhat different values of $\Delta_t H^\circ$.

Table 44. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{FA})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{FA}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
Li ⁺	LiBr	1.1	0.6	-2.2	-4.0	-5.2	-6.1	-6.6	-7.4	-7.7	-7.5	-5.7
Na ⁺	NaBPh ₄	2.0	1.2	-2.3	-6.4	-9.3	-11.0	-11.6	-11.9	-12.9	-14.0	-14.4
K ⁺	K(I,NO ₃)	1.6	0.6	-3.1	-7.0	-9.8	-11.6	-12.6	-13.2	-14.5	-15.7	-16.6
Rb ⁺	RbBr	0.5	-0.7	-4.8	-7.7	-9.7	-11.1	-12.1	-13.3	-14.5	-16.1	-17.4
Cs ⁺	CsNO ₃	-0.7	-1.0	-4.0	-6.7	-8.8	-10.5	-12.0	-13.2	-14.6	-16.0	-17.4
NH ₄ ⁺	NH ₄ NO ₃	1.4	0.6	-2.8	-5.7	-7.7	-9.2	-10.3	-11.1	-12.0	-13.0	-14.0
Me ₄ N ⁺	Me ₄ NBr	1.7	1.9	0.3	-0.4	-0.4	-0.1	0.3	0.3	0.3	0.2	0.1
Ph ₄ P ⁺	Ph ₄ PBPh ₄	3.0	4.0	3.0	2.0	1.1	0.7	0.4	0.0	-0.3	-0.9	-1.2
Y ³⁺	YI ₃		34.8	32.0			8.1			21.6		
Gd ³⁺	GdBr ₃		31.4	30.7			17.9			13.4		
Ho ³⁺	HoI ₃		26.6	14.2			-4.5			6.1		
Er ³⁺	ErBr ₃		42.2	38.1			27.2			30.6		
F ⁻	CsF	0.6	0.9	4.0	7.1	9.7	12.1	14.4	16.5	18.8	21.2	23.4
Cl ⁻	(Li,Na)Cl	-2.9	-3.5	-2.3	-0.7	0.4	0.6	0.3	-0.4	-0.7	-2.0	-3.4
Br ⁻	Ph ₄ PBr	-2.9	-3.9	-3.3	-3.0	-2.9	-2.8	-2.8	-2.4	-2.0	-1.3	-1.2
I ⁻	NaI	-4.6	-6.1	-6.4	-5.4	-4.9	-5.4	-6.7	-8.0	-8.4	-8.4	-8.6
NO ₃ ⁻	(Li,NaNO ₃)	-3.8	-5.2	-5.3	-5.1	-5.0	-5.0	-5.0	-5.0	-4.8	-4.6	-4.4
BPh ₄ ⁻	Ph ₄ PBPh ₄	3.0	4.0	3.0	2.0	1.1	0.7	0.4	0.0	-0.3	-0.9	-1.2

**Figure 10.** Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, from water into aqueous-FA mixtures at 25 °C of the halide ions: ● F⁻, ▲ Cl⁻, ◆ Br⁻, ■ I⁻.

behavior of $\Delta_t H^\circ(X^-)$ is generally systematic, $F^- \gg Cl^- > Br^- > I^-$, but there is a crossover between Cl^- and Br^- at $x_{\text{FA}} \approx 0.9$. Comparisons with other protic solvents, for which $\Delta_t H^\circ(F^-, w \rightarrow w + s)$ are not generally large,⁵⁸ suggests that the F^- results may be a little too positive, but further investigation is required.

There is insufficient information on the R_4N^+ ions, with only values for Me_4N^+ available, to make any generalizations. Similarly, the values for $\Delta_t H^\circ(M^{3+}, w \rightarrow w + \text{FA})$ are too widely spaced to draw definite conclusions, although at low x_{FA} they appear to follow a trend similar to that of the alkali metal ions. The effects of increasing charge, as for other systems, are large.

3. Entropies of Transfer

There do not appear to have been any entropy values published for the transfer of electrolytes from water to aqueous FA solutions. The values that can be calculated for $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{FA})$ via the GHSE using the $\Delta_t H^\circ(\text{ion})$ information in Table 44, based on the TPTB assumption, with the limited

Table 45. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{FA})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TATB/TPTB Assumption, as a Function of $100x_{\text{FA}}$

ion	5	10	20	30	40	50	60	70	80	90	100
Na ⁺	8	13	6	-5	-12	-15	-16	-17	-18	-20	-21
K ⁺	8	12	4	-7	-13	-17	-19	-20	-23	-26	-28
Rb ⁺	5	7	-3	-10	-14	-17	-20	-22	-24	-28	-32
Cs ⁺	5	7	-1	-8	-14	-19	-23	-26	-30	-34	-38
Me ₄ N ⁺	7	11	7	5	5	6	7	7	5	5	5

range of values available for $\Delta_t G^\circ(M^{n+})$, based on the TATB assumption,¹ are listed in Table 45. The ionic entropies of transfer are similar in all respects to the corresponding enthalpies except that they are somewhat smaller. That is, there is (at least partial) $\Delta_t H^\circ/\Delta_t S^\circ$ compensation in these mixtures.

M. Transfers from Water to Water + *N,N*-Dimethylformamide (DMF)

1. Enthalpy Data for Electrolytes

Enthalpies of transfer from water to aqueous-DMF solutions have been reported for more than twenty 1:1 electrolytes (Table 46). No studies have appeared for higher valent electrolytes. Further information may be available (see the references cited in Korolyov et al.⁶⁶) but was not accessible to the reviewers. Many of the values have been confirmed by independent calorimetric measurements, although only one report⁶⁵ has been made of salts suitable for application of the TATB/TPTB assumption.

Transfer enthalpies for many of the alkali metal halides are well characterized. For NaCl, two studies^{65,274} are in excellent agreement where comparison is possible ($x_{\text{DMF}} \leq 0.3$). At higher x_{DMF} only the values of Booij and Somsen⁶⁵ are available and have therefore been accorded a Tentative status. For NaI, the two independent calorimetric studies^{140,267} are in excellent agreement over the entire solvent composition range, so their averaged values are Recommended. The earlier potentiometric results on this salt²⁷⁵ differ somewhat and have been rejected. Independent calorimetric studies of KI^{140,276} are also in excellent agreement at $x_{\text{DMF}} \leq 0.8$; at higher DMF concentrations, only the data of Klopov et al.¹⁴⁰ are available. For both CsBr and CsI, independent data

Table 46. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{DMF})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{DMF}}$

MX	$\Delta_{\text{sln}} H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
NaCl	3.88	-0.49	-0.57										22
NaBr	-0.1	-1.0	-1.8	-3.6	-6.1	-9.3	-13.6	-17.1	-20.4	-23.6	-26.4	-28.6	65
NaBr	-0.60	-1.28	-2.06	-3.22	-5.48								274
NaBr		-1.1	-1.9	-3.4	-5.8	{-9.3}	{-13.6}	{-17.1}	{-20.4}	{-23.6}	{-26.4}	{-28.6}	
NaI		[-4.48]	[-7.57]	[-9.57]									275
NaI	-7.57	-2.43	-4.98	-10.25	-15.65	-21.13	-26.57	-31.84	-36.86	-41.51	-45.73	-49.41	273
NaI	-7.53	-2.23	-4.64	-9.83	-15.44	-21.21	-26.86	-32.26	-37.24	-41.76	-45.81	-49.37	267, 272 ^d
NaI		-2.3	-4.8	-10.0	-15.5	-21.2	-26.7	-32.0	-37.0	-41.6	-45.8	-49.4	
NaBPh ₄	-19.6	15.2	22.1	11.4	-3.2	-17.1	-30.4	-37.1	-42.5	-46.4	-49.3	-52.1	65
KBr	20.06	-2.03	-3.44	-5.21	-7.08								274
KI	20.50	-3.14	-6.19	-12.26	-18.24	-24.10	-29.79	-35.27	-40.46	-45.35	-49.87	-53.97	273
KI	20.3	-2.84	-5.76	-11.54	(-17.27)	(-22.95)	-28.58	(-34.16)	(-39.68)	(-45.15)			276
KI		-3.0	-6.0	-11.9	-17.8	-23.4	-29.2	-34.7	-40.0	-45.2	{-49.9}	{-54.0}	
RbCl	17.21	-1.02	-1.29	-1.01	-0.83	-1.81	-4.42					-16.32	277, 278
RbI	25.44	-3.10	-5.90	-11.63	-17.41	-23.18	-28.83	-34.35	-39.58	-44.52	-49.08	-53.14	273
CsF	26.3	-2.0	-3.3	-7.0	-9.0	-11.8	-15.0	-19.5	-22.0	-25.8	-29.8	-33.3	24
CsCl	17.25	-0.20	-0.29	-0.75	-1.57	-2.76	-4.31	-6.23	-8.52	-11.17	-14.19	(-17.58)	279
CsBr	26.06	-1.45	-2.69	-5.33	-8.15	-11.17	-14.37	-17.77	-21.35	-25.12	-29.09	(-33.24)	279
CsBr	26.3	-1.6	-3.2	-6.2	-9.2	-12.2	-15.4	-18.7	-22.3	-26.1	-30.2	-33.8	25 ^a
CsBr		-1.5	-3.0	-5.8	-8.7	-11.7	-14.9	-18.3	-21.8	-25.6	-29.6	-33.5	
CsI	33.01	-3.35	-6.44	-12.34	-17.95	-23.30	-28.41	-33.28	-37.93	-42.37	-46.61	-50.68	273
CsI	33.18	-3.39	-6.41	-12.29	-17.93	-23.34	-28.52	-33.47	-38.18	-42.66	-46.91	(-50.93)	279
CsI		-3.4	-6.4	-12.3	-17.9	-23.3	-28.5	-33.4	-38.1	-42.5	-46.8	-50.8	
NH ₄ Br	16.72	-1.98	-3.93	-7.92	-12.30								274
NH ₄ Br	17.28	-1.68	-3.66	-8.16	-12.94	-17.56	-21.70	-25.17	-27.91	-29.99	-31.59	-33.03	280
NH₄Br		-2.0	-4.0	-8.1	-12.5	{-17.1}	{-21.1}	{-24.4}	{-27.9}	{-30.3}	{-31.9}	{-33.0}	
Me ₄ NBr	24.57	-1.1	-1.8	-2.3	-2.1	-1.8	-1.6	-2.1	-3.3	-5.5	-8.7	-13.3	269
Me ₄ NBr	24.57	-1.51	-2.29	-2.39	-1.81	-1.44	-1.60	-2.32	-3.54	-5.34	-8.20	-13.22	278
Me ₄ NBr	24.6	-0.5	-1.1	-1.6	-1.9	-2.2	-2.5	-2.9	-3.6	-4.6	-6.1	-8.2	25 ^a
Me₄NBr		{-1.0}	{-1.7}	{-2.1}	{-1.9}	{-1.8}	{-1.9}	{-2.4}	{-3.5}	{-5.1}	{-7.7}	{-13.3}	
Et ₄ NBr	6.2	0.79	1.88	4.49	7.05	9.04	10.15	10.21	9.26	7.50	5.32	3.29	269, 278
Et ₄ NBr	6.2	1.5	2.9	5.6	7.8	9.4	10.3	10.5	10.0	8.7	6.5	3.2	25 ^a
Et₄NBr		{1.2}	{2.4}	{5.1}	{7.4}	{9.2}	{10.2}	{10.4}	{9.6}	{8.1}	{5.9}	{3.3}	
Pr ₄ NBr	-4.25		[1.33]	[9.4]	24.3	24.95	24.47	23.23	21.41	19.18	16.17	14.18	278
Pr ₄ NBr	-4.25		9.5	18.2	23.2	24.7	24.4	23.1	21.1	19.0	16.4	12.2	281 ^c
Pr ₄ NBr	-4.3	6.0	11.1	18.5	22.9	24.8	24.8	23.3	21.1	18.6	16.3	14.2	25
Pr₄NBr		{6.0}	{10.3}	{18.3}	{23.5}	{24.8}	{24.6}	{23.2}	{21.2}	{18.9}	{16.3}	{13.5}	
MeBu ₃ NBr	-12.2		12.9	22.6	26.1	26.8	25.1	22.9	20.6	17.9	15.2	12.4	24
Me ₃ DcNBr	32.0	6.1	d										
Bu ₄ NBr	-8.58	12.7	22.0	33.3	38.1	37.5	36.0	33.0	30.1	27.5	24.8	21.0	277
Bu ₄ NBr	-8.58		22.3	33.8	38.2	38.2	35.4	32.7	30.1	27.1	23.8	20.5	281 ^c
Bu ₄ NBr	-7.9	12.7	22.3	34.3	37.9	37.5	35.0	32.1	29.3	26.4	23.6	20.7	65
Bu ₄ NBr			22.5		38.7		36.2		30.6		24.6	21.3	66
Bu ₄ NBr	-8.4	10.9	19.9	32.3	38.7	40.4	38.6	34.7	29.8	25.2	22.1	20.9	25
Bu₄NBr		12.2	21.8	33.4	38.3	38.4	36.2	33.1	30.0	26.6	23.8	20.9	
Pe ₄ NBr	2.7	16.4	29.4	42.5	45.6	43.2	38.5	33.9	30.4	27.8	25.2	20.0	281
Pe ₄ NBr	2.7	11.9	21.9	33.3	38.2	39.1	37.6	34.6	30.5	26.1	22.5	20.2	25
Pe₄NBr		{16.4}	{29.4}	{42.5}	{45.6}	{43.2}	{38.0}	{34.2}	{30.5}	{27.0}	{23.7}	{20.1}	
Ph ₄ PBr	8.6	7.0	10.7	11.1	8.2	5.0	2.1	-0.7	-4.3	-7.1	-10.0	-12.5	65

^a Interpolated graphically by reviewers. ^b Cf. ref 282. ^c Cf. refs 269 and 278. ^d Data up to $x_{\text{DMF}} = 0.058$ conform to $\Delta_t H^\circ = 275x + 784x^2 - 76710x^3$. ^d Data also available at $278.15 \leq T/\text{K} \leq 308.15$.

sets are in excellent agreement and the averaged values have been Recommended at all cosolvent concentrations.

An unusually extensive set of data exists for $\Delta_t H^\circ(\text{R}_4\text{NBr}, w \rightarrow w + \text{DMF})$ with $\text{R} = \text{H} - \text{Pe}$. However, with the exception of NH_4Br ²⁷⁴ and Bu_4NBr ,⁶⁶ all of the data were measured by Somsen and co-workers.^{24,25,269,277,278,281} While all this work appears to be of high quality, the results cannot be considered as having been independently confirmed. Consequently, most of the averaged values for these systems must be classified as Tentative, pending independent verification.

2. Ionic Enthalpies of Transfer

The values of $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{DMF})$ for 12 cations and 5 anions (all monovalent) that could be derived by application of the TPTB assumption⁶⁵ to the data in Table 46 are summarized in Table 47.

Plots against x_{DMF} of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + \text{DMF})$ for the alkali metal ions (not shown) are remarkably similar to those observed for many protic solvents such as the higher alcohols (e.g., 1-PrOH) and FA. Thus, there is a small maximum (<ca. 5 kJ mol⁻¹) at $x_{\text{DMF}} \approx 0.1$ followed by a steady decrease thereafter, with almost no dependence on the cation size. The only difference is that $\Delta_t H^\circ(\text{M}^+)$ is much more negative in the aprotic DMF because of its much greater donor (cation solvating) ability, cf. ROH.

The extensive series of data for $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + \text{DMF})$ are very systematic with values increasing with cation size and showing a pattern similar to that observed in most aqueous-organic solvent mixtures.

