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Gibbs Energies of Transfer of Cations from Water to Mixed Aqueous Organic Solvents

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I. Introduction

A. Gibbs Energies of Transfer and the Solvent Medium Effect

A large number of quantitative studies have been made of the Gibbs energy of transfer (the solvent medium effect) for cations transferring from water into mixed aqueous−organic solvent systems, mainly at 25 °C. Nevertheless, no systematic effort appears to have been made to compile and analyze these data, particularly for multivalent cations. A critical review of this information and its presentation in a manner that permits comparison of different cations in a given solvent mixture and of a given cation transferring into different mixtures is therefore of value.

The solvent medium effect is a measure of the change in the total solvation energy (chemical potential) of a solute *i* when it is transferred from one solvent (S1) to another (S2). The magnitude of this effect defines the relative stability of the solute in the two solvents and thus the consequences of changing the solvent on the redox, acid−base, and complexation characteristics of the solute, as well as the kinetics and mechanisms of its reactions. In this context, the solvent medium effect (hereafter simply the “medium effect”) is probably one of the most useful parameters available for quantifying and understanding solute behavior in both pure (neat) and mixed solvents. The significance of this parameter only became widely appreciated in the 1960s, as a result of the increased use of nonaqueous and mixed solvents in analytical chemistry and for physicochemical measurements in organic and inorganic chemistry. A number of reviews, stressing various aspects of the solvent medium effect, appeared during the 1970s[1−8] and subsequently.[9−15]

As defined, the medium effect is directly related to the standard molar Gibbs energy of transfer of the solute *i*, $\Delta_t G°(i,S1 \rightarrow S2)$, shortened in the following to Gibbs energy of transfer, and most recent work has used this quantity as a readily understood measure for discussion and interpretation. The transfer is normally considered to occur under the conditions of infinite dilution of the solute in both solvents, so as to remove the complicating effects of solute−solute interactions. The reference solvent (S1) is chosen arbitrarily but is usually taken as water.

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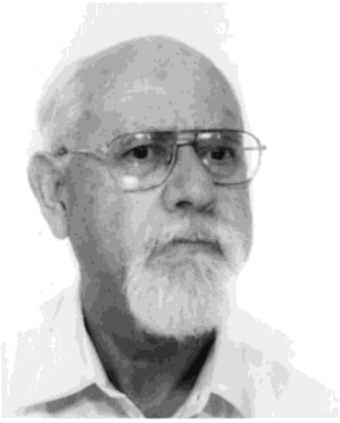

Yizhak Marcus, born in Germany and having immigrated to Israel as a child, obtained his M.Sc. degree in 1952 and Ph.D. degree in 1956 from the Hebrew University of Jerusalem, where he has been Professor of inorganic and analytical chemistry since 1965. He has been a visiting professor in universities in several countries and has recently stayed at Murdoch University in Australia, where 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), and *Properties of Solvents* (1998).

There is no restriction on the target solvent S2; however, for this review S2 is limited to a selection of organic solvents and their mixtures with water over (wherever possible) their entire composition range. Excluded, therefore, are media such as solutions of electrolytes (e.g., 1 mol dm^{-3} $NaClO_4$) or nonelectrolytes (e.g., 6 mol dm^{-3} urea) sometimes employed for the study of medium effects.

Being a thermodynamic quantity, the medium effect applies to any solute but is especially significant for electrolytes because of the high solvation energies of ions.[10] This is manifest in the frequently dramatic effects of solvent on the relative stabilities of oxidation states of ions (and hence redox potentials), their rates of reaction, formation of complex species, the solubility of salts, etc.

Although it is often found that the largest medium effects are observed for the transfer of electrolytes between neat solvents, heteroselective solvation (see later) may result in even larger effects occurring for transfer to mixed solvents.[14] Solvent mixtures, especially those involving water, are also of considerable technological interest because of their reduced purification requirements, greater ease of manipulation, and lower cost compared to pure nonaqueous solvents. The use of mixed solvents also permits the solvent composition to be used as an additional variable to achieve desired chemical ends. An example of this is the Parker process[16] which exploits the spectacular changes in the relative stabilities of the oxidation states of copper in acetonitrile (CH_3CN)−water mixtures

$$\mathrm{Cu(0)} + \mathrm{Cu(II)} \underset{\mathrm{H_2O}}{\overset{\mathrm{CH_3CN}}{\rightleftharpoons}} 2\mathrm{Cu(I)}$$

to create a low-energy route for the hydrometallurgical processing of copper, alternative to those traditionally based on Cu(II).

The medium effect for the transfer of ions from water to neat solvents has been surveyed in a number of publications, and reasonably comprehensive compilations of Gibbs energies of transfer are available.[8,13,17−20] The transfer of ions into mixed (mainly aqueous/organic) solvents has also been reviewed.[14,21,22] However, these reviews have been limited in their scope and have not attempted an overview of the available numerical data. An exception is the survey[22] of Gibbs energies of transfer of electrolytes and ions from water to aqueous alcohol mixtures, prepared by Marcus on behalf of IUPAC. However, this report was not concerned with the interpretation of the data, and no comparable compilations are available for other important classes of solvent.

Thus, the major purpose of the present review is to provide a wide-ranging, critically evaluated compilation of the Gibbs energies of transfer (medium effects) of cations from water to aqueous/organic mixtures. These quantities will then be discussed and interpreted in terms of current views of ion solvation. The review deals mainly with monatomic cations, as these provide a series of ions of well-defined electronic configuration with systematically varying size and charge, which provides a useful basis for comparison and interpretation. The symmetric tetraalkylammonium cations have also been included for similar reasons. Exclusion of entirely nonaqueous mixtures is partly in order to limit the scope of the review but, more importantly, because such mixtures have not been sufficiently well investigated to enable the data to be critically evaluated. For the same reason, no attempt is made to be exhaustive with respect to the organic cosolvents: as wide a selection as possible of representative cosolvents for which reasonable amounts of data exist are included. The literature has been surveyed to the end of 1996 or later in some cases.

B. Thermodynamic Description

The chemical potential (partial molar Gibbs energy), μ_i, at a stoichiometric molality m_i (mol of solute/kg of solvent) or molarity c_i (mol solute/L solution) in a solvent s at a specified temperature and pressure is given by

$$\mu_i = {}_s\mu^\circ{}_{i(m)} + RT \ln m_i + RT \ln {}_s\gamma_{i(m)} \quad (1a)$$

$$\mu_i = {}_s\mu^\circ{}_{i(c)} + RT \ln c_i + RT \ln {}_s\gamma_{i(c)} \quad (1b)$$

where γ_i is the activity coefficient of the solute on the relevant concentration scale, the pre-subscript s refers to the solvent, and the superscript ° indicates the standard state (taken customarily to be unit concentration of *i* but with properties as in the reference state of infinite dilution of *i* in s).

The medium effect (presubscript m), $RT \ln {}_m\gamma_i$, is then defined as the difference in the standard state chemical potentials of *i* in the solvent (or solvent mixture) and the reference solvent, on the appropriate concentration scale. As noted above, the selection of the reference solvent is arbitrary, but for convenience, especially for the discussion of aqueous/organic mixtures, water (presubscript w) is the most obvious choice. The choice of concentration scale is also optional. However, although some authors[3,5,23,24] have discussed the solvent medium effect in terms of the molality scale, for reasons given below, the molarity scale will be used here wherever possible. Thus, in terms of eq 1b the medium effect is (note the change to the customary decadic logarithm):

$$\log {}_{\mathrm{m}}\gamma_{\mathrm{i(c)}} = [{}_{\mathrm{s}}\mu^{\circ}{}_{\mathrm{i(c)}} - {}_{\mathrm{w}}\mu^{\circ}{}_{\mathrm{i(c)}}]/2.303RT \qquad (2)$$

An analogous expression is obtained if the treatment is performed in terms of molalities but the numerical values of the quantities will differ. Since $\log {}_{\mathrm{m}}\gamma_{\mathrm{i(c)}}$ is defined in terms of standard state quantities, it is independent of the solute concentration and reflects ***only*** ion−solvent interactions. The activity coefficients ${}_{\mathrm{s}}\gamma_{\mathrm{i(c)}}$ and ${}_{\mathrm{w}}\gamma_{\mathrm{i(c)}}$ on the other hand reflect both ion−solvent and ion−ion interactions.

Thus, to summarize, the medium effect is the change in Gibbs energy of a solute when it is transferred under standard state conditions (infinite dilution) from one solvent to another. As such, it is a measure of the difference in the total (standard) solvation energy of that solute in the two solvents. That is, assuming water is the reference solvent (S1), the medium effect for the solute i is $\Delta_t G^{\circ}(i, \mathrm{w}\rightarrow\mathrm{s})$, where s can be any solvent other than water, including any mixed solvent.

The description up to this point has been applicable to any solute. However, the focus of this review is on ions and this involves some special problems. For an electrolyte dissociating into its ions as

$$\mathrm{M}_{\nu+}\mathrm{A}_{\nu-} \rightleftharpoons \nu^{+}\mathrm{M}^{z+} + \nu^{-}\mathrm{A}^{z-} \qquad (3)$$

with the total number of ions per formula unit of electrolyte being $\nu = \nu^{+} + \nu^{-}$, the Gibbs energy of transfer from w to s refers to the whole salt and is therefore related to the standard solubility product, $K_{\mathrm{sp}}{}^{\circ}$, of the electrolyte in the two solvents

$$\Delta_t G^{\circ}\,(\mathrm{M}_{\nu+}\mathrm{A}_{\nu-}, \mathrm{w}\rightarrow\mathrm{s}) = 2.303RT \log [K_{\mathrm{sp}}{}^{\circ}{}_{(\mathrm{w})}/K_{\mathrm{sp}}{}^{\circ}{}_{(\mathrm{s})}] \qquad (4)$$

which in turn is related to the mean ionic medium effect ${}_{\mathrm{m}}\gamma_{\pm}$

$$\Delta_t G^{\circ}\,(\mathrm{M}_{\nu+}\mathrm{A}_{\nu-}, \mathrm{w}\rightarrow\mathrm{s}) = \nu 2.303RT \log {}_{\mathrm{m}}\gamma_{\pm} \qquad (5)$$

Equation 4 shows that $\Delta_t G^{\circ}(i, \mathrm{w}\rightarrow\mathrm{s})$ is a determinable quantity (the ratio of two solubility products) for any given electrolyte. Using the usual methods of chemical thermodynamics, it is also readily shown that $\Delta_t G^{\circ}(i, \mathrm{w}\rightarrow\mathrm{s})$ can be determined, in principle, for any electroneutral combination of ions, such as the difference between two cations or two anions of the same charge. However, there is ***no*** thermodynamic method for separating (determinable) electrolyte properties into their ionic components. Although they cannot be measured, the reality of these ionic Gibbs energies is well established.[25] The means by which they can be estimated are discussed in detail in section II.B.

C. Significance and Applications of the Medium Effect

Chemical reactions commonly take place in solution, many of them involving solvents other than neat water; hence, the impact of the medium effects is very far-reaching. Only some of the more general applications are briefly considered here; more detailed descriptions can be found elsewhere.[9,26]

1. pH Scales

Estimation of the medium effect for the proton (H^{+}) provides a means of comparing Brönsted−Lowry acidities and basicities in different solvents. In other words, it enables the development of a single, solvent-independent, ‘universal’ pH scale in which all acidities and basicities are related to those in a single reference solvent (customarily, but as discussed above not necessarily, taken as water).

A detailed description of the measurement of pH in neat and mixed solvents has been presented in a number of publications[5,27−29] and is beyond the scope of the present review. The principles involved can be illustrated by consideration of the following cell

$$\mathrm{Pt, H_2\ (g, 0.1\ MPa)|HCl\ in\ s|AgCl, Ag, Pt} \qquad \mathrm{I}$$

In principle, this cell can be used to establish a pH scale in any solvent s. However, the hydrogen-ion activities so obtained, $\mathrm{p_sH}$ [$\equiv -\log {}_{\mathrm{s}}a(\mathrm{H}^{+})$], are not comparable between solvents because of the difference in the standard state chemical potentials. That is, measurements with such cells result in the creation of a separate pH scale for each solvent. Although useful for many purposes, the limitations of such a plethora of scales are self-evident. Use of the solvent medium effect enables all $\mathrm{p_sH}$ values to be referred to the usual aqueous $\mathrm{p_wH}$ scale, since

$$\mathrm{p_sH} = \mathrm{p_wH} + \log {}_{\mathrm{m}}\gamma(\mathrm{H}^{+}) \qquad (6)$$

thereby establishing a single ‘universal’ acidity/basicity scale.

2. Electrode Potential Scales

Comparison of redox strengths in different solvents[30,31] is of considerable interest for the rational selection of synthetic reagents, the development of new hydrometallurgical reactions, the rationalization of oxidation state stabilities, etc. As the aqueous standard hydrogen electrode (SHE) is generally taken as the ultimate reference electrode, the problems of establishing a single universal scale for all redox potentials are similar to those discussed above in relation to pH scales (see cell I).

It is readily shown that the potential of the SHE in solvent s referred to the aqueous SHE, ${}_{\mathrm{w}}E^{\circ}({}_{\mathrm{s}}\mathrm{H}^{+})$, is given by

$${}_{\mathrm{w}}E^{\circ}\,({}_{\mathrm{s}}\mathrm{H}^{+}) = (RT/F) \ln {}_{\mathrm{m}}\gamma(\mathrm{H}^{+}) \qquad (7)$$

noting the usual convention that the standard potential of the aqueous SHE, ${}_{\mathrm{w}}E°({}_{\mathrm{w}}\mathrm{H}^+) \equiv 0$ V. Since all other potentials in a given solvent can be referred to the SHE in that solvent in the usual way, it is also true that for a redox couple *i* involving *n* electrons

$$ {}_{\mathrm{w}}E°_{\mathrm{i,s}} = {}_{\mathrm{s}}E°_{\mathrm{i,s}} + (RT/nF)\ln {}_{\mathrm{m}}\gamma_{\mathrm{H}^+} = {}_{\mathrm{s}}E°_{\mathrm{i,s}} + (1/n)_{\mathrm{w}}E°_{\mathrm{H}^+,\mathrm{s}} \quad (8)$$

which corresponds to a universal scale for the comparison of standard electrode potentials in any solvent.

3. Liquid Junction Potentials

In principle, it is possible to establish universal scales for both electrode potentials and pH by measurements on cells such as

$$\underset{\text{in solvent, s}}{\mathrm{Pt, H_2\,(g, 0.1\,MPa), H^+\,}(a=1)}\ \underset{E_{\mathrm{j}}}{\Big\|}\ \underset{\text{in water, w}}{\mathrm{H^+\,}(a=1)\mathrm{, H_2\,(g, 0.1\,MPa), Pt}}\quad \mathrm{II}$$

provided that the liquid junction potentials, E_{j}, which arise at the liquid-phase boundaries M, can be rendered negligible or be estimated reliably in some way. Neither of these options is possible; indeed, it can be shown that both approaches involve making some assumption about the medium effect for single ions. Conversely, if the medium effects for the appropriate ions are known, it becomes possible to estimate E_{j}. Since galvanic cells with liquid junctions are in practice much more diverse and useful than those without them, such a capability is quite useful.[32]

4. Solubilities

It is apparent from eq 4 that the medium effect can be used to predict the solubility (or $K°_{\mathrm{sp}}$) of an electrolyte in a solvent, given its value in another solvent. Popovych and Friedman[33] first exploited this possibility to calculate the solubility of very sparingly soluble salts such as $\mathrm{Bu_4NBPh_4}$ in water from their solubility products in MeOH and the medium effects for their ions. Similar calculations for other tetraalkylammonium salts have been reported in EtOH/$\mathrm{H_2O}$ mixtures.[34] Reliable solubility measurements are generally labor-intensive and time-consuming; hence, such data are frequently unavailable for many systems of interest and the possibility of calculating such values is very attractive.

5. Kinetics and Other Applications

The role of the medium effect on the kinetics and mechanisms of both organic and inorganic substrates has long been recognized and has been reviewed in several publications.[1,35] The effects are usually greatest for reactions involving charged species. Knowledge of the medium effects and their dependence on charge, size, and other properties of the ions is especially useful when considering the role of the transition state as such states are generally not amenable to direct study.

As noted above, an exhaustive discussion of the applications of the medium effect is inappropriate here, but they include the development of high-energy density batteries,[36] nonaqueous electrodeposition,[9] corrosion[37] and hydrometallurgical reactions,[16] solvent extraction,[10] ion-exchange,[38] and analytical titrimetry.[39]

The overarching importance of medium effects of ions lies in their ability to correlate and predict a vast array of experimental facts as pointed out by Parker,[1] Bates,[5] Strehlow,[30] and many others.

II. Measurement and Treatment of the Data

A. Determination of Medium Effects

As already noted (section I.B), the medium effect or the Gibbs energy of transfer of an electroneutral solute or combination of ions can be determined experimentally and has exact thermodynamic significance. It is beyond the scope of this review to provide a comprehensive account of the great variety of methods which can be or have been used to determine medium effects, but it is appropriate to briefly outline the advantages and drawbacks of the more commonly employed and reliable methods.

1. Solubility

In this method the solubility of the solute *i* is measured at the desired temperature (generally 25 °C) in the reference solvent (w) and the target solvent or solvent mixture (s). The thermodynamic relationship in eq 4 forms the basis of this method and requires the determination of the solubility products of the electrolyte in the two media. The advantage of the solubility approach is its universal applicability, provided that the electrolyte is not too soluble in the two media, so that the activity coefficient ratio can be reliably estimated, and no crystal solvates are formed in w and s.[3,40]

There are, however, a number of drawbacks and pitfalls in using solubility measurements[41] for the present purpose. Such determinations are time-consuming and labor-intensive, since attainment of equilibrium must be checked by successive measurements. Ideally, saturation should be approached from both above and below to check for possible supersaturation. Sampling of the saturated solution should be made at the equilibration temperature to avoid changes in composition, and this may require specialized apparatus.[42] Unfortunately, these necessary precautions to obtain true equilibrium solubilities are not always taken. On the other hand, the logarithmic form of eq 4 permits reasonable results to be obtained even from solubility measurements of only modest accuracy.

The optimal range of salt solubilities is ca. 10^{-5} to 10^{-2} mol dm^{-3}, which reduces the possible effects of ion pairing and permits reliable estimation of activity coefficients. Since solubility is a characteristic property of a given salt/solvent system at a given temperature, the researcher lacks the freedom of choosing the desirable concentration level, except through a judicious selection of the anion (in the present context of interest in the cations).

A variant of the solubility method is based on liquid−liquid distribution, where the solute is allowed to distribute between immiscible reference and target solvents. This has the advantage of permitting arbitrarily low solute concentrations to be used. Also, equilibration in such cases is generally rapid. In the present context of cation transfer into aqueous solvent mixtures, reference and target solvent immiscibility is precluded (but see section III.J concerning propylene carbonate). Some authors have used this method for ion transfers into so-called "wet" solvents, e.g., water-saturated nitrobenzene or 1,2-dichloroethane,[43,44] but their consideration is beyond the scope of this review.

2. Potentiometry

Potentiometry is attractive for the measurement of medium effects because of its accuracy and experimental convenience.[32] The latter is emphasized when using the NLJP assumption (see section II.B.5) as values of $\Delta_t G°(\text{ion})$ are obtained directly from the experimental emf data.[45]

A great variety of electrochemical cells can be employed to measure Gibbs energies of transfer, the choice being limited only by the availability of suitable, reversible, electrodes (e.g., ion selective ones[46,47]) and experimental ingenuity. Detailed discussions of successful approaches can be found in standard texts,[9,48] with the following given as a simple illustration.

Consider cell III, with one electrode responsive to the cation M^{n+} and the other to the anion A^-:

$$\text{M}|\text{MA}_n \text{ in w or s}|\text{A} \qquad \text{III}$$

Measurements of the cell emf's, ${}_wE_{III}$ in the reference solvent w and ${}_sE_{III}$ in the target solvent s, as a function of the salt concentration $c(\text{MA}_n)$, permits the determination of the standard emf's ${}_wE_{III}°$ and ${}_sE_{III}°$ by extrapolation to $c(\text{MA}_n) = 0$ or by calculation, using an appropriate expression for the activity coefficients if $c(\text{MA}_n)$ is low enough. It follows from the relationship between cell emf and the Gibbs energy of the cell reaction that

$$\Delta_t G°(\text{MA}_n, \text{w}\rightarrow\text{s}) = nF({}_wE_{III}° - {}_sE_{III}°) \qquad (9)$$

If one of the electrodes employed allows this (e.g., an alkali metal amalgam electrode), the cells with solvents w and s can be coupled back to back, so that the emf of the 'double' cell yields the Gibbs energy of transfer directly.

The major disadvantage with the potentiometric method is that suitable electrodes cannot always be found, although the situation has improved with the development of ion-selective electrodes.[47,49] When traditional electrodes based on redox equilibria are used, two or more species must be present and stable at the macroscopic level at the electrode/solution interface.

3. Voltammetry

Voltammetric methods enable the need for macroscopic stability to be circumvented to some degree. Polarography, preferably in one of its more modern forms,[50] is probably the most appropriate form of voltammetry for this purpose. This is due to the high reproducibility of the dropping mercury electrode (dme) and its wide cathodic range. For the reversible reduction of an amalgam-forming metal ion at the dme, the half-wave potential $E_{1/2}$ is related to the standard cell potential

$$E_{1/2} = E°(\text{M}^{n+}|\text{M(Hg)}) + (RT/nF)\ln a_{\text{Hg}} + (RT/nF)\ln[(D_R/D_O)^{1/2}(\gamma_O/\gamma_R)] \qquad (10)$$

where D is the diffusivity (diffusion coefficient) and the subscripts O and R designate the oxidized and reduced forms of the electroactive species. The last two terms on the right-hand side of in eq 10 are generally small and are often neglected. In this case, $\Delta E_{1/2}$, the difference in $E_{1/2}$ in w and s, is directly related to the Gibbs energy of transfer[9,13]

$$\Delta E_{1/2} \approx {}_sE°(\text{M}^{n+}|\text{M(Hg)}) - {}_wE°(\text{M}^{n+}|\text{M(Hg)}) = \Delta_t G°(\text{M}^{n+}, \text{w}\rightarrow\text{s})/nF \qquad (11)$$

A newer voltammetric method that appears promising is VITIES (*v*oltammetry for *i*on *t*ransfer at the *i*nterface of two immiscible *e*lectrolyte *s*olutions).[51,52] Here the dme is replaced by an electrolyte solution in a solvent such as nitrobenzene that is immiscible with water as well as the target (aqueous) solvent. When coupled with a tetraphenylborate reference electrode, this technique can give values directly on the TATB scale (see section II.B.3).

The advantages of voltammetric methods include the ease and speed of measurement and in many cases the need for only trace amounts of one of the electroactive species to be present. Furthermore, some reference electrodes often used, such as ferrocene/ferrocinium (Fc)[53] or bis(biphenyl)chromium(0/I) (BBCr),[54] lead to Gibbs energies of transfer of individual cations if their potentials are assumed to be independent of the solvent (see section II.B.2). The major drawbacks of voltammetric methods for measuring medium effects are that the species of interest must be electroactive and the electrode process should be fully reversible (Nernstian response of the polarographic wave) in all the solvent (mixtures) of interest. It is generally also necessary to have a significant concentration of a (inert) supporting electrolyte present to minimize ohmic losses and migration currents.[50]

4. Spectrophotometry

Spectrophotometric methods have found some use for the determination of medium effects and have been employed in mainly two manners. One is the determination of solubilities of electrolytes or their distribution ratios between immiscible solvents by the use of a highly colored counterion, such as picrate.[55,56] The other mode is the use of Hammett indicators *B*, especially 4-nitroaniline, to estimate the transfer Gibbs energy of the hydrogen ion. The ratio $[\text{BH}^+]/[\text{B}]$ is determined spectrophotometrically as a function of the concentration of added strong acid, $[\text{H}^+]$, and the medium composition.[5,57] The Gibbs energy of transfer of the hydrogen ion is obtained at a given total acidity in water (w) and the new medium (s), provided $[\text{H}^+] \gg [\text{BH}^+]$ and the activity coefficient ratio is assumed to be unity, as

$$\Delta_t G°(\mathrm{H}^+, \mathrm{w} \rightarrow \mathrm{s}) = -RT \ln\{[\mathrm{BH}^+]_s[\mathrm{B}]_w/[\mathrm{BH}^+]_w[\mathrm{B}]_s\} \quad (12)$$

This method has been further elaborated by Wells.[58]

B. Evaluation of Single-Ion Medium Effects

1. Background

As noted earlier, Gibbs energies of transfer (medium effects) are determinable only for molecular solutes, electrolytes, and electroneutral combinations of ions. Standard Gibbs energies of transfer imply the condition of infinite dilution of the electrolyte and, hence, the additivity of the individual ionic contributions. It is, therefore, necessary only to fix the value for one ion; those of all other ions are then obtainable from appropriate thermodynamic cycles. However, Gibbs energies of transfer of single ions, in common with other individual ionic thermodynamic quantities, can only be evaluated by resorting to an appropriate extrathermodynamic assumption, i.e., an assumption outside the realm of thermodynamics. In essence, the role of such an assumption is to split the (measurable) whole electrolyte thermodynamic property into its (nonmeasurable) individual ionic contributions.

It should be noted that although extrathermodynamic assumptions can be checked for self-consistency (precision) by the use of appropriate thermodynamic cycles, their correctness (accuracy) cannot be determined. Still, chemical intuition and theoretical understanding can lead to a preference for certain assumptions for the determination of $\Delta_t G°$(ion) values from the wide array of proposals that have been made since 1947, when Pleskov[59] attempted to develop a universal scale of electrode potentials. These assumptions have been reviewed and their various merits and demerits discussed in detail elsewhere[10,60,61] and thus will be only briefly summarized here.

Virtually all of the assumptions for evaluating $\Delta_t G°$(ion) are, to some extent, either explicitly or implicitly based on an insight which stems from the Born equation. In his original treatment of 1920, Born[62] calculated the (Gibbs) energy possessed by a spherical conducting ion of charge number z and radius r located within a dielectric continuum of relative permittivity (dielectric constant) ϵ. The expression obtained can be written, per mole of ions, as

$$G°(\mathrm{ion}) = -(N_A e^2/8\pi\epsilon_o)(z^2/r)(1/\epsilon) \quad (13)$$

where N_A is Avogadro's number, e is the charge of the electron, and ϵ_o is the permittivity of vacuum.

As has been demonstrated by many authors, this approach is far too crude to provide a quantitative account of ion-solvation phenomena and various modifications have been proposed over the years.[26] Nevertheless, the Born equation should model to some extent the electrostatic part of ion–solvent interactions. More importantly for the present discussion, the Born equation suggested to earlier workers that ions of a low charge-to-radius ratio should have relatively low solvation energies. It follows that when such ions are transferred from one solvent to another, the changes in solvation energy should also be minimal. It is this insight which underlies, to some degree, all of the assumptions which will be discussed below.

2. Reference Ion Assumptions

These assumptions postulate that a selected ('reference') ion has a negligible Gibbs energy of transfer from the reference solvent to all other solvents

$$\Delta_t G°(\text{reference ion, S1} \rightarrow \text{S2}) \equiv 0 \quad (14)$$

Following the original suggestion of Rb^+ by Pleskov,[59] various other reference ions have been proposed over the years. Abraham[63] proposed $\mathrm{Me_4N^+}$ in the sense of a "conventional" reference from which to report the $\Delta_t G°$ values of other ions, without necessarily implying that $\Delta_t G°(\mathrm{Me_4N^+}, \mathrm{S1} \rightarrow \mathrm{S2}) \equiv 0$. It is now generally accepted that no one ion can have the required solvent-independent properties for all solvents.

3. Reference Couple Assumptions

Here it is assumed that the Gibbs energies of transfer of both species of a chemically related couple are negligible

$$\Delta_t G°(\text{reference couple, S1} \rightarrow \text{S2}) \equiv 0 \quad (15)$$

Redox couples, acid/base couples, and complexation couples have generally been used for this purpose. Redox couples which have been used in this way include ferrocene/ferricinium (Fc),[64] Fe(II/III) phenanthroline,[65,66] and bisbiphenylchromium(0/I) (BBCr).[54] Acid/base couples, originally proposed by Hammet[67] for establishing a universal pH scale, are generally large dye molecules in the protonated and unprotonated forms (the latter being anionic or neutral). Complexation couples consist of an encapsulating macrocyclic ligand, such as 2,2,2-cryptand, and its metal-ion-containing analogue.[68]

It is noteworthy that in addition to most of these species being of low charge/radius ratio (cf. eq 13), they typically have their charge 'buried' inside a large organic 'cage' and thereby shielded from direct interaction with the solvent in which the species are dissolved. Despite the inevitable charge difference, the two species of the couple are chemically similar and thus relatively little affected by transfer from solvent to solvent. It should also be noted that if one of the species of a couple is neutral, its transfer properties are measurable and can be factored out of the assumption. Depending on how such considerations are implemented, the use of such a couple may then amount to a reference ***ion*** assumption. Experimental convenience is an advantage when the reference redox couple assumption is used in electrochemical determinations of Gibbs energies of transfer.

4. Reference Electrolyte Assumptions

This approach assumes that the (measurable) Gibbs energy of transfer of a suitable electrolyte (CA) can be split appropriately between its cation and anion. The electrolytes chosen for this type of assumption have cations and anions with low charge/radius ratios and a ‘buried’ charge, that are as chemically similar as possible. Most commonly the split is even, so that the assumption can be expressed as

$$\Delta_t G°(\text{CA, S1} \rightarrow \text{S2}) = 2\Delta_t G°(\text{C}^+\text{, S1} \rightarrow \text{S2}) = 2\Delta_t G°(\text{A}^-\text{, S1} \rightarrow \text{S2}) \quad (16)$$

Some authors[69,70] have preferred unequal splits, taking into account small differences in the sizes of the reference ions and their quadrupole moments. Although the justifications for the unequal split seem reasonable, the cation:anion weightings do not differ greatly from 1:1 (eq 16) and the simpler even splitting is used here. The salts used most widely for this purpose are tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4, TATB) and its phosphorus analogue tetraphenylphosphonium tetraphenylborate (Ph_4PBPh_4, TPTB), although others have been employed from time to time. When solubility measurements are employed for the implementation of the reference electrolyte approach, their laborious nature is a disadvantage.

5. Liquid Junction Potential Assumptions

This approach assumes that the potential difference (E_j) which develops at the phase boundary between solutions in a galvanic cell such as cell II can be rendered negligible (or, more accurately, independent of the solvent) by separating them with an appropriate salt bridge solution. This procedure was proposed as long ago as 1927 by Bjerrum and Larsson[71] and others[72] but became widely adopted only after Parker and co-workers[45] advocated the use of cells such as (pic = picrate):

$$\begin{array}{c||c||l} \text{Ag, AgClO}_4\text{(0.01 M)} & \text{0.1 M Et}_4\text{Npic} & \text{AgClO}_4\text{(0.01 M), Ag} \quad \text{IV} \\ \text{in S1} & \text{in the reference} & \\ & \text{(bridge) solvent} & \end{array}$$

The basis of this negligible liquid junction potential (NLJP) assumption is that the large ions of the salt bridge solution have similar electrical mobilities and (low) solvation energies in many solvents. The theory of liquid junction potentials[73] suggests this should lead to $E_j \approx 0$. If this can be achieved, then cells such as II (with, of course, an appropriate salt bridge) and III can be used directly to obtain $\Delta_t G°$ for H^+ and Ag^+, respectively.

The choice of the bridge electrolyte and solvent is to some extent arbitrary, within the constraints just discussed, but also depends on the nature of S1 and S2 (clearly, all of the cell components must be chemically and electrochemically compatible). A solution of 0.1M Et_3Npic in CH_3CN[45] has been widely adopted, but satisfactory results have been reported using other solutions too. The major advantage of the NLJP approach is its experimental simplicity, but the disadvantage is that it is unclear under what conditions the assumption breaks down.

6. Other Assumptions

Many other assumptions for determining $\Delta_t G°$(ion) have been put forward over the years. However, most of them have been rejected as unreliable and are now of historical interest only. Such approaches are discussed in detail elsewhere[10,60.61] and include calculations[3,26,30] and extrapolations[26,74,75] based on the Born equation and its various modifications and various spectroscopic indicator methods,[5,57] involving also the Born equation in one such method.[58] In general, $\Delta_t G°$(ion) values based on such assumptions have been excluded from this review. For aqueous alcohol systems, such data can be found in the compilation by Marcus.[22]

7. Adopted Assumption

All extrathermodynamic assumptions for the determination of $\Delta_t G°$(ion), or indeed any single-ion thermodynamic property,[76] can be objected to on some basis. Essentially only three of the methods mentioned above have survived the passage of time, namely, the NLJP, BBCr, and TATB (or TPTB) ones. The others are very rarely employed nowadays. Careful analysis indicates that the reference electrolyte approach employing TATB or TPTB (see above) is based on sound considerations[3,60,61,69] and is the least objectionable assumption currently available for the estimation of $\Delta_t G°(\text{ion, w} \rightarrow \text{s})$. Accordingly, this approach has been adopted in this review wherever possible. This is consistent with the work of many research groups and with a number of other reviews of $\Delta_t G°$(ion) from water to neat[8,17,19,20] and mixed[14,22] solvents and also of other single-ion transfer thermodynamic properties[77,78] and electrode potentials.[31]

Values of $\Delta_t G°$ (TATB or TPTB), for establishing the values of $\Delta_t G°(\text{TA}^+\text{, TP}^+\text{, or TB}^-)$ and hence all other values of $\Delta_t G°$(ion), are usually determined by solubility measurements. However, both TATB and TPTB have extremely low solubilities in water and water-rich mixtures and cannot usually be measured directly. The required information is obtained, albeit with the expenditure of considerably more experimental effort and with some loss of precision, by employing the additivity of standard thermodynamic properties of more soluble salts

$$\Delta_t G°(\text{Ph}_4\text{AsBPh}_4) = \Delta_t G°(\text{Ph}_4\text{AsX}) + \Delta_t G°(\text{MBPh}_4) - \Delta_t G°(\text{MX}) \quad (17)$$

where M^+ and X^- are some appropriate cation and anion. Developments in ultratrace analysis using techniques such as plasma-enhanced atomic emission-mass spectroscopy will hopefully facilitate more direct measurements in the future.

In the absence of values based on the TATB (or TPTB) assumptions, the NLJP assumption is also considered relatively reliable (see above) and values given on their basis are included in the present review. Data obtained via the Fc assumption (or its equivalent) are also included but are much less reliable and in the absence of corroboration should be viewed with caution.

8. Comparison of the TATB, NLJP, and Fc Assumptions

Comparisons between the ionic Gibbs energies of transfer from water to *neat* organic solvents obtained by the TATB assumption and those based on the NLJP and Fc assumptions (as well as the BBCr one, rarely used for aqueous solvent mixtures) have been made by several authors.[45,46] Agreement between the TATB and NLJP results is generally within 10 kJ mol^{-1}, although in some cases much worse. As noted above, such discrepancies are unpredictable, which represents a major drawback of the NLJP method. Disagreements between the TATB and Fc methods, on the other hand, are in many cases considerably larger than 10 kJ mol^{-1}, which makes moot the continued use of the latter (a trend noted in recent years).

The only direct comparison of these assumptions in aqueous organic mixtures is that of Kundu and Parker,[79] who showed that the TATB- and NLJP-derived values of $\Delta_t G^\circ$(ion) for aqueous AN, DMF, and DMSO (see Table 3 below for solvent abbreviations) were ≤6 kJ mol^{-1} apart whereas the differences between the TATB- and Fc-derived values were much larger. The present compilation sheds little further light on this issue, since the $\Delta_t G^\circ$(ion) based on the Fc assumption are too limited for reasonable comparisons to be made (except for aqueous AN and DMSO).

Ideally, comparisons of results on any two scales require at least two independent determinations of $\Delta_t G^\circ$(ion) by each assumption. The most useful data in this context are the values of $\Delta_t G^\circ(Ag^+, w\rightarrow w+AN)$ and $\Delta_t G^\circ(Cu^{2+}, w\rightarrow w+DMSO)$ derived via the TATB and NLJP assumptions, given in Tables 16 and 21 below. Both sets of data for each cosolvent show good agreement (prior to application of any addends). On the other hand, values of $\Delta_t G^\circ(Cu^{2+}, w\rightarrow w+AN)$, Table 16, differ by up to 16 kJ mol^{-1}. In hydroxylic solvents, data for $\Delta_t G^\circ(Cu^{2+})$ obtained by the TATB and NLJP assumptions agree fairly well (within 3 kJ mol^{-1}) in aqueous MeOH but differ by >20 kJ mol^{-1} beyond 50 mol % aqueous EtOH.

As a result of Kundu and Parker's work,[79] it is possible to convert $\Delta_t G^\circ$(ion) values obtained on the NLJP scale for EG, AN, DMF, and DMSO and on the Fc scale for AN and DMSO to the TATB scale by the addition of the addends listed in Table 1. Such conversions were made in the appropriate tables in section III, where both the original and the converted values are shown.

C. Solute Concentration and Solvent Composition Scales

1. Solute Concentrations

The concept of the medium effect was developed originally in terms of the molality scale, leading to values of ${}_{m}\gamma_{i(m)}$. However, a given mass (1 kg) of solvent does not represent any fundamental chemical quantity: the number of water and solvent molecules per kilogram differs and so does the average volume per molecule. There are good reasons, therefore, to use other concentration scales, as many authors have done.

Table 1. Conversion Factors (addends, in kJ mol^{-1}) for Converting Gibbs Energies of Transfer of Cations Obtained by the NLJP and Fc Assumptions to the TATB Scale (DMSO = dimethyl sulfoxide, AN = acetonitrile, DMF = *N*,*N*-dimethylformamide, EG = ethylene glycol)

	DMSO		AN		DMF	EG
$100x_{\text{co-solvent}}$	NLJP	Fc	NLJP	Fc	NLJP	NLJP
10	0.3	0.0	0.0	8.0	0.4	0.1
20	0.5	2.0	−4.0	(10.2)	2.1	0.3
30	1.5	4.0	−4.0	11.0	0.5	0.6
40	2.2	4.0	−5.0	(11.0)	−3.7	0.5
50	(2.1)	7.5	−4.0	11.0	−2.9	0.5
60	(1.8)	10.0	−6.0	(12.0)	−2.1	0.7
70	1.5	9.0	−5.0	13.0	−1.3	0.8
80	2.0	9.0	−5.0	13.0	−0.5	0.6
90	2.5	11.0	−5.0	12.0	0.6	0.4
100	2.9	11.0	−6.0	13.0	2.5	0.3

One such is the mole fraction scale, *x*, where the fractional number of moles of solute per mole of solvent is employed (strictly per mole of solvent plus solute(s), but at infinite dilution this converges to per mole of solvent). Medium effects on the mole fraction scale, ${}_{m}\gamma_{i(x)}$, are related to those on the molality scale, ${}_{m}\gamma_{i(m)}$, by

$$\log {}_{m}\gamma_{i(x)} = \log {}_{m}\gamma_{i(m)} - \log({}_{w}M/{}_{s}M) \qquad (18)$$

where *M* is the molar mass of the solvent (or its mean value for a solvent mixture).

There are, however, reasons to prefer the use of the molarity scale for representing the Gibbs energy of transfer. One is that the physicochemical interpretation of the solvation energies of solutes by means of statistical thermodynamics requires the use of the number density of the particles of the solute.[80] Molarities *c* in mol dm^{-3} are proportional to the number densities ρ. (If SI units are used for the number density, i.e., m^{-3}, then $c/\rho = 1000\ N_A$.) Another reason is that more recent extensive compilations of values of $\Delta_t G^\circ$ of ions from water to neat solvents[19,20] and to aqueous alcohols[22] have consistently used the molarity scale.

Thus, in this review all values of $\Delta_t G^\circ$ reported on other scales were converted to the molarity scale. The conversion from the molality scale is according to

$$\Delta_t G^\circ_{(c)} = \Delta_t G^\circ_{(m)} + 2.303\ RT \log({}_{s}d/{}_{w}d) \qquad (19)$$

where *d* is the density of the indicated solvent or solvent mixture at the temperature where the transfer energetics are measured. Conversion from the mole fraction scale is according to

$$\Delta_t G^\circ_{(c)} = \Delta_t G^\circ_{(x)} + 2.303\ RT \log({}_{w}M\ {}_{s}d/{}_{s}M\ {}_{w}d) \qquad (20)$$

2. Solvent Composition

As this review deals with the transfer of cations into mixed solvents, it is also necessary to adopt an appropriate scale to express the solvent composition. The scales that have been commonly employed are the mole fraction, mass fraction, and volume fraction (or their equivalent percentages). Each scale has its own merits and problems, and individual researchers

Table 2. Relevant Properties of the Ions Transferred[20]

univalent ions	ionic radius, r/pm	softness parameter, σ	multivalent ions	ionic radius, r/pm	softness parameter, σ
H^+	30[a]	0.00	Mg^{2+}	72	−0.41
Li^+	69	−1.02	Ca^{2+}	100	−0.66
Na^+	102	−0.60	Sr^{2+}	113	−0.64
K^+	138	−0.58	Ba^{2+}	136	−0.66
Rb^+	149	−0.53	Mn^{2+}	83	−0.15
Cs^+	170	−0.54	Fe^{2+}	78	−0.16
Cu^+	95	−0.22 (0.28)[b]	Co^{2+}	75	−0.11
Ag^+	115	0.18 (0.68)[b]	Ni^{2+}	69	−0.11
Au^+	137	0.44 (0.94)[b]	Cu^{2+}	73	0.38
Tl^+	150	0.20	Zn^{2+}	75	0.35
Me_4N^+	280		Cd^{2+}	95	0.58
Et_4N^+	337		Hg^{2+}	102	1.27
Pr_4N^+	379		Pb^{2+}	118	0.41
Bu_4N^+	413		Eu^{2+}	117	−0.62
i-Pe_3BuN^+	436		Fe^{3+}	65	0.33
Ph_4P^+	424		In^{3+}	79	0.48
Ph_4As^+	425		La^{3+}	105	−0.75

[a] Not for the bare proton but inferred from the thermodynamics of hydration. [b] The values in parentheses express the interactions with soft donors better than the values obtained from the ionization potential and enthalpy of hydration, which express the interactions with hard donors for these two d^{10} cations.

have selected a particular scale on the basis of experimental convenience, tradition, desired theoretical interpretation, or envisaged usage.

For aqueous/organic mixtures, the various solvent composition scales can be expressed as follows. When n_w mol of water of mass $n_w M_w$ are mixed with n_{org} mol of the organic cosolvent of mass $n_{org}M_{org}$, then the mole fraction of the latter component is

$$x_{org} = n_{org}/(n_{org} + n_w) \tag{21}$$

The mass (weight) fraction of the cosolvent is

$$w_{org} = n_{org}M_{org}/(n_{org}M_{org} + n_w M_w) \tag{22}$$

When V_{org} is the volume of the neat organic component used in making up a volume V_s of the solvent mixture, then its volume fraction is

$$\phi_{org} = V_{org}/V_s \tag{23}$$

Note that some authors have used ideal volume fractions, $\phi_{org,id} = V_{org}/(V_{org} + V_w)$, to express solvent composition. This introduces uncertainties into the experimental data, due to the contraction of the mixture with respect to its ideal volume, without providing any significant advantage; its use should be avoided.

The solvent composition scale adopted for this review is mole fraction, expressed for convenience as mole percent, $100x_{org}$, since this appears to best express the ability of the ions to sort the solvent molecules around them.[14,81,82] Data reported on other scales were therefore converted to the mole fraction scale. The density data required for conversions from volume-based scales were obtained from literature sources or by assuming a linear dependence of density on solvent (mol fraction) composition. Comparison of densities calculated via this assumption with experimental data for several known systems indicates the errors introduced are <1 kJ mol^{-1}. Mass fraction data were converted using mean molar masses, $(n_{org}M_{org} + n_w M_w)/(n_{org} + n_w)$.

For tabulation purposes, the original $\Delta_t G°$ data, converted where required by means of eqs 19 and 20 to the molarity scale, were interpolated numerically or graphically to evenly spaced values of $100x_{org}$.

D. Relevant Properties of the Transferred Ions and of the Solvents

This review deals with the transfer of uni- and multivalent cations from water to aqueous/organic mixtures. Explanations of the observed trends must ultimately be made in terms of the properties of the ions and solvents involved. Table 2 lists relevant ionic properties: their size, expressed by their radius r, and their hard/soft interaction preferences, expressed by their softness parameter σ.[20] Not included in Table 2 are cations for which $\Delta_t G°$ information is available only in water-rich mixtures of a few solvents and where little discussion in terms of cation−solvent interactions can consequently be made.

The relevant properties of the solvents appear to be[15,83] their (a) Lewis basicity, i.e., electron density donation ability, represented here by the Kamlet−Taft β parameter. Note that since this review is concerned only with the solvation of cations, the Lewis acidity (electron density acceptance ability) should not be significant; (b) ‘Polarity’/polarizability, expressed by the Kamlet−Taft π^* parameter; and (c) hard/soft interaction preferences, taken as the Marcus μ parameter.[84]

These properties for the neat solvents are listed in Table 3. More useful for this review would be the values of β, π^*, and μ for the relevant aqueous−organic solvent mixtures. However, values of β and π^* are currently known only for some of the mixtures[85] and μ values are known only for neat solvents.[84] The data available for the β values of aqueous mixtures are shown for convenience in Table 4.

Table 3. Relevant Properties of the Solvents[84]

solvent	Kamlet−Taft β	Kamlet−Taft π^*	Marcus μ
water	0.47	1.09	0.00
methanol (MeOH)	0.66	0.60	0.02
ethanol (EtOH)	0.75	0.54	0.08
2-propanol (i-PrOH)	0.84	0.48	
tert-butyl alcohol (t-BuOH)	0.93	0.41	
ethylene glycol (EG)	0.52	0.92	−0.03
propylene glycol (PG)		unavailable	
tetrahydrofuran (THF)	0.55	0.58	0.00
dioxane (DX)	0.37	0.55	
acetone (AC)	0.43	0.71	0.03
propylene carbonate (PC)	0.40	0.83	−0.09
pyridine (PY)	0.64	0.87	0.66
acetonitrile (AN)	0.40	0.75	0.34
formamide (FA)	0.48	0.97	0.09
N,*N*-dimethylformamide (DMF)	0.69	0.88	0.11
N-methylpyrrolidin-2-one (NMP)	0.77	0.92	0.13
hexamethyl phosphoric triamide (HMPT)	1.05	0.87	0.29
dimethyl sulfoxide (DMSO)	0.76	1.00	0.22

Table 4. Kamlet−Taft Donation Ability (basicity) β Parameters of Aqueous Mixtures (smoothed values from ref 85)

$100x_{\text{co-solvent}}$	10	20	30	40	50	60	70	80	90	100
water + MeOH	0.46	0.56	0.64	0.70	0.73	0.70	0.68	0.65	0.64	0.64
water + EtOH	0.46	0.63	0.66	0.66	0.66	0.66	0.66	0.68	0.72	0.75
water + *i*PrOH	0.59	0.66	0.68	0.70	0.71	0.74	0.77	0.80	0.82	0.84
water + THF	0.64	0.58	0.50	0.44	0.41	0.43	0.42	0.44	0.49	0.55
water + DX	0.39	0.47	0.50	0.51	0.52	0.55	0.55	0.50	0.45	0.37
water + AC	0.53	0.56	0.58	0.59	0.60	0.58	0.56	0.54	0.52	0.43
water + PY	0.53	0.57	0.60	0.63	0.66	0.68	0.69	0.70	0.68	0.64
water + AN	0.55	0.56	0.56	0.54	0.54	0.54	0. 55	0.53	0.48	0.40
water + FA	0.50	0.52	0.53	0.53	0.54	0.54	0.54	0.54	0.53	0.48
water + DMF	0.58	0.63	0.65	0.68	0.69	0.72	0.74	0.73	0.72	0.69
water + DMSO	0.57	0.59	0.59	0.61	0.66	0.68	0.70	0.75	0.79	0.76

E. Organization of the Data

In order for comparisons of the data to be as meaningful as possible, choices were made regarding the extrathermodynamic assumption and the concentration scales to be used, as described in sections II.B and II.C above.

To develop a unified presentation and an understanding of cation solvation in binary mixed aqueous−organic solvents, the present reviewers undertook the following steps. (1) Compilation of the available Gibbs energy of transfer (medium effect) data of as many monatomic and symmetrical tetraalkylammonium cations as possible, in the most commonly used and representative aquo-organic solvent mixtures over the complete range of solvent compositions (as far as available), based on the TATB, NLJP, and Fc (or BBCr or cobaltocene) extrathermodynamic assumptions. (2) Recalculation, where required, of the data in units of kJ mol^{-1}, conversion of $\log_m\gamma_i$ values to $\Delta_t G°$, and their conversion, if necessary, to the molarity scale. (3) Conversion of the data where possible to the preferred extrathermodynamic assumption, i.e., the TATB (or TPTB) method. (4) Commenting on the availability and an assessment of the reliability of the data. (5) Discussion of the trends of ion−solvent interactions based on the charge, size, and hard/soft nature of ions and the polarity, H-bond donation ability, acid−base nature, and structure of the solvent mixtures so as to arrive at general conclusions.