As for many other systems, the plots (not shown) of $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + \text{DMF})$ against x_{DMF} for the halide ions look rather different from those of the alkali metal ions. At low x_{DMF} there is some cation/anion compensation with a small minimum (>ca. -10

Table 47. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{DMF})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{DMF}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
Na ⁺	NaBPh ₄	3.5	4.7	-1.6	-8.4	-15.7	-23.0	-26.7	-29.3	-31.4	-32.8	-34.1
K ⁺	KI	3.8	4.1	-3.5	-11.4	-18.2	-25.1	-29.3	-32.6	-36.2	-39.2	-42.2
Rb ⁺	RbI	3.7	4.2	-3.2	-11.0	-18.0	-24.7	-29.0	-32.2	-35.5	-38.4	-41.3
Cs ⁺	CsBr	3.2	3.7	-3.9	-11.5	-18.1	-24.4	-28.0	-30.7	-33.5	-36.1	-39.0
NH ₄ ⁺	NH ₄ Br	2.7	2.7	-6.2	-15.3	-23.5	-30.6	-34.1	-36.8	-38.2	-38.4	-38.5
Me ₄ N ⁺	Me ₄ NBr	3.7	5.0	-4.0	-4.7	-8.2	-11.6	-13.1	-12.4	-13.0	-14.2	-18.8
Et ₄ N ⁺	Et ₄ NBr	5.9	9.1	7.0	4.6	2.8	0.7	0.7	0.7	0.2	-0.6	-2.2
Pr ₄ N ⁺	Pr ₄ NBr	10.7	17.0	20.2	20.7	18.4	14.9	13.5	12.3	11.0	9.8	
Bu ₄ N ⁺	Bu ₄ NBr	16.9	28.5	35.3	35.5	32.0	26.7	23.4	21.1	18.7	17.3	15.4
Pe ₄ N ⁺	Pe ₄ NBr	21.1	36.1	44.4	42.8	36.8	28.5	24.5	21.6	19.1	17.2	14.6
Ph ₄ P ⁺	Ph ₄ PBPh ₄	11.7	17.4	13.0	5.4	-1.4	-7.4	-10.4	-13.2	-15.0	-16.5	-18.0
F ⁻	CsF	-5.2	-7.0	-3.9	2.5	6.3	9.4	8.5	8.7	7.7	6.3	5.7
Cl ⁻	CsCl	-3.4	-4.0	3.1	9.9	15.3	20.1	21.8	22.2	22.3	21.9	21.4
Br ⁻	Ph ₄ PBr	-4.7	-6.7	-1.9	2.8	6.4	9.5	9.7	8.9	7.9	6.5	5.5
I ⁻	CsI	-6.8	-10.1	-8.4	-6.4	-5.2	-4.1	-5.4	-7.4	-9.0	-10.7	-11.8
BPh ₄ ⁻	Ph ₄ PBPh ₄	11.7	17.4	13.0	5.4	-1.4	-7.4	-10.4	-13.2	-15.0	-16.5	-18.0

Table 48. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{DMF})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{DMF}}$

MX	5	10	20	30	40	50	60	70	80	90	100	ref
NaBr	-8.3	-15.6	-32.6	-45.4	-62.4	-80.9	-105.0	-114.9	-129.1	-147.5	-160.3	65
NaI	-16.1	-27.4	-36.4									275
NaBPh ₄	79.6	110.6	106.4	80.9	56.7	27.0	2.8	-1.4	-5.7	-7.1	-9.9	65
KPi	35	-20	-17	-15	-14	-15						283
KBPh ₄	200	175	140	145	220	380						283
RbCl	-9.4	-19.6	-33.6	-49.3	-67.8	-84.1						277
Ph ₄ PBr	35.0	56.7	72.3	70.9	68.1	61.0	49.6	36.9	22.7	7.1	-9.9	65
Ph ₄ AsPi	65	105	140	130	105	90						283

kJ mol⁻¹) at $x_{\text{DMF}} \approx 0.1$, although there is considerable variation (up to 30 kJ mol⁻¹) among the halides. At higher cosolvent concentrations and consistent with the absence of H-bond donor ability of DMF, the values of $\Delta_t H^\circ(X^-)$ become positive. An exception is $\Delta_t H^\circ(I^-)$, which remains (weakly) negative over the whole composition range. The results for fluoride (\approx bromide) do not follow the pattern $\text{Cl}^- > \text{Br}^- > \text{I}^-$ set by the other halides. They are almost certainly in error since $\Delta_t H^\circ(\text{F}^-, w \rightarrow s)$ values are invariably more positive than those of the other halide ions.⁵⁸

It may be noted that it is possible to use the GHSE to calculate values of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + \text{DMF})$ for $\text{M}^+ = \text{Ag}^+$ or Tl^+ since the values of $\Delta_t G^\circ(\text{M}^+)$ are available¹ and $\Delta_t S^\circ(\text{M}^+)$ are known from NICE measurements.⁶⁰ However, in view of the uncertainties in the latter (see below), this is left to the interested reader.

3. Entropy Data for Electrolytes

As with other systems, relatively few values exist for the entropies of transfer of electrolytes from water to aqueous–DMF mixtures. The available data are listed in Table 48. Little can be said of them except the values for KBPh₄ and Ph₄AsPi²⁸³ seem to be rather different from those for related salts.

4. Ionic Entropies of Transfer

The values of $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{DMF})$ that can be derived via the GHSE from the $\Delta_t H^\circ(\text{ion})$ estimates in Table 47 and the corresponding $\Delta_t G^\circ(\text{ion})$ values¹ are summarized in Table 49. As anticipated above, the present values for BPh₄⁻ and Ph₄P⁺ (and K⁺) differ markedly (by up to 122 J K⁻¹ mol⁻¹ or ~ 36 kJ mol⁻¹ in terms of $298\Delta_t S^\circ$) from those derived by Ray et al.²⁸³ from temperature-dependent solubility and

emf measurements. The present results are almost certainly more realistic.

Agreement is also rather poor between the present GHSE results for $\Delta_t S^\circ(\text{Na}^+, w \rightarrow w + \text{DMF})$ and those obtained by Gritzner and Lewandowski⁶⁰ using NICE measurements, with differences of up to ca. 65 J K⁻¹ mol⁻¹ (~ 20 kJ mol⁻¹ for $298\Delta_t S^\circ$). Little can be said of the remaining values except the need for further study. Plots (not shown) of $\Delta_t S^\circ(\text{M}^+, w \rightarrow w + \text{DMF})$ against x_{DMF} are almost identical to those of the corresponding enthalpies. That is, there is strong $\Delta_t H^\circ/\Delta_t S^\circ$ compensation for the alkali metal cations in water/DMF mixtures.

Plots (not shown) of $\Delta_t S^\circ(X^-, w \rightarrow w + \text{DMF})$ against x_{DMF} for the halide ions using the rather more limited data available (Table 49) also show a broad similarity to the corresponding enthalpies: an initial decrease to $x_{\text{DMF}} \approx 0.15$ followed by a maximum (at least for Br⁻) at $x \approx 0.5$ and then a rather large decrease down to the neat DMF value.

N. Transfers from Water to Water + *N,N*-Dimethylacetamide (DMA)

1. Enthalpy Data for Electrolytes

Very few studies have been reported on the enthalpies of transfer of electrolytes from water to aqueous–dimethylacetamide (DMA) solutions. The available data, for ten 1:1 electrolytes and Ni(ClO₄)₂, are collected in Table 50. All values were determined calorimetrically from heats of solution measurements. None has been confirmed. The only additivity checks possible, using (MCl–MI), indicate good consistency, but little further comment can be made.

Table 49. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{DMF})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TATB/TPTB Assumption, as a Function of $100x_{\text{DMF}}$

ion	5	10	20	30	40	50	60	70	80	90	100	ref
Na ⁺	-0.7	-1.6	-3.3	-5.1	-7.0	-8.8	-10.3	-11.4	-12.2	-12.6	-12.8	60
Na⁺	13*	21	9	-8	-32	-57	-68	-73	-77	-78	-79	
K ⁺	90	40	-15	10	65	105						283
K⁺	10*	18	-1	-22	-48	-73	-84	-92	-100	-105	-111	
Rb ⁺	10*	18	0	-22	-48	-72	-81	-87	-93	-99*	-101*	
Cs ⁺	11*	18	3	-18	-39	-64	-71	-76	-82	-86	-91	
Ag ⁺	-0.7	-1.4	-2.6	-3.8	-5.0	-6.1	-7.0	-7.7	-8.2	-8.3	-8.1	60
Tl ⁺	3.9	3.8	-0.6	-2.3	-4.6	-7.1	-9.5	-11.5	-13.2	-14.2	-14.5	60
Ph ₄ As ⁺		92	150	145	94	85	79	75	74	74	80	65
Ph ₄ As ⁺	110	150	145	155	180	205					106	283
Ph₄(P,As)⁺	66*	100	112	103	93	83	77	72	70	67	71	
Cl ⁻												
Cl⁻	-19	-38	-34	-27	-20	-12						
Br⁻	-26	-40	-41	-35	-28	-23	-32	-39	-50	-55	-81	
I⁻	-29	-48	-45									
Pi ⁻	-60	-45	-20	-40	-80							283
BPh ₄ ⁻	110	150	145	155	180	205					106	283
BPh₄⁻	66*	100	112	103	93	83	77	72	70	67	71	

Table 50. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{DMA})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{DMA}}$

MX	$\Delta_{\text{sin}} H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
NaCl	3.89	0.60	1.83	4.24									33
NaBr	-0.60	-0.45	-0.12	-0.79	-2.42	-4.96	-8.28	-12.15	-16.26	-20.21	-23.50	-25.54	284
NaI	-7.58	-1.91	-3.72	-7.96	-12.60	-18.67	-24.95	-29.41	-34.16	-38.41	-41.63	-44.17	32
NaClO ₄	13.89	0.25	-2.69	-10.26	-19.85	-29.60	-38.20	-44.90	-49.50	-52.54	-54.36	-56.99	284
NaBPh ₄	-20.28	25.06	28.20	11.71	-8.13	-21.57	-31.46	-41.21	-49.47	-51.46	-54.26	-55.48	284
KCl	17.29	0.50	1.29	2.38									33
KI	20.26	-2.37	-4.87	-9.64	-14.70	-20.04	-25.58	-31.21	-36.70	-41.80	-46.17	-49.42	22
CsI	33.29	-2.96	-6.45	-12.02	-17.32	-22.13	-26.78	-31.85	-36.78	-41.72	-46.66	-51.38	32
Bu ₄ NBr	-8.42	15.50	27.04	40.70	45.39	44.73	41.48	37.56	34.06	31.20	28.35	24.02	281,25
Ph ₄ PBr	8.18	15.94	18.79	20.24	16.16	11.93	9.13	7.07	4.30	0.08	-2.09	-2.97	284
Ni(ClO ₄) ₂	-164.01	-3.65	-13.59	-32.14	-51.00	-67.86	-81.23	-90.40	-95.47	-97.33	-97.66	-98.96	284

Table 51. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{DMA})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{DMA}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
Na ⁺	NaBPh ₄	4.6	4.7	-4.7	-14.6	-21.1	-24.5	-30.2	-35.0	-34.9	-37.8	-39.0
K ⁺	KI	4.1	4.5	-6.3	-16.7	-24.4	-26.1	-30.6	-34.9	-38.3	-42.4	-44.2
Cs ⁺	CsI	3.5	2.9	-8.7	-19.3	-24.5	-27.3	-31.3	-35.0	-38.2	-42.9	-46.2
Bu ₄ N ⁺	Bu ₄ NBr	20.1	31.7	36.9	35.7	32.3	25.4	19.5	16.8	15.5	14.4	10.5
Ph ₄ P ⁺	Ph ₄ PBPh ₄	20.5	23.5	16.4	6.5	-0.5	-7.0	-11.0	-14.5	-15.6	-16.5	-16.5
Ni ²⁺	Ni(ClO ₄) ₂	4.9	1.2	-20.9	-40.4	-50.9	-53.8	-66.1	-64.5	-64.1	-63.5	-63.0
Cl ⁻	NaCl	-4.0	-2.9	8.9								
Br ⁻	Ph ₄ PBr	-4.6	-4.7	3.8	9.7	12.4	16.1	18.1	18.8	15.7	14.4	13.5
I ⁻	NaI	-6.5	-9.4	-3.3	2.0	2.4	0.5	-0.6	-1.8	-3.5	-3.8	-5.2
ClO ₄ ⁻	NaClO ₄	-4.3	-7.4	-5.6	-5.3	-8.5	-13.7	-14.7	-15.5	-16.6	-17.6	-18.0
BPh ₄ ⁻	Ph ₄ PBPh ₄	20.5	23.5	16.4	6.5	-0.5	-7.0	-11.0	-14.5	-15.6	-16.5	-16.5

2. Ionic Enthalpies of Transfer

Application of the TPTB assumption using the data of Gusev et al.²⁸⁴ enabled estimation of $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{DMA})$ values for 10 monovalent ions and Ni²⁺, although some only extend to low cosolvent concentrations (Table 51).

The behavior of $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + \text{DMA})$, plotted as a function of x_{DMA} (not shown), is almost identical with that observed for DMF: a small maximum (<6 kJ/mol) at $x_{\text{DMA}} \approx 0.07$ followed by a steady decrease through to neat DMA, with very small differences between the cations. Again as for DMF, plots of $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + \text{DMA})$ against x_{DMA} (not shown) are rather different from those of the alkali metal ions. Such plots show a small minimum at $x_{\text{DMA}} \approx 0.07$ followed by a maximum (at least for Br⁻ and I⁻) and then a steady decrease. There are also substantial differences between the halides with

respect to the position and magnitude (up to 18 kJ/mol between Br⁻ and I⁻) of the extrema. Measurements on Cl⁻ (at higher x_{DMA}) and F⁻ would be interesting for these mixtures.

3. Entropies of Transfer

No data appear to have been published for the entropies of transfer of electrolytes between water and aqueous–DMA mixtures. Further, as the values for $\Delta_t G^\circ(\text{ion}, w \rightarrow w + \text{DMA})$ are not readily available,¹ it was not possible to utilize the values of $\Delta_t H^\circ(\text{ion})$ in Table 51 to calculate $\Delta_t S^\circ(\text{ion})$ via the GHSE.