The Gibbs energy of transfer data, $\Delta_t G°(M^{n+}, w \rightarrow w+s)$ in kJ mol^{-1}, at 298.15 K (or 303.15 K for a few solvent mixtures) on the molarity scale are reported in Tables 5−21 (one for each cosolvent s). The order of the cations in each Table is that in Table 2 and the order of the cosolvents (Tables) is as given in Table 3. Wherever possible, data are quoted on the TATB (or TPTB), NLJP, Fc, and BBCr extrathermodynamic assumptions, according to which they have been reported in the literature. In a few solvent mixtures, where comparative measurements are available, the $\Delta_t G°(M^{n+})$ data based on the NLJP and the Fc assumptions have been converted to those on the TATB scale, using the addends in Table 1. In cases where only data obtained on the basis of a less satisfactory extrathermodynamic assumption are available, the values are still reported so as to provide a qualitative picture of the nature of ion−solvent interactions.

Data shown in Tables 5−21 in ordinary type are as reported in the original publications, converted where necessary to the molarity scale (using eqs 19 and 20), at (generally) evenly spaced decadic mole percentages of the cosolvent, using the specified extrathermodynamic assumption. If reported at other solvent compositions, the values were interpolated by the reviewers graphically or numerically, lengthy interpolations being indicated by placing values in parentheses. Data that were considered unreliable, for reasons given in the detailed comments in section II, were placed in square brackets and not used in the calculation of averaged values. For some systems that have been comprehensively reviewed previously, the “selected” values of $\Delta_tG°(M^{n+})$ of the original authors are shown in *italics* for the purpose of comparison with, but are not included in the calculation of, the present average values.

The values in Tables 5−21 at each (rounded) solvent composition were averaged for those cations where results are available from at least two independent studies, giving equal weight to each reported value. The averaged values have been classified as Recommended (indicated by the letter **R** in the status column and shown in **bold** type) when estimated by the reviewers to be accurate, within the constraints of the TATB assumption, to ±3 kJ mol^{-1}. If over some of the solvent composition range there were insufficient data to average, i.e., only one set of data is available on the TATB scale, these data are classified as Tentative, put in curly brackets, and the entire row is designated as **R**{**T**} in the status column. To the Tentative category (**T**) also belong results from (a) one set only of data based on TATB or (b) an average of one or more sets of data based on NLJP, or (c) the average of two or more sets of TATB or NLJP data differing by more than 5 kJ mol^{-1}. The likely accuracy is estimated to be ±10 kJ mol^{-1}. Data obtained using only the Fc, BBcr, or indicator methods have not been given a designation. Rejected data are identified by enclosure in square brackets [] and the reason(s) stated in the text. Some of the Recommended and Tentative data have been plotted against the solvent composition and are shown in Figures 1−12 as smoothed curves. In a few cases the smoothed values rather than averages are shown in Tables 5−21. These are marked by asterisks.

III. Detailed Presentation of the Data

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

1. Comments on the Data

Of all aqueous/organic solvent mixtures, those of water + MeOH are probably the most well studied. Data of $\Delta_tG°(M^{n+}, w \rightarrow w+MeOH)$ for a wide variety of monovalent and divalent cations over the entire solvent composition range, mostly based on the TATB/TPTB and NLJP assumptions, are given in Table 5. In addition, data are also shown for all 14 rare earth cations up to 30 mol % MeOH. The many values for these mixtures listed by Marcus[22] included those based on less reliable extrathermodynamic assumptions to which zero weights were assigned. These have not been repeated here.

It is noteworthy that previous compilations[22,104] of $\Delta_tG°(\text{cation}, w \rightarrow w+MeOH)$, based on more limited data, arrived at recommended values (shown *italicized* in Table 5) similar to the present ones. Selected data from Table 5 are plotted in Figures 1 and 2.

Three[89,90,97] of the four independent studies of $\Delta_tG°(Ph_4As^+, w \rightarrow w+MeOH)$ are in almost quantitative agreement, permitting their averages to be Recommended over the entire solvent composition range. The data of Villermaux and Delpuech[87] deviate significantly, especially at lower x_{MeOH}, and have therefore been rejected.

Water/methanol mixtures are notable in that TPTB data are also available in three independent studies.[89,104,108] The agreement among the reported values of $\Delta_tG°(Ph_4P^+, w \rightarrow w+MeOH)$ is even better than for $\Delta_tG°$ (Ph_4As^+). Still more pleasing is the fact that $\Delta_tG°(Ph_4P^+) = \Delta_tG°(Ph_4As^+)$ within 0.7 kJ mol^{-1} over the entire composition range. This provides some indirect support for the use of the reference electrolyte approach. The present values of $\Delta_tG°(Ph_4P^+)$ and $\Delta_tG°(Ph_4As^+)$ are similar to, but more broadly based than, those suggested in previous compilations.[22,104]

The numerous independent studies of the hydrogen ion (Table 5) are generally in good agreement over the entire composition range. The values of Villermaux and Delpuech[87] are again aberrant and have therefore been rejected. The averaged, Recommended, values of $\Delta_tG°(H^+)$ are close to those proposed in earlier compilations.[22,104]

The situation for the alkali metal and silver ions is similar to that for the hydrogen ion, and the averaged values generally have been classified as Recommended. The averaged values of $\Delta_tG°(Rb^+)$ are rather ‘bumpy’ (Figure 1) with significant discrepancies among the values at higher x_{MeOH}, and perhaps unexpectedly, $\Delta_tG°(Rb^+) > \Delta_tG°(Cs^+)$. Therefore, the averaged data at $x_{MeOH} \geq 0.7$ for these two ions are classified as Tentative. The data of Covington and Thain[93] for Rb^+ appear to be high at $x_{MeOH} > 0.4$ and have been rejected. For the other univalent cations, relatively fewer data are available so these have been given a Tentative classification, pending future verification.

The data for the divalent cations are generally unsatisfactory. Few studies cover the whole composition range and disagreements among independent studies are often considerable, especially for methanol-rich solutions. Values for $\Delta_tG°(Cu^{2+})$ are an exception, and so their average is Recommended. No comments are possible on the values of $\Delta_tG°(M^{3+})$ as all the data are from a single source.[88] However, these values were determined from the solubility of the iodate salts, and no allowance was made for incomplete dissociation or possible hydrolysis.

It is pertinent to point out here the difficulties of estimating the values of $\Delta_tG°(\text{ion})$ for multivalent ions. In particular, the role of ion pairing, which can profoundly affect the apparent values of $\Delta_tG°$ for salts containing multiply charged ions, demands but seldom receives special care and attention. Such considerations are especially important in solubility and electrochemical measurements. It is noteworthy that the independently determined values of $\Delta_tG°(M^{2+}, w \rightarrow w+MeOH)$ show much greater variation than the corresponding values for the M^+ ions (Table 5). Indeed, a different selection of these data would produce results that contradict some of the points made below.

2. Discussion of the Transfer Energetics

The values of $\Delta_tG°(H^+)$ show that aqueous methanol mixtures are slightly more basic ($\Delta_tG°(H^+) < 0$) than water in the intermediate solvent composition region $0.2 \leq x_{MeOH} \leq 0.8$ but less basic in the more water-rich and, especially, the more MeOH-rich

Table 5. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Methanol (MeOH) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	0.6	0.5	−0.2	−1.0	−1.5	−1.8	−2.1	(−2.4)			TPTB[a]	86	
	[−3.5]	[−5.6]	[−6.8]	[−7.5]	[−7.6]	[−7.1]	[−5.5]			8.5	TATB	87	
	0.2	0.2	−0.4	−1.0	−1.3	−1.5	−1.4	−0.9	2.2	9.1	TPTB[a]	88	
	0.0	0.4	0.3	−0.2	0.5	−2.4	−2.9	−2.2	1.2	8.6	TATB	89	
	−0.3	−0.8	−1.4	−2.1	−2.9	−3.9					TATB	90	
	0.8	*0.8*	*0.3*	*−0.4*	*−0.9*	*−1.0*	*−0.3*	*1.6*	*5.1*	*10.3*	TATB	22	
	0.1	**0.1**	**−0.4**	**−1.1**	**−1.6**	**−2.4**	**−2.1**	**−1.8**	**1.8**	**8.7**	**TATB**		**R**
Li^+	1.7	2.6	3.1	3.3	3.4	3.5	(3.5)				TATB	91	
	1.1	2.0	2.5	2.7	2.6	2.7	2.7	2.5	2.4	2.2	TPTB[a]	92	
	1.6	2.3	2.6	2.8	2.5	2.6	2.7	2.7	2.6	1.9	TPTB[a]	86	
	1.2	1.5	1.5	1.3	0.9	0.9	0.9	0.9	0.8	0.2	TPTB[a]	93	
	0.7	1.8	2.9	3.5	4.0	4.2	4.2	4.1	4.0	3.8	TATB	94	
	1.7	2.5	3.0	3.1	3.2	3.2	3.2	3.2	3.3	3.4	TATB	95	
	1.6	2.5	2.8	2.9	2.6	2.7	2.8	2.9	3.3	3.6	TATB	89	
	1.5	*2.5*	*3.1*	*3.4*	*3.6*	*3.6*	*3.6*	*3.7*	*4.0*	*4.5*	TATB	22	
	1.4	**2.3**	**2.8**	**3.1**	**3.1**	**3.2**	**3.1**	**3.1**	**3.1**	**3.0**	**TATB**		**R**
Na^+	2.0	3.8	4.8	5.7	6.3	6.8	7.0	7.2	7.3	7.2	TPTB[a]	92	
	2.5	4.1	5.0	5.8	6.3	6.8	7.3	7.7	7.8	7.1	TPTB[a]	86	
	2.0	3.4	4.1	4.7	5.0	5.2	5.3	5.3	5.2	4.6	TPTB[a]	93	
	2.4	4.1	5.1	5.8	6.4	6.8	7.3	7.7	7.9	7.7	TATB	89	
	2.4	4.1	5.2	6.3	6.7	7.5	7.9	8.8	9.0	8.6	TATB	96	
	2.2	*3.7*	*5.1*	*6.2*	*7.1*	*7.7*	*8.2*	*8.3*	*8.3*	*8.0*	TATB	22	
	2.3	**3.9**	**4.8**	**5.7**	**6.1**	**6.6**	**7.0**	**7.3**	**7.4**	**7.0**	**TATB**		**R**
K^+	2.0	3.9	4.9	5.8	6.7	7.5	8.3	8.4	8.4	8.5	TPTB[a]	92	
	2.4	4.1	5.1	5.9	6.7	7.5	8.3	8.7	8.9	8.4	TPTB[a]	86	
	1.9	3.2	4.0	4.7	5.3	5.8	6.5	6.9	7.2	7.3	TPTB	93	
	1.8	3.5	5.0	6.4	7.5	8.5	9.2	9.8	10.3	10.5	TATB	97	
	2.1	3.7	4.8	5.9	6.7	7.4	8.2	8.6	8.9	8.6	TATB	89	
	1.6	2.8	3.8	4.5	5.0	5.2					TATB	90	
	2.2	*3.9*	*5.3*	*6.6*	*7.7*	*8.5*	*9.1*	*9.5*	*9.7*	*9.7*	TATB	22	
	2.0	**3.5**	**4.6**	**5.5**	**6.3**	**7.0**	**8.1**	**8.4**	**8.7**	**8.4**	**TATB**		**R**
Rb^+	2.0	3.6	4.7	5.6	6.5	7.4	8.2	8.6	8.9	8.9	TPTB[a]	92	
	2.6	2.1	3.1	6.2	6.2	7.1	8.3	9.0	9.2	8.8	TPTB[a]	86	
	2.4	4.4	6.0	7.8	[9.7]	[11.8]	[14.0]	[15.9]	[17.3]	[17.4]	TPTB[a]	93	
	2.4	4.1	5.2	6.2	7.2	8.3	9.5	10.6	11.4	12.2	TPTB[a]	98	
	3.4	5.6	6.9	7.7	8.1	8.4	9.4	9.8	11.2	13.1	TATB	89	
	2.2	*3.9*	*5.4*	*6.7*	*7.7*	*8.6*	*9.2*	*9.6*	*9.7*	*9.7*	TATB	22	
	2.6	**4.0**	**5.2**	**6.2***	**7.0**	**7.8**	**9.0**	{**9.8**}	{**10.6**}	{**11.3**}	**TATB**		**R**{**T**}
Cs^+	1.8	3.2	4.2	5.1	6.0	6.9	7.7	8.0	8.3	8.3	TPTB[a]	92	
	2.2	3.6	4.4	5.2	5.9	6.7	(7.8)				TPTB[a]	86	
	2.9	4.6	5.4	6.0	6.5	7.1	7.9	8.7	9.2	9.1	TATB	89	
	2.1	*3.6*	*4.9*	*6.1*	*7.0*	*7.8*	*8.4*	*8.8*	*9.0*	*9.1*	TATB	22	
	2.3	**3.8**	**4.7**	**5.4**	**6.1**	**6.9**	**7.8**	{**8.4**}	{**8.8**}	{**8.7**}	**TATB**		**R**{**T**}
Ag^+	1.8	2.9	3.4	(3.8)							TATB	99	
	1.6	2.7	3.8	4.6	4.8						TATB[b]	100	
	0.9	1.5	2.4	3.4	4.8	6.2	7.4	8.6	9.7	10.8	TATB	103	
	1.0	2.1	3.2	4.0	4.6	5.2	5.6	5.8	6.1	6.2	TPTB[a]	104	
	1.2	2.3	3.6	4.5							TATB	105	
	1.4	*2.7*	*3.8*	*4.7*	*5.5*	*6.1*	*6.5*	*6.7*	*6.8*	*6.7*	TATB	22	
	1.3	**2.3**	**3.3**	**4.1**	**4.8**	**5.7**	**6.5**	**7.2**	**7.9**	**8.5**	**TATB**		**R**
Tl^+	**2.5**	**3.6**	**4.5**	**5.1**	**5.5**	**5.6**	**5.5**	**5.2**	**4.6**	**4.2**	**TPTB**	105	**T**
NH_4^+	**1.7**	**2.3**	**2.8**	**3.5**	**4.1**	**4.6**	**5.0**	**6.0**	**8.0**	**11.3**	**TATB**	106	**T**
Me_4N^+	0.8	(1.4)	2.1					6.1	(7.0)	8.0	TATB[c]	107	
	0.7	1.0	1.6	1.9	2.4	3.2	4.0	4.5	5.1	5.9	TPTB	104	
	0.8	**1.4***	**1.9**	{**2.3***}	{**2.9***}	{**3.6***}	{**4.5***}	**5.3**	**6.1**	**7.0**	**TATB**		**R**{**T**}
Pr_4N^+	−1.4	(−2.8)	−3.8					−7.4	(−7.5)	−7.7	TATB[c]	107	
	−2.6	−3.5	−4.6	−5.8	−6.8	−7.6	−8.4	−9.8	−10.3	−9.9	TPTB	104	
	−1.5	**−3.2**	**−4.5***	{**−5.8**}	{**−6.8**}	{**−7.6**}	{**−8.2***}	**−8.8***	**−8.9**	**−8.8**	**TATB**		**R**{**T**}
Bu_4N^+	**−2.7**	**−5.2**	**−7.6**	**−10.2**	**−12.5**	**−14.6**	**−16.6**	**−19.1**	**−21.3**	**−23.1**	**TPTB**	104	**T**
Ph_4P^+	−3.7	−8.2	−12.6	−15.5	−18.0	−19.9	−21.4	−22.4	−23.1	−23.8	TPTB	108	
	−4.3	−8.3	−12.2	−15.4	−18.0	−20.0	−21.3	−22.2	−22.9	−24.0	TATB	89	
	−4.3	−8.3	−11.8	−14.8	−17.3	−19.3	−20.8	−21.8	−22.3	−22.3	TPTB	104	
	−4.1	**−8.3**	**−12.2**	**−15.2**	**−17.8**	**−19.7**	**−21.2**	**−22.1**	**−22.8**	**−23.4**	**TPTB**		**R**
Ph_4As^+	[−10.6]	[−16.3]	[−19.5]	[−21.5]	[−22.8]	[−23.6]	[−23.7]			[−24.0]	TATB	87	
	−3.8	−7.3	−10.4	−13.2	−15.7	−17.7	−19.5	−20.8	−21.9	−22.5	TATB	97	
	−4.2	−8.2	−12.1	−15.3	−18.0	−20.1	−21.4	−22.4	−23.2	−24.3	TATB	89	
	−4.9	−9.3	−13.3	−16.7	−19.7	−22.2					TATB	90	
	−4.2	*−8.1*	*−11.5*	*−14.5*	*−17.0*	*−19.1*	*−20.6*	*−21.8*	*−22.4*	*−22.5*	TATB	22	
	−4.3	**−8.3**	**−11.9**	**−15.1**	**−17.8**	**−20.0**	**−20.5**	**−21.6**	**−22.6**	**−23.4**	**TATB**		**R**
Mg^{2+}	**2.0**	**3.3**	**4.2**	**4.7**	**4.8**	**4.3**	**3.8**	**3.3**	**2.7**	**2.0**	**TATB**[d]	109	**T**

Table 5 (Continued)

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion \ 100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
Ca^{2+}	4.5	5.5	5.7	6.0							TATB	105	
	3.9	6.5	8.4	9.7	10.7	11.2	11.3	11.2	11.1	11.2	TATB[d]	109	
	4.2	**6.0**	**7.5**	**8.9***	{**10.4**}*	{**11.2**}	{**11.3**}	{**11.2**}	{**11.1**}	{**11.2**}	**TATB**		**R**{**T**}
Sr^{2+}	3.9	6.2	8.1								TATB	104	
	6.4	7.7	8.9								TATB	105	
	4.3	6.8	7.7	8.5	9.3	9.1	8.4	8.0	7.5	7.1	TATB[d]	109	
	5.3	**7.2**	**8.2**	{**8.5**}	{**9.3**}	{**9.1**}	{**8.4**}	{**8.0**}	{**7.5**}	{**7.1**}	**TATB**		**R**{**T**}
Ba^{2+}	3.2	5.7	7.6	9.2							TATB[e]	110	
	3.9	6.2	8.6	11.0	12.4	14.3	15.7	17.0	17.1	17.2	TATB	104	
	4.2	6.5	8.4	9.8	10.8	11.0	10.5	8.6	7.1	6.0	TATB[d]	109	
	3.8	**6.1**	**8.2**	**10.0**	**11.6**	{**12.5**}	{**13.1**}				**TATB**		**R**{**T**}
Cu^{2+}	1.1	1.8	2.9	4.5	6.1	7.7	9.7	12.4	15.6	24.7	NLJP	46	
	1.9	3.2	4.6	6.8	8.7	10.8	13.2	15.5	20.4	29.1	NLJP	111	
	1.9	3.0	4.0								TATB	105	
	3.7	6.1	7.1	8.0	8.9	10.0	11.2	12.6	16.1	21.8	TATB[d]	109	
	2.2	**3.5**	**4.7**	**6.4**	**7.9**	**9.5**	**11.4**	**13.5**	{**17.4**}	{**25.2**}	**TATB**		**R**{**T**}
Zn^{2+}	2.7	5.2	7.6	9.0	11.4	12.8	14.1				TPTB[e]	112	
	2.4	5.7	7.6	9.5	11.4	13.3	(15.0)	(19.5)	(22.9)	26.4	TPTB	104	
	2.4	4.2	4.4	4.3	4.7	5.1	5.5	6.3	6.4	13.0	TATB[d]	109	
	2.5	**5.0**	**6.5**								**TATB**		**T**
Cd^{2+}	2.2	4.2	5.6	6.6							TPTB[e]	113	
	2.4	4.2	5.9	8.8	12.9	16.6	20.2	23.5	27.4	31.4	TPTB	104	
	2.7	4.7	5.6	6.0	6.5	7.1	7.7	8.3	9.7	9.6	TATB[d]	109	
	2.4	**4.4**	**5.7**	**6.9**							**TATB**		**R**
Hg^{2+}	9.7	12.3	15.3								TATB	114	
	2.8	4.7	5.4	5.5	6.4	6.8	7.2	7.3	8.2	6.8	TATB[d]	109	
Pb^{2+}	5.2	6.2	6.1	7.0	7.2						TATB	105	
	3.2	5.3	6.2	6.8	7.4	7.9	8.4	9.4	9.8	10.3	TATB[d]	109	
	4.1	**5.8**	**6.2**	**6.9**	**7.3**	**7.9**	**8.4**	**9.4**	**9.8**	**10.3**	**TATB**		**R**{**T**}
La^{3+}	5.4										TATB	105	
Ce^{3+}	1.6	6.1	8.9								TATB[f]	88	
Pr^{3+}	1.1	7.1	11.2								TATB[f]	88	
Nd^{3+}	0.8	7.1	10.9								TATB[f]	88	
Sm^{3+}	0.8	7.1	10.9								TATB[f]	88	
Eu^{3+}	0.6	6.6	11.2								TATB[f]	88	
Gd^{3+}	0.3	6.1	10.4								TATB[f]	88	
Tb^{3+}	0.6	7.4	11.9								TATB[f]	88	
Dy^{3+}	0.6	7.1	10.7								TATB[f]	88	
Ho^{3+}	0.3	6.6	12.4								TATB[f]	88	
Er^{3+}	1.6	7.9	12.2								TATB[f]	88	
Tm^{3+}	0.3	7.6	12.9								TATB[f]	88	
Yb^{3+}	1.3	8.1	12.9								TATB[f]	88	
Lu^{3+}	2.3	7.6	12.4								TATB[f]	88	

[a] Using $\Delta_t G°$(MCl) combined with $\Delta_t G°(Cl^-)$ based on the TPTB scale from ref 108, quoted in ref 104. [b] See also, refs 101 and 102. [c] Recalculated in ref 22 from the data in ref 107. [d] Authors' "selected values" smoothed by the reviewers. [e] Using $\Delta_t G°(MCl_2)$ combined with $\Delta_t G°(Cl^-)$ based on the TATB scale from ref 104. [f] Using $\Delta_t G°[M(IO_3)_3]$ combined with $\Delta_t G°(IO_3^-)$ based on the TATB scale from ref 105.

regions. In the neat solvents, H^+ forms a strong solvate (H_3O^+ or $CH_3OH_2^+$) with one solvent molecule that is further solvated by additional solvent molecules. In the mixtures, the resulting basicity depends on the interaction of H_3O^+ or $CH_3OH_2^+$ with the other solvent molecules present, both H_2O and CH_3OH. Such interactions may be expressed in terms of the equilibrium

$$H_3O^+ + CH_3OH \rightleftharpoons H_2O + CH_3OH_2^+$$

These interactions are finely balanced in $H_2O + CH_3OH$ mixtures and are affected, for example, by the replacement of the three-dimensional hydrogen-bonded network of water with the one-dimensional methanol structure;[89] hence, quite complex behavior might be anticipated in the presence of dissolved H^+.

The values of $\Delta_t G°$ for the alkali metal ions, which are in the order $Li^+ < Na^+ < K^+ \approx Cs^+ < Rb^+$, are increasingly positive (corresponding to less favorable solvation of the ions compared with neat water) as the MeOH concentration in the mixtures rises. The simple effect of ionic radius, which might be expected for the interaction of hard ions with hard solvents, is muted here because both solvents are O-donors of similar donor strength. Thus, although the values of $\Delta_t G°$ (ion) for the smaller cations parallel their ionic radii (Table 2), the larger cations show no such effect. Furthermore, the overall magnitudes of $\Delta_t G°$ for all of these cations are rather small (<12 kJ mol^{-1}) and might, for example, simply be reflecting the packing abilities of H_2O and CH_3OH molecules in the primary solvation sheaths of the ions.[115] Further discussion of these data is probably better made in terms of the more dramatic changes that take place in the ionic transfer enthalpy and entropy data in these mixtures,[77] but this is beyond the scope of this review.

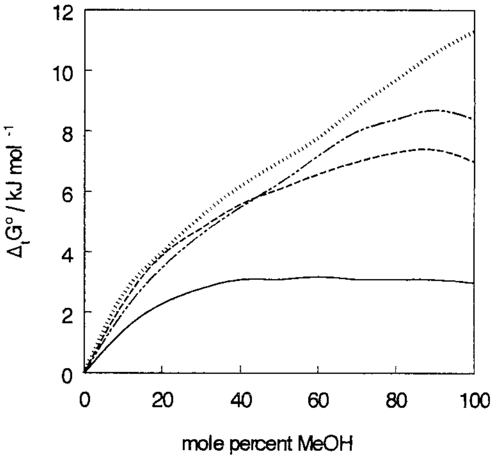

Figure 1. Gibbs energy of transfer of cations from water to aqueous methanol as a function of the mole percentage of methanol: (—) Li^+, (- - -) Na^+, (—··—) K^+, and (···) Rb^+.

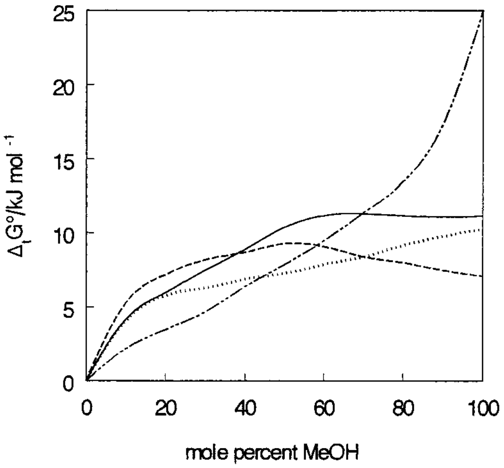

Figure 2. Gibbs energy of transfer of cations from water to aqueous methanol as a function of the mole percentage of methanol: (—) Ca^{2+}, (- - -) Sr^{2+}, (—··—) Cu^{2+}, and (···) Pb^{2+}.

The data for $\Delta_t G°(Ag^+$ or $Tl^+)$ are similar to those of the alkali metal ions. The tetraalkylammonium cations, on the other hand, show more complex behavior. Thus, $\Delta_t G°(Me_4N^+)$ becomes increasingly positive with increasing MeOH content like an alkali metal ion. In marked contrast, for the larger R_4N^+ ions (as well as for Ph_4As^+ and Ph_4P^+), $\Delta_t G°$ becomes more negative. This suggests that the hydrophobic effects of these bulky cations and their increased dispersion interactions with the methyl groups of the MeOH molecules outweigh any electrostatic considerations. Data for $\Delta_t G°(Et_4N^+)$ would be interesting but do not appear to have been measured.

The values of $\Delta_t G°(M^{2+}, w \rightarrow w+MeOH)$ are all positive, consistent with more favorable solvation of these ions by water molecules, but show some puzzling anomalies. As for the alkali metal ions, there is some evidence of an ionic size effect with the order $Mg^{2+} < Sr^{2+} < Ca^{2+} < Ba^{2+}$; however, the position of Sr^{2+} is anomalous and not easily explained. Similarly, if electrostatic interactions alone are important, it is hard to understand why $\Delta_t G°(Pb^{2+}) < \Delta_t G°(Cd^{2+})$ at high x_{MeOH} or why the $\Delta_t G°$ values for Cu^{2+} and Zn^{2+} appear to be almost 20 kJ mol^{-1} more positive than that of the similarly sized Mg^{2+}. The data for Hg^{2+} differ markedly from the other M^{2+} ions, again for no obvious reason. In view of these anomalies and the disagreements in the data discussed above, further experimental effort is clearly required in this area.

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

1. Comments on the Data

With a few notable exceptions, far fewer data for ionic Gibbs energies of transfer are available for aqueous EtOH mixtures (Table 6) than in the corresponding MeOH solutions (Table 5). The Gibbs energies of transfer of univalent cations, $\Delta_t G°(M^+, w \rightarrow w+EtOH)$, have been studied extensively over the entire composition range, mainly via the TATB method (Table 6), which allows many of the averaged values to be Recommended. In contrast, the $\Delta_t G°$ values for multivalent cations are rather less extensive, with few independent studies. Selected values of $\Delta_t G°(M^+, w \rightarrow w+EtOH)$ are shown graphically in Figures 3 and 4. Also included (*italicized*) in Table 6 for comparison are the selected values of Marcus,[22] which are in general similar to the present Recommended data.

The values of $\Delta_t G°(Ph_4As^+, w \rightarrow w+EtOH)$ have been estimated via the TATB assumption in a number of independent reports[90,120,122,129,130] and are in good agreement ($\sigma < 1$ kJ mol^{-1}), enabling their average values to be Recommended. The notable exception is at lower EtOH concentrations ($x_{EtOH} = 0.1$) where two sets of values differ by about 6 kJ mol^{-1}. One set of data for $\Delta_t G°(Ph_4Sb^+, w \rightarrow w+EtOH)$ also exists[122] and is in good agreement with those for Ph_4As^+ except at $x_{EtOH} \leq 0.3$.

Data for $\Delta_t G°(H^+, w \rightarrow w+EtOH)$ are not fully satisfactory, with two independent studies[117,118] reporting considerably more positive values than those of others[116,120] and, for one group,[118] of their own later work.[90,121] As the bulk of the data in these mixtures (Table 6) and in pure EtOH[133] favors the less positive values, the results of Juillard et al.[117] and the earlier work of Kundu's group[118] were rejected.

Numerous studies of $\Delta_t G°$ of K^+, Rb^+, and Cs^+ are available (Table 6) and are in good agreement, which means that their average values can be Recommended at all solvent compositions. Data for Na^+ and especially for Li^+ are not so well substantiated, except at low x_{EtOH}. Independent studies of $\Delta_t G°(R_4N^+, w \rightarrow w+EtOH)$ for the tetraalkylammonium cations up to Bu_4N^+ and for $i$$Pe_3BuN^+$ show good agreement and systematic behavior, enabling their average values to be classified as Recommended at all solvent compositions.

Data for the divalent cations are relatively few, with Cu^{2+} being an exception. However, for this ion there is a major disagreement between the values estimated via the TATB[132] and NLJP[46,111] assumptions. Interestingly, this is not the case for Pb^{2+}, where independent NLJP[132]- and TATB[131]-based data are in good agreement. Little can be said about the reliability of the remaining data, except that there

Table 6. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Ethanol (EtOH) Mixtures at 298.15 K

	$\Delta_tG°$(ion)/kJ mol^{-1}, molarity-scale												
ion \ 100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	−1.8	−4.7	−6.4	−6.7	−5.8	−4.7	−4.4	−2.9	1.2	8.6	TATB	116	
	[−0.2]	[−0.6]	[1.0]	[2.2]	[3.6]	[5.5]	[8.5]	[13.5]	[18.9]	[25.7]	TATB	117	
	[1.0]	[1.8]	[2.7]	[3.7]	[4.6]	[5.9]	[7.2]	[8.9]	[11.6]	[22.4]	TATB	118	
	0.1	−1.5									TATB[a]	119	
	−0.1	−1.6	−3.2	−3.4	−3.2	−2.6	−1.3	1.0	5.5	12.7	TATB	120	
	−0.4	−1.6	−3.7								TATB	90	
	0.2	−1.6		−3.0							TATB	121	
	−0.2	−1.7	−3.4	−3.7	−3.6	−3.0	−1.8	0.5	5.0	12.1	TATB	122	
	−0.6	*−2.0*	*−3.4*	*−4.5*	*−5.1*	*−4.9*	*−3.5*	*0.7*	*3.8*	*10.3*	TATB	22	
	−0.4	**−2.1**	**−4.2**	**−4.2**	**−4.2**	**−3.4**	**−2.5**	**−0.5**	**3.9**	**11.1**	**TATB**		**R**
Li^+	1.9	2.3									TATB[a]	119	
	2.9	**2.3**	**0.9**	**1.1**	**2.5**	**3.9***	**5.2**	**6.4**	**8.1**	**10.3**	**TATB**[b]	123	**T**
Na^+	2.6	3.4									TATB[a]	119	
	3.0	3.4	4.2	4.8	6.0	8.0					TATB	124	
	2.9	2.9	2.7	3.3	4.4	6.0	7.7	9.9	12.4	14.9	TATB[b]	123	
	2.8	**3.2**	**3.4**	**4.0**	**5.2**	**6.4***	{**7.7**}	{**9.9**}	{**12.4**}	{**14.9**}	**TATB**		**R**{**T**}
K^+	0.2	0.6	1.4	2.8	4.5	6.7	9.1	11.6	13.8	15.6	TATB	116	
	1.4	1.1	1.7	2.7	4.1	6.1	7.5	9.4	11.7	13.9	TATB[a]	125	
	3.0	3.2	3.9								TATB[a]	124	
	1.8	3.0	4.1	5.4	7.0	8.8	11.0	13.0	15.5	18.4	TATB	120	
	1.4	2.4	2.7	2.8	2.8						TATB	90	
	(1.7)	2.8	3.9	5.1	6.6	8.4	10.6	12.5	15.0	17.8	TATB	122	
	2.1	*3.2*	*4.4*	*5.6*	*6.8*	*8.3*	*9.9*	*11.9*	*14.1*	*16.8*	TATB	22	
	1.6	**2.2**	**3.0**	**3.8**	**5.0**	**7.1***	**9.5**	**11.6**	**14.0**	**16.4**	**TATB**		**R**
Rb^+	2.9	3.4	3.8	4.1	5.5	7.9	10.9				TATB[c]	98	
	0.6	1.3	2.1	3.8	5.9	7.9	9.6	11.6	13.4	15.1	TATB[c]	107	
	1.5	2.7	3.9	5.0	6.5	8.3	10.2	12.4	14.9	17.6	TATB	120	
	(1.4)	2.5	3.6	4.7	6.2	7.8	9.7	12.9	14.3	17.0	TATB	122	
	2.3	*3.5*	*4.6*	*5.6*	*6.7*	*8.0*	*9.5*	*11.4*	*14.1*	*16.5*	TATB	22	
	1.6	**2.5**	**3.4**	**4.4**	**5.9**	**8.0**	**10.1**	**12.3**	**14.2**	**16.6**	**TATB**		**R**
Cs^+	3.0	3.0	3.8	4.6	5.4						TATB[a]	124	
	0.2	0.4	1.3	3.4	5.5	7.6	9.5	11.6	13.3	15.1	TATB	107	
	−0.3	4.2									TATB[d]	114	
	1.4	2.2	3.3	4.7	5.7	7.8	9.5	11.7	14.2	17.0	TATB	120	
	(1.4)	2.0	3.1	4.4	5.8	7.4	9.1	11.2	13.8	16.4	TATB	122	
	1.1	**2.5**	**2.8**	**4.2**	**5.5**	**7.7**	**9.5**	**11.7**	**13.8**	**16.1**	**TATB**		**R**
Ag^+	**−1.2**	**−2.3**	**−2.7**	**−2.4**	**−1.4**	**0.1**	**1.7**	**2.8**	**3.3**	**4.5**	TATB	126	**T**
Au^+	**−1.9**	**−3.6**	**−4.3**	**−3.7**	**−2.0**	**−0.1**	**0.7**	**3.9**	**6.5**	**7.4**	TATB	127	**T**
Me_4N^+	−1.4	−1.6	−1.3	0.8	2.6	4.8	7.0	9.3	11.4	14.8	TATB	107	
	−1.5	−1.0	0.3	1.8	3.9	6.2	8.4	11.0	13.8	16.4	TATB	120	
	(−1.6)	−1.2	0.1	1.5	3.5	5.8	7.9	10.5	13.2	15.8	TATB	122	
	−1.5	**−1.3**	**−0.5**	**1.3**	**3.3**	**5.5**	**7.8**	**10.2**	**12.6**	**15.6**	**TATB**		**R**
Et_4N^+	−1.9	−2.5	−2.3	−2.0	−1.3	−0.6	0.2	1.1	2.3	3.8	TATB	120	
	−2.0	−2.7	−2.6	−2.3	−1.7	−1.1	−0.8	0.6	1.7	3.2	TATB	122	
	−2.0	**−2.6**	**−2.5**	**−2.2**	**−1.5**	**−0.9**	**−0.3**	**0.9**	**2.0**	**3.5**	**TATB**		**R**
Pr_4N^+	−3.6	−6.4	−8.1	−8.0	−7.0	−6.0	−5.4	−4.8	−4.5	−4.1	TATB	107	
	−3.8	−5.3	−6.0	−5.9	−5.7	−5.3	−4.2	−3.2	−1.7	0.1	TATB	120	
	−3.9	−5.4	−6.0	−6.2	−6.0	−5.7	−4.7	−3.7	−2.3	−0.5	TATB	122	
	−3.7	**−5.9**	**−7.1**	**−7.0**	**−6.4**	**−5.7**	**−4.8**	**−4.0**	**−3.1**	**−2.0**	**TATB**		**R**
Bu_4N^+	−4.8	−9.4	−13.8	−18.2							TATB	107	
	−4.2	−5.9	−6.5	−6.9	−7.5	−8.3	−9.1	−10.0	−10.8	−11.7	TATB	120	
	−4.3	−6.0	−6.7	−7.2	−7.9	−8.8	−9.6	−10.5	−11.4	−12.3	TATB	122	
	−4.3	**−6.0**	**−6.6**	**−7.1**	**−7.7**	**−8.5**	**−9.3**	**−10.3**	**−11.1**	**−12.0**	**TATB**		**R**
iPe_3BuN^+	−5.5	−10.6	−14.7	−17.8	−19.8	−20.8	−21.1	−21.0	−21.3	−22.4	TATB	116	
	2.9	−7.6	−12.3	−16.3	−18.6	−20.2	−21.4	−22.2	−22.9	−23.1	TATB[c]	128	
	−4.1	**−9.1**	**−13.5**	**−17.1**	**−19.2**	**−20.5**	**−21.3**	**−21.6**	**−22.1**	**−22.7**	**TATB**		**R**
Ph_4As^+	−6.8	−14.0	−17.4	−19.2	−20.0	−20.2	−21.6	−22.2	−22.8	−21.3	TATB	129	
	−11.7	−15.9	−18.6	−20.3	−21.4	−21.9	−22.2	−22.4	−22.5	−22.6	TATB	120	
	−6.6	−13.9	−16.1								TATB	130	
	−6.9	−12.6	−17.0	−20.0	−21.7						TATB	90	
	−11.8	−16.1	−18.9	−20.6	−21.7	−22.4	−22.7	−22.9	−23.0	−23.2	TATB	122	
	−7.2	*−12.8*	*−16.6*	*−18.8*	*−20.0*	*−20.3*	*−20.3*	*−20.2*	*−20.5*	*−21.4*	TATB	22	
	{**−8.8**}	**−14.5**	**−17.6**	**−20.0**	**−21.2**	**−21.5**	**−22.2**	**−22.5**	**−22.9**	**−22.4**	**TATB**		{**T**}**R**
Ph_4Sb^+	−21.0	−22.5	−22.6	−22.8	−23.0	−23.1	−23.2	−23.6	−24.0	−24.6	TATB	122	
Ca^{2+}	3.8										TATB	131	
Cu^{2+}	2.3	4.1	6.5	9.9	12.8	16.0	20.6	26.0	37.9	51.7	NLJP	111	
	1.5	2.9	4.5	6.9	9.3	12.6	16.2	20.8	31.5	44.8	NLJP	46	
	1.3	**1.9**	**2.5**	**2.9**	**3.8**	**4.7**	**6.6**	**10.0**	**13.9**	**19.1**	**TATB**	132	**T**
Zn^{2+}	**2.1**	**3.0**	**3.1**	**(3.1)**	**(3.6)**	**5.3**	**8.7**	**(14.6)**	**23.5**	**(36.0)**	**TATB**	132	**T**
Hg^{2+}	11.1	15.4	19.0								TATB	131	
	18.0	15.6									TATB	114	

Table 6 (Continued)

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
Pb^{2+}	2.3	3.4	3.7	(3.8)	(4.0)	5.0	7.2	(10.9)	16.8	25.2	NLJP	131	
	4.8	**6.6**					**6.9**	**11.5**	**16.4**	**21.8**	**TATB**	132	**T**
UO_2^{2+}	−6.0	−1.4	3.5	9.4	13.3						TATB	131	
U^{4+}	3.1	7.1	13.0	21.7	30.3	37.7					TATB	131	

[a] Using $\Delta_t G°$(MCl) combined with $\Delta_t G°(Cl^-)$ based on the TATB scale from ref 22. [b] Calculated in ref 123 from the data in ref 126. [c] Using $\Delta_t G°$(MCl) combined with $\Delta_t G°(Cl^-)$ based on the TATB scale from ref 129. [d] Using $\Delta_t G°(MBPh_4)$ combined with $\Delta_t G°(BPh_4^-)$ based on the TATB scale from ref 129.

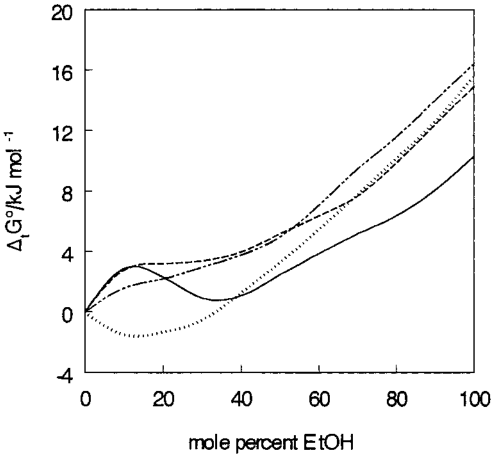

Figure 3. Gibbs energy of transfer of cations from water to aqueous ethanol as a function of the mole percentage of ethanol: (—) Na^+, (- - -) K^+, (—··—) Rb^+, and (···) Me_4N^+.

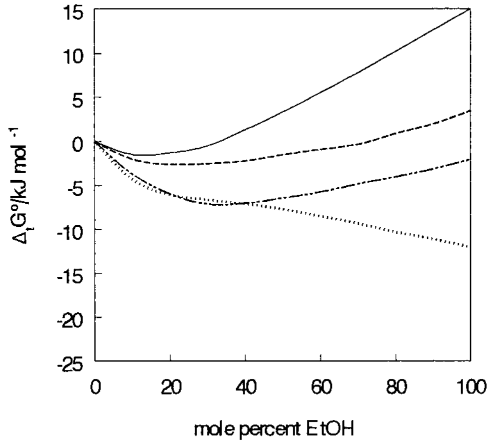

Figure 4. Gibbs energy of transfer of cations from water to aqueous ethanol as a function of the mole percentage of ethanol: (—) Me_4N^+, (- - -) Et_4N^+, (—··—) Pr_4N^+, and (···) Bu_4N^+.

is clearly a need for renewed experimental effort in this area.

2. Discussion of the Transfer Energetics

The values of $\Delta_t G°(H^+)$ from water to aqueous ethanol are broadly similar to, but show some significant differences from, those for transfer into aqueous methanol. Thus, whereas $\Delta_t G°(H^+)$ is slightly positive at low x_{MeOH} in the latter mixtures, only a small kink is apparent at similar compositions in the former. At intermediate solvent compositions, both aqueous methanol and ethanol mixtures are more basic ($\Delta_t G°(H^+) < 0$) than pure water. In both mixtures $\Delta_t G°(H^+)$ eventually becomes positive at higher alkanol contents, although considerably earlier in aqueous ethanol ($x_{EtOH} \approx 0.65$) than in aqueous methanol ($x_{MeOH} \approx 0.80$). For the interactions responsible for this behavior, see the discussion above of $\Delta_t G°(H^+, w \rightarrow w+MeOH)$, noting that, compared with methanol, ethanol has a somewhat higher β value (Table 3) and proton affinity of the isolated molecule,[84] but is also bulkier, i.e., it has a larger hydrophobic group.

The $\Delta_t G°(M^+)$ data for the alkali metal cations, particularly Li^+ and Na^+, show definite anomalies (extrema or inflection points, Figure 3) at low x_{EtOH}, where the water−water interactions are dominant. As for aqueous methanol, but without the Rb^+/Cs^+ anomaly, the sizes of the cations, responsible for the electrostatic effect, lead to the order $Li^+ < Na^+ < K^+ \approx Rb^+ \approx Cs^+$.

The tetraalkylammonium cations show a more or less systematic variation with increasing chain length. The values of $\Delta_t G°(Me_4N^+)$ are similar to those of the larger alkali metal cations, except at low x_{EtOH} where water structural effects are prominent. For the larger and more hydrophobic R_4N^+ cations, $\Delta_t G°$ is more negative, corresponding to more favorable solvation than in pure water, as a result of the increasing break-up of the water structure and increasing dispersion interactions with the ethanol component. These effects are even greater for $iPeBu_3N^+$ and Ph_4As^+. Interestingly, $\Delta_t G°$ of these two ions are similar, especially at higher x_{EtOH}, which provides some indirect justification for the extrathermodynamic assumption $\Delta_t G°(iPeBu_3N^+) \equiv \Delta_t G°(Ph_4B^-)$ used by some authors.[116,128]

The limited data available for the divalent cations are broadly similar to those of the alkali metal cations, with some inflections at low ethanol content in the mixtures, followed by a steady increase. Consistent with their higher charge, $\Delta_t G°(M^{2+})$ are much more positive than those for the univalent cations of similar size. On the other hand, the order with respect to size is anomalous: $Zn^{2+} < Pb^{2+} < Cu^{2+}$, which cannot be readily explained. Furthermore, $\Delta_t G°(Cu^{2+})$ and $\Delta_t G°(Zn^{2+})$ are well correlated up to $x_{EtOH} = 0.7$ but then rapidly diverge, which seems implausible.

C. Transfers from Water to Water + 2-Propanol (*i*-PrOH)

Since Marcus's review,[22] and in contrast to aqueous *n*-PrOH for which almost no data exist, a reasonable body of data on $\Delta_t G°$(ion, w→w+*i*-PrOH) has built

Table 7. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + 2-Propanol (*i*-PrOH) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale									
ion\100*x*	10	20	30	40	50	60	70	method	ref	status
H^+	−1.9	−3.0	(−3.5)					TATB	90	
	−1.4	−2.6	−3.8					TATB	131	
	−2.1	−3.8						TATB	118	
	−1.7	−2.7	−3.2	−3.3	−3.3	−3.2	−3.2	IND	57	
	−3.8	−6.1	−7.3	−7.7	−7.7	−7.6	−7.7	IND	103	
	−1.8	**−3.1**	**−3.7**					**TATB**		**R**
K^+	1.0	1.7	(2.4)	3.0				TATB	90	
	1.5	2.2	2.2					TATB	131	
	1.0	1.0						TATB	118	
	1.2	**1.6**	**2.3**					**TATB**		**R**
Rb^+	1.2	1.8	1.8					TATB	131	
	0.9	1.7	2.1	2.8	4.3	5.8	8.3	IND[a]	98	
	1.0	**1.8**	**2.0**					**TATB**		**R**
NH_4^+	−0.8	−0.8						IND[b]	134	
Ph_4As^+	−11.3	−17.8						TATB	130	
	−10.8	−14.9	(−18.1)	−19.1				TATB	90	
	−11.5	−16.8	(−15.4)					TATB	131	
	−11.2	**−16.5**	**−16.8**					**TATB**		**R**
Cu^{2+}	1.9	4.3	7.2	10.5	14.3	18.6	23.3	NLJP	46	
Zn^{2+}	**0.3**	**1.6**	**0.1**					**TATB**	131	**T**

[a] Using $\Delta_t G°$(HCl) from ref 157 and $\Delta_t G°(H^+)$ from ref 57 to obtain $\Delta_t G°(Rb^+)$ values from $\Delta_t G°$(RbCl) data. [b] Using $\Delta_t G°$(HI) from ref 179 and $\Delta_t G°(H^+)$ from ref 57 to obtain $\Delta_t G°(NH_4^+)$ values from $\Delta_t G°(NH_4I)$ data.