O. Transfers from Water to Water + Urea (UR)

1. Enthalpy Data for Electrolytes

Data have been reported for the enthalpies of transfer of more than 20 electrolytes from water to

Table 52. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{UR})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{UR}}$

MX	$\Delta_{\text{sln}} H^\circ$	2.5	5	7.5	10	15	ref
HCl		-3.04	-4.55	-5.13	-5.39	-7.40	285 ^a
HBr		-3.39	-4.76	-5.57	-6.51	-7.61	286
HI		-3.65	-4.84	-5.74	-7.14	-7.45	286
NaCl	4.12	-1.22	-2.25	-3.06	-3.70	-4.56	287
NaCl	3.85	-1.29	-2.30	-3.09	-3.70	-4.53	288
NaCl	3.90	-1.40	-2.39	-3.11	-3.71		289
NaCl		-1.3	-2.3	-3.1	-3.7	-4.5	
NaBr	-0.50	-1.56	-2.62	-3.47	-4.26	-5.76	290
NaBr	-0.53	-1.57	-2.83	-3.80	-4.49		289
NaBr		-1.6	-2.7	-3.6	-4.4	{ -5.8 }	
NaI	-7.58	-2.19	-3.34	-4.21	-5.16	-6.98	290
NaI	-7.62	-1.67					291
NaI	-7.54	-1.55	-2.80	-3.82	-4.66		289
NaI		-1.8	-3.1	-4.0	-4.9	{ -7.0 }	
NaBPh ₄	-19.26	1.84	3.25	4.31	5.14		289
NaBPh ₄	-20.10	2.58	3.76	4.08	4.06	5.14	294 ^b
NaBPh₄		2.2	3.5	4.2	4.6	{ 5.1 }	
KCl	17.22	-1.37	-2.43	-3.25	-3.87	-4.77	288
KBr	20.15	-1.74	-2.91	-3.81	-4.63	-6.19	290
KI	20.40	-2.28	-3.50	-4.38	-5.32	-7.18	290
KPi		-17.38	-25.47	-28.34	-26.00		194
KBPh ₄			38.93	29.21	28.13		194
RbCl	17.28	-1.73	-3.02	-3.97	-4.67	-5.63	288
CsCl	17.78	-2.30	-3.91	-5.01	-5.77	-6.92	288
CsBr	26.00	-2.68	-4.22	-5.32	-6.38	-8.47	290
CsI	33.10	-3.32	-4.93	-6.02	-7.23	-9.68	290
NH ₄ Cl	14.85	-1.33	-2.39	-3.23	-3.89	-4.93	288
Bu ₄ NBr	-8.60	2.41	4.91				30
Bu ₄ NBPh ₄	24.10	3.40	7.60	12.67			176
Ph ₄ AsCl	-10.62	0.50	0.06	-0.27	-0.45		289
Ph ₄ AsPi			[-15.10]	[-10.49]	[-11.01]		194
AgCl		-1.35	-2.76	-3.75	-4.32	-4.23	292
AgBr		-0.64	-1.35	-2.02	-2.64	-3.76	292
AgI		-1.64	-2.95	-4.04	-4.91	-6.01	292

^a Same data also listed in refs 293, 194. ^b Solvent compositions converted from mol/L (density data, Waghorne, W. E., unpublished).

aqueous–urea mixtures but only at low urea concentrations (Table 52). For the sodium halides there is excellent agreement among independent data sets, and their averages are listed as Recommended. No duplicate data sets are available for the remaining electrolytes. However, additivity checks using (NaX–KX) indicate that the data for the potassium halides are reasonable. On the other hand, there are clearly inconsistencies in the (MCl–MPi) data and for additivities involving KBPh₄. Careful examination indicates that there are serious discrepancies in the data of Talukdar et al.,¹⁹⁴ based on solubility measurements, and data for a number of salts have not been included in Table 52.

The numerous data reported by Dash and co-workers^{240,295,364} from emf measurements at different temperatures are problematic. The enthalpy (and entropy) data are presented as single-ion values but without a stated assumption. There are also inconsistencies in the reporting of the signs of $\Delta_t H^\circ$, some being exothermic and others endothermic. Thus, in general, these data have not been listed in Table 52.

2. Ionic Enthalpies of Transfer

Because of the inconsistencies in the enthalpy of transfer data for some of the electrolytes needed for the TATB assumption, the number of acceptable routes to the ionic values is limited. There is, however, reasonable agreement between values cal-

Table 53. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{UR})/\text{kJ mol}^{-1}$, 298.15 K, TATB Assumption, as a Function of $100x_{\text{UR}}$

ion	MX data	2.5	5	7.5	10	15
H ⁺	HCl	-1.5	-1.8	-1.3	-1.0	-1.9
Na ⁺	NaBPh ₄	0.2	0.6	0.7	0.7	0.0
K ⁺	KCl	0.1	0.4	0.5	0.5	-0.3
Rb ⁺	RbCl	-0.2	0.2	0.2	0.3	-1.1
Cs ⁺	CsCl	-0.8	-1.1	-1.2	-1.3	-2.4
Ag ⁺	AgCl	-0.1	0.0	0.0	0.1	0.3
NH ₄ ⁺	NH ₄ Cl	0.2	0.4	0.6	0.5	-0.4
Bu ₄ N ⁺	Bu ₄ NBPh ₄	1.4	4.7	9.2		
Ph ₄ As ⁺	Ph ₄ AsBPh ₄	2.0	2.9	3.5	3.9	5.1
Cl ⁻	Ph ₄ AsCl	-1.5	-2.8	-3.8	-4.4	-4.5
Br ⁻	NaBr	-1.8	-3.3	-4.3	-5.1	-5.8
I ⁻	NaI	-2.0	-3.7	-4.7	-5.6	-7.0
BPh ₄ ⁻	Ph ₄ AsBPh ₄	2.0	2.9	3.5	3.9	5.1

culated using the NaBPh₄ and Bu₄NBPh₄ data, where comparison is possible. Accordingly, values of $\Delta_t H^\circ(\text{ion})$ calculated using the former are reported in Table 53, since they cover the greater composition range. In general, all of the values are small in magnitude. The values for $\Delta_t H^\circ(\text{ion})$ at $x_{\text{UR}} = 0.15$ were ultimately obtained by a short extrapolation of the $\Delta_t H^\circ(\text{Ph}_4\text{AsBPh}_4)$ values at lower cosolvent compositions and so are a little less certain.

3. Entropy Data for Electrolytes

Data for entropies of transfer reported for over 10 electrolytes are summarized in Table 54, including ones suitable for the application of the TATB as-

Table 54. $\Delta_t S^\circ(\text{MX}, \text{w} \rightarrow \text{w} + \text{UR})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{UR}}$

MX	2.5	5	7.5	10	15	ref
HCl	-0.2	0.5	2.2	4.8	2.5	285
HBr	0.2	0.8	1.5	2.4	4.4	286
HI	0.1	0.5	1.1	2.0	4.4	286
LiCl	-2.8	-5.2	-7.3	-9.1	-11.6	288
NaCl	-4.1	-7.7	-10.8	-13.5	-17.6	288
KCl	-4.5	-8.4	-11.9	-14.9	-19.5	288
KCl	-3.8	-6.7	-8.9	-11.0		194
KCl	-4.2	-7.6	-10	-13	{-20}	
KPi	-50.8	-81.6	-83.9	-49.4		194
KBPh ₄	140.8	142.6	97.1	95.3		194
RbCl	-5.5	-10.1	-14.1	-17.4	-22.0	288
CsCl	-6.1	-10.9	-15.1	-18.4	-23.1	288
NH ₄ Cl	-3.8	-7.0	-9.9	-12.4	-16.3	288

Table 55. $\Delta_t S^\circ(\text{ion}, \text{w} \rightarrow \text{w} + \text{UR})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TATB Assumption, as a Function of $100x_{\text{UR}}$

ion	2.5	5	7.5	10
H ⁺	-0.5	1.2	4.9	10.8
Na ⁺	-5.3	-8.5	-9.5	-8.6
K ⁺	-5.1	-8.2	-9.3	-8.3
Rb ⁺	-6.0	-9.7	-11.2	-10.4
Cs ⁺	-7.4	-12.0	-13.9	-13.1
NH ₄ ⁺	-4.0	-6.4	-7.2	-6.4
Ph ₄ As ⁺	8.2	15.1	20.5	24.5
Cl ⁻	0.3	-0.6	-2.7	-6.0
Br ⁻	0.1	-1.1	-3.6	-7.2
I ⁻	0.4	-0.6	-2.9	-6.4
Pi ⁻	[-51.6]	[-59.6]	[-50.4]	[-30.0]
BPh ₄ ⁻	8.2	15.1	20.5	24.5

sumption. Only for KCl are there independent sets of data,^{194,288} and these are in good agreement where comparison is possible, enabling their averages to be Recommended. As for the enthalpies, there appear to be inconsistencies in the data of Dash and co-workers,^{237,295,296,364} and so these have not been included.

4. Ionic Entropies of Transfer

The entropy data for the electrolytes required for the TATB assumption come from the temperature coefficients of the solubilities. As noted above, there are problems with the $\Delta_t H^\circ$ for the picrate salts and for KBPh₄ that are presumably transmitted to the $\Delta_t S^\circ$ values. In fact, $\Delta_t S^\circ(\text{ion})$ values calculated from the electrolyte entropies are absurdly large (ca. +70 J K⁻¹ mol⁻¹ for cations and -70 J K⁻¹ mol⁻¹ for anions at 0.025 mol % urea). An alternative route suggested by Hakin and Beswick²⁸⁹ is to combine $\Delta_t H^\circ(\text{ion})$ values with $\Delta_t G^\circ$ values calculated from the solubility products reported by Talukdar et al.¹⁹⁴ This is preferred since the solubility products are inherently more precise than their temperature coefficients. Thus, the values reported in Table 55 are taken from the work of Hakin and Beswick²⁸⁹ or calculated from them using data in Table 53. With the exception of the values for Pi⁻, the $\Delta_t S^\circ(\text{ion})$ values seem reasonable. It is interesting that, as with $\Delta_t H^\circ(\text{ion})$, the $\Delta_t S^\circ(\text{ion})$ values are small and practically monotonic for transfers from water to aqueous-urea mixtures.

P. Transfers from Water to Water + Hexamethyl Phosphoric Triamide (HMPT)

1. Enthalpy Data for Electrolytes

Data have been reported for the enthalpies of transfer between water and aqueous-HMPT mixtures for about 15 1:1 electrolytes, in several cases across the whole solvent composition range (Table 56). No data are available for higher valent electrolytes. For NaCl, NaI, and KI there are duplicate sets of data but from the same laboratory,^{298,299} and thus the averaged values must be classified as Tentative. For KCl (and at one solvent concentration, KI) data from the Lodz group^{298,299} are in excellent agreement with those of Vorob'ev et al.³⁰⁰ The key salt, NaBPh₄, has been extensively studied by two groups^{268,297,299} across the whole range of solvent composition. The relationship between the two data sets reported by Vandyshev et al.^{268,297} is unclear; the reported data differ, but it is not obvious whether the later data involve new measurements or a recalculation of the earlier results. Nevertheless, the differences are generally small (apart from the data at $x_{\text{HMPT}} \leq 0.2$) and the values are in good agreement with those of Taniewska-Osinska and Jozwiak,²⁹⁹ enabling the averaged values to be Recommended. Further data for NaI and KBr at 298.15 K and $x_{\text{HMPT}} \leq 0.1$ are available.³⁰³

There are large discrepancies in the (MI-MNO₃) additivities. Since the other additivity checks are reasonable, it seems likely that either the CsNO₃ or NaNO₃ data are incorrect. Similarly, (MCl-MBr) additivities indicate that there is a problem with the data for either Ph₄PBi²⁹⁷ or Ph₄PCl.²⁹⁹

2. Ionic Enthalpies of Transfer

In addition to the well-established data for NaB-Ph₄, there are data for Ph₄PCl, up to 30 mol % HMPT, and for Ph₄PBr across the whole solvent composition range. There is good agreement between the ionic values recovered from these at the low HMPT concentrations, but they diverge above 10 mol % HMPT, with the values calculated via the chlorides being more exothermic than those calculated via the bromides. This is consistent with the problem in the (MCl-MBr) additivities noted above. It is not possible to determine which set of data are preferred, and so, since the bromide data extend to all solvent compositions, these were used to calculate ionic transfer enthalpies.

The values of $\Delta_t H^\circ(\text{ion}, \text{w} \rightarrow \text{w} + \text{HMPT})$ so derived are listed for seven cations and six anions in Table 57. It can be noted that, as with virtually all aqueous-organic systems, there are maxima in the cation values and minima in those of the anions at low HMPT concentrations. As expected from the very large donor number of HMPT, the $\Delta_t H^\circ$ data for cations are strongly exothermic at higher HMPT concentrations. Similarly, $\Delta_t H^\circ$ for the smaller anions are endothermic into the aqueous mixtures, as expected for transfer to mixtures containing an aprotic cosolvent. Interestingly, $\Delta_t H^\circ$ for I⁻ is negative into the mixtures, possibly reflecting a significant soft-soft interaction with HMPT, which has a higher

Table 56. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{HMPT})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{HMPT}}$

MX	$\Delta_{\text{sin}} H^\circ$	5	10	20	30	40	50	60	70	80	90	100	ref
LiNO ₃	-2.49	-2.15	-7.27	-15.06	-20.45	-24.34	-27.48	-30.49	-33.82	-37.80	-42.60	-48.25	297
NaCl	3.83	4.35	5.68	2.45	-2.43								298
NaCl		4.35	5.68	2.83									299
NaCl		{4.4}	{5.7}	{2.6}	{-2.4}								
NaBr	-0.60	0.82	1.37	0.74	-3.32	-9.34	-13.04	-15.22	-16.62	-17.98	-20.04	-23.37	297
NaI	-7.55	-2.89	-9.48	-20.47	-28.52						-56.63	-58.65	298
NaI		-2.34	-8.99	-19.96	-28.50	-35.41	-41.23	-46.29	-50.53	-53.98	-56.51	-57.96	299
NaI		{-2.6}	{-9.2}	{-20.2}	{-28.5}	{-35.4}	{-41.2}	{-46.3}	{-50.5}	{-54.0}	{-56.6}	{-58.3}	
NaNO ₃	20.19	1.92	-2.52	-9.31	-14.22	-18.14	-21.70	-25.30	-29.10	-33.02	-36.74	-39.71	297
NaBPh ₄	-19.36	26.91	-19.25	-59.23	-62.11	-64.91	-67.62	-70.25	-72.79	-75.26	-77.64	-79.95	268
NaBPh ₄	-20.02	37.56	-22.61	-43.83	-54.95	-61.30	-64.31	-69.17	-72.77	-75.36	-76.92	-77.50	299
NaBPh ₄	-19.36	34.25	-22.04	-52.07	-62.90	-65.51	-67.92	-70.22	-72.49	-74.82	-77.29	-79.96	297
NaBPh₄		32.9	-21.3	-51.7	-60.0	-63.9	-66.6	-69.9	-72.7	-75.1	-77.3	-79.1	
KCl	17.17	3.43	4.30	-3.44									298
KCl		3.43	4.30	-3.44									299
KCl		2.91	3.86										300
KCl		3.3	4.2	{-3.4}									
KI	20.02	-1.83		-21.50	-29.39	-35.37	-39.81	-43.08	-45.53	-47.53	-49.56	-51.73	298
KI		-1.83	-9.30	-24.21	-30.83	-35.93	-39.81	-42.80	-45.19	-47.29	-49.40	-51.96	299
KI		-2.81											300
KI		-2.2	{-9.3}	{-22.9}	{-30.1}	{-35.7}	{-39.8}	{-42.9}	{-45.4}	{-47.4}	{-49.5}	{-51.9}	
CsF	-36.54	8.59	15.12	23.62	26.04	20.31	22.50	23.31	22.64				268
CsI	33.09	-2.76	-12.30	-26.60	-35.49	-40.37	-42.82	-44.14	-45.05	-46.14	-47.84	-49.63	299
CsNO ₃	39.60	-0.18	-12.07	-24.29	-27.84								268
NH ₄ NO ₃	25.68	-2.67	-11.48	-24.67	-33.30	-38.82	-42.41	-45.01	-47.35	-49.87	-52.80	-56.12	297
Me ₄ NBr	24.57	0.96	-0.97	-3.18	-7.97								301
Bu ₄ NBr	8.45	(32.0)	(48.0)	(50.5)	(46.5)	(43.0)	(40.0)	(37.0)	(34.0)	(31.5)	(28.5)	25.40	302
Ph ₄ PCl	-8.90	26.45	24.34	21.83	22.07								299
Ph ₄ PBr	8.56	23.84	20.09	14.67	11.08	8.41	6.00	3.42	0.53	-2.57	-5.52	-7.72	297