Table 8. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + *tert*-Butyl Alcohol (*t*-BuOH) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100*x*	2	5	10	20	30	40	60	80	90	100	method	ref	status
H^+	0.2	−0.9	−2.9	−4.0							TATB	118	
	0.1	−1.3	−3.4	(−4.8)							TATB	117	
	−0.6	−2.3	−4.5	−6.5							TATB[a]	135	
	−0.1	−1.4	−3.2	−3.4							TATB[a]	98	
	0.2		−2.7	−3.1							TATB	121	
	−0.1	−1.6	−3.4	−5.2							TATB	90,118	
	−0.1	**−1.5**	**−3.4**	**−4.5**							**TATB**		**R**
Li^+	0.2	0.2	−0.4	−0.2							TATB[a]	136	
Na^+	0.8	0.9	0.7	0.6							TATB[a]	136	
	1.2	1.5	1.0	0.4	−0.1						TATB[b]	137	
	1.0	**1.2**	**0.9**	**0.5**	{**−0.1**}						**TATB**		**R**{**T**}
K^+	0.8	0.8	0.5	0.7							TATB[a]	136	
	1.6	1.9	0.7	1.3							TATB	138	
	0.3	0.0	0.3	1.4							TATB	118	
	0.3	−0.4	−0.3	−0.2							TATB	90,118	
	0.8	**0.6**	**0.3**	**0.8**							**TATB**		**R**
Rb^+	**0.5**	**0.6**	**0.2**	**0.5**							**TATB**[c]	136	**T**
Cs^+	**0.6**	**0.5**	**0.1**	**0.3**							**TATB**[a]	136	**T**
Ag^+	**0.5**	**0.3**	**−0.4**	**(−3.0)**							**TATB**[a]	139	**T**
NH_4^+	**0.4**	**−0.3**	**−0.8**	**−0.8**							**TATB**[a]	138	**T**
Me_4N^+	**1.0**	**1.3**	**0.7**								**TATB**[c]	140	**T**
Et_4N^+	**2.5**	**3.7**	**3.2**								**TATB**[c]	140	**T**
Pr_4N^+	**1.6**	**2.7**	**2.0**								**TATB**[c]	140	**T**
Bu_4N^+	**3.0**	**6.3**	**6.6**								**TATB**[c]	140	**T**
Ph_4As^+	−2.6	−7.4	−14.2	−16.2							TATB	118	
	−3.0	−7.9	−14.4								TATB	140	
	−1.8	−6.9	−13.6	−16.1							TATB	138	
	−2.9	−8.4	−13.8	−17.2							TATB	130	
	−2.4	−8.9	−14.7	−17.5							TATB	90,118	
	−2.5	**−7.9**	**−14.1**	**−16.8**							**TATB**		**R**
Mg^{2+}	**2.7**	**1.2**	**−3.2**								**TATB**	117	**T**
Ca^{2+}	**3.0**	**1.8**	**−0.6**								**TATB**	117	**T**
Sr^{2+}	**4.0**	**4.2**	**1.5**								**TATB**	117	**T**
Ba^{2+}	**4.0**	**4.2**	**1.5**								**TATB**	117	**T**
Cu^{2+}			3.1	5.9	9.3	13.7	23.5	36.4	45.3	55.0	NLJP	111	
Hg^{2+}	3.5	12.1	(17.1)	(17.3)							TATB[a]	114	

[a] Using $\Delta_t G°(MCl_x)$ from the designated references and $\Delta_t G°(Cl^-)$ based on the TATB assumption from ref 118. [b] Using $\Delta_t G°(MCl_x)$ from ref 137 and $\Delta_t G°(Cl^-)$ based on the TATB assumption from ref 22. [c] $\Delta_t G°[M(BPh_4)_x]$ from refs 114 and 140, combined with the average value of $\Delta_t G°(BPh_4^-)$ based on the TATB scale from refs 118 and 138.

up. Table 7 summarizes the available values. Contrary to the other systems, values obtained via indicator methods (IND) have been included, since where comparisons are possible such results are in

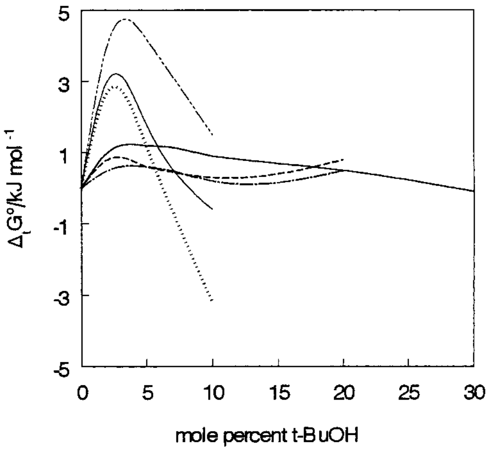

Figure 5. Gibbs energy of transfer of cations from water to aqueous *tert*-butyl alcohol as a function of the mole percentage of *tert*-butyl alcohol: (—) Na^+ (extending to 30%), (- - -) K^+, (—•—) Rb^+, (•••) Mg^{2+}, (—) Ca^{2+} (with sharp peak), and (—••—) Sr^{2+}.

surprisingly good accord with the TATB-based values.

At low $x_{i\text{-PrOH}}$, independently determined values of $\Delta_t G°(M^+, w \rightarrow w+i\text{-PrOH})$ for Ph_4As^+, H^+, K^+, and Rb^+ based on the TATB assumption[90,118,130,131] are in good agreement and the averaged data are Recommended. Insufficient data are available for other solvent compositions and for other cations to make a reliable assessment. However, as in other aqueous alkanol mixtures (e.g., section III.B), it is possible that the values of $\Delta_t G°(Cu^{2+}, w \rightarrow w+i\text{-PrOH})$ obtained by the NLJP assumption[46] are too positive.

Little discussion of the significance of the data is possible at the present time. It is noteworthy, however, that as in aqueous ethanol and *tert*-butyl alcohol mixtures, the hydrogen ion is better solvated at low $x_{i\text{-PrOH}}$ than in pure water.

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

1. Comments on the Data

The Gibbs energies of transfer of cations are generally limited to ≤20 mol % *tert*-butyl alcohol, except for the study of $\Delta_t G°(Cu^{2+}, w \rightarrow w+t\text{-BuOH})$[111] which covers the entire composition range. One of the reasons for this focus on the low x_{tBuOH} region is that significant changes in solvent structure take place there. The available data are summarized in Table 8, and selected data are plotted in Figure 5.

Within the restricted composition range studied, independent determinations of $\Delta_t G°$ for Ph_4As^+, H^+, Na^+, and K^+ are in good agreement and their averaged values have been classified as Recommended. In the absence of confirmatory studies, little can be said about the quality of the remaining data.

2. Discussion of the Transfer Energetics

As noted above, the values of $\Delta_t G°(M^{n+}, w \rightarrow w+t\text{-BuOH})$ undergo remarkable changes as the concentration of *t*-BuOH increases (Figure 5). The reality of such effects depends, of course, on the reliability of the TATB assumption, but it is hard to see why this assumption would fail here, given that it appears to work well in other aqueous/organic mixtures. It is well-known that relatively featureless plots of $\Delta_t G°$(ion, w→w+s) against x_s may result from dramatic but opposing changes in the corresponding enthalpies and entropies of transfer.[77,141] Even larger effects are exhibited by the heat capacities, $\Delta_t C_p°$(ion, w→w+*t*-BuOH), and volumes, $\Delta_t V°$(ion, w →w+*t*-BuOH), of transfer in the same solvent composition region.[142] Such effects have been attributed to strong mutual interactions of water and *t*-BuOH, even to the point of the development of solution nanoheterogeneity.[142]

The values of $\Delta_t G°(H^+, w \rightarrow w+t\text{-BuOH})$ indicate that except perhaps at very low x_{tBuOH}, aqueous *t*-BuOH is significantly more basic than pure water. This is attributable to the break-up of the three-dimensional hydrogen-bonded structure of water by the bulky, hydrophobic *t*-BuOH molecules. For the alkali metal and even more so for the alkaline earth cations, the values of $\Delta_t G°$(ion) have very definite maxima near $x_{t-BuOH} = 0.03$ (Figure 5). It is known[143] that *t*-BuOH enhances the water structure more and at lower mole fractions than MeOH and EtOH. Therefore, at $x_{t-BuOH} < 0.1$ where the $\Delta_t G°$ of these and the tetraalkylammonium ions are available, the work of cavity creation to accommodate the cations is greater than in water and increases with cation size, hence the observed extrema. However, further discussion of these effects is unwarranted pending confirmation of the data and their extension to a much wider range of solvent compositions.

The $\Delta_t G°(Cu^{2+}, w \rightarrow w+t\text{-BuOH})$ data,[111] which are available over the entire composition range though not in the important very water-rich region, $x_{tBuOH} < 0.1$, were obtained via the NLJP assumption and must be viewed with caution. As with data obtained by this procedure in other aqueous alkanol mixtures, the $\Delta_t G°$ values seem to be somewhat too positive, in view of the rather strong donor properties of *t*-BuOH (Table 3). Circumstantial evidence for this view comes from a calculation of $\Delta_t G°(Cu^{2+}, w \rightarrow t\text{-BuOH}) = 19$ kJ mol^{-1}, based on a multiparameter ion solvation model.[15,83] On the other hand, the large positive values of $\Delta_t G°(Cu^{2+}, w \rightarrow w+t\text{-BuOH})$ may reflect solvent packing effects in the coordination sphere of the copper cation.

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

The available data from the few studies made of the Gibbs energies of transfer of cations from water into aqueous ethylene glycol, mainly based on the TATB assumption, are shown in Table 9. As there is only one estimation[144] of the values of $\Delta_t G°(Ph_4As^+)$, which appears reliable, the data for this system have been classified as Tentative. For most other cations, insufficient independent data are available to assess their reliability. Exceptions are $\Delta_t G°(H^+)$, $\Delta_t G°(K^+)$, and $\Delta_t G°(Cu^{2+})$, where independent data are in good agreement over the entire composition range.

As in aqueous ethanol solutions (Table 6), $\Delta_t G°(H^+)$ is slightly negative at low cosolvent concentrations, the mixed solvent being slightly more basic than pure water, and becomes steadily more positive

Table 9. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Ethylene Glycol Mixtures (EG) at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	−0.5	0.0	0.3	−0.3	0.0	0.9	1.9	3.6	5.7	8.5	TATB	144	
	−0.6	−1.0	−1.6	−1.8	−1.8	−1.5	−1.1	0.0	1.8	4.1	TATB[a]	103	
	−0.5	**−0.5**	**−0.7**	**−1.1**	**−0.9**	**−0.3**	**0.4**	**1.8**	**3.8**	**6.3**	**TATB**		**T**
Li^+	**0.3**	**1.2**	**2.4**	**2.7**	**3.0**	**3.4**	**3.9**	**4.2**	**3.7**	**3.3**	**TATB**	144	**T**
Na^+	**0.1**	**0.4**	**1.0**	**1.6**	**1.7**	**1.7**	**1.8**	**1.9**	**1.5**	**1.3**	**TATB**	144	**T**
K^+	0.3	1.3	2.0	2.0	2.0	2.0	2.0	2.1	1.6	1.3	TATB	144	
	0.1	1.3	1.5	1.6	1.8	2.2	2.8	3.4	2.7	1.8	TATB[b]	125	
	0.3	1.5	2.1	2.0	(1.7)						TATB	145	
	0.3	**1.4**	**1.9**	**1.9**	**1.8**	**2.1**	**2.4**	**2.7**	**2.2**	**1.6**	**TATB**		**T**
Ph_4As^+	**−4.8**	**−8.0**	**(−11.2)**	**−13.7**	**(−15.9)**	**(−17.8)**	**−19.3**	**(−20.2)**	**(−20.9)**	**−21.3**	**TATB**	144	**T**
Cu^{2+}	0.7	1.2	1.7	2.3	2.8	3.4	3.9	(4.7)	(5.8)	7.1	NLJP	111	
	0.2	0.3	0.4	0.8	0.9	1.3	1.8	2.2	3.8	4.7	NLJP	46	
	0.6	**1.1**	**1.7**	**2.1**	**2.4**	**3.1**	**3.7**	**4.1**	**5.2**	**6.2**	**TATB**[c]		**T**
Zn^{2+}	[−2.0]	[−5.4]	[−9.3]	[−11.4]	[−14.8]	[−17.8]	[−20.3]				Fc	146	
Cd^{2+}	[−1.6]	[−4.7]	[−8.0]	[−10.6]	[−13.3]	[−15.0]	[−18.0]			[−6.6]	Fc	147	

[a] Recalculated via the TATB assumption from values presented according to the spectrophotometric indicator approach. [b] Using $\Delta_t G°$(KCl) from ref 125 with $\Delta_t G°$(Cl^-) based on the TATB scale from ref 22. [c] Averaged NLJP data from the previous rows adjusted to the TATB scale using conversion addends from Table 1.

Table 10. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Propylene Glycol (PG) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	[−14.0]	[−10.8]	[−9.7]	[−8.6]	[−7.4]	[−6.5]	[−5.7]	[−2.3]	2.1	6.5	TATB	55	
K^+	2.5	2.9	4.3	5.6	6.0	5.7	5.3	5.3	5.2	5.2	TATB	55	
Cs^+	2.0	3.3	4.1	4.5	4.5	4.4	4.3	4.3	4.6	5.2	TATB	148	
Ag^+	−16.2	−13.6	−12.4	−11.4	−11.4	−11.7	−12.2	−11.7	−11.4	−10.8	TATB	55	
Ph_4As^+	−5.0	−9.3	−11.5	−13.3	−14.6	−15.4	−17.0	−17.9	−18.6	−19.3	TATB	55	
	−6.1	−10.6	−13.7	−15.7	−16.9	−17.5	−17.8	−18.0	−18.4	−19.2	TATB	148	
	−5.6	**−10.0**	**−12.6**	**−14.5**	**−15.7**	**−16.5**	**−17.4**	**−18.0**	**−18.5**	**−19.3**	**TATB**		**R**
Cu^{2+}	2.5	4.8	6.5	7.6	8.9	(9.9)	11.1	(13.0)	(15.3)	17.7	NLJP	111	
Zn^{2+}	−2.4	−8.6	−14.7	−16.7	−19.1	−20.5	−22.7				Fc	149	

at $x_{EG} > 0.5$. The reasons for such behavior are presumably the same for both cosolvents (see section II.B.2).

The values of $\Delta_t G°(M^{n+}$, w→w+EG) for the other cations are generally quite small and positive, consistent with the similarity of the solvation characteristics of ethylene glycol and water. The values for the alkali metal cations do not show a consistent order. The values of $\Delta_t G°(Ph_4As^+)$ are quite strongly negative, similar to those for other aqueous organic solvent mixtures, and their dependence on the solvent composition is characteristic of preferential interaction with the organic component. The magnitude of $\Delta_t G°(Cu^{2+})$ is somewhat positive, more than for the alkali metal cations, but still rather small compared with those for transfer into aqueous monohydric alkanols. In contrast, $\Delta_t G°(Zn^{2+})$ and $\Delta_t G°(Cd^{2+})$, obtained by the Fc assumption, are highly negative (also when compared with the positive $\Delta_t G°(Zn^{2+})$ for aqueous MeOH and EtOH) and are considered unreliable.

F. Transfers from Water to Water + Propylene Glycol (PG)

The available data for the Gibbs energies of transfer of cations from water to aqueous propylene glycol are given in Table 10. Surprisingly, none of the papers quoted specify whether the 1,2- or the 1,3-isomer of propylene glycol was used, with the exception of that of Brillas et al.,[147,149] who used 1,2-PG. There are somewhat fewer data than for transfer into aqueous ethylene glycol (Table 9), and consequently little can be said about them. An exception is $\Delta_t G°(Ph_4As^+)$, for which two independent studies[55,148] are in good agreement over the whole composition range.

The values of $\Delta_t G°(H^+)$ at lower x_{PG}[55,148] are very negative, both in an absolute sense and when compared with those for transfer into aqueous EG (Table 9) and must therefore be regarded with caution. Such negative values may stem from an incorrect estimation of $\Delta_t G°(Cl^-)$ used in their derivation. A similar caveat appears appropriate for the corresponding values of $\Delta_t G°(Ag^+)$ by the same authors.[63] The major differences, up to 40 kJ mol^{-1}, between $\Delta_t G°(Cu^{2+})$ and $\Delta_t G°(Zn^{2+})$ are anomalous and possibly reflect an inconsistency between the extrathermodynamic assumptions employed rather than a real difference in the solvation energies of these two cations.

G. Water to Water to Water + Tetrahydrofuran (THF)

The rather few data available for $\Delta_t G°(M^{n+}$, w→w+THF) are summarized in Table 11. The data are restricted to low cosolvent compositions ($x_{THF} \leq 0.2$), probably because of the low relative permittivity of THF ($\epsilon = 7.58$ at 25 °C) with its consequent problems of ion pairing in more THF-rich solutions. It is not possible to comment on the reliability of the

Table 11. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Tetrahydrofuran (THF) Mixtures at 298.15 K

	$\Delta_tG°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100x	2	5	10	15	20	40	60	80	90	100	method	ref	status
H^+	−2.6	(−5.0)	−6.9	(−7.6)	−8.0						TATB	150	
	−2.6	−7.4	−11.5	−10.2	−8.2						IND	151	
Li^+	−2.2	−4.0	−5.4	−6.2	−6.4						TATB	152	
Na^+	−2.0	−3.7	−5.0	−5.2	−5.2						TATB	152	
	−1.8	−5.1	(−7.1)								IND	151	
K^+	−2.0	−3.4	−4.3	−4.8	−4.9						TATB	152	
Rb^+	−2.2	−5.8	−8.1	(−5.1)							IND	151	
	−2.0	−3.7	−5.1	−5.7	−5.8						TATB	152	
Bu_4N^+	−3.3	−8.2	−13.9	−13.7	−12.4						IND[a]	151	
	−2.4	−3.9	−5.0	(−6.2)	−7.3						TATB[b]	153	
Ph_4As^+	−5.6	−12.0	−20.1	−24.7	−18.9						TATB	152	
Cu^{2+}	(0.4)	(0.7)	1.4	(1.8)	2.3	3.7	4.9	9.5	15.7	23.5	NLJP	154	

[a] Data for asymmetrically substituted alkylammonium ions are also available in ref 151. [b] Using $\Delta_tG°(Br^-)$ based on the TATB scale from ref 150 to obtain the cation value.

data as there are no independent studies based on the TATB assumption. It is noteworthy, however, that the values of $\Delta_tG°(M^+)$ estimated by the TATB assumption[152] and the indicator method of Wells[151] are in reasonably good agreement (Table 11), although the latter method cannot be said to yield reliable results. This agreement, however, does not exist for $\Delta_tG°(Bu_4N^+)$.

The magnitude of $\Delta_tG°(H^+, w\rightarrow w+THF)$ indicates that (water-rich) aqueous THF is more basic than pure water, as is the case for the alkanols and alkanediols. Little can be said about the trends in the remaining data, except that the $\Delta_tG°(M^+)$ values for the alkali metal cations are slightly negative and essentially independent of cation size. Surprisingly, $\Delta_tG°(Bu_4N^+)$ is similar to those of the alkali metal cations. The values of $\Delta_tG°(Cu^{2+})$ are, on the contrary, positive and show, when plotted against x_{THF}, the shape characteristic for selective solvation by water. This is consistent with the greater donor strength of water (Table 3). It is puzzling, therefore, that similar effects are not apparent in the transfer Gibbs energies of the univalent cations.

H. Transfers from Water to Water + 1,4-Dioxane (DX)

The data available for $\Delta_tG°(M^{n+}, w\rightarrow w+DX)$, summarized in Table 12, are largely confined to low cosolvent concentrations ($x_{DX} \leq 0.2$), a fact ascribable to the very low relative permittivity of dioxane ($\epsilon = 2.21$ at 25 °C).

Two independent investigations[120,152] of $\Delta_tG°(Ph_4As^+)$ are in reasonable agreement over the limited solvent composition range studied, and the values obtained are supported by the results reported for $\Delta_tG°(Ph_4P^+)$.[161] The equivalence $\Delta_tG°(Ph_4As^+) \approx \Delta_tG°(Ph_4P^+)$, having been established for a number of aqueous organic cosolvent systems, permits the averaging of the three sets of data to produce a set of Recommended values for $\Delta_tG°(Ph_4As^+)$. Independent studies of $\Delta_tG°(H^+)$ and of the Gibbs energy of transfer of the alkali metal cations are also in agreement, and the averaged values have accordingly been classified as Recommended.

The small negative values of $\Delta_tG°(H^+, w\rightarrow w+DX)$ indicate that as for THF and the alcohols, the (water-rich) mixtures are slightly more basic than pure water. Again, as for THF, the Gibbs energies of transfer of the alkali metal cations are small and negative and vary little with cation size. For the tetraalkylammonium cations, $\Delta_tG°(Me_4N^+)$ closely resembles those of the alkali metal cations whereas those of the higher homologues show a systematic (increasingly negative) variation with size, consistent with their increasing interactions with the organic component.

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

1. Comments on the Data

Although there have been numerous studies of ion solvation energetics in aqueous acetone solutions, few cover the entire solvent composition range. The available data, based mainly on the TATB assumption, are summarized in Table 13 and selected data are shown in Figure 6.

A number of independent studies of $\Delta_tG°(M^+)$ for the hydrogen and alkali metal ions up to $x_{AC} = 0.7$ have been published and are in good agreement. However, as only one study[166] of $\Delta_tG°(Ph_4As^+)$ has been reported, the averages of mutually agreeing data for other cations must be classified as Tentative. Two independent studies of $\Delta_tG°(Cu^{2+})$, using the NLJP assumption, are also in agreement, and their average is also classified as Tentative. In contrast, an investigation of $\Delta_tG°(Zn^{2+})$ using the notionally similar cobaltocene (analogous to Fc) and BBCr assumptions[168] produced discordant results, of which the more negative ones obtained by the cobaltocene assumption appear to be incompatible with the behavior expected for transfer of Zn^{2+} into aqueous solvents of similar donor strength.

2. Discussion of the Transfer Energetics

The negative values of $\Delta_tG°(H^+)$ and the evidence for an upturn at $x_{AC} > 0.4$ are similar to the observed behavior in other aqueous organic mixtures. Despite the greater donor strength of water compared with acetone, the values of $\Delta_tG°(M^+, w\rightarrow w+AC)$ for the

Table 12. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + 1,4-dioxane (DX) Mixtures at 298.15 K

	$\Delta_tG°$(ion)/kJ mol^{-1}, molarity-scale											
ion\100x	5	10	15	20	30	40	50	60	70	method	ref	status
H^+	−1.5	−2.1	−2.1	−1.7	0.8	5.3	(11.1)			IND	155	
	(−3.1)	−4.7	−3.5							TATB	152	
	(−3.2)	−5.1	−4.3							TATB[a]	98	
	(−3.0)	−3.7	−2.6							TATB[b]	156	
	−3.9	−6.5	−6.8	−7.1						TATB[b]	157	
	−1.3	−1.4	−1.4	−1.4						TATB	87	
	−2.9	**−4.3**	**−3.7**	{**−4.3**}						**TATB**		**R**{**T**}
Li^+	**−2.6**	**−2.8**	**(−2.1)**							**TATB**	152	**T**
Na^+	−2.0	−2.0	(−0.7)							TATB	152	
	0.0	−0.3	−0.8	−2.1						TATB	87	
	−1.0	**−1.2**	**−0.8**	{**−2.1**}						**TATB**		**R**{**T**}
K^+	−1.6	−2.3	−1.2							TATB	152	
	−1.4	−2.1	0.4							TATB[a]	158	
	−1.5	**−2.2**	**−0.4**							**TATB**	152	**R**
Rb^+	−1.9	−1.7	(−0.6)							TATB[a]	98	
	−1.6	−2.1	0.2							TATB[a]	158	
	−1.4	−1.8	0.4							TATB	152	
	−1.8	**−1.9**	**−0.2**							**TATB**		**R**
Cs^+	−2.0	−2.2	(−0.9)							TATB	152	
	−1.6	−2.3	−0.1							TATB[a]	158	
	−1.8	**−2.3**	**−0.5**							**TATB**		**R**
Ag^+	2.0	1.7	−1.3							NLJP	159	
Me_4N^+	**(−2.4)**	**−3.1**	**−1.1**							**TATB**[a]	158	**T**
Pr_4N^+	**−4.4**	**−7.1**	**−6.8**	**−5.7**						**TATB**[a]	158	**T**
Bu_4N^+	**−5.2**	**−9.2**	**−10.5**							**TATB**[a]	158	**T**
Fc^+	**−9.4**	**−11.9**	**(−12.7)**							**TATB**[c]	160	**T**
Ph_4P^+	**−11.4**	**−19.9**	**−25.7**	**−28.7**						**TATB**	161	**T**
Ph_4As^+	−8.9	−15.5	−18.7	(−20.5)						TATB	152	
	−13.8	−19.5	−22.9	−25.3						TATB	120	
	−11.4	**−18.3**	**−22.4**	**−24.8**						**TATB**		**R**
Ba^{2+}	12.2									IND[d]	162	
Cu^{2+}	0.4	0.8		2.4	3.6	4.5	5.6	7.1	8.1	NLJP	154	

[a] Using $\Delta_tG°(MCl_x)$ from ref 158 and $\Delta_tG°(Cl^-)$ based on the TATB assumption from ref 152. [b] Using $\Delta_tG°$(HX) from refs 156 and 157 together with $\Delta_tG°(Cl^{-\,-})$ based on the TATB assumption, ref 152. [c] Using $\Delta_tG°(Fc^+) - \Delta_tG°(H^+)$ from ref 163 combined with $\Delta_tG°(H^+)$ based on the TATB assumption from this table. [d] Using $\Delta_tG°(Ba(IO_3)_2)$ from ref 162 with $\Delta_tG°(IO_3^-)$ based on the indicator scale.

alkali metal cations are also negative, albeit less so than for hydrogen ions, but given the values of $\Delta_tG°(M^+, w \rightarrow AC)$, they eventually become positive. Up to $x_{AC} = 0.7$ they show little variation with size, lying in the order $Li^+ < Cs^+ < Rb^+ \approx K^+ < Na^+$. The anomalous position of Li^+ is difficult to explain.

As for many other aqueous organic systems, the values of $\Delta_tG°(Me_4N^+)$ are very similar to those of the alkali metal cations. The very negative values for $\Delta_tG°(Pr_4N^+)$ and $\Delta_tG°(Ph_4As^+)$ are consistent with the preferential solvation of these large hydrophobic cations by the organic constituent via dispersion interactions.

As in other O-donor organic mixtures with water (such as THF, DX, and DMF), the values of $\Delta_tG°(Cu^{2+})$ are much more positive than those of the alkali metal cations, consistent with preferential solvation by the water component of the mixtures. The differences of up to 30 kJ mol^{-1} between $\Delta_tG°(Cu^{2+})$ derived from the NLJP assumption and $\Delta_tG°(Zn^{2+})$ obtained by the cobaltocene assumption[168] emphasize the uncertainty of the latter values.

J. Transfers from Water to Water + Propylene Carbonate (PC)

Water and propylene carbonate are not completely miscible at 25 °C, the mutual solubilities corresponding to $x_{PC} = 0.0362$ in the water-rich phase and $x_{PC} = 0.661$ in the PC-rich phase.[84] This miscibility gap is reflected in most of the available data for the Gibbs energies of transfer of cations from water to aqueous PC, which are summarized in Table 14. Surprisingly, Coetzee and Istone[46] report $\Delta_tG°(Cu^{2+}, w \rightarrow w{+}PC)$ over the entire solvent composition range. Although these measurements seem to have been made with a background electrolyte (0.01 mol dm^{-3} Et_4NClO_4), it is implausible that the solutions were homogeneous. Accordingly, the data in the midrange of solvent compositions[46] have been rejected and are not included in Table 14.

All of the remaining data are reported in one publication,[171] using the Fc assumption. Consequently, for comparison, values of $\Delta_tG°(M^+, w \rightarrow PC)$ based on the TATB scale[19] are also included in Table 14. These differ from the Fc-based data by up to 15 kJ mol^{-1} (although many of the differences are smaller), so that all the data listed in Table 14 should be viewed with caution.

At $x_{PC} \geq 0.7$, the values of $\Delta_tG°(M^+, w \rightarrow w{+}PC)$ for the alkali metal cations show systematic variation in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The complexity of the ion−solvent interactions is reflected in the fact that these $\Delta_tG°(M^+)$ values remain negative even up to pure PC, despite the weaker donor

Table 13. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Acetone (AC) Mixtures at 298.15 K

	$\Delta_tG°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100*x*	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	−5.4	−9.1	−11.3	−12.1	−11.0						TATB[a]	98	
	−5.4	−9.2	−11.7	−12.4	−11.8	(−10.3)					TATB[a]	164	
	−5.4	**−9.2**	**−11.5**	**−12.3**	**−11.4**	**(−10.3)**					**TATB**		**T**
Li^+	−3.3	−6.0	−6.6								TATB[a]	165	
	−3.4	−5.8	−6.9	−7.2	−6.4	(−6.1)					TATB[a]	164	
	−3.3	**−5.9**	**−6.8**	{**−7.2**}	{**−6.4**}	{**−5.8**}*				**10**[b]	**TATB**		**R**{**T**}
Na^+	−2.8	−4.5	−4.1								TATB[a]	165	
	−2.7	−4.5	−5.2	−4.6	−3.3	(−2.3)					TATB[a]	164	
	−2.8	**−4.5**	**−4.7**	{**−4.6**}	{**−3.3**}	{**−2.3**}				**10**[b]	**TATB**		**R**{**T**}
K^+	−3.2	−5.0	−5.6	−5.4	−5.1	−4.4	(−3.8)				TATB	166	
	−3.0	−4.8	−5.7	−5.2	−4.0	(−3.7)					TATB[a]	164	
	−3.1	**−4.9**	**−5.7**	**−5.3**	**−4.6**	**−4.1**	{**−3.8**}			**4**[c]	**TATB**		**R**{**T**}
Rb^+	−3.1	−4.9	−5.4	−4.9	−4.5	−3.9	(−3.2)				TATB	166	
	−3.0	−4.8	−5.7	−5.3	−4.5	−4.3					TATB[a]	164	
	−3.1	**−4.9**	**−5.6**	**−5.1**	**−4.5**	**−4.1**	{**−3.2**}			**4**[c]	**TATB**		**R**{**T**}
Cs^+	−3.4	−5.6	−6.1	−5.8	−5.3	−4.4	(−3.7)				TATB	166	
	−3.2	−5.0	−6.2	−6.0	−5.3	−4.9					TATB[a]	164	
	−3.3	**−5.3**	**−6.2**	**−5.9**	**−5.3**	**−4.7**	{**−3.7**}			**4**[c]	**TATB**		**R**{**T**}
Ag^+	**−3.1**	**−6.2**	**−6.8**	**−6.5**	**−6.1**	**−5.5**	**(−4.9)**			**9**[c]	**TATB**	166	**T**
Me_4N^+	**−4.3**	**−7.1**	**−7.8**	**−7.6**	**−7.2**	**−6.6**	**(−5.9)**			**3**[c]	**TATB**	166	**T**
Pr_4N^+	**−8.6**	**−14.3**	**(−17.5)**								**TATB**	166	**T**
Bu_4N^+	**(−11.3)**										**TATB**	166	**T**
Fc^+	**−7.1**	**−9.9**									**TATB**[d]	163	**T**
Ph_4As^+	**−12.8**	**−20.4**	**−25.6**	**−28.0**	**−30.1**	**−31.6**	**(−33.0)**			**−32**[c]	TATB	166	**T**
Cu^{2+}	0.7	1.9	2.5	3.6	4.2	6.4	8.1	12.9	22.9	42.2	NLJP	154	
	3.8	7.6	7.5	8.7	9.7	11.2	13.1	16.4	21.9	44.8	NLJP	167	
	2.3	**4.8**	**5.0**	**6.1**	**7.0**	**8.8**	**10.6**	**14.7**	**22.4**	**43.5**	NLJP		**T**
Zn^{2+}	−7.2	(−13.1)	−18.5	−21.1	(−22.3)	−22.8	−15.9	−14.3	−12.1	18.8	Fc[e]	168	
	−1.2	(−2.1)	−4.5	−4.1	(−3.3)	−1.8	6.3	9.9	11.9	44.8	BBCr	168	
In^{3+}	−0.3	−1.0	−1.1	3.6	11.3	22.3	35.6				NLJP	169	

[a] Using $\Delta_tG°(MCl)$ data from ref 164 combined with $\Delta_tG°(Cl^-)$ data based on the TATB scale, ref 166. [b] Recommended value from ref 170 based on the TATB scale. [c] Recommended value from ref 19 based on the TATB scale. [d] Using $\Delta_tG°(Fc^+) - \Delta_tG°(H^+)$ from ref 163 combined with $\Delta_tG°(H^+)$ based on the TATB scale from this table. [e] Cobaltocene was used rather than ferrocene.

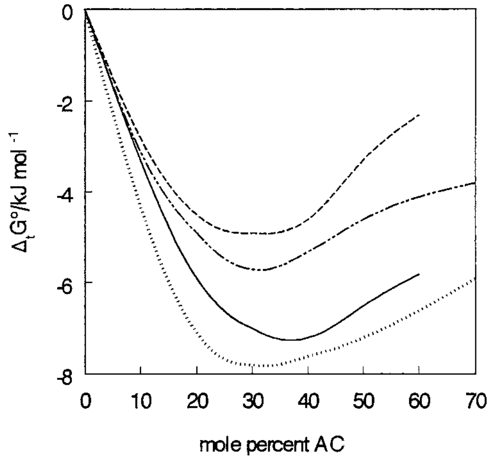

Figure 6. Gibbs energy of transfer of cations from water to aqueous acetone as a function of the mole percentage of acetone: (—) Li^+, (- - -) Na^+, (—••—) K^+, and (•••) Me_4N^+.

ability (but not dipole moment and polarizability) of PC relative to water (Table 3). In contrast, the data for $\Delta_tG°(Cu^{2+}, w \rightarrow w+PC)$ are much more positive and show a dependence on solvent composition characteristic of preferential solvation by water, similar to those of other aqueous O-donor cosolvent mixtures.

K. Transfers from Water to Water + Pyridine (PY)

The few data available for the Gibbs energies of transfer of cations from water to aqueous pyridine, mostly based on the NLJP assumption and measured at 30 °C, are collected in Table 15. Little can be said about the reliability of these data in the absence of independent investigations and especially studies based on the TATB assumption. As would be expected from the high basicity and strong electron-donor characteristics of pyridine, all the reported values of $\Delta_tG°(M^+, w \rightarrow w+PY)$ are negative and show a dependence on the pyridine content of the mixtures typical of preferential solvation of the cations by the pyridine component.

It is interesting that $\Delta_tG°(Zn^{2+}, w \rightarrow w+PC)$ at low x_{PY} is much less favorable (less negative by up to 25 kJ mol^{-1}) than for the almost identically sized Cu^{2+} cation. This is consistent with the usual Irving−Williams order of stability of the $[M(PY)_n]^{2+}$ complexes measured in extremely dilute ($x_{PY} \ll 0.1$) aqueous solutions,[178] which is largely related to a difference in the ligand field stabilization energy of the d^9 Cu^{2+} and d^{10} Zn^{2+} cations. The increasingly favorable values of $\Delta_tG°(Zn^{2+})$ at higher x_{PY} are noteworthy and might be related to changes in the coordination number of this ion.

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

1. Comments on the Data

Gibbs energies of transfer of cations from water to aqueous acetonitrile mixtures are among the most extensively studied of all aqueous−organic systems.

Table 14. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Propylene Carbonate (PC) Mixtures at 298.15 K

ion\100*x*	2	miscibility gap	$\Delta_tG°$(ion)/kJ mol^{-1}, molarity-scale				method	ref	status
			70	80	90	100			
H^+	−1.6						Fc	171	
						50	TATB	19	
Li^+	−1.3		−2.0	4.4	5.5	18.7	Fc	171	
						24	TATB	19	
Na^+	−2.2		−2.5	1.0	3.3	4.0	Fc	171	
						15	TATB	19	
K^+	−1.0		−6.5	−3.0	−3.3	−3.5	Fc	171	
						5	TATB	19	
Rb^+	−1.3		−8.2	−5.3	−5.6	−5.8	Fc	171	
						−1	TATB	19	
Cs^+	−2.2		−9.9	−6.4	−7.3	−8.0	Fc	171	
						−7	TATB	19	
Ag^+	−1.6		−6.0	−0.4	2.7	9.9	Fc	171	
						19	TATB	19	
Tl^+	−1.3		−6.5	−7.3	−6.4	−4.3	Fc	171	
						11	TATB	19	
Cu^{2+}	0.5		10.8	16.3	27.6	75.4	NLJP	46	
						73	TATB	19	

Table 15. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Pyridine (PY) Mixtures at 303.15 K (except where otherwise indicated)

ion\100*x*	$\Delta_tG°$(ion)/kJ mol^{-1}, molarity-scale										method	ref	status
	10	20	30	40	50	60	70	80	90	100			
H^+	−30.0									−28[b]	NLJP[a]	172	
	−38.8										Fc[a]	172	
	−30.2										NLJP	173	
Ag^+	−33.4	−37.4	−41.4	−45.0	−47.6	−49.6	−51.3	−52.0	−52.6	−52.8	NLJP	174,175	
Cu^{2+}	−43.7	−48.9	−52.8	−55.8	−60.7	−62.8	−66.3	−71.6	−74.6	−77.5	NLJP	176	
Zn^{2+}	−18.6	−24.4	−34.4	−38.6	−42.4	−49.9	−59.0	−66.8	−73.2	−79.6	NLJP	177	

[a] At 298.15 K. [b] From ref 11, based on the TATB assumption.

The existing data, based mainly on the TATB assumption, are listed in Table 16, and selected values are plotted in Figures 7 and 8.

Four independent studies[80,140,179,186] of $\Delta_tG°(Ph_4As^+$, w→w+AN) are in excellent agreement, which allows their averaged values to be classified as Recommended over the entire solvent composition range. For the alkali metal, copper(I), and silver cations, independent studies based on the TATB assumption are in good agreement too. They are also well supported by other estimates, based on the Fc and NLJP assumptions, that can be adjusted to the TATB scale using the addends given in Table 1. Accordingly, the averaged values of $\Delta_tG°$ for these ions have been classified as Recommended at all solvent compositions. Data for $\Delta_tG°(R_4N^+)$ from two independent studies[140,185] exist up to $x_{AN} = 0.4$ and are in good agreement, so that their averages are also classified as Recommended.

The situation regarding $\Delta_tG°(H^+)$ is less straightforward. The values given by Villermaux and Delpuech[87] at $x_{AN} \leq 0.4$ are at variance with those in other studies[98,179] and have therefore been rejected. The latter two studies are in good agreement at $x_{AN} \leq 0.7$ but diverge at $x_{AN} = 0.8$. Because of this and as only a single study[179] is available at $x_{AN} > 0.8$, the data beyond $x_{AN} = 0.7$ must be considered doubtful at this stage.

Data for the remaining univalent and the divalent cations, with the exception of copper(II), have not been independently confirmed and so have been classified as Tentative. There are a plethora of data for $\Delta_tG°(Cu^{2+})$ based on the NLJP assumption.[46,132,181,183] All the data are in good agreement, with the exception of the values given by Parker et al.[183] at $x_{AN} \leq 0.4$, which must be rejected. However, when the averaged NLJP values are converted to the TATB scale by means of the addends in Table 1, they are in poor agreement with those determined directly via the TATB assumption (differing by up to 20 kJ mol^{-1}), the latter being preferred.

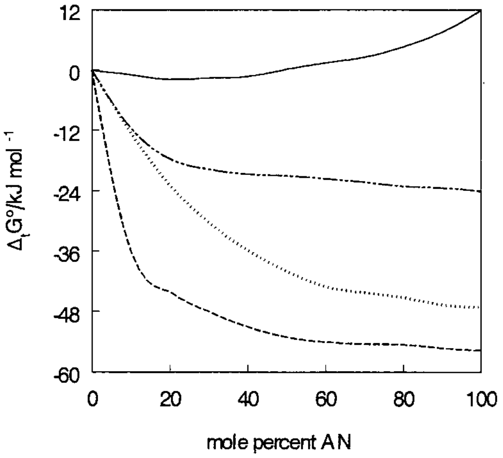

Figure 7. Gibbs energy of transfer of cations from water to aqueous acetonitrile as a function of the mole percentage of acetonitrile: (—) Na^+, (- - -) Cu^+, (−··−) Ag^+, and (···) Au^+.

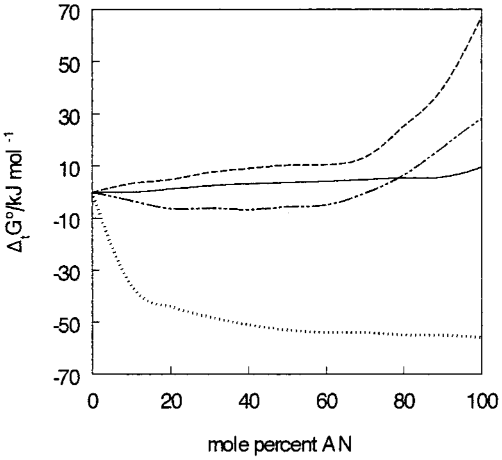

Figure 8. Gibbs energy of transfer of cations from water to aqueous acetonitrile as a function of the mole percentage of acetonitrile: (—) Tl^+, (- - -) Cu^{2+}, (—··—) Zn^{2+}, and (···) Cu^+.

2. Discussion of the Transfer Energetics

As for many other aqueous organic solvent systems, $\Delta_tG°(H^+, w \rightarrow w+AN)$ is slightly negative at low cosolvent compositions ($x_{AN} < 0.7$), indicating that the mixtures are mildly more basic than pure water. This presumably results from the enhancement of the three-dimensional hydrogen-bonded structure of water by the acetonitrile molecules. At $x_{AN} > 0.7$, where the data are less reliable (see above), the mixtures appear to become steadily less basic ($\Delta_tG°(H^+)$ is positive) as water is replaced by acetonitrile in the immediate solvation shell of the hydrogen ion.

The values of $\Delta_tG°(M^+)$ for the alkali metal cations are similar to those of the hydrogen ion but become positive at lower cosolvent compositions, $x_{AN} \approx 0.5$. These data generally show a systematic variation with cation size, being in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$, although the differences are not large, except for the smaller cations at $x_{AN} > 0.7$.

As in many other aqueous organic solvent systems, the values of $\Delta_tG°(Me_4N^+, w \rightarrow w+AN)$ mimic those of the alkali metal cations but the similarity appears to be a little weaker (the data have not been independently confirmed though). Certainly the values of $\Delta_tG°(R_4N^+, w \rightarrow w+AN)$ for the bulkier, more hydrophobic R_4N^+ cations appear quite different, in particular if a smooth variation of $\Delta_tG°(R_4N^+)$ is assumed in the range $0.4 < x_{AN} < 1.0$ where data are not available.

Arguably the most noteworthy feature of the Gibbs energies of transfer of cations from water to aqueous acetonitrile mixtures is the very large stabilization (negative $\Delta_tG°$) of the univalent d^{10} cations Cu^+, Ag^+, and Au^+. This well-known effect[190] is brought about by a specific 'soft' interaction: 'back-donation' of electron density from the filled $d_\pi(t_{2g})$ orbitals of the metal cations to low lying p_{π^*} orbitals of the cyano moiety of the acetonitrile molecule. This effect is superimposed on the usual σ bond formed by donation of electron density from acetonitrile to the metal cation.

The values of $\Delta_tG°(M^{2+})$ roughly parallel those of the alkali metal cations, although they became much more positive at high acetonitrile concentrations, where this much weaker donor begins to replace water in the coordination sphere of the cations. This effect becomes very marked (Table 16) for $\Delta_tG°(Fe^{3+})$. As for many other aqueous organic solvent systems, $\Delta_tG°(Zn^{2+})$ is much more negative than $\Delta_tG°(Cu^{2+})$, although both cations have similar sizes and softness parameters (Table 2).

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

The changes in Gibbs energies for cations transferring from water to aqueous formamide are summarized in Table 17. Almost all of the data have been reported on the TATB scale in a single study,[52] using the novel method of VITIES.[51]

Consistent with the strong donor characteristics of formamide (Table 3), $\Delta_tG°(M^+, w \rightarrow w+FA)$ are all mildly negative, but in marked contrast to most other aqueous organic solvent mixtures, the values of $\Delta_tG°(Me_4N^+, w \rightarrow w+FA)$ are not close to those of the alkali metal cations nor is there a significant difference between the latter and $\Delta_tG°(Cu^{2+})$.

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

1. Comments on the Data

Available data for the Gibbs energies of transfer of cations from water to aqueous *N*,*N*-dimethylformamide, mainly based on the TATB assumption, are listed in Table 18, and selected values are plotted in Figure 9.

Four studies[186,193,195,196] of $\Delta_tG°(Ph_4As^+, w \rightarrow w+DMF)$ by two groups of workers are in good agreement over the entire solvent composition range, and thus, their averaged values are classified as Recommended. Reasonable amounts of data also exist for the hydrogen ion, most of the alkali metal, silver, and copper(II) cations, also permitting their averaged values to be classified as Recommended or Tentative. The values of $\Delta_tG°(K^+)$ from one study[196] differ considerably from those of two earlier reports[193,195] and have been rejected. In the absence of confirmatory studies, no critical evaluation of the remaining data presented in Table 18 is possible.

2. Discussion of the Transfer Energetics

Consistent with the strong donor character of DMF (Table 3), the values of $\Delta_tG°(M^{n+}, w \rightarrow w+DMF)$ are all favorable (negative), indicating that cations are better solvated in the mixtures than in neat water. The values of $\Delta_tG°(H^+)$ decrease rather sharply at low x_{DMF} before passing through a shallow minimum at $x_{DMF} \approx 0.4$. This indicates that aqueous DMF is considerably more basic than water and that the hydrogen ion is preferentially solvated by the DMF (which has a higher proton affinity than water in the gaseous state[84]), although other factors such as solvent structural effects are doubtless important.