Table 57. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{HMPT})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{HMPT}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
Li ⁺	LiNO ₃	0.6	-24.8	-37.3	-43.4	-47.0	-48.6	-49.4	-49.6	-50.1	-51.8	-55.9
Na ⁺	NaBPh ₄	4.7	-20.0	-31.5	-37.2	-40.8	-42.8	-44.3	-44.9	-45.3	-45.9	-47.4
K ⁺	KI	5.1	-20.3	-35.8	-38.8	-41.1	-41.4	-40.9	-39.8	-38.7	-38.9	-41.3
Cs ⁺	CsI	4.6	-23.1	-37.9	-44.2	-45.8	-44.4	-42.1	-39.4	-37.4	-37.2	-38.7
NH ₄ ⁺	NH ₄ NO ₃	0.1	-29.0	-46.9	-56.3	-61.5	-63.5	-64.0	-63.2	-62.1	-62.0	-63.8
Me ₄ N ⁺	Me ₄ NBr	4.9	-22.4	-35.4	-41.8	-31.5	-29.8	-29.0	-28.3	-27.3	-25.9	-24.0
Ph ₄ P ⁺	Ph ₄ PBPh ₄	28.0	-1.3	-18.9	-22.8	-23.1	-23.8	-25.6	-27.8	-29.9	-31.4	-31.7
F ⁻	CsF	4.0	38.2	61.5	70.2	66.1	66.9	65.4	62.1			
Cl ⁻	Ph ₄ AsCl	-0.4	25.7	34.1	34.8							
Br ⁻	NaBr	-3.9	21.4	32.2	33.9	31.5	29.8	29.0	28.3	27.3	25.9	24.0
I ⁻	NaI	-7.3	10.8	11.3	8.7	5.4	1.6	-2.0	-5.6	-8.7	-10.7	-10.9
NO ₃ ⁻	NaNO ₃	-2.8	17.5	22.2	23.0	22.7	21.1	19.0	15.8	12.3	9.2	7.7
BPh ₄ ⁻	Ph ₄ PBPh ₄	27.7	-1.3	-17.6	-22.8	-23.1	-23.8	-25.6	-27.8	-29.9	-31.4	-31.7

Table 58. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{HMPT})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, TPTB Assumption, as a Function of $100x_{\text{HMPT}}$

ion	5	10	20	30	40	50	60	70	80	90	100
K ⁺	14	-64	-103	-103	-118	-126	-128	-126	-124	-125	-133
Cs ⁺	12	-66	-94	-99	-109	-109	-104	-98	-93	-96	-104
Ph ₄ P ⁺	137	66	36	33	32	39	36	32	27	24	25

softness parameter, $\mu = 0.29$, than other oxygen-donor dipolar aprotic solvents.¹

3. Entropies of Transfer

No entropy data have been reported for electrolytes in aqueous HMPT systems. Thus, Table 58 reports ionic $\Delta_t S^\circ$ values for Ph₄P⁺, K⁺, and Cs⁺ calculated via the GHSE using the $\Delta_t H^\circ(\text{ion})$ data in Table 57 and $\Delta_t G^\circ$ data reported previously.¹

Q. Transfers from Water to Water + Dimethyl Sulfoxide (DMSO)

1. Enthalpy Data for Electrolytes

Enthalpy of transfer data from water to aqueous-DMSO mixtures are available for almost thirty 1:1,

five 1:2, and two 2:1 electrolytes, often with independent data sets extending over the whole range of solvent composition (Table 59). Almost all the data were obtained by calorimetry. No data were found for the hydrohalic acids, which is probably a reflection of the increased solubility of the silver halides in the presence of excess halide ion in the presence of DMSO (cf. AN, section IV.K.1). The enthalpy of dissociation of water has also been measured in aqueous-DMSO mixtures.¹⁸⁰

There is poor agreement between the two available data sets for LiCl.^{305,306} Additivity checks using (MCl-MX) indicate that the data of Cox et al.³⁰⁶ are out of line and hence are rejected. There is good agreement among three independent sets of data for

Table 59. $\Delta_t H^{\circ}(\text{MX}, w \rightarrow w + \text{DMSO})/\text{kJ mol}^{-1}$, 298.15 K, as a Function of $100x_{\text{DMSO}}$

MX	$\Delta_{\text{sm}} F^{\circ}$	5	10	20	30	40	50	60	70	80	90	100	ref
HClO ₄		0.30	-2.00	-13.90	-28.10								304
LiCl	-37.03	-0.03	-0.65	-2.33	-4.49	-6.89	-9.20	-11.01	-11.79	-11.31	-10.02	-8.57	305
LiCl	-35.77	[-1.89]	[-3.27]	[-4.32]	[-4.67]	[-5.17]	[-5.82]	[-6.67]	[-7.57]	[-8.47]	[-9.31]	[-10.04]	306
LiBr	-48.83	-1.06	-2.56	-6.13	-9.96	-13.55	-16.57	-18.82	-20.30	-21.12	-21.59	-22.14	305
LiI	-63.30	-2.10	-4.66	-10.41	-16.54	-22.56	-28.05	-32.68	-36.19	-38.41	-39.25	-38.69	305
LiNO ₃	-2.48	-1.60	-3.58	-8.73	-14.44	-19.78	-24.10	-27.06	-28.57	-28.89	-28.53	-28.32	268 ^a
NaCl	3.89	-0.15	0.15	0.17	-1.02	-3.58	-5.98	-7.75	-9.26	-10.55	-11.28	-10.75	305
NaCl		-0.11	-0.20	-0.67	-1.45	-2.45	-3.59					-8.79	306
NaCl		-0.10	-0.75	-1.51	-0.43								307
NaCl		-0.1	-0.7	-1.0	-1.2	-3.0	-4.8	{-7.8}	{-9.3}	{-10.6}	{-11.3}	-9.8	
NaBr	-0.5	-1.8	-2.6	-4.0	-7.1	-11.0	-14.9	-17.9	-20.0			-25.4	308, 315
NaBr	-0.59	-1.36	-2.20	-3.67	-6.18	-10.57	-14.52	-17.37	-19.76	-21.93	-23.69	-24.43	305
NaBr	-0.59	-0.90	-1.82	-4.00	-6.57	-9.40	-12.38	-15.40	-18.34	-21.08	-23.50	-25.52	306
NaBr		-1.4	-2.2	-3.9	-6.6	-10.3	-13.9	-16.9	-19.4	-21.5	-23.6	-25.1	
NaI	-7.5	-3.2	-5.5	-8.8	-14.2	-19.5	-25.1					-40.6	308
NaI	-7.53	-1.85	-3.57	-8.01	-13.57	-18.35	-23.75	-28.64	-32.75	-36.03	-38.60	-40.82	305
NaI	-7.53	-2.20	-4.51	-9.35	-14.36	-19.37	-24.23	-28.77	-32.83	-36.24	-38.86	-40.58	306
NaI		-2.4	-4.5	-8.7	-14.0	-19.1	-24.4	-28.7	-32.8	-36.1	-38.7	-40.7	
NaOH	-43.9	0.0	0.5	12.6	19.9	25.8	30.1	32.9	34.8			43.9	308, 315
NaClO ₄	13.9	-0.4	-1.3	-7.6	-17.6	-27.9	-35.1	(-41.5)	-44.5	(-47.2)	-48.9	-49.0	309
NaBPh ₄	-18.8	14.7	16.8	13.9	-2.6	-16.3	-26.3	-32.7	-35.8			-41.0	308, 315
KCl	17.15	-0.86	-0.84	-1.11	-3.50	-6.33	-9.18	-11.76	-13.90	-15.57	-16.85	-17.96	305
KCl	17.41	0.32	0.33	-0.54	-2.34	-4.78	-8.23	-10.34	-12.88	-13.87	-14.88	-15.90	306
KCl		-1.76	-2.66	-1.10	-0.89								307
KCl		-0.8	-1.1	-0.9	-2.2	-5.6	-8.7	-11.1	-13.4	-14.7	-15.9	-16.9	
KBr	19.87	-1.75	-2.80	-4.81	-8.52	-12.77	-16.84	-20.30	-23.07	-25.40	-27.86	-31.36	305
KBr	19.87	-1.72	-2.50	-4.21	-8.67	-14.96	-17.69	-20.88	-23.60	-25.84	-27.95	-30.53	306
KBr		-1.7	-2.7	-4.5	-8.6	-13.9	-17.3	-20.6	-23.3	-25.6	-27.9	-30.9	
KI		-2.65	-4.80	-8.79	-14.42	-20.98	-27.71	-33.86	-38.67				310
KI	20.33	-2.96	-5.13	-9.38	-15.28	-21.89	-28.11	-33.84	-38.64	-42.49	-45.57	-48.33	305
KI	20.33	-2.24	-4.40	-9.59	-15.54	-21.82	-28.04	-33.85	-38.93	-43.01	-45.85	-47.25	306
KI		-2.6	-4.8	-9.3	-15.1	-21.6	-28.0	-33.8	-38.7	-42.7	-45.7	-47.8	
RbCl	16.74	-1.27	-1.11	-1.34	-3.26	-6.18	-9.38	-12.36	-14.87	-16.84	-18.42	-19.96	305, 316
RbCl	17.28	-0.28	-1.05	-2.16	-3.50							-14.64	306
RbCl		-0.8	-1.1	-1.3	-3.4	{-6.2}	{-9.4}	{-12.4}	{-14.9}	{-16.8}	{-18.4}	-17.3	
RbBr	21.88	-2.13	-3.06	-4.88	-8.39	-12.68	-16.96	-20.75	-23.94	-26.71	-29.55	-33.31	305, 316
RbI	25.10	-3.02	-4.89	-9.27	-14.62	-21.06	-27.64	-33.49	-38.28	-42.13	-45.69	-50.08	305, 316
Rb ₂ SO ₄		-3.18	-8.39	-4.54	17.70	45.08		62.85	27.05				311
CsCl	17.41	-1.64	-1.74	-2.17	-4.21	-4.84	-8.10	-11.43	-14.24	-16.04	-16.49	-15.36	305, 316
CsCl	17.78	-0.39	-0.43	-0.62	-2.23							-13.39	306
CsCl		-1.0	-1.1	-1.4	-3.2	{-4.8}	{-8.1}	{-11.4}	{-14.2}	{-16.0}	{-16.5}	-14.4	
CsBr	26.19	-2.46	-3.71	-5.78	-8.66	-11.36	-15.76	-19.87	-23.31	-25.89	-27.62	-28.70	305, 316
CsI	33.26	-3.29	-5.55	-10.26	-15.86	-19.57	-25.78	-32.30	-37.76	-41.54	-43.80	-45.44	305, 316
Cs ₂ SO ₄		-2.19	-6.93	-2.16									311
NH ₄ I		-0.23	-3.43	-9.39	-22.89	-34.05	-39.77						312
NH ₄ I	13.70	-2.15	-5.31		-23.03								92
NH₄I		-1.2	-4.4	{-9.4}	-23.0	{-34.0}	{-39.8}						
NH ₄ NO ₃	25.69	-1.23	-2.57	-6.76	-13.62	-19.99	-25.04	-30.29	-33.01	-34.93	-36.59	-38.45	268 ^a
Bu ₄ NCl	-30.54						49.01	48.51	47.63	45.21		43.10	313
Bu ₄ NCl	-31.0	14.3	25.5	36.8	43.5	47.4	49.0					41.8	308
Bu ₄ NBr	-9.20						39.02	36.60	34.66	33.35		30.54	313
Bu ₄ NBr	-8.4	12.3	22.1	29.3	37.6	38.4	36.4					26.4	308
Bu ₄ NI	15.90						18.90	17.93	17.11	15.58		14.23	313
Bu ₄ NI	16.7	12.7	25.7	29.3	32.5	33.0	30.11					13.4	308
Bu ₄ NBBu ₄	-50.21						104.21	105.38	95.55	95.78		91.63	313
DcMe ₃ NBr	32.00	-4.6											30
Ph ₄ PBr	8.0	9.5	11.3	13.4	9.9	6.1	2.8	0.2	-1.1			-6.5	308
MgCl ₂	-159.83	-2.25	(-4.32)	-7.96									314
CaCl ₂	-80.80	-5.43	(-8.93)	-10.16									314
SrCl ₂	-51.24	-3.47		-6.90									44
BaCl ₂	-14.30	-2.94		-3.41									44
CuCl ₂	-50.9	-0.6	-2.5	-4.3	-8.4	-14.4	-16.1	(-18.7)	-21.3	(-22.4)	-23.7	-25.8	318
Ni(ClO ₄) ₂	163.6	-1.0	-5.9	-24.4	-47.1	-68.5	-84.9	(-95.2)	-97.9	(-100.0)	-101.0	-101.3	309

^a Slightly different values are given by the same authors elsewhere.³⁶⁷

each of the sodium and potassium halides and between two sets for rubidium and cesium chlorides at most solvent compositions. The averaged values are therefore classified as Recommended or Tentative according to the availability of the data.

The Kharkov group published two sets of data for NH₄I^{92,312} that are in good agreement; the averaged values are classified Tentative pending independent confirmation. The data reported by Krestov's group for NH₄NO₃²⁶⁸ include earlier²⁹⁷ and additional data.

Table 60. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{DMSO})/\text{kJ mol}^{-1}$, 298.15 K, TPTB Assumption, as a Function of $100x_{\text{DMSO}}$

ion	MX data	5	10	20	30	40	50	60	70	80	90	100
H ⁺	HClO ₄	2.6	0.9	-8.0	-20.0							
Li ⁺	Li(Cl,Br,I)	2.1	1.4	-3.6	-12.7	-19.9	-25.1	-27.9	-29.3	-29.5	-28.6	-27.8
Na ⁺	NaBPh ₄	1.9	1.6	-1.7	-9.5	-16.4	-21.5	-24.9	-27.0	-28.6	-29.5	-29.8
K ⁺	K(Cl,Br,I)	1.5	1.1	-2.2	-11.0	-19.2	-25.1	-28.9	-31.7	-33.6	-34.8	-36.5
Rb ⁺	Rb(Cl,Br,I)	1.2	1.0	-2.5	-11.1	-18.9	-25.1	-29.3	-32.3	-34.4	-36.2	-38.2
Cs ⁺	Cs(Cl,Br,I)	0.9	0.5	-3.1	-11.6	-17.5	-23.7	-28.3	-31.7	-33.7	-34.3	-34.1
NH ₄ ⁺	NH ₄ NO ₃	2.9	2.4	-2.6	-12.1	-20.1	-26.6	-31.0	-34.1	-35.9	-36.7	-37.9
Ag ⁺	Ag(Cl,Br,I)	-0.9	-4.8	-14.5	-25.2	-35.9	-42.0	-46.1	-48.4	-49.8	-50.5	-51.5
Bu ₄ N ⁺	Bu ₄ N(Cl,Br,I)	16.3	28.4	34.5	35.5	34.0	30.4	27.3	26.6	25.5	(-26.6)	23.3
DcMe ₃ N ⁺	DcMe ₃ NI	-1.4										
Ph ₄ P ⁺	Ph ₄ PBPh ₄	12.8	15.1	15.6	6.9	0.1	-4.8	-7.8	-8.8	(-10.1)	(-10.5)	-11.2
Mg ²⁺	MgCl ₂	1.8	-0.5	-10.1								
Ca ²⁺	CaCl ₂	-1.4	-5.1	-12.3								
Sr ²⁺	SrCl ₂	0.6		-9.0								
Ba ²⁺	BaCl ₂	1.1		-5.5								
Ni ²⁺	NiClO ₄	3.6	0.0	-12.7	-31.0	-45.4	-57.7	-61.9	-63.0	-62.8	-62.2	-62.9
Cu ²⁺	CuCl ₂	3.4	1.3	-6.4	-25.6	-41.1	-49.5	-52.9	-56.9	-58.5	-60.1	-65.9
Cl ⁻	NaCl	-2.0	-1.9	1.1	8.6	13.3	16.7	17.1	17.8	18.1	18.2	20.0
Br ⁻	NaBr	-3.3	-3.8	-2.1	2.9	6.0	7.6	8.0	7.7	7.1	5.9	4.7
I ⁻	NaI	-4.3	-6.2	-7.0	-4.5	-2.7	-2.9	-3.8	-5.7	-7.5	-9.2	-10.9
OH ⁻	NaOH	-1.9	-1.2	14.4	29.4	42.1	51.6	57.8	61.8			73.7
NO ₃ ⁻	LiNO ₃	-4.0	-5.0	-4.9	-1.6	0.1	1.0	1.0	0.9	0.7	0.0	-0.5
ClO ₄ ⁻	NaClO ₄	-2.3	-2.9	-5.9	-8.1	-11.5	-13.6	-16.6	-17.5	-18.6	-19.4	-19.2
BBu ₄ ⁻	Bu ₄ NBBu ₄						73.8	78.1	69.0	70.3		68.4
BPh ₄ ⁻	Ph ₄ PBPh ₄	12.8	15.1	15.6	6.9	0.1	-4.8	-7.8	-8.8	(-10.1)	(-10.5)	-11.2

Fuchs and co-workers reported results for some tetrabutylammonium salts in two publications;^{308,313} the data overlap at only one composition $x_{\text{DMSO}} = 0.5$. They are in good agreement except for Bu₄NI. A detailed consideration of the (MBr–MI) and (MCl–MBr) additivities indicates that all these data may have uncertainties of 2–4 kJ/mol but that the earlier study of Bu₄NI³¹³ is certainly too low by ~8 kJ/mol.