Although $\Delta_tG°(Li^+) < \Delta_tG°(Na^+)$, the values of $\Delta_tG°(M^+)$ for the larger alkali metal cations show almost no dependence on ionic radius. This is unexpected for such 'hard' interactions (see section II.Q). Equally important, the $\Delta_tG°(M^+)$ values do not vary

Table 16. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Acetonitrile (AN) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100*x*	10	20	30	40	50	60	70	80	90	100	method	ref	status
H$^+$	−2.8	−3.7	−3.5	−3.3	−2.6	−2.0	0.5	6.9	19.4	44.8	TATB	179	
	−2.6	−2.8	−3.5	−2.7	−2.1	−1.1	−2.5	[−7.2]			TATB^a	98	
	[−3.6]	[−8.3]		[−11.4]							TATB	87	
	−2.7	**−3.3**	**−3.5**	**−3.0**	**−2.4**	**−1.6**	**−1.0**	**{6.9}**	**{19.4}**	**{44.8}**	**TATB**		**R{T}**
Li$^+$	−1.4	−1.4	−1.3	−1.1	−0.2	1.0	3.9	10.0	18.6	28.5	TATB	179	
	−0.8	−0.8	−0.4	1.6	2.5	5.2	7.9	11.4	19.7	28.5	TATB^a	180	
	−1.1	**−1.1**	**−0.9**	**0.3**	**1.2**	**3.1**	**5.9**	**10.7**	**19.2**	**28.5**	**TATB**		**R**
Na$^+$	0.4	0.8	1.3	2.1	3.1	3.7	5.0	6.6	9.8	16.1	NLJP	181	
	0.4	−3.2	−2.7	−2.9	−0.9	−2.3	0.0	1.6	4.8	10.1	TATB^b		
	0.2	0.6	2.0	2.7	3.5	4.3	5.5	6.9	9.2	14.5	BBCr	182	
	−1.4	−1.4	−1.0	−0.4	0.2	1.2	3.2	6.2	9.4	13.0	TATB	179	
	−1.8	−0.8	−0.9	−0.4	1.2	1.0	4.7	6.4	8.4	12.6	TATB^a	180	
	−0.9	**−1.8**	**−1.5**	**−1.2**	**0.2**	**1.5***	**2.6**	**4.7**	**7.6**	**11.9**	**TATB**		**R**
K$^+$	−1.8	−2.3	−1.4	0.2	0.3	0.3	1.0	2.1	3.9	6.4	TATB	179	
	−3.3	−1.8	−1.7	−0.6	−0.2	1.5	2.6	3.3	3.7	6.6	TATB^a	180	
	−2.1	−2.8	(−2.6)	−2.1	(−1.5)	−1.0					TATB	90	
	−2.4	**−2.3**	**−1.9**	**−0.8**	**−0.5**	**0.3**	**1.8**	**2.7**	**3.8**	**6.5**	**TATB**		**R**
Rb$^+$	−2.1	−2.9	−2.4	−1.9	−0.9	0.0	1.0	1.7	3.6	5.4	TATB	179	
	−1.8	−1.4	−1.4	0.1	0.9	1.7					TATB^a	98	
	−2.0	**−2.2**	**−1.9**	**−0.9**	**0.0**	**0.9**	**{1.0}**	**{1.7}**	**{3.6}**	**{5.4}**	**TATB**		**R{T}**
Cs$^+$	−2.1	−2.9	−2.5	−1.9	−1.4	−0.7	0.2	1.2	2.4	3.9	TATB	179	
	−2.3	−2.8	−3.4	−2.6	−1.5	0.3	1.7	1.9	2.7	5.0	TATB^a	180	
	−2.2	**−2.8**	**−3.0**	**−2.3**	**−1.5**	**−0.1**	**1.0**	**1.6**	**2.6**	**4.5**	**TATB**		**R**
Cu$^+$	−39.0	−42.7	−46.5	−46.9	−47.4	−48.5	−48.5	(−48.5)	(−48.6)	−48.7	NLJP	181	
	−42.0	−46.6	(−47.9)	−49.9	(−53.5)	(−56.6)	−56.0	−51.5	−47.7	−53.7	NLJP	132	
	−33.1	−39.2	−40.3	−43.4	−47.4	−50.0	(−50.3)	−50.5	(−50.6)	−50.6	NLJP	183	
	−36.1	**−44***	**−48***	**−51***	**−53***	**−54***	**−54.4**	**−54.5**	**−55.2**	**−55.7**	**TATB^b**		**T**
Ag$^+$	−11.5	−14.9	−16.3	−17.1	−17.5	−17.9	−18.2	−18.2	−18.6	−19.0	NLJP	184	
	−11.6	−14.7	−16.4	−17.1	−17.4	−17.7	−17.7	−18.0	−18.1	−18.2	NLJP	181	
	−11.6	−18.8	−20.5	−22.1	−21.4	−23.7	−22.7	−22.2	−23.6	−24.6	TATB^b		
	−19.1	(−26.0)	−30.4	(−31.4)	−31.4	(−33.5)	−34.5	(−34.0)	−34.6	−35.6	Fc^c	30	
	−11.1	−16.0	−19.4	−20.2	−20.4	−21.0	−21.5	−22.3	−22.6	−22.6	TATB^d		
	−13.4	−15.6	−15.2	−15.7	−16.7	−17.8	−19.2	−20.6	−22.0	−23.7	BBCr	182	
	−11.5	−18.9	−20.7	−22.1	−21.5	−21.9	−23.2	−23.2	−23.6	−25.0	TATB	79	
	−12.1	−16.7	−18.4	−18.4	−19.1	−19.8	−21.9	−23.7	−23.8	−24.0	TATB^e	180	
	−11.6	**−17.6**	**−19.7**	**−20.7**	**−21.0***	**−21.6**	**−22.3**	**−23.1**	**−23.4**	**−24.1**	**TATB**		**R**
Au$^+$	**−12.5**	**−22.9**	**−30.4**	**−35.8**	**(−39.9)**	**−43.0**	**(−44.0)**	**−45.2***	**(−46.6)**	**(−47.1)**	**TATB**	127	**T**
Tl$^+$	0.1	1.3	2.6	3.2	3.7	4.2	4.8	5.6	6.8	9.6	BBCr	182	
Me$_4$N$^+$	0.2	−3.3	−5.0	−3.7							TATB^f	185	
	−1.8	−2.8	(−3.1)	−2.8							TATB	140	
	−0.8	**−3.1**	**−4.1**	**−3.3**						**3.0^g**	**TATB**		**R**
Et$_4$N$^+$	2.7	0.2	−2.5	−2.7							TATB^f	185	
	0.3	0.1	(−0.5)	−1.7							TATB	140	
	1.5	**0.2**	**−1.5**	**−2.2**						**−7.0^g**	**TATB**		**R**
Pr$_4$N$^+$	1.7	0.2	−2.3	−5.2							TATB^f	185	
	−1.8	−3.1	(−4.0)	−4.4							TATB	140	
	−0.1	**−1.5**	**−3.2**	**−4.8**						**−13.0^g**	**TATB**		**R**
Bu$_4$N$^+$	5.7	3.7	0.2	−1.7							TATB^f	185	
	3.3	4.2	(2.7)	−1.3							TATB	140	
	4.5	**4.0**	**1.5**	**−1.5**						**−32.0^h**	**TATB**		**R**
Ph$_4$As$^+$	−14.6	−20.5	−25.0	−28.4	−30.6	−32.2	−33.0	−33.7	−34.8	−34.9	TATB	186	
	−14.8	−20.6	−23.4	−25.1	−26.6	−28.0	−29.4	−30.9	−32.5	−33.9	TATB^i	80	
	−10.9	−20.7	−25.5	−27.9	−29.4	−30.5	−31.5	−32.5	−33.3	−33.9	TATB	179	
	−11.8	−20.2	(−25.3)	−27.1							TATB	140	
	−13.4	**−20.4**	**−24.6**	**−27.1**	**−28.9**	**−30.2**	**−31.3**	**−32.4**	**−33.5**	**−34.2**	**TATB**		**R**
Mn^{2+}	−5.2	−8.4	−10.6	−11.3	−9.8	−7.4	−2.5	4.0	14.3	26.3	Fc	187	
	2.8	**2.1**	**0.4**	**0.5**	**1.2**	**5.1**	**10.5**	**17.0**	**26.3**	**39.3**	**TATB^d**		**T**
Fe^{2+}	1.5	−1.9	0.4	2.1	5.7	11.1	19.0	30.0	51.8	97.5	NLJP	154	
	−1.5	**−5.9**	**−3.6**	**−2.8**	**−2.5**	**5.1**	**14.0**	**25.0**	**46.8**	**91.5**	TATB^b		**T**
Cu^{2+}	0.3	1.8	1.7	2.6	5.1	8.5	13.0	19.0	32.8	54.0	NLJP	181	
	[12.7]	[14.2]	[12.0]	[10.1]	7.1	7.9	10.8	14.0	22.3	49.3	NLJP	183	
	1.6	3.1	5.1	7.5	10.4	14.1	18.3	23.8	31.8	58.2	NLJP	46	
	1.2	3.3	4.7	2.6	1.6	3.8	7.3	12.8	23.6	50.8	NLJP	132	
	[1.0]	[−1.3]	[−0.5]	[−0.8]	[2.1]	[2.6]	[7.4]	[10.4]	[22.6]	[47.1]	TATB^b		
	3.4	**4.9***	**7.7**	**9.1**	**10.4**	**10.6**	**13.5**	**25.5**	**39.8**	**66.8**	TATB	188	**T**
Zn^{2+}	−3.2	−2.4	−2.1	−1.7	−1.6	1.1	4.8	11.7	22.3	30.3	NLJP	132	
	−3.2	**−6.4**	**−6.1**	**−6.7**	**−5.6**	**−4.9**	**−0.2**	**6.7**	**17.3**	**28.3**	TATB^b		**T**
Pb^{2+}	−2.7	−2.4	−3.1	−3.0	−1.8	0.4	3.5	9.4	19.3	36.2	NLJP	132	
	−2.7	**−6.4**	**−7.1**	**−8.0**	**−5.8**	**−5.6**	**−1.5**	**4.4**	**14.3**	**30.3**	TATB^b		**T**
Fe^{3+}	2.1	−3.1	0.1	3.4	8.3	14.8	25.0	40.8	78.2	223.2	NLJP	154	
	2.1	**−7.1**	**−3.9**	**−1.6**	**4.3**	**8.8**	**20.0**	**35.8**	**73.2**	**218.2**	TATB^b		**T**

[a] Using $\Delta_t G°$(MCl) data combined with $\Delta_t G°$(Cl$^-$) data on the TATB scale from ref 179. [b] The NLJP data from the previous row(s) adjusted to the TATB scale using conversion factors from Table 1. [c] Data available also for 303.15 K. [d] The Fc data from the previous row(s) adjusted to the TATB scale using conversion factors from Table 1. [e] Using $\Delta_t G°$(AgBr) data combined with $\Delta_t G°$(Br$^-$) data on the TATB scale from ref 179. [f] Using $\Delta_t G°$(R$_4$NBPh$_4$) data combined with $\Delta_t G°$(BPh$_4{}^-$) data on the TATB scale from ref 179. [g] From ref 19. [h] From ref 189. [i] Using $\Delta_t G°$(Ph$_4$AsI) data combined with $\Delta_t G°$(I$^-$) data on the TATB scale from ref 179.

Table 17. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Formamide (FA) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	−14.8	−20.0	−23.2	−25.6	−27.0	−28.0	−28.4					191	
Na^+	−2.8	−4.2	−5.0	−5.8	−6.4	−6.9	−7.3	−7.7	−8.0	−8.2	TATB	52	
K^+	−3.1	−4.3	−5.0	−5.8	−6.4	−6.9	−7.3	−7.7	−8.0	−8.3	TATB	52	
Rb^+	−2.8	−3.9	−4.7	−5.5	−6.0	−6.6	−7.0	−7.4	−7.7	−7.9	TATB	52	
Cs^+	−3.0	−3.7	−4.3	−4.7	−4.9	−5.3	−5.6	−5.8	−6.0	−6.0	TATB	52	
$Me_4N^{+\,a}$	−1.3	−1.7	−1.8	−1.9	−1.9	−1.9	−1.7	−1.3	−1.3	−1.3	TATB	52	
$Et_4N^{+\,a}$	−2.8	−3.9	−4.6	−5.2	−5.5	−5.8	−6.1	−6.4	−6.8	−7.1	TATB	52	
Cu^{2+}	−3.5	−3.6	−4.5	−5.1	−5.8	−6.3	−6.9	−7.6	−8.2	−8.4	NLJP	192	

[a] Data for unsymmetrical tetraalkyl-, phenyltrimethyl-, and benzyltrimethylammonium cations are also available in ref 52.

Table 18. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + *N,N*-dimethylformamide (DMF) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion\100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	−5.0	−10.7	−14.9	−15.6	−16.2	−16.0	−15.8	−15.5	−15.1	−14.4	TATB	193	
	−5.3	−10.9	−15.1	−16.3	−16.1						TATB[a]	98	
	−5.2	**−10.8**	**−15.0**	**−16.0**	**−16.2**	**{−16.0}**	**{−15.8}**	**{−15.5}**	**{−15.1}**	**{−14.4}**	**TATB**		**R{T}**
Li^+	**−2.5**	**−6.8**	**−9.5**	**−10.5**	**−10.9**	**−12.6**	**−14.6**	**−17.3**	**−19.8**	**−22.4**	**TATB**	193	**T**
Na^+	4.7	5.1	3.8	2.0	0.1	−2.1	−4.4	−5.5	−6.4	−7.1	BBCr	194	
	−1.7	**−4.3**	**−6.0**	**−6.0**	**−5.9**	**−6.5**	**−7.4**	**−8.5**	**−9.6**	**−10.6**	**TATB**	193	**T**
K^+	−1.3	−3.8	−5.2	−5.2	−5.1	−5.8	−6.7	−7.6	−8.7	−9.8	TATB	193	
	−1.1	−2.3	−4.3	−2.8	−1.7	−3.0	−3.9	−4.9	−7.0	−8.4	TATB[b]	195	
	[−2.6]	[−6.4]	[−8.8]		[−10.9]					[−17.6]	TATB	196	
	−1.2	**−3.1**	**−4.8**	**−4.0**	**−3.4**	**−4.4**	**−5.3**	**−6.3**	**−7.9**	**−9.1**	**TATB**		**R**
Rb^+	−1.5	−3.6	−4.9	−4.6	−4.3	−4.9	−6.4	−7.7	−9.0	−10.2	TATB	193	
	−1.0	−3.0	−3.7	−3.0	−2.1						TATB[a]	98	
	−1.3	**−3.3**	**−4.3**	**−3.8**	**−3.2**	**{−4.9}**	**{−6.4}**	**{−7.7}**	**{−9.0}**	**{−10.2}**	**TATB**		**R{T}**
Cs^+	−1.3	−4.0	−5.4	−5.2	−4.6	−5.0	−5.9	−7.1	−8.1	−9.4	TATB[a]	98	
	−2.3	−5.3	−6.8	−7.5	−6.2	−8.5	−9.9	−11.2	−13.0	−14.3	TATB[b]	195	
	−1.8	**−4.7**	**−6.1**	**−6.4**	**−5.4**	**−6.8**	**−7.9**	**−9.2**	**−10.6**	**−11.9**	**TATB**		**R**
Ag^+	1.5	0.9	−0.9	−3.2	−5.4	−7.6	−10.1	−11.9	−13.4	−15.1	BBCr	194	
	−3.3	−5.2	−7.2	−8.8	−10.5	−11.9	−12.9	−13.9	−14.5	−14.5	NLJP[c]	79	
	−3.3	**−7.5**	**−11.3**	**−13.7**	**−14.7**	**−15.6**	**−16.1**	**−16.6**	**−17.1**	**−17.2**	**TATB**[d]		**T**
Tl^+	4.2	3.5	2.1	−0.2	−2.4	−4.6	−7.0	−8.6	−9.7	−10.8	BBCr	194	
Ph_4As^+	−10.5	−20.3	−25.7	−29.5	−32.4	−34.8	−36.6	−38.3	−39.8	−40.6	TATB	186	
	−12.5	−19.0	−23.5	−26.5	−28.6	−31.1	−33.3	−35.3	−37.1	−38.3	TATB	193	
	−13.2	−21.7	−26.2	−31.0	−35.0	−34.7	−34.3	−33.8	−32.7	−31.6	TATB[b]	195	
	−12.8	−20.6	−25.9	(−29.7)	−32.5					−45.8	TATB	196	
	−12.3	**−20.4**	**−25.3**	**−29.2**	**−32.1**	**−33.5**	**−34.7**	**−35.8**	**−36.5**	**−39.1**	**TATB**		**R**
Ph_4Sb^+	**−11.1**	**−20.7**	**−28.3**	**−34.0**	**−38.3**	**−41.5**	**−43.9**	**−45.9**	**−47.7**	**−49.8**	**TATB**	195	**T**
Mn^{2+}	−11.5	−22.5	−29.5	−37.1	−45.1	−48.6	−49.9	−51.0	−51.7	−53.3	Fc	197	
Cu^{2+}	−1.3	−2.8	−3.5	−4.6	−6.6	−8.1	−9.6	−11.2	−12.7	−14.7	NLJP	192	
	−5.4	−10.5	−13.8	−17.7	−20.1	−22.8	−22.8	−22.0	−20.7	−19.0	NLJP[c]	46	
	−2.9	**−4.6**	**−8.2**	**−14.9**	**−16.3**	**−17.6**	**−17.0**	**−16.1**	**−16.1**	**−14.4**	**TATB**[d]		**T**
Zn^{2+}	−9.0	−18.0	−26.0	−41.6	−50.1	−53.1	−55.1	−57.2	−57.2	−57.3	Fc	133	
Eu^{2+}	−5.0	−18.8	−25.0	−28.6	−33.4	−40.2	−44.3	−53.3	−55.7	−57.3	Fc[e]	198	

[a] Using $\Delta_t G°$(MCl) data combined with $\Delta_t G°$(Cl^-) data on the TATB scale from ref 193. [b] Using $\Delta_t G°$($RbBPh_4$) data combined with $\Delta_t G°$(BPh_4^-) data on the TATB scale from ref 195. [c] Data available also for 303.15 K. [d] The NLJP data from the previous row(s) adjusted to the TATB scale using conversion factors from Table 1. [e] Cobaltocene used rather than ferrocene.

monotonically with solvent composition (Figure 9), which is again indicative that the cation solvation energetics are being significantly influenced by effects other than donor−acceptor (coordinative) interactions of the cations with the solvent molecules. Similar effects are also apparent in the less well-established values of other univalent cations.

The very large differences, up to 43 kJ mol^{-1}, between the NLJP- and TATB-based values of $\Delta_t G°$(Cu^{2+}) and the Fc-based data for $\Delta_t G°$(Zn^{2+}) may imply a significant discrepancy between these two assumptions rather than a real difference in the solvation energetics of these two cations. It is also noteworthy that unlike the equivalence observed between $\Delta_t G°$(Ph_4P^+) and $\Delta_t G°$(Ph_4As^+) in a number of pure and mixed solvents, the values of $\Delta_t G°$(Ph_4Sb^+) are rather different from those of $\Delta_t G°$(Ph_4As^+) at $x_{DMF} > 0.3$.

O. Transfers from Water to Water + *N*-Methylpyrrolidin-2-one (NMP)

The available data for the Gibbs energies of transfer of cations from water to aqueous *N*-methylpyrrolidin-2-one, mainly based on the TATB assumption and mostly determined at 30 °C, are listed in Table 19.

Serious discrepancies of up to 25 kJ mol^{-1} exist between the values of $\Delta_t G°$(Ph_4As^+, w→w+NMP) determined independently at 30 °C by Kalidas and

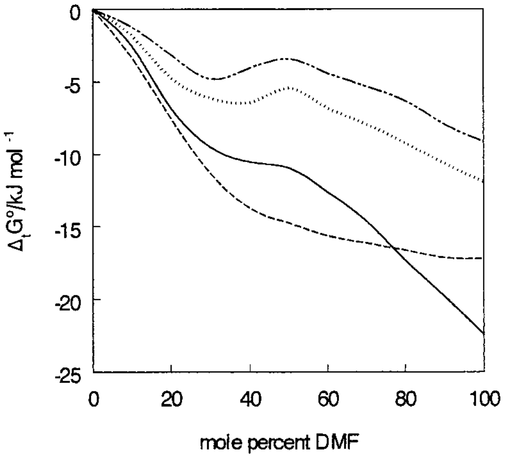

Figure 9. Gibbs energy of transfer of cations from water to aqueous *N*,*N*-dimethylformamide as a function of the mole percentage of *N*,*N*-dimethylformamide: (—) Li^+, (- - -) Ag^+, (−··−) K^+, and (···) Cs^+.

co-workers[24,199] and at 25 °C by Gomaa,[200] both using the TATB assumption. These are unlikely to be due to the small difference in temperature. The former show a variation with solvent composition which is quite unusual for this ion in aqueous organic solvent mixtures. It is also difficult to see how the values of $\Delta_t G°(M^+)$ determined by these two groups of workers for the alkali metal cations can show the expected similarity, when the values of $\Delta_t G°(Ph_4As^+)$ on which they ought to have been based differ so markedly.

In the absence of further studies, all the data should be viewed with caution and a discussion of the transfer energetics is inappropriate at this time.

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

The available data for the Gibbs energies of transfer of cations from water to aqueous hexamethyl phosphoric triamide are listed in Table 20. Since there are no confirmatory studies, no critical evaluation of the data is possible. However, the TATB-based values appear reasonable and have been classified as tentative.

Consistent with the very strong donor properties of HMPT (Table 3), all the values of $\Delta_t G°(M^{n+}$, w→w+HMPT) are negative (favorable for transfer). The shape of the curves of $\Delta_t G°(M^{2+})$ against x_{HMPT}, obtained by the less reliable Fc assumption, are characteristic of strong preferential solvation by HMPT. The curves of $\Delta_t G°(M^+)$ for the alkali metal cations are more complex, however, showing an unusual minimum at $x_{HMPT} \approx 0.3$.

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

1. Comments on the Data

All the available data for $\Delta_t G°(M^{n+}$, w→w+DMSO) based on the NLJP, Fc, or TATB assumptions are reported in Table 21. Also incorporated into Table 21 are the $\Delta_t G°$ values obtained by converting the NLJP and Fc data to the TATB scale (Table 1). Selected values of $\Delta_t G°$ are plotted as functions of solvent composition in Figures 10−12.

Two independent studies[202,205] of $\Delta_t G°(Ph_4As^+$, w→w+DMSO) are in excellent agreement, permitting the averaged values to be classified as Recommended over the whole composition range. Reasonably extensive data for hydrogen ions and the alkali metal, silver, and copper(II) cations, mainly based on the TATB assumption, are also in good agreement for each cation, and the averaged values are Recommended at all solvent compositions.

Independent estimates of $\Delta_t G°(M^{2+})$ for zinc and lead have been obtained using the Fc and NLJP assumptions. After conversion to the TATB scale, employing the addends in Table 1, these data are generally in good agreement, allowing the averaged values to be classified as Recommended or, where the agreement is poorer, as Tentative. Unconfirmed values for other cations which appear reasonable have been classified as Tentative too.

2. Discussion of the Transfer Energetics

The value of $\Delta_t G°(H^+)$ is negative at all solvent compositions, decreasing sharply at first before passing through a shallow minimum at $x_{DMSO} \approx 0.55$. Thus, all the aqueous DMSO mixtures are more basic than pure water, with maximum basicity occurring at the composition of the minimum in the curve. This arises from three effects: the breakdown of the three-dimensional H-bonded network of water by the DMSO, the interaction of DMSO with water molecules to form a fairly stable 1:1 adduct, and the greater proton affinity of isolated DMSO molecules.[84]

The values of $\Delta_t G°(M^+)$ for the alkali metal ions are also negative, in the order $Li^+ < Cs^+ < Na^+ < K^+ < Rb^+$ (least negative), corresponding to more favorable solvation of these ions by DMSO, which is consistent with its higher donor properties compared with water (Table 3). With the exception of Cs^+, this order is consistent with the increasing ionic radii (Table 2), as would be expected for the interaction of these relatively 'hard' ions with the hard O-donor site of the DMSO. The position of Cs^+ is interesting and may indicate that this rather less 'hard' ion is interacting with the π^* orbitals of the >S=O moiety.

The values of $\Delta_t G°(Ag^+)$ are more negative than those of most other cations; Ag^+ is a typical soft d^{10} cation and probably either interacts with DMSO as suggested for Cs^+ or with the 'soft' S-donor site of the DMSO. The data for Cu^+, another soft d^{10} cation, are even more negative than for Ag^+.

Almost no data exist for the tetraalkylammonium cations. However, the limited values for $\Delta_t G°(Bu_4N^+)$, up to 50 mol % DMSO, show the effect of the diminishing three-dimensional water structure as the DMSO concentration increases. This enables this rather large, hydrophobic ion to be better accommodated within the solvent mixtures than in neat water. In addition, an increase in dispersion interactions of this ion with the DMSO molecules would also be expected to occur with increasing amounts of DMSO. Similar but even larger effects are observed for the more polarizable Ph_4As^+.

All the divalent cations studied are more favorably solvated in aqueous DMSO than in neat water ($\Delta_t G°$ is negative), consistent with DMSO being a stronger

Table 19. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + *N*-Methylpyrrolidin-2-one (NMP) Mixtures at 303.15 K (unless otherwise noted)

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale											
ion \ 100x	10	20	30	40	50	60	70	80	90	100	method	ref
K^+	−2.2	(−5.5)	−8.0	(−9.6)	−10.5	(−10.9)	−10.8	(−10.7)	−10.2	−1.7	NLJP	24, 199
	−3.2	(−4.9)	−6.1	(−7.0)	−7.3	(−8.5)	−9.8	(−10.0)	−9.1	−5.8	TATB	24, 199
Rb^+	0.7	0.4	−2.5	−3.9	−4.3	−4.7	−4.9	−5.1	−4.9	−4.6	TATB	200[a]
Cs^+	−0.3	−4.5	−7.9	−9.5	−9.1	−7.4	−6.1	−5.5	−4.7	−4.1	TATB	200[a]
Ag^+	−2.3	(−4.4)	−6.3	(−8.9)	−11.1	(−13.7)	−15.8	−17.4	−17.8	−18.3	NLJP	24, 199
	−3.4	(−4.2)	−4.4	(−6.4)	−7.9	(−10.7)	−14.9	(−15.9)	−16.7	−26.8	TATB	24, 199
Ph_4As^+	−1.1	(−4.9)	−9.7	(−11.9)	−13.3	(−14.9)	−15.7	(−17.4)	−18.0	−10.2	NLJP	24, 199
	−2.2	(−5.4)	−7.8	(−9.4)	−10.1	(−11.9)	−14.8	(−15.9)	−16.7	−22.4	TATB	24, 199
	−19.9	−29.4	−32.4	−34.4	−36.4	−37.9	−38.9	−39.4	−39.9	−40.0	TATB	200[a]
Cu^{2+}	−4.2	(−11.6)	−18.3	(−21.6)	−23.8	(−24.8)	−25.0	(−25.3)	−24.7	−26.5	NLJP	24, 199
	−7.2	(−8.0)	−8.2	(−11.8)	−15.7	(−18.8)	−21.8	(−23.3)	(−26.3)	−38.3	TATB	24, 199

[a] At 298.15 K.