2. Ionic Enthalpies of Transfer

Despite the large number of salts that have been studied in this system (Table 59), relatively few ionic $\Delta_t H^\circ$ values can be derived. Table 60 summarizes the values for 11 monovalent and 6 divalent cations and 8 monovalent anions, calculated via the TPTB assumption using the data for NaBPh₄, Ph₄PBr, and NaBr. It is interesting to note that the equal division of $\Delta_t H^\circ$ for Bu₄NBBu₄ between its cation and anion results in $\Delta_t H^\circ(\text{ion})$ values that differ from the TPTB values by some 50 kJ mol⁻¹. This is surely outside the experimental error of the data and the uncertainty in the TPTB assumption.

As with other strong donor cosolvents, the $\Delta_t H^\circ(M^{n+})$ values are negative for transfer into the mixtures, although they pass through a small maximum at low DMSO concentrations. Similarly, the anion values pass through a small minimum before increasing as the concentration of the aprotic (weak acceptor) DMSO increases. Similar to the HMPT system (section IV.P), $\Delta_t H^\circ(\text{ion})$ is exothermic for I⁻ and, in this case at least, also for ClO₄⁻. The $\Delta_t H^\circ(\text{ion})$ values for BBu₄⁻ and Bu₄N⁺, both of which are hydrophobic, are very endothermic. There is no clear reason the value for BBu₄⁻ is approximately twice that of Bu₄N⁺ on the TPTB scale, even though DMSO undoubtedly interacts more strongly with cations than anions. This difference implies either a problem with the TPTB assumption in these mixtures or that the $\Delta_t H^\circ(\text{Bu}_4\text{NBBu}_4)$ on which the ionic values are

based are in error. Measurements with salts of the rather unstable BBu₄⁻ are difficult.

3. Entropy Data for Electrolytes

Entropy data are available for 14 1:1 electrolytes (Table 61), although there are independent sets for only NaCl and KCl; in both cases agreement is excellent, within $\pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$. Additivity checks, where possible, suggest that the data are reasonably consistent, but no further assessment is possible.

4. Ionic Entropies of Transfer

There are no $\Delta_t S^\circ$ data for the electrolytes necessary to apply the TA(P)TB assumption. Thus, ionic $\Delta_t S^\circ$ values were obtained via the GHSE using the $\Delta_t H^\circ(\text{ion})$ values in Table 59 based on the TPTB assumption and the previously reported $\Delta_t G^\circ$ values¹ based on the TATB assumption in combination with the electrolyte $\Delta_t S^\circ$ values from Table 61. The values so obtained are summarized in Table 62.

With the exception of the large hydrophobic organic ions and NH₄⁺, the $\Delta_t S^\circ(\text{ion})$ values are mostly negative for transfer into the mixtures, becoming more so as the size of the ion increases. The positive $\Delta_t S^\circ$ for the hydrophobic ions are typical. That for NH₄⁺ may reflect strong hydrogen bonding to DMSO.

R. Transfers from Water to Water + Tetramethylene Sulfone (TMS)

The enthalpy of transfer data between water and aqueous–TMS mixtures for eight 1:1 electrolytes at 30° C, reported by Castagnolo et al.,³¹⁹ are summarized in Table 63. Additivity (MCl–MClO₄) indicates that the data are internally consistent. However, in the absence of any independent confirmation, no further assessment is possible. These data allow the estimation of $\Delta_t H^\circ$ for the three cations and five anions (including BPh₄⁻ = Ph₄P⁺) up to 60 mol %

Table 61. $\Delta_t S^\circ(\text{MX}, w \rightarrow w + \text{DMSO})/\text{J K}^{-1} \text{mol}^{-1}$, 298.15 K, mol/L Scale, as a Function of $100x_{\text{DMSO}}$

MX	5	10	20	30	40	50	60	70	80	90	100	ref
LiCl	-5.0	-10.0	-19.3	-28.1	-37.0	-46.3	-56.5	-67.6	-80.1	-94.0	-109.5	306
NaCl	-5.9	-12.2	-24.5	-36.7	-48.7	-60.7	-72.5	-84.3	-96.2	-108.3	-120.7	306
NaCl	-7.2	-16.3	-31.7	-38.9								307
NaCl	-7	-14	-28	-38								
NaBr	-6.6	-12.9	-26.3	-40.5	-54.8	-68.7	-81.8	-94.1	-105.2	-115.4	-124.8	306
NaI	-6.8	-14.0	-30.8	-48.9	-66.6	-82.6	-96.2	-107.5	-116.9	-125.4	-134.7	306
KCl	-5.7	-12.9	-30.0	-48.6	-67.1	-84.0	-98.7	-111.1	-121.6	-131.3	-141.8	306
KCl	-12.7	-21.8	-30.9	-41.0								307
KCl	-9	-17	-30	-45								
KBr	-8.2	-17.0	-35.9	-55.4	-74.0	-90.9	-105.8	-118.8	-130.6	-142.4	-155.7	306
KI	-7.9	-15.8	-34.0	-54.5	-76.0	-97.2	-117.1	-134.6	-148.8	-158.9	-164.1	306
RbCl	-6.7	-14.5	-32.3	-51.5	-70.2	-87.3	-102.1	-114.3	-124.3	-133.0	-141.7	306
CsCl	-6.4	-12.7	-26.5	-41.6	-57.9	-74.9	-91.7	-107.3	-120.4	-129.2	-131.9	306
AgCl	-10.3	-20.4	-37.4	-51.4	-63.6	-74.9	-85.9	-96.8	-107.3	-117.0	-124.9	306
AgBr	-15.5	-29.5	-51.0	-66.6	-78.9	-89.8	-100.4	-111.0	-121.0	-129.2	-133.3	306
AgI	-17.0	-31.3	-54.6	-73.2	-88.9	-102.8	-115.5	-126.9	-136.2	-141.8	-141.7	306
NH ₄ I	-2.2	1.9	5.8	22.7	36.3	44.0						312
Bu ₄ NBr	32.6	59.9	98.5	119.1	126.1	123.7						306

Table 62. $\Delta_t S^\circ(\text{ion}, w \rightarrow w + \text{DMSO})/\text{kJ mol}^{-1}$, 298.15 K, mol/L Scale, TPTB Assumption, as a Function of $100x_{\text{DMSO}}$

ion	5	10	20	30	40	50	60	70	80	90	100
H ⁺	15	16	5	-19							
Li ⁺	13	14	9	-8	-19	-30	-37	-45	-45	-40	-35
Na ⁺	8	8	2	-15	-28	-38	-47	-53	-57	-58	-57
K ⁺	6	6	-3	-26	-46	-57	-68	-76	-78	-79	-82
Rb ⁺	5	4	-2	-25	-43	-60	-75	-84	-88	-87	-94
Cs ⁺	5	4	-3	-22	-32	-46	-58	-68	-73	-73	-71
Ag ⁺	5	-5	-21	-40	-58	-67	-73	-71	-68	-66	-65
NH ₄ ⁺	15	25	38	55	70	84					
Bu ₄ N ⁺	61	105	140	160	166	159					
Ph ₄ P ⁺	60	80	107	97	87	81	81	83	(87)	(91)	91
Cl ⁻	-14	-19	-25	-20	-10	-11	-11	-16	-22	-29	-34
Br ⁻	-17	-23	-30	-27	-25	-29	-33	-41	-51	-61	-70
I ⁻	-17	-23	-32	-32	-33	-40	-47	-56	-66	-74	-79
BPh ₄ ⁻	60	80	107	97	87	81	81	83	(87)	(91)	91

Table 63. $\Delta_t H^\circ(\text{MX}, w \rightarrow w + \text{TMS})/\text{kJ mol}^{-1}$, 303.15 K, as a Function of $100x_{\text{TMS}}$

MX	$\Delta_{\text{sln}} H^\circ$	5	10	20	30	40	50	60	100	ref
NaCl	3.89	-2.72	-4.55	-7.08	-8.41	-8.90	-8.92	-8.83		319
NaBr	-0.59	-4.45	-7.26	-10.44	-11.93	-16.79	-19.43	-19.86		319
NaI	-7.53	-5.99	-10.34	-15.82	-18.47			-26.65		319
NaClO ₄	13.89	-6.07	-10.91	-17.57	-21.43			-30.70		319
NaBPh ₄	-19.96	1.72	-8.37	-15.83	-20.21	-24.19	-27.77	-30.94	-25.65	319
KCl	17.20	-4.61	-7.77	-11.88	-13.93			-18.35		319
KClO ₄	51.04	-8.09	-14.33	-22.69	-27.27			-38.33		319
Ph ₄ PBr	10.42	3.39	0.16	-3.56	-4.97	-6.43	-7.93	-9.48	-3.01	319

Table 64. $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{TMS})/\text{kJ mol}^{-1}$, 303.15 K, as a Function of $100x_{\text{TMS}}$

ion	MX data	5	10	20	30	40	50	60
Na ⁺	NaBPh ₄	-3.1	-7.9	-11.4	-13.6	-17.3	-19.6	-20.7
K ⁺	KCl	-4.9	-11.1	-16.1	-19.1			-30.2
Ph ₄ P ⁺	Ph ₄ PBPh ₄	4.8	-0.5	-4.5	-6.6	-6.9	-8.1	-10.3
Cl ⁻	NaCl	0.3	3.3	4.3	5.2	8.4	10.87	11.8
Br ⁻	Ph ₄ PBr	-1.4	0.6	0.9	1.6	0.5	0.2	0.8
I ⁻	NaI	-2.9	-2.4	-4.5	-4.9			-6.0
ClO ₄ ⁻	NaClO ₄	-3.1	-3.2	-6.5	-8.2			-8.1
BPh ₄ ⁻	Ph ₄ PBPh ₄	4.8	-0.5	-4.5	-6.6	-6.9	-19.6	-20.7

TMS (Table 64). No entropy data have been reported in this system.

V. Discussion

A. Transfer Energetics

1. Energetics of Solvent Replacement

It is convenient to divide the surroundings of an ion into two regions: (i) the near-neighbor solvent

molecules that occupy the coordination or first solvation shell of the ion and (ii) the remaining solvent molecules beyond the coordination sphere.

The interaction of an ion with the solvent molecules in its coordination shell is primarily an acid–base (acceptor–donor) interaction, with cations interacting strongly with basic (strong donor) solvents such as DMSO or the amides and anions with acidic (strong acceptor) solvents such as water or the alcohols. This

is born out by the single-ion transfer enthalpies for cations between water and the neat solvents, which are negative to strongly basic solvents such as DMSO, DMF, and HMPT (donor numbers 30, 27, and 39, respectively⁷¹) but positive to weakly basic solvents such as AN (donor number 14). Similarly, the transfer enthalpies of anions from water to (neat) aprotic solvents such as DMSO, DMF, and AN (acceptor numbers 19, 16, and 10, respectively) are strongly positive, while those to the lower alcohols (with acceptor numbers of ~ 40) are less positive or, in the case of large anions, even slightly negative. In addition, there are significant effects from soft-soft interactions,³²⁰ most strikingly in the cases of the d^{10} ions (such as Ag^+), which have large negative transfer enthalpies to AN.

In mixed solvents, the possibility of preferential solvation arises; that is, the composition of the coordination sphere of the ion may differ from that of the surrounding bulk solvent. In the simplest case the ion will be preferentially solvated by the component with which it interacts more strongly and the transfer enthalpy is then determined largely by the composition of the coordination shell as

$$\Delta_t H^\circ(\text{ion}, A \rightarrow A+B) = x_B^L \Delta_t H^\circ(\text{ion}, A \rightarrow B) \quad (25)$$

where x_B^L represents the local mole fraction of component B, i.e., in the coordination shell of the ion.

The difference in composition between the coordination shell of the ion and the bulk solvent also leads to an unfavorable entropy of transfer. In effect this is an entropy arising from demixing of the solvent and has the form

$$\Delta_t S^\circ(\text{ion}, A \rightarrow A+B) = -n_A R \ln(x_A^L/x_A) - n_B R \ln(x_B^L/x_B) \quad (26)$$

where n_A and n_B are the numbers of molecules of components A and B in the coordination shell of the ion.

These relationships take no account of changes in solvent-solvent interactions nor of changes in the interactions of coordinated solvent molecules with the surrounding medium. They also take no account of changes in the permittivity of the solvent, although this could be readily included. The applicability of these relationships has been demonstrated for ions in simple mixtures of nonaqueous solvents.^{321,322}

In more complex mixed solvents, solvent-solvent interactions are composition dependent, which will affect the standard transfer enthalpy and entropy. Thus, considering the enthalpy, an ion occupies a cavity in the solvent in which it is surrounded by some number, n , of solvent molecules, each of which will have broken some fraction, α , of its solvent-solvent interactions. This will make an endothermic contribution, $-\alpha n \Delta H^*$ (where ΔH^* is the enthalpy of solvent-solvent interaction) to the enthalpy of solution. In a mixed solvent the cavity is surrounded by n_A and n_B molecules of components A and B. The transfer enthalpy from pure component A to a mixture of A and B will then contain a contribution from changes in the enthalpy of cavity formation as

$$\Delta_{t,\text{cav}} H(\text{ion}, A \rightarrow A+B) = -\alpha_A n_A \Delta H_A^* - \alpha_B n_B \Delta H_B^* + \alpha_A^\circ n_A^\circ \Delta H_A^{\circ*} \quad (27)$$

where the superscript o refers to values in pure solvent A.

The ion may influence the interactions between solvent molecules, for example, by strengthening or weakening hydrogen bonds between them. If it is assumed that the effect on solvent-solvent interactions is some fraction β of the solvent-solvent interaction enthalpy, then the transfer enthalpy arising from solvent reorganization can be written as

$$\Delta_{t,\text{reorg}} H(\text{ion}, A \rightarrow A+B) = -\beta_A N_A \Delta H_A^* - \beta_B N_B \Delta H_B^* + \beta_A^\circ N_A^\circ \Delta H_A^{\circ*} \quad (28)$$

where N ($= n$) represents the number of solvent molecules affected and β is the average proportionality constant (note β is negative if solvent-solvent bonds are strengthened). Logically, cavity formation and solvent reorganization will also make contributions to the transfer entropy. These have forms similar to those of eqs 27 and 28.

Making the assumptions that α , β , n , and N are the same for both components of the mixture and are composition independent leads to eqs 29 and 30 for the transfer enthalpies and entropies

$$\Delta_t H^\circ(\text{ion}, A \rightarrow A+B) = x_B^L \Delta_t H^\circ(\text{ion}, A \rightarrow B) - (\alpha n + \beta N)(x_A^L L_A + x_B^L L_B) \quad (29)$$

$$\Delta_t S^\circ(\text{ion}, A \rightarrow A+B) = x_B^L \Delta_t S^\circ(\text{ion}, A \rightarrow B) - (\alpha n + \beta N)(x_A^L \Delta S_A + x_B^L \Delta S_B) - NR[x_A^L \ln(x_A^L/x_A) + x_B^L \ln(x_B^L/x_B)] \quad (30)$$

In eqs 29 and 30, L_i and ΔS_i are, respectively, the partial molar excess enthalpy and entropy of component i in the mixed solvent. These equations have been discussed in detail elsewhere³²²⁻³²⁴ In the present case, they are written retaining x_i^L to make clear their inter-relationships; in previous work the x_i^L values were calculated from the solvent composition, using a simple mass action treatment

$$(n_B/n_A) = p(x_B/x_A)$$

which gives

$$x_A^L = x_A/(x_A + px_B) \text{ and } x_B^L = px_B/(x_A + px_B) \quad (31)$$

This has been demonstrated to hold for electrolytes in aqueous methanol systems, where the transfer enthalpies and entropies were fitted to eqs 29 or 30 assuming that the ions are randomly solvated. The case of random solvation is particularly straightforward since, for example, eq 29 reduces to

$$\Delta_t H^\circ(\text{ion}, A \rightarrow A+B) = x_B \Delta_t H^\circ(\text{ion}, A \rightarrow B) - (\alpha n + \beta N) \Delta H^E \quad (32)$$

where ΔH^E is the excess enthalpy of mixing of the

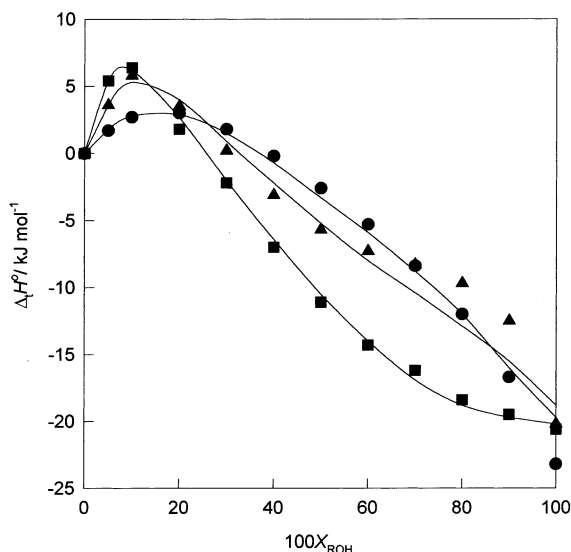


Figure 11. Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, of NaI at 25 °C from water into aqueous mixtures with various alcohols: ● MeOH, ▲ EtOH, ■ 2-PrOH. Lines are calculated via eq 32; see text.

solvents at composition x_B . In the aqueous alcohol systems a number of 1:1 electrolytes follow eq 32, suggesting that they are randomly solvated. This is illustrated in Figure 11, which shows the fits to eq 32 of the $\Delta_t H^\circ$ values for NaI in aqueous methanol, ethanol, and 2-propanol.

2. Entropy–Enthalpy Compensation

The question of entropy–enthalpy compensation, when significant changes in the entropies ($T\Delta_t S^\circ$) and enthalpies ($\Delta_t H^\circ$) accompanying a chemical process largely cancel each other, leading to relatively small changes in the corresponding Gibbs energies ($\Delta_t G^\circ$), has been studied for many systems and types of processes. Examples of this effect have been reported for protein unfolding, protein–DNA interactions, drug–acceptor interactions, chiral recognition, supramolecular host–guest chemistry, and surfactant micellization, and it has also been used for understanding chromatographic separations. Some recent references to such studies include those in refs 271 and 325–334. It should also be noted that when entropy–enthalpy compensation occurs, even though the changes in $\Delta_t G^\circ$ are much smaller than those for $\Delta_t H^\circ$ and $T\Delta_t S^\circ$ they may still have significant chemical impacts.

The transfer of electrolytes and ions from water to aqueous–organic solvent mixtures may also exhibit such compensation effects. Entropy–enthalpy compensation for the transfer processes must usually be sought at reasonably high values of x_s since, by definition, $\Delta_t Y^\circ = 0$ at $x_s = 0$ and the values of $\Delta_t Y^\circ$ at low x_s are generally small for electrolytes containing relatively small ions. An exception to this may occur when large ions are involved, as the magnitudes of $\Delta_t Y^\circ$ for electrolytes containing such ions may be large even at very low x_s . However, because the effects for cations and anions may be quite different (see below), it is more appropriate to look for compensation effects with respect to the transfer of individual ions rather than of electrolytes.

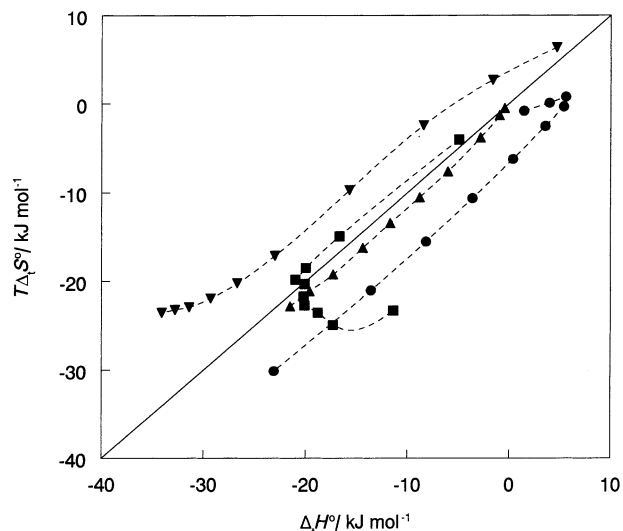


Figure 12. Entropy–enthalpy compensation ($\Delta_t H^\circ$ and $T\Delta_t S^\circ$ at 25 °C, in kJ mol^{-1}) for the transfer at 25 °C of Na^+ from water into aqueous mixtures of various solvents: ● MeOH, ▲ EG, ▼ DMF, ■ AN.

The behavior of differing ions is quite diverse. Figure 12 demonstrates that entropy–enthalpy compensation does indeed take place for small cations such as Na^+ in many solvents. Such effects are most evident for transfer between water and aqueous EG, where the magnitude of $\Delta_t G^\circ$ ($< 2 \text{ kJ mol}^{-1}$) is much smaller than those of $\Delta_t H^\circ$ and $T\Delta_t S^\circ$ (which are as large as -20 kJ mol^{-1}). Comparable effects are obtained for small cations in other protic solvents, such as MeOH, and in aprotic solvents, such as DMF and AN. Similar trends are also noted for larger monatomic cations, such as Cs^+ (see for example the data available for MeOH, DMF, and AN) and likewise for Me_4N^+ , where the entropy–enthalpy compensation is pronounced in the three solvents for which data are available. For the larger Bu_4N^+ , some compensation takes place at low x_s but the entropy and enthalpy diverge significantly at higher x_s , with the (positive) entropy contribution being considerably higher than the (positive) enthalpy contribution, thereby producing appreciable (negative) $\Delta_t G^\circ$ values.

On the other hand, quite different trends are noted for the monatomic anions, such as Cl^- (plotted in Figure 13). The mostly negative values of $T\Delta_t S^\circ$ for Cl^- are much larger in magnitude than the mostly positive $\Delta_t H^\circ$ values, especially for aqueous–AN mixtures. Similar although somewhat smaller diverging effects are observed for I^- . For the much larger BPh_4^- anion (and necessarily, according to the extrathermodynamic assumption employed, for the large cations Ph_4P^+ and Ph_4As^+), the invariably positive $T\Delta_t S^\circ$ values are considerably larger in magnitude than the $\Delta_t H^\circ$ values. Thus, for anions and very large cations (at least at high x_s) the entropies and enthalpies of transfer diverge and little entropy–enthalpy compensation is apparent.

The interactions that take place when an ion i is transferred from highly structured water to an aqueous–organic solvent mixture having its own structure, are very complex. Such interactions include the breaking (subscript b) of direct ion–water bonds and making (subscript m) of direct ion–organic solvent

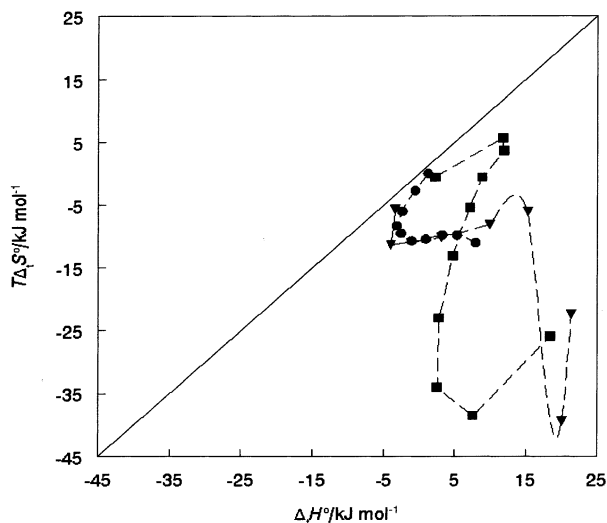


Figure 13. Entropy–enthalpy compensation ($\Delta_t H^\circ$ and $T\Delta_t S^\circ$ at 25 °C, in kJ mol^{-1}) for the transfer of Cl^- from water into aqueous mixtures of various solvents: ● MeOH, ▼ DMF, ■ AN.

bonds as well as the formation of new water–water H-bonds and the breaking of solvent–solvent attractive interactions and the affecting (subscript af) of any solvent–water interactions in the vicinity of the ion. Therefore, the enthalpies of transfer can be considered as being made up of the following five terms

$$\Delta_t H^\circ = \Delta_{b,i-w}H + \Delta_{m,i-s}H + \Delta_{m,w-w}H + \Delta_{b,s-s}H + \Delta_{af,w-s}H \quad (33)$$

These terms have +ve, -ve, -ve, +ve, and unknown signs, respectively. It is expected that the sum of the first two terms may often be negative, but the value of this sum relative to the sum of the remaining three terms may make the overall $\Delta_t H^\circ$ either positive or negative, depending on the ion i and the solvent s .

Similarly, the entropies of transfer can be written as a sum of terms for all the processes that occur

$$\Delta_t S^\circ = \Delta_{b,i-w}S + \Delta_{m,i-s}S + \Delta_{m,w-w}S + \Delta_{b,s-s}S + \Delta_{af,w-s}S \quad (34)$$

where the signs of the terms should be the same as those of the enthalpies, except that the breaking of solvent–solvent interactions usually has a relatively small entropy (since nearly all the solvents are less structured than water). It should be possible to distinguish between the entropy changes of hydrophobic and hydrophilic ions. The former should have a large positive value of $\Delta_{b,i-w}S$ because of their hydrophobic hydration and a smaller negative $\Delta_{m,i-w}S$, so that the sum of these two terms should be positive. As $\Delta_{m,i-s}S$ would also be relatively small for these large ions, the overall value of $\Delta_t S^\circ$ should therefore be positive. For hydrophilic ions, on the other hand, the entropic effects of the water molecules released upon breaking their i – w bonds are largely counterbalanced when these molecules join the structured bulk water, i.e., $\Delta_{b,i-w}S + \Delta_{m,w-w}S \approx 0$. The dominant entropy term is therefore the moderately negative contribution from $\Delta_{m,i-s}S$.

Because of the complexity of these effects, it is not possible at present to compare the overall $T\Delta_t S^\circ$ and $\Delta_t H^\circ$ values and predict whether entropy–enthalpy compensation or divergence should take place, based on the properties of the ions and/or of the solvents. However, it is clear that, contrary to early assertions,³³⁸ the phenomenon of entropy–enthalpy compensation is *not* characteristic of solutions in water nor due exclusively to its structuredness but is manifested in rather unstructured mixed aqueous–organic solvents and even in neat organic solvents. For example, the transfer of Cs^+ from water into AN or high x_{AN} mixtures of AN with water (which exhibits compensation) contrasts with that of Cl^- (which exhibits divergence). If leaving the structured aqueous environment by the ions were the dominant factor, both ions would show similar behavior. Indeed, complexation reactions in nonaqueous AN and DMF, for example, have recently been shown to exhibit entropy–enthalpy compensation.³³⁰

B. Behavior of Specific Systems

1. Protic Solvents: Alcohols

The shape of the $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{ROH})$ vs x_{ROH} curves depends on the properties of the ions, on one hand (discussed further below), and on those of the aqueous–organic mixed solvents, on the other. The alcohols, in addition to accepting H-bonds from water, are also capable of H-bond donation: to other alcohol molecules, to water, and to anions. This characteristic distinguishes them as a class (along with the non- and monosubstituted amides) from other water-miscible solvents. The alcohols are, however, weaker H-bond donors than water, with their donor strength (for example as measured by the Kamlet–Taft α parameter) decreasing in the order methanol > primary > secondary > tertiary alcohol. On the other hand, the ability of ROH to accept H-bonds (e.g., as measured by the Kamlet–Taft β parameter) increases in the reverse order.⁷¹

These statements pertain to the neat solvents, so the question arises as to whether the properties of the aqueous mixtures change in proportion to their composition. In fact, they do not: a gradual increase of α and a decrease of β is observed when water is added to 2-PrOH or t -BuOH. However, a steep increase in α and a steep decrease in β are noted at $x_w > 0.95$ for 2-PrOH and 0.975 for t -BuOH.³³⁹ This means that for $x_{2-\text{PrOH}} \leq 0.050$ and $x_{t-\text{BuOH}} \leq 0.025$ the H-bonding properties of the mixtures change rather abruptly. Smoother changes are noted for aqueous EtOH and aqueous MeOH, for which the α vs x_s curves have a shallow minimum and β changes gradually as a function of x_s .³⁴⁰ These facts are applicable to the $\Delta_t H^\circ(\text{ion}, w \rightarrow w + \text{ROH})$ curves, where for cations it is the β and for anions the α of the mixtures that would be the major factors involved,³⁶² provided the ions are affected in the same manner as the solvatochromic indicators used for the measurement of these parameters. This presumption, which underlies the attempts to develop ‘universal’ scales of donor and acceptor strength, is by no means self-evident.