Table 20. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Hexamethyl Phosphoric Triamide (HMPT) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion \ 100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
K^+	**−1.0**	**−3.4**	**−8.0**	**−6.0**	**−3.7**	**−2.6**	**−2.0**	**−1.7**	**−1.4**	**−1.1**	TATB	70	**T**
Rb^+	**−1.9**	**−6.4**	**−9.8**	**−8.5**	**−7.2**	**−6.3**	**−5.3**	**−4.7**	**−4.4**	**−3.8**	TATB	70	**T**
Cs^+	**−3.3**	**−9.9**	**−14.8**	**−13.2**	**−11.8**	**−11.0**	**−10.2**	**−9.1**	**−8.6**	**−7.8**	TATB	70	**T**
Ph_4As^+	**−21.0**	**−29.5**	**−32.6**	**−32.6**	**−35.3**	**−36.4**	**−37.2**	**−38.0**	**−38.7**	**−39.3**	TATB	70	**T**
Zn^{2+}	−14.5	−32.0	−45.0	−58.5	−64.9	−70.0	−75	−80	−84.5	−87.5	Fc	171	
Cd^{2+}	−15.0	−28.0	−10.5	−49.5	−56.4	−61.0	−65	−68	−71	−73.5	Fc	201	
Pb^{2+}	−20.0	−37.5	−52.0	−63	−70	−79.4	−89	−95	−100	−105	Fc	171	

donor than water. The values of $\Delta_t G°$ for the harder ions are in the order $Cu^{2+} \approx Zn^{2+} < Mn^{2+}$, consistent with their radii (Table 2). The data for the softer Pb^{2+} and Cd^{2+} do not conform to this pattern. Indeed, at $x_{DMSO} > 0.5$, $\Delta_t G°(Pb^{2+}) < \Delta_t G°(Cd^{2+})$ even though Cd^{2+} is considerably smaller. This sort of behavior is expected when 'soft' (specific covalent bonding) interactions are important.

IV. General Discussion

A. Comparison of Hydrogen-Ion Medium Effects in Different Solvent Mixtures

The medium effect on hydrogen ions, expressed here as its Gibbs energy of transfer $\Delta_t G°(H^+, w \rightarrow w+s)$, is an expression of the relative stability or acidity of the proton in water and aqueous organic solvent mixtures. As such, it is a parameter of great significance in analytical and electroanalytical chemistry. In view of this importance, it is pertinent to compare its variation with the nature of the solvent and its composition for as many diverse cosolvents as possible. Data for $\Delta_t G°(H^+)$ into aqueous MeOH, EtOH, EG, AC, AN, FA, DMF, and DMSO, based on the TATB assumption, are shown in Figure 13.

The Gibbs energies of transfer of the hydrogen ion from water to the aqueous mixtures of ***aprotic*** solvents (except AN) studied to date are negative. In this respect, FA appears to behave as an aprotic solvent, which is rather surprising given its rather 'water-like' properties. In both aqueous DMSO and aqueous DMF mixtures, the $\Delta_t G°(H^+)$ values decrease sharply initially, up to about 30 mol % organic solvent, then slightly increase (become less negative) up to the pure solvent. Thus, all these aqueous DMSO and DMF mixtures are more basic than water with the basicity maximum being around 50 mol % organic solvent. This may be due to the higher electron-pair donicities (measured by β, Tables 3 and 4) of these O-donor polar solvents compared with water and to the breakdown of the H-bonded network of water by the added organic component. Note that non-hydrogen-bonded water molecules have a much smaller β value (0.18) than bulk water (0.47), showing that they are much weaker electron-pair donors. The destruction of the H-bonded network of water may predominate for aqueous AC and aqueous FA mixtures, whose β values are commensurate with that of bulk water, their maximal basicities being near 30 and probably 80 mol % cosolvent, respectively. Tetrahydrofuran and dioxane behave in this respect as typical aprotic polar cosolvents, but the data extend only to low cosolvent contents.

In contrast to the other aprotic cosolvents, in aqueous acetonitrile $\Delta_t G°(H^+)$ is only slightly negative up to ca. 65 mol % AN, before rapidly becoming positive. Thus, water + AN mixtures are more basic than water up to 65 mol % AN, due to enhancement of the H-bonded structure of water, but the hydrogen-ion activity is significantly increased at high AN concentrations. In acetonitrile-rich mixtures AN, which is a weaker proton acceptor than the O-donor cosolvents FA, DMF, DMSO, AC, and bulk water, disrupts the water structure and finally replaces water molecules in the solvation shell of the proton.

The Gibbs free energies of transfer of hydrogen ions for the aqueous ***protic*** solvent mixtures are small ($|\Delta_t G°(H^+)| < 3$ kJ mol^{-1}) up to 70 mol % cosolvent. The values of $\Delta_t G°(H^+)$ are slightly negative over at least some of this range but increase and become positive as the neat cosolvent is approached. It is

Table 21. Standard Molar Gibbs Energies of Transfer of Cations from Water to Water + Dimethyl Sulfoxide (DMSO) Mixtures at 298.15 K

	$\Delta_t G°$(ion)/kJ mol^{-1}, molarity-scale												
ion \ 100x	10	20	30	40	50	60	70	80	90	100	method	ref	status
H^+	−4.4	−9.5	−14.8	−18.8	−21.3	−21.7	−21.4	−20.4	−19.3	−17.9	TATB[a]	202	
	−4.3	−10.0	−15.8	−19.8	−22.0						TATB[a]	203	
	−3.4	−10.3	−15.7	−19.8	−22.2						TATB[a]	98	
	−2.7	−10.1	−15.8	−21.5	−24.3	−27.1	−28.8	−29.9	−31.2	−31.8	Fc	204	
	−2.7	−8.1	−11.8	−17.5	−16.8	−17.1	−19.8	−20.9	−20.2	−20.8	TATB[b]		
	−4.4	−9.6	−14.9	−20.1	−25.3						TATB	87	
	−3.7	**−9.5**	**−14.5**	**−19.0**	**−21.6**	**{−19.3}**	**−20.6**	**−20.7**	**−19.8**	**−19.4**	**TATB**		**R**
Li^+	−2.9	−6.3	−10.5	−15.0	−17.5	−18.8				−18.8	TATB	205	
	−2.4	−6.0	−10.1	−13.5	−15.9	−15.5	−16.0	−16.2	−16.8	−15.7	TATB[a]	202	
	−2.7	**−6.2**	**−10.3**	**−14.1**	**−16.0***	**−16.6***	**−16.0**	**−16.2**	**−16.8**	**−17.3**	**TATB**		**R**
Na^+	−0.9	−2.5	−5.3	−8.5	−11.0	−12.3	−12.7	−13.3	−13.3	−13.5	TATB	205	
	−0.4	−2.0	−4.6	−7.5	−9.3	−9.1	−9.7	−10.1	−11.3	−11.9	TATB[a]	202	
	−1.9	−4.9	−9.1								TATB	90	
	−0.7	**−2.3**	**−5.0**	**−8.0**	**−10.2**	**−10.7**	**−11.2**	**−11.7**	**−12.3**	**−12.7**	**TATB**		**R**
K^+	−0.9	−1.3	−3.5	−5.5	−8.8	−9.5	−9.7	−10.2	−10.8	−11.6	TATB	205	
	−0.4	−1.0	−3.1	−5.5	−7.3	−7.6	−8.5	−10.1	−11.3	−12.7	TATB[a]	202	
	−0.7	**−1.2**	**−3.3**	**−5.5**	**−8.1**	**−8.6**	**−9.2**	**−10.2**	**−11.1**	**−12.2**	**TATB**		**R**
Rb^+	−0.4	−1.8	−3.8	−6.0	−7.3	−8.8				−8.9	TATB	205	
	−0.4	−2.5	−4.3	−6.8	−6.9	−5.5					TATB[a]	98	
	−1.1	−1.3	−2.8	−5.3	−7.3	−6.7	−7.2	−8.3	−10.1	−11.5	TATB[a]	202	
	−0.3	**−1.9**	**−3.6**	**−6.0**	**−7.2**	**−7.0**	**−7.2**	**−8.3**	**−10.1**	**−10.2**	**TATB**		**R**
Cs^+	−0.9	−2.5	−5.3	−8.5	−10.8	−12.3	−12.7	−13.1	−13.0	−12.6	TATB	205	
	−0.6	−2.0	−4.8	−7.3	−9.3	−9.6	−10.0	−10.8	−12.1	−13.4	TATB[a]	202	
	−0.8	**−2.3**	**−5.1**	**−7.9**	**−10.1**	**−11.0**	**−11.4**	**−12.0**	**−12.6**	**−12.9**	**TATB**		**R**
Cu^+					−37.8	(−42.3)	−44.8	(−46.3)	−46.8	−47.8	NLJP	167	
					−35.7	**−40.5**	**−43.3**	**−44.3**	**−44.3**	**−44.9**	TATB[c]		**T**
Ag^+	−4.3	−8.6	−12.7	−16.7	−20.6	−23.8	−26.4	−28.6	−30.6	−31.6	NLJP	79	
	−4.4	−9.3	−15.1	−19.3	−23.3	−26.2	−28.3	−30.3	−21.6	−32.0	NLJP	181	
	−4.1	−8.5	−12.4	−15.8	−20.5	−22.9	−25.9	−27.5	−28.6	−28.9	TATB[c]		
	−2.9	−9.8	−17.8	−23.8	−29.8	−35.8	−36.8	−39.8	−42.8	−44.8	Fc[d]	206	
	−1.6	−10.1	−16.9	−23.8	−28.3	−31.9	−36.9	−39.2	−42.6	−43.7	Fc	204	
	−2.3	−7.9	−13.3	−19.8	−22.1	−24.4	−27.9	−31.0	−31.7	−33.3	TATB[b]		
	−2.9	−7.8	−13.8	−19.8	−23.3	−25.8	−27.8	−29.8	−31.8	−33.8	TATB	180	
	−3.2	**−8.1**	**−13.2**	**−18.5**	**−21.9**	**−24.4**	**−27.2**	**−29.4**	**−30.7**	**−32.0**	**TATB**		**R**
Tl^+		−4.9	−11.2	−15.8	−20.9	−24.3	−27.2	−30.0	−31.2	−32.9	Fc	167	
		−2.9	**−7.2**	**−11.8**	**−13.8***	**−16.0***	**−18.2**	**−19.5***	**−20.2**	**−21.9**	TATB[b]		**T**
Bu_4N^+	**−3.0**	**−7.2**	**−12.3**	**−15.5**	**−17.1**						**TATB**[e]	202	**T**
Ph_4As^+	−9.4	−16.3	−21.6	−26.0	−28.9	−31.6	−33.6	−35.6	−36.8	−37.6	TATB	205	
	−8.2	−16.4	−22.4	−25.8	−29.1	−32.4	−33.6	−36.6	−38.1	−39.0	TATB	202	
	−8.8	**−16.4**	**−21.9**	**−25.9**	**−29.0**	**−32.0**	**−33.6**	**−36.1**	**−37.5**	**−38.3**	**TATB**		**R**
Mn^{2+}	−9.8	−19.7	−30.6	−40.5	−49.5	−55.5	−62.5	−67.5	−74.5	−79.0	Fc	207	
	−9.8	**−17.7**	**−26.6**	**−36.5**	**−42.0**	**−46.5***	**−53.5**	**−58.5**	**−63.5**	**−68.0**	**TATB**[b]		**T**
Cu^{2+}	−4.3	−8.7	−13.1	−17.5	−22.5	−27.5	−32.0	−34.5	−38.3	−42.9	NLJP[d]	154	
	−3.8	−9.2	−13.1	−17.5	−24.5	−33.5	−36.0	−37.5	−37.5	−40.5	NLJP	181	
	−6.9	−13.9	−20.9	−27.1	−33.0	−37.6	−42.2	−45.1	−47.2	−48.0	NLJP	46	
	−8.1	−16.3	(−24.6)	−32.5	(−39.5)	−45.8	(−50.9)	(−54.6)	−56.4	(−56.3)	NLJP	132	
	−8.8	(−15.7)	−21.2	(−27.0)	−30.5	(−35.5)	−39.5	(−41.5)	−42.5	−47.5	NLJP	167	
	−5.6	−10.1	−16.5	−20.8	−26.3	−31.5	−35.9	−37.0	−39.2	−41.8	TATB[c]		
	−3.3	−9.7	−17.6	−23.0	−27.5	−31.3	−34.5	−37.5	−40.0	−42.5	TATB	188	
	−4.5	**−9.9**	**−17.1**	**−21.9**	**−26.9**	**−31.4**	**−35.2**	**−37.3**	**−39.6**	**−42.2**	**TATB**		**R**
Zn^{2+}	−8.1	−18.0	−25.5	−32.8	−37.9	−42.9	−46.3	−49.5	−52.9	−54.4	Fc	208	
	−8.1	−16.0	−21.5	−28.8	−30.4	−29.9	−37.3	−40.5	−41.9	−43.4	TATB[b]		
	−4.8	−9.9	−15.1	(−20.0)	−25.2	(−29.7)	−34.0	−36.8	(−39.4)	−40.8	NLJP	132	
	−6.5	−10.6	−14.1	−17.8	−22.0	−27.0	−32.5	−34.8	−36.5	−37.1	TATB[c]		
	−7.3	**−13.4**	**−17.8**	**−23.3**	**−26.2**	**−29.9**	**−34.9**	**−37.6**	**−39.2**	**−40.3**	**TATB**		**R**
Cd^{2+}	−9.8	−21.4	−29.6	−39.5	−44.6	−52.0	−59.5	−64.6	−69.7	−71.4	Fc	209	
	−9.8	**−19.4**	**−25.6**	**−33***	**−39***	**−44***	**−50.5**	**−55.6**	**−58.7**	**−60.4**	**TATB**[c]		**T**
Pb^{2+}	−11.8	−26.7	−39.1	−47.5	−55.0	−61.5	−67.5	−74.0	−79.5	−83.5	Fc	209	
	−11.8	−24.7	−35.1	−43.5	−47.5	−51.5	−58.5	−65.0	−68.5	−72.5	TATB[b]		
	−6.6	−14.7	−22.6	(−31.2)	−39.5	−47.1	−53.6	(−58.5)	−61.5	(−61.8)	NLJP	132	
	−7.1	−14.2	−19.6	−28.3	−35.5	−42.0	−50.5	−54.8	−58.0	−58.9	TATB[c]		
	−9.5	**−19.5**	**−27.4**	**−35.9**	**−41.5**	**−46.8**	**−54.5**	**{−59.9}**	**{−63.3}**	**{−65.7}**	**TATB**		**R{T}**

[a] Using $\Delta_t G°$(MCl) and $\Delta_t G°$(Cl$^-$) data based on the TATB scale from ref 205. [b] The Fc data from the previous row(s) adjusted to the TATB scale using conversion factors from Table 1. [c] The NLJP data from the previous row(s) adjusted to the TATB scale using conversion factors from Table 1. [d] Data also available at 303.15 K for Cu^{2+} in ref 176 and for Ag^+ in ref 210. [e] As for footnote d, but using MI and I^- data.

pertinent to point out at this juncture that Feakins et al.[211] arrived at different conclusions on the basicity of methanol−water mixtures using their (less reliable) extrapolation method. Although the basicities (β values, Tables 3 and 4) of the protic solvents are generally higher than that of water, their hydro-

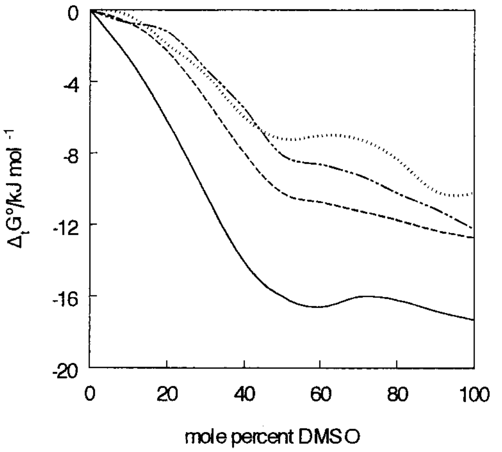

Figure 10. Gibbs energy of transfer of cations from water to aqueous dimethyl sulfoxide as a function of the mole percentage of dimethylsulfoxide: (—) Li$^+$, (- - -) Na$^+$, (—··—) K$^+$, and (···) Rb$^+$.

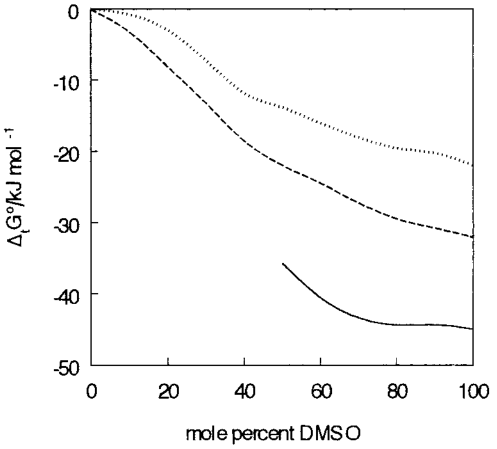

Figure 11. Gibbs energy of transfer of cations from water to aqueous dimethyl sulfoxide as a function of the mole percentage of dimethylsulfoxide: (—) Cu$^+$, (- - -) Ag$^+$, and (···) Tl$^+$.

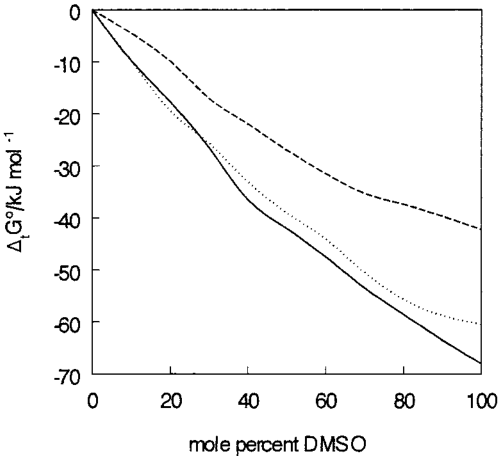

Figure 12. Gibbs energy of transfer of cations from water to aqueous dimethyl sulfoxide as a function of the mole percentage of dimethylsulfoxide: (—) Mn^{2+}, (- - -) Cu^{2+}, and (···) Cd^{2+}.

phobic groups ($-CH_2-$ and $-CH_3$) enhance the three-dimensional hydrogen-bonded structure of the water at low cosolvent contents, augmenting the inherent basicity of the cosolvent (see above). This probably accounts for the small negative $\Delta_t G°(H^+)$ values at these compositions. The data for *i*-PrOH and *t*-BuOH are limited to low cosolvent contents, where they act as water structure makers. The positive $\Delta_t G°(H^+)$ values as the neat organic solvent is approached are harder to explain. Pure ethanol is even less basic than methanol contrary to what is indicated by their donor character. Both pure PG and EG are less basic than water and behave like methanol and ethanol.

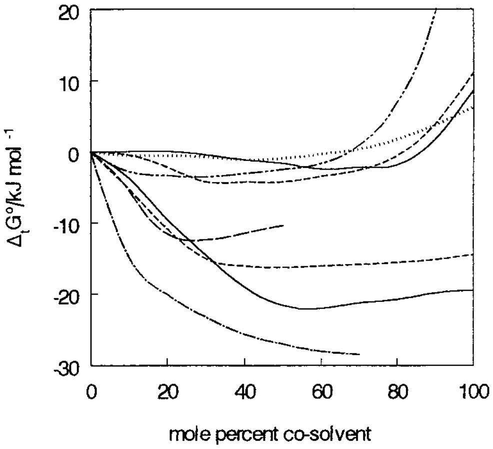

Figure 13. Gibbs energy of transfer of hydrogen ions from water to aqueous solvents as a function of the mole percentage of the cosolvent: (—) (upper) MeOH, (- - -) (upper) EtOH, (···) EG, (— — —) AC, (—··—) **AN**, (—·—) FA, (- - -) (lower) DMF, and (—) (lower) DMSO.

B. Concluding Remarks

This review has been restricted to studies of the differences in stabilities (solvent medium effects) of cations in water and mixed aqueous−organic solvents by means of their $\Delta_t G°(M^{n+}, w \rightarrow w+s)$ values. Despite the great wealth of studies since the pioneering work of the 1960s,[1,33,65,66,75,184,211] the solvation energetics of ions in aqueous−organic mixtures remains rather poorly quantified. For univalent cations, satisfactory data are available only for aqueous mixtures of MeOH, EtOH, AN, DMF, and DMSO and over only the water-rich part of the composition range, for EG, DX, and AC. For divalent cations, the situation is much less satisfactory, with reliable values being available for transfer of only few ions into very few aqueous mixtures. Data are virtually nonexistent for cations of higher valence.

An overall view of, for example, the effects of ionic size, charge, and chemical character on the solvation energetics of cations in mixed aqueous−organic solvents is yet to emerge. Pending more systematic studies of $\Delta_t G°$ for a wider range of ions and solvents, it is premature to attempt a detailed analysis of such effects. Obtaining reliable data for multivalent cations is certainly a significant challenge, since careful attention needs to be paid to the possible effects of ion-pairing and hydrolysis. It may well be that the effects of cationic charge on solvation energetics, which must be regarded at present as poorly characterized, can only be investigated by the use of nonlabile complex ions.

As has been noted in a number of places in this review, the $\Delta_t G°(M^{n+}, w \rightarrow w+s)$ values may give the impression that the differences in stabilities are minor: the values are relatively low and their variation with solvent composition is frequently monotonic. However, the division of $\Delta_tG°$ into its component enthalpy, $\Delta_tH°$, and entropy, $\Delta_tS°$, contributions often reveals that the relatively unremarkable plots of $\Delta_tG°$ as a function of solvent composition result from the compensation of quite dramatic but largely opposing changes in $\Delta_tH°$ and $\Delta_tS°$.[141] The magnitude and shape of plots of the latter quantities may provide important information about preferential solvent binding and the effects of solvent structure on the solvation of the cations. The availability of such data is very limited, however, and their detailed discussion is outside the scope of this review.

An example of the diverse modes of behavior with respect to the enthalpy and entropy of transfer in different solvent mixtures is given in the work of Gritzner and Lewandowski.[194] For transfers of Na^+, Ag^+, and Tl^+ between *N*,*N*-dimethylformamide (DMF) and its mixtures with *N*,*N*-dimethylthioformamide, $T\Delta_tS°$ is generally much smaller than $\Delta_tH°$, so that $\Delta_tG°$ reflects quite accurately the energetics of the transfer. However, for the transfer of the same cations from DMF to its mixtures with water (or vice versa), $T\Delta_tS°$ is >50% of $\Delta_tH°$, so that extensive entropy–enthalpy compensation takes place. Gritzner and Lewandowski's[194] data indicate that the signs of $\Delta_tS°$, $\Delta_tH°$, and $\Delta_tG°$ are the same for all these cations. In contrast, for the transfer of K^+ between water and aqueous DMF, the measurements of Ray et al.[196] show that the sign of $\Delta_tS°$ at some target solvent compositions is opposite to that of $\Delta_tG°$. In the absence of confirmatory results from independent sources, it is impossible to know whether this apparent difference (between, say, Na^+ and K^+) is real or an experimental artifact. This illustrates the difficulty with regard to the critical evaluation of the enthalpy and entropy data of the kind which has been possible in this review for the Gibbs energies of transfer.

A further difficulty arises from the fact that more accurate enthalpy of transfer data are usually obtainable from calorimetric measurements rather than from the temperature dependence of the Gibbs energy of transfer. The latter, derived, e.g., from the temperature dependence of electrode or polarographic half-wave potentials, yield the entropy of transfer. Combinations of $\Delta_tH°$ and $\Delta_tG°$ in the former case to yield $T\Delta_tS°$ and of $\Delta_tG°$ and $T\Delta_tS°$ in the latter case to yield $\Delta_tH°$ may lead to considerable uncertainties in the derived values. The methodologies employed to obtain these thermodynamic quantities are frequently not available in the same laboratories, so that the data may not be compatible. This difficulty is compounded by the different extrathermodynamic assumptions that have been employed in obtaining $\Delta_tH°$ from calorimetry (generally the TATB assumption) and $T\Delta_tS°$ from electrochemical measurements (commonly the BBCr assumption). Although these assumptions are usually reasonably compatible with respect to $\Delta_tG°$, as illustrated in the present review, this need not be so when the differences $\Delta_tH° - \Delta_tG°$ or $\Delta_tG° - (-T\Delta_tS°)$ are formed.

There is, therefore, a need to obtain enthalpy and entropy of transfer data in as compatible a manner as possible for their thorough evaluation. This is a prerequisite for a meaningful discussion of the enthalpy–entropy compensation effect, where it exists, and the relationships of these quantities to properties of the ions, such as charge, size, and softness, and of the solvent mixtures.

Even larger effects can be obtained for the corresponding heat capacity, $\Delta_tC_p°$, and volume, $\Delta_tV°$, parameters. These quantities appear to be especially sensitive to solvent structural effects, which, as noted in the text, play an important role in the solvation preferences of ions in the water-rich region of the aqueous organic mixtures. With some notable exceptions,[142] few systematic studies have been made of such variables. Renewed experimental efforts in all these areas are therefore highly desirable.

V. References

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