A further aspect that is important for the aqueous–alcohol mixtures is the reputed water structure enhancement caused by low concentrations of the alcohols. This effect was invoked by Franks and Ives³⁴¹ to explain the behavior of several thermodynamic properties of these mixtures, such as their excess enthalpies and partial molar volumes. Subsequently, this phenomenon has been used to account for other thermodynamic, transport, and spectroscopic properties of these mixtures.^{340,342,343} More recently, computer simulations using molecular dynamics calculations have confirmed the enhancement of the water H-bonding in dilute aqueous mixtures with alcohols.³⁴⁴ This enhanced H-bonding is not necessarily reflected in the structure of the water in these mixtures, for example, as represented by the monodimensional radial distribution function obtained by, i.e., neutron diffraction,³⁴⁵ but is clearly reflected in the spatial distribution functions.³⁴⁶ The enhanced water structure in these mixtures is analogous to that of heavy water, for which the $\Delta_t H^\circ$ (ion, $\text{H}_2\text{O} \rightarrow \text{D}_2\text{O}$) data have been reported and analyzed by Friedman and Krishnan.³⁴⁷ The values for the alkali metal ions as well as Me_4N^+ , Et_4N^+ , Br^- , and I^- are positive, generally increasing with ion size (except for Et_4N^+). Those for the larger tetraalkylammonium ions as well as F^- and Cl^- are negative. Further aspects of this analogy are given under the discussions of these groups of ions below.

2. Dipolar Aprotic Solvents

The remainder of the solvents for which $\Delta_t H^\circ$ data are available are dipolar aprotic, i.e., they have no proton that can be donated toward the formation of a hydrogen bond but do have a fairly large dipole moment. (Exceptions are FA and UR that are not aprotic and DX that has a low net dipole moment.) Furthermore, many of these solvents have high electron-pair donorities (in many cases higher than that of water) as measured, for example, by the Kamlet–Taft solvatochromic parameter β .^{1,71} These characteristics make them good solvating agents for cations due to ion–dipole interactions and, ultimately, to coordinative bonds with divalent and higher valent cations. By the same token, they are poor solvating agents for anions, lacking the ability to donate hydrogen bonds to them and also because the positive end of their dipoles (the electron density acceptor site) is generally far from the outer edge of the van der Waals envelope of the solvent molecule.

However, since only completely water-miscible solvents are dealt with in this review, they are hydrophilic and interact with the water in the aqueous mixtures, accepting hydrogen bonds from it. The electron pair donicity (hydrogen bond acceptance), β , and hydrogen bond donating ability, α , have been measured for aqueous mixtures with several dipolar aprotic solvents.³⁴⁸ The β values increase gradually with increasing x_s , though not linearly, from that of water to that of the cosolvent (or have a broad maximum in the cases of THF and pyridine) without notable features. The α values decrease from that of water to zero as x_s is increased, with an initial larger negative slope up to $x_s \approx 0.3$ and a more moderate

slope beyond this. In a few cases (THF, AN) the α values have a plateau at intermediate x_s values before going more steeply down to zero. This plateau has been interpreted as indicating the occurrence of microheterogeneity in these mixtures,³⁴⁹ see section V.B.3. Note that the α and β values pertain directly to the solvatochromic indicators used for measuring them. As noted above, it is only by implication that they also apply to ions and other solutes.

In any case, the cations must compete with water molecules for the electron pair donating sites on the dipolar aprotic solvents in the mixtures. Anions must compete in these mixtures with the cosolvent molecules for the hydrogen bonding water molecules. It is the balance of the competing abilities of the species, relative to the situation in purely aqueous media, that determines whether $\Delta_t H^\circ$ is positive or negative.

A further aspect that should be considered with respect to the $\Delta_t H^\circ$ of the larger ions, which break the water structure³⁶⁵ or have extensive hydrophobic hydration³⁴⁷ in aqueous solutions, is whether (in water-rich mixtures with dipolar aprotic solvents) the water structure is unaltered, enhanced, or broken. The evidence concerning this issue is not very clear: apparently conflicting results from various methods of measurement and computer simulations having been reported. It is generally accepted that at very low x_s (at least the smaller) cosolvent molecules can fit into the open spaces in the low-density tetrahedral hydrogen-bonded water structure. As x_s increases beyond ~ 0.02 , these spaces are no longer sufficiently available and the dipoles of the cosolvent molecules orient the water molecules in a manner that is incompatible with this structure. Hence water-structure breaking by the cosolvents takes place, as was found by low-frequency Raman spectroscopy³⁵² for aqueous AC at $x_s \leq 0.06$, by molecular dynamics computer simulations³⁵³ for aqueous DMSO at $x_s = 0.04$ and 0.2 , and various methods³⁴⁹ for aqueous AN at $x_s \geq 0.2$. The consequences of this structure breaking, if it is general for the dipolar aprotic solvents, for the $\Delta_t H^\circ$ of various classes of ions are discussed further below.

3. Microheterogeneous Mixtures

Certain organic solvents, though completely miscible with water at 298 K, split into two liquid phases at higher or lower temperatures. Thus, aqueous–AN mixtures have an upper critical solution temperature of ~ 272 K, whereas aqueous–triethylamine mixtures have a lower critical solution temperature of ~ 290 K. In addition, aqueous–organic mixtures at 298 K may also show microheterogeneity.³⁵⁴ Such mixtures, although being macroscopically a single liquid phase, have microscopic regions where one or another of the components is dominant. The existence of such domains is consistent with X-ray and neutron diffraction studies^{355–359} in a number of aqueous–organic mixtures including (w + AN). The presence of microheterogeneity in (w + AN) is also consistent with light-scattering experiments³⁶¹ and can be inferred from other kinds of data, including NMR chemical shifts, tracer diffusion, reaction kinetics, wavelength shifts of probe absorbances, and the

thermodynamic functions of mixing.³⁴³ Such data show that there are extensive regions of composition of the solvent mixtures where the variation of these functions is minimal. This is interpreted in terms of there being domains of predominance of one or another of the components with substantially invariant composition, even though the relative amounts of these domains may depend on the overall solvent composition. Mixtures of *w* + AN are an example of such a system. Such mixtures have been studied by a great variety of methods, leading to a congruent conclusion about the occurrence of microheterogeneity, though not about the exact composition limits between which it exists.³⁴⁹ In such systems, molecules of one component, i.e., water, tend to be surrounded by molecules of the same type (water in this case) to the essential exclusion of the other component. That is, molecular level domains are formed where molecules of one of the components of a solvent mixture are surrounded mainly by molecules of their own kind. At the boundaries between such domains, individual molecules of the two components mix more freely. Of course, such boundaries are diffuse and changing dynamically.

The local environment of a molecule of a given kind in binary solvent mixtures may be established via Kirkwood–Buff integrals, calculated from the thermodynamic excess functions of mixing.³⁶⁰ The resulting data, either of the local mole fraction of, i.e., water around a water molecule, $x_{w(w)}^L$, or the preferential solvation parameter, $\Delta x_{w(w)} = x_{w(w)}^L - x_w$, are large and positive when preferential solvation takes place; hence, the deficiency of water molecules around a cosolvent molecule, $\Delta x_{w(s)}$, is large and negative. Preferential solvation studied by the use of Kirkwood–Buff integrals confirms evidence from other sources that 1-PrOH, 2-PrOH, *t*-BuOH, THF, DX, and AN have microheterogeneous composition ranges.³⁶⁰

4. Transfer of Alkali Metal Cations

The $\Delta_t H^\circ(M^+, w \rightarrow w + ROH)$ vs x_{ROH} curves, where M^+ is an alkali metal cation (Li^+ to Cs^+) and ROH is MeOH, EtOH, 1-PrOH, 2-PrOH, *t*-BuOH, and EG, show broad similarities that are largely independent of the cation. Typically, these curves show an initial maximum of 2 to 10 kJ mol⁻¹ at low x_{ROH} , followed by a general decrease to ca. -10 to -20 kJ mol⁻¹. The position of the maximum depends on the alcohol but not on the cation. On the other hand, the magnitude of the maximum depends mainly on the alcohol but also decreases somewhat from Li^+ to Cs^+ .

The characteristics of the maximum vary systematically among the alcohols. Thus, its position decreases from $x_{ROH} \approx 0.33$ for MeOH to ~ 0.14 for EtOH and ~ 0.10 for 1-PrOH. A similar trend is observed for the series of methyl-substituted carbinols: MeOH, EtOH, 2-PrOH, and *t*-BuOH. Such effects are illustrated in Figure 14 for K^+ . The magnitude of the maximum increases in the sequence MeOH < EtOH \approx 2-PrOH (for K^+ , the only cation for which reliable data are available in this solvent) < *t*-BuOH. However, the maximum for 1-PrOH does not fit this sequence, being too low. There is also a

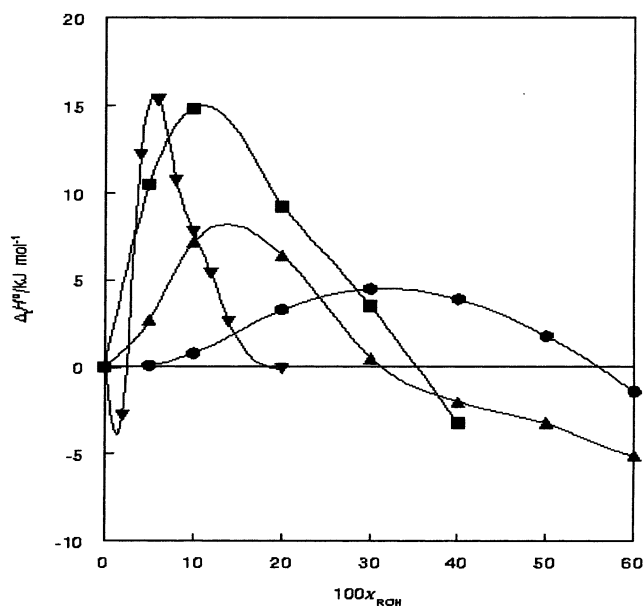


Figure 14. Standard molar enthalpy of transfer, $\Delta_t H^\circ/\text{kJ mol}^{-1}$, of K^+ at 25 °C from water into aqueous mixtures of various alcohols: ● MeOH, ▲ EtOH, ■ 2-PrOH, ▼ *t*-BuOH.

general dependence of the height of the maximum on the cation, with $Na^+ > K^+ > Rb^+ > Cs^+$ and a range of ~ 2 kJ mol⁻¹. However, $Li^+ > Na^+$ for MeOH and EG but $Li^+ < Cs^+$ for the other alcohols for which the data are available. The values of $\Delta_t H^\circ(M^+, w \rightarrow w + ROH)$ for transfer at high x_{ROH} and to the neat cosolvent show a clear-cut reversal with $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

Formamide is a highly structured protic solvent, and the shape of the $\Delta_t H^\circ(M^+, w \rightarrow w + FA)$ vs x_{FA} curves resemble those of the highly structured EG, although the maximum is somewhat higher and occurs at a lower x_s . The curve for Cs^+ transferring into aqueous FA has no maximum, in common with that for EG. The ordering of the cations at low x_{FA} is the same as for the alcohols, but no crossovers occur at high x_{FA} . The curve for Li^+ in FA shows an unusual trend, which is not observed for the alcohols. At low x_{FA} , $Li^+ < Na^+$ but $\Delta_t H^\circ(Li^+, w \rightarrow w + FA)$ curves upward nearing neat FA.

The dipolar aprotic (DPA) solvents AN, DMF, DMA, HMPT, and DMSO have $\Delta_t H^\circ(M^+, w \rightarrow w + s)$ vs x_s curves that are similar to each other and also resemble those for the alcohols. Thus, a maximum occurs near $x_s \approx 0.05$, its height increasing from ~ 2 kJ mol⁻¹ for DMSO to ~ 7 kJ mol⁻¹ for HMPT. The ordering of the curves for the alkali metal cations at low x_s is again $Na^+ > K^+ > Rb^+ > Cs^+$, with $Li^+ > Na^+$ in *w* + AN but with $Li^+ < Cs^+$ for transfer to aqueous HMPT and DMSO (no data are available for DMF and DMA). The reversal of the order of the alkali metal ions noted for the alcohols is repeated for HMPT but not for the other DPA solvents. Aqueous HMPT and AN mixtures have an additional feature in that the values of $\Delta_t H^\circ(M^+, w \rightarrow w + s)$ are nearly constant over a wide composition range, before turning slightly upward as $x_s \rightarrow 1$. The (relatively sparse) data available for THF, DX, and TMS are unusual in several ways. The curve for THF follows a course similar to that noted for the other

DPA solvents, but the maximum, still at $x_s \approx 0.05$, is considerably higher, at $\sim 16 \text{ kJ mol}^{-1}$. The curves for DX and TMS, however, have no maximum for no discernible reason except perhaps the inadequacy of the available data.

For all the cosolvents for which transfer data from water to the neat solvents are known, the $\Delta_t H^\circ(\text{M}^+, w \rightarrow s)$ values are negative, on the order of -10 to -40 kJ mol^{-1} . This effect is more easily understood by considering the reverse transfer, i.e., from the neat cosolvent to water. Such a transfer clearly involves an appreciable positive enthalpy change. The donor atom of all the cosolvents for which data are currently available is oxygen, with the exception of AN. The more bulky solvents, such as HMPT and *t*-BuOH, have larger donicities (expressed for example by the Kamlet-Taft β parameter) than water, but there will be fewer of them around a small ion. Hence, for the transfer of M^+ from $s \rightarrow w$, the terms $\Delta_{m,t-w}H$ and $\Delta_{b,t-s}H$ in the reverse of eq 33 largely cancel each other. Furthermore, for the $s \rightarrow w$ transfer $\Delta_{af,w-s}H$ is necessarily zero and $\Delta_{m,s-s}H$ would be expected to be small for solvents with no or little structure. The remaining term, $\Delta_{b,w-w}H$, then carries the burden of explaining the observed positive $\Delta_t H^\circ(\text{M}^+, s \rightarrow w)$ values. The commonly accepted explanation is that this term arises from the energy that has to be invested to create a cavity to accommodate the ion in highly H-bonded water. The more strongly H-bonded the aqueous solvent, the more positive $\Delta_t H^\circ(\text{M}^+, s \rightarrow w)$. Therefore, if the water structure is enhanced relative to that in neat water (e.g., as is the case for D_2O),² then $\Delta_t H^\circ(\text{M}^+, s \rightarrow w + s)$ will be greater than $\Delta_t H^\circ(\text{M}^+, s \rightarrow w)$. That is, a maximum in the $\Delta_t H^\circ(\text{M}^+, s \rightarrow w + s)$ curve should be observable at or near the value of x_s at which the structure is maximally enhanced in enthalpic terms, as is in fact found.

The more or less horizontal portions in the $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + s)$ curves for AN and HMPT noted above possibly originate from microheterogeneity. This phenomenon is well established for $w + \text{AN}$ mixtures³⁴⁹ and would not be unexpected for HMPT with its six methyl groups, despite its high polarity. This effect is more fully described with respect to the behavior of the R_4N^+ ions below.

Entropy curves $\Delta_t S^\circ(\text{M}^+, w \rightarrow w + s)$ vs x_s are available for fewer solvents than for the corresponding enthalpies, but they follow rather similar patterns. Most show a positive maximum at the same x_s values as the enthalpy curves and then go on to rather negative values: from -70 to $-130 \text{ J K}^{-1} \text{ mol}^{-1}$. This general behavior pattern can be understood along the lines described above for the enthalpies. Again, it is useful to consider the $s \rightarrow w$ transfer. When an ion is transferred from a cosolvent to water, it is necessary to create a cavity to accommodate the ion in the structured water. This results in a net destruction of (hydrogen) bonds with an increase in randomness, and thus, $\Delta_t S^\circ(\text{M}^+, s \rightarrow w)$ will be positive. When the transfer is to an aqueous-solvent mixture with enhanced water structure, the increase in entropy is larger and a maximum in the curve is observed. The $\Delta_t S^\circ(\text{M}^+, w \rightarrow w + \text{MeOH})$ curves for

the heavier alkali metal cations have a shallow minimum at $x_{\text{MeOH}} \approx 0.1$, i.e., at lower cosolvent compositions than those corresponding to the maximum. This minimum is much more clearly discernible in the $\Delta_t S^\circ(\text{M}^+, w \rightarrow w + t\text{-BuOH})$ curves, where it corresponds with the minimum in the $\Delta_t H^\circ$ curves. This extra minimum is difficult to understand and may simply be a reflection of the more comprehensive data available for *t*-BuOH at very high dilutions, cf. other solvents.

5. Transfer of Tetraalkyl/Phenylonium Ions

The systematic effects of ion size on the transfer thermodynamics of ions from water to aqueous-organic mixtures are well illustrated by means of the standard molar enthalpies of transfer of the tetraalkylammonium cations, for which a reasonably comprehensive body of data exists. The plots of $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + s)$ vs x_s for Me_4N^+ , Et_4N^+ , Pr_4N^+ , Bu_4N^+ , and, where available, also Pe_4N^+ , Hx_4N^+ , and Hp_4N^+ are essentially parallel and become increasingly endothermic along this series. All $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + s)$ curves show a maximum in all solvents, except for Me_4N^+ transferring into aqueous 1-propanol. The value of x_s at which this maximum occurs increases with the size of the cation, e.g., from 0.14 (Me_4N^+) to 0.19 (Bu_4N^+) for EtOH, from 0.04 (Me_4N^+) to 0.10 (Hp_4N^+) for AN, and from 0.09 (Me_4N^+) to 0.23 (Pe_4N^+) for DMF. The $\Delta_t H^\circ$ of all R_4N^+ larger than Et_4N^+ are positive at all x_s but $\Delta_t H^\circ$ is negative at high x_s for the transfer of Me_4N^+ and Et_4N^+ into most solvents.

Transfers of R_4N^+ into MeOH and DMF are, apart from the initial maximum, largely featureless; the small fluctuations and inflections probably reflecting uncertainties in the data. However, transfers of R_4N^+ into aqueous 1-PrOH and (to a lesser degree due to the incomplete database) EtOH show an incipient second maximum. This second maximum is fully developed for transfers into aqueous AN. Its location is somewhat dependent on the cation size, Figure 7, shifting from $x_{\text{AN}} \approx 0.9$ for Me_4N^+ to $x_{\text{AN}} \approx 0.8$ for Hx_4N^+ (although Bu_4N^+ is aberrant). This feature of the $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + s)$ vs x_s curves may be related to solvent microheterogeneity (section V.B.3), which is well documented³⁵⁵⁻³⁵⁹ in aqueous-AN mixtures for the region $0.25 \leq x_{\text{AN}} \leq 0.75$. Where microheterogeneity exists, $\Delta_t H^\circ$ might be expected to change only slightly with x_s , since although the relative amounts of the microphases vary, their compositions probably remain nearly constant. The Hp_4N^+ ion, for which $\Delta_t H^\circ$ increases steadily (by $\sim 20 \text{ kJ mol}^{-1}$) over the region $0.25 \leq x_{\text{AN}} \leq 0.75$, does not fit this pattern of behavior. This is probably because this very large ion disturbs the (solvent) composition balance when it distributes between the two microphases.

The range of x_s for which data for $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + s)$ exist for transfer to aqueous *t*-BuOH and DX is short ($x_s \leq 0.14$ and 0.20 , respectively), but the same features are observed for these solvents. These features include an essential parallelism of the curves, an increase in $\Delta_t H^\circ$ with increasing ion size, a shift of the maximum with ion size, from 0.05

(Me_4N^+) to 0.07 (Pe_4N^+) in *t*-BuOH and from 0.05 (Me_4N^+) to 0.10 (Hx_4N^+) in DX, and an incipient second maximum in DX and for Pe_4N^+ in *t*-BuOH. For the other solvents there are data only for one ion, either Me_4N^+ or Bu_4N^+ , so that no systematic pattern can be discerned. Nevertheless, the values of $\Delta_t H^\circ$ for these ions follow closely those for other solvents.

It is generally accepted that the addition of small amounts of alcohols having significant hydrophobic character enhances the structure of the remaining water: the more hydrophobic the alcohol, the larger the enhancement and the lower the alcohol concentration that produces maximal enhancement.^{341–343,346} Further, it has been argued above (section V.B.2) that addition of a typical DPA cosolvent to water (partly) *destroys* the water structure. Despite this difference, the values of $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow w + s)$ are invariably positive, at least for the larger R_4N^+ ions, and there is little difference in the size or position of the maximum regardless of the solvent. This effect is consistent with cosolvent molecules interacting, via van der Waals forces, with the alkyl chains of the (larger) R_4N^+ ions, thereby disrupting the hydrophobic hydration sheath that would otherwise exist around the alkyl chains. Thus, regardless of whether the cosolvent is water structure enhancing or breaking, there is a net loss of *w*–*w* H-bonding in the hydrophobic solvation sheath around the R_4N^+ ions. The longer the alkyl chains, the greater their surface area and hence the extent of their solvation sheath and thus the greater the endothermic effect. These results contrast with the values reported for $\Delta_t H^\circ(\text{R}_4\text{N}^+, w \rightarrow \text{D}_2\text{O})$ where for $\text{R} \geq \text{Pr}$ the enthalpy of transfer is negative.³⁴⁷ This is because in D_2O there are no cosolvent molecules to interact with the alkyl chains and break up the solvation sheath. Clearly there are subtle balances among these various effects that cause the maximum in the curves to depend on the solvent.

The ‘tetraphenyl’ ions, Ph_4P^+ , Ph_4As^+ , and BPh_4^- , have the same values of $\Delta_t H^\circ$ for transfer to a given solvent mixture, according to the extrathermodynamic assumption adopted here. The sizes of these ions, ~ 0.42 nm, are similar to each other and to Bu_4N^+ , 0.41 nm.¹ The tetraphenyl ions might therefore be expected to show $\Delta_t H^\circ$ values similar to those of Bu_4N^+ , if the ion size and its hydrophobic nature were the only considerations. At low x_s the $\Delta_t H^\circ$ values of the tetraphenyl ions are invariably positive and show the characteristic maximum. This maximum generally occurs at appreciably lower cosolvent concentrations than for the R_4N^+ ions ($x_s \approx 0.4$ for DMF, DMA, and DMSO but as low as $x_s \approx 0.15$ for AN, HMPT, and TMS). In contrast to the larger R_4N^+ ions, the values of $\Delta_t H^\circ$ for the tetraphenyl ions are usually negative at higher x_s . This is most likely to be a reflection of the much stronger (exothermic) dipole-induced dipole forces that exist between the very polarizable tetraphenyl ions and the cosolvent dipoles. The protic solvents (ROH and FA), although also highly polar, form hydrogen bonds among their molecules and with water. These bonds are disrupted by the presence of the large tetraphenyl ions; hence, their $\Delta_t H^\circ$ values remain essentially positive up to

the highest cosolvent concentrations. Consistent with the extrathermodynamic assumption adopted in this review, there does not appear to be any reason these interactions should depend significantly on the *sign* of the centralized charge on these large ions for either aprotic or protic cosolvents.

The large hydrophobic R_4N^+ ions show great similarity between the shape of their $\Delta_t S^\circ$ and $\Delta_t H^\circ$ vs x_s curves. Thus, little additional insight about the interactions taking place can be obtained from the entropy curves. However, the tetraphenyl ions have positive $\Delta_t S^\circ$ to all solvent mixtures, contrary to their $\Delta_t H^\circ$. The slopes of the $\Delta_t S^\circ$ vs x_{org} curves beyond the maximum are only moderately negative, and for some solvents a second maximum or an upturn at higher x_{org} is found. The above-mentioned direct solvent–ion interactions thus interfere with the water–solvent or solvent–solvent interactions without totally disrupting them, causing increases in the entropy but allowing for negative enthalpies.

6. Transfer of Halide Ions

At high cosolvent concentrations, in all the solvents for which data are available, the values of $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + s)$ for the halide ions become more endothermic (less negative) with increasing x_s . This effect is most noticeable for Cl^- (or F^- where such data exist), with $\Delta_t H^\circ$ becoming very positive, and least for I^- , for which $\Delta_t H^\circ$ usually remains negative as x_s increases. Thus, the trend in $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + s)$ is in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ in all solvents. The overall increase in $\Delta_t H^\circ$ is readily understandable in terms of the loss of H-bonding when X^- is transferred from water to the weaker H-bond donor (electron acceptor) cosolvents. On the other hand, the large anions strongly break the water structure³⁶⁵ and thus gain energy ($\Delta_t H^\circ$ is negative) when they are transferred from water. Apart from this general trend, there are significant differences between protic and aprotic solvents with respect to their values of $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + s)$ and therefore they will be discussed separately.

Typical protic solvents such as the alcohols (in this respect FA and UR behave more like typical aprotic solvents, see below) tend to enhance the structure of water at low x_s (section V.B.1). Thus, anions find it harder to compete for H-bonds and $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + \text{ROH})$ goes through a small endothermic maximum in the low x_s region. This occurs at approximately the same cosolvent compositions as for the alkali metal ions (see previous section) but is somewhat smaller in magnitude ($< \text{ca. } 10 \text{ kJ mol}^{-1}$).

It might be expected that there would be a regular variation of both the position and height of the maximum in $\Delta_t H^\circ(\text{X}^-, w \rightarrow w + \text{ROH})$ according to the solvent. Systematic behavior is indeed observed for thermodynamic properties such as the excess enthalpies and volumes in *w* + ROH mixtures.³⁴² While there is some pattern in the characteristics of the maximum in $\Delta_t H^\circ$, exceptions are also observed. For example, the propanols do not fit the sequence established by the series MeOH, EtOH, and *t*-BuOH, with respect to the position and height of their maximum. Ethanol also has a lower maximum than might be expected for such a sequence.

The maximum in $\Delta_t H^\circ(X^-, w \rightarrow w + s)$ at low x_s is followed by a minimum at higher cosolvent concentrations for both Cl^- and Br^- but not necessarily for I^- . These observations reflect the competing effects of enthalpy loss arising from the breaking of H-bonds between X^- and water (partially compensated for by the making of H-bonds with the weaker H-bond donor ROH molecules) and the effects of (water) structure breaking by the larger anions. As the size of X^- increases, its propensity for H-bond acceptance decreases and its structure-breaking proclivity increases.

For the mixtures of DPA solvents (along with FA and UR) with water, $\Delta_t H^\circ(X^-, w \rightarrow w + s)$ exhibits a *minimum* at low x_s for I^- and Br^- and, for most solvents, Cl^- (data are not usually available for the more difficult to measure F^-). The depth of the minimum follows the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$ but shows no apparent systematic dependence on the nature of the cosolvent. Similarly, the position of the minimum depends only slightly on the nature of X^- but varies among cosolvents, apparently unsystematically, over the approximate range $0.04 \leq x_s \leq 0.15$.

At higher x_s , the values of $\Delta_t H^\circ(\text{Cl}^-, w \rightarrow w + s)$ become positive, showing a broad maximum at $x_s \approx 0.7$. The corresponding data for Br^- are less positive but also exhibit a broad maximum or at least a plateau in most solvents. The values of $\Delta_t H^\circ(\text{I}^-, w \rightarrow w + s)$ remain negative (or, for some solvents, become somewhat positive) but also usually show a broad maximum before reaching the invariably negative values associated with transfer to the neat solvent. It is noted that the deepest minimum, of ca. -17 kJ mol^{-1} , occurs for $\Delta_t H^\circ(\text{Br}^- \text{ or } \text{I}^-, w \rightarrow w + \text{THF})$ while the greatest maximum, of ca. 34 kJ mol^{-1} , occurs for $\Delta_t H^\circ(\text{Cl}^- \text{ or } \text{Br}^-, w \rightarrow w + \text{HMPT})$.

The initial minimum in $\Delta_t H^\circ(X^-, w \rightarrow w + s)$ in aqueous dipolar aprotic mixtures can be explained if it is assumed that these solvents have a water structure *breaking* effect at low x_s . Evidence for such an effect has been obtained for $\text{AN} + \text{H}_2\text{O}$ from a variety of measurements (ref 349 and references therein), for $\text{DMSO} + \text{H}_2\text{O}$ from molecular dynamics simulations,³⁵³ and for $\text{AC} + \text{H}_2\text{O}$.³⁵² If this structure breaking is a general phenomenon of aqueous-dipolar aprotic mixtures at low x_s , an anion being transferred from water will have less water structure to break and more freely available water with which to H-bond, leading to negative values of $\Delta_t H^\circ(X^-, w \rightarrow w + s)$.

This effect is opposite to that observed for the alkali metal ions (see previous section) for which $\Delta_t H^\circ(\text{M}^+, w \rightarrow w + s)$ show a small endothermic maximum. This difference may be thought of as stemming from the directional requirements of H-bonds between X^- and water molecules. Such bonds are effective only when the $X^- \cdots \text{H} \cdots \text{O}$ bond angle is $> 150^\circ$ and preferably fully straight (ref 366, p 19). On the other hand, the directional requirements for alkali metal ion $\text{M}^+ \cdots \text{OH}_2$ bonds are less. Thus, the transfer of an anion from water to an aqueous-dipolar aprotic mixture will produce an enhanced (more exothermic) interaction with the 'freed' water molecules than would be expected for a cation.

C. Concluding Remarks

This review has shown that there is a considerable body of data available that relates to enthalpies and, to a lesser extent, entropies of transfer of electrolytes from water to a variety of aqueous-organic mixtures. Nevertheless, much remains to be done. Only a few of the cosolvent systems investigated to date (MeOH, EtOH, AN, and DMSO) can be considered as having reasonable amounts of good quality data, and even for these mixtures relatively few values have been independently confirmed and there are often significant gaps. Relatively little has been done on salts containing cations of higher charge and almost nothing is known about the corresponding anions. Of course the accurate measurement of such data is not trivial because of the effects of ion pairing and (for the cations) hydrolysis. Similarly, very few studies have been made on key ions such as F^- and OH^- . More systematic studies are required for ions of varying size, hydrophobicity, polarizability, etc., to more clearly identify the relative importance of these factors in determining the thermodynamics of ion transfer.

Much more work needs to be done with respect to determining entropies of transfer. The present situation is, however, not quite as bad as it appears. An up-to-date critical review of the Gibbs energies of transfer of electrolytes, comparable to that recently published for cations,¹ would enable many entropies to be calculated via the GHSE using the corresponding enthalpy data presented here. Unfortunately, such an undertaking was beyond the scope of both the present and previous reviews.

Development of new methods for deriving single-ion enthalpies and entropies of transfer that are not based on the TATB/TPTB assumption would be welcome. Of course, such assumptions should be at least as chemically reasonable as that with which they are to be compared. Along these lines, further nonisothermal cell emf measurements on systems for which good quality TA(P)TB data exist would be useful to enable a more detailed comparison of these two assumptions to be made.

Extension of the existing database to other solvents would also be useful. Of most interest would be solvents whose properties expand on those already studied with respect to, for example, their donor/acceptor properties, polarizability, 'softness', etc. The goal of such studies would be to characterize the contributions of such effects to the thermodynamics of ion solvation. Of course, explanation of the often complex thermodynamic effects that are observed when ions are transferred from water to aqueous-organic mixtures must ultimately be in terms of what is happening at the molecular level. Spectroscopic, theoretical, and computer simulation studies are invaluable for such purposes.

Finally, it should not be forgotten that one of the major underlying purposes for studying aqueous-organic mixtures as solvents is to better understand the behavior of water. It is well-known, but worth repeating, that one of the best ways of appreciating the remarkable properties of water as a solvent is to replace it (wholly or in part) by another. Aqueous-

organic mixtures provide a means of doing this in a systematic and controlled manner.

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VII. References

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