Monatshefte für Chemie 134, 669–677 (2003)
DOI 10.1007/s00706-002-0578-4

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Invited Review

Gibbs Energies of Transfer of Fluoride Salts from Water to Aqueous Alcohol Mixtures

Gamini Senanayake[1] and **Glenn Hefter**[2,*]

[1] Department of Mineral Science and Extractive Metallurgy, Murdoch, WA 6150, Australia
[2] Department of Chemistry, Murdoch University, Murdoch, WA 6150, Australia

Received October 29, 2002; accepted November 8, 2002

Summary. *Gibbs* energy of transfer data for LiF and NaF from water to aqueous alcohol mixtures, obtained from solubility measurements, are examined via the *Born* equation. In spite of its well-known deficiencies, the simple *Born* model accounts for much of the observed variation of $\Delta_t G^\circ$(MF, w → w + ROH), particularly for NaF. This unexpected success of the *Born* model appears to result from the fortuitous cancellation of the donor and acceptor contributions to the solvation of the cations and anions by these closely related co-solvents. Examination of the deviations between the observed and calculated $\Delta_t G^\circ$ values also suggests that they are partly due to uncompensated ion-pairing effects, especially for LiF.

Keywords. Solubility; Fluoride salts; *Born* equation; Ion solvation; Donor–acceptor properties.

Introduction

The solvation of ions involves complex processes that have, despite extensive efforts, proven to be difficult to model accurately [1, 2]. Nevertheless, useful insights into ion-solvation phenomena can be obtained by using quite simple approaches. One of the most popular of these has been the *Born* model [3, 4], which calculates the energy required to charge a hard sphere (ion) of radius r in a dielectric continuum (solvent) of relative permittivity ε.

Because of the very large magnitude of ion-solvation energies, typically many hundreds or even thousands of kJ mol^{-1}, it is customary to discuss *differences* in solvation energies between solvents by means of the standard *Gibbs* energy of transfer, $\Delta_t G^\circ$, rather than the solvation energies themselves [1]. The quantity $\Delta_t G^\circ(i)$ represents the change in the overall solvation of an ion (i) when it is

---

[*] Corresponding author. E-mail: hefter@chem.murdoch.edu.au

Dedicated to Prof. Dr. *Heinz Gamsjäger* on the occasion of his 70th birthday transferred from a reference solvent, usually but arbitrarily chosen as water (w), to the solvent or solvent mixture of interest (s) under standard state (infinite dilution) conditions.

It is readily shown [1, 4, 5] that the *Born* model predicts that $\Delta_t G^\circ(i)$ is given by Eq. (1),

$$\Delta_t G(i, \mathrm{w} \to \mathrm{s}) = N_A Z^2 e^2 (8\pi\varepsilon_o r_i)^{-1} (\varepsilon_s{}^{-1} - \varepsilon_w{}^{-1}) \tag{1}$$

where N_A is *Avogadro*'s number, Ze is the ionic charge, ε_o is the permittivity of free space, and ε_w and ε_s are the permittivities of the solvents w and s.

This model, if not necessarily in the exact form of Eq. (1), has been utilised by many investigators to rationalize a variety of experimental observations related to ion-solvation. For example, *Davis* and *Ricci* [6] used it to account for the variation in the solubility of silver salts in dioxane-water mixtures. *DeLigny et al.* used the *Born* model as a basis for estimating $\Delta_t G^\circ$ values for single ions [7], whereas many authors routinely 'correct' their data for "*Born* effects" prior to further theoretical analysis [8]. An indication of the enduring importance of the *Born* equation, as well as a more extensive list of its applications in many areas of chemistry, is given in the recent review by *Conway* [4].

In spite of its successes, a number of problems have been identified with the *Born* approach [1, 4, 5]. The first is the appropriateness (and constancy) of the crystallographic radius. The second, and undoubtedly more significant, is the treatment of the solvent as a structureless dielectric continuum having the permittivity of the bulk solvent right up to the surface of the ion [4]. Although such a model may adequately account for long-range coulombic interactions, it represents a very primitive view of the predominant short-range (bonding and structural) interactions that take place when an ion is dissolved in a solvent or solvent mixture.

As often occurs with simple electrostatic models, attempts to make the *Born* equation more physically realistic have met with only limited success [1, 4, 5]. This has led researchers to seek alternative, albeit mostly semi-empirical, models of ion-solvation such as the donor–acceptor approach [9]. Nevertheless, the *Born* model continues to provide an underpinning for various concepts in ion-solvation studies [4]. As such it is of interest to investigate the extent to which the simple *Born* model can account for the behaviour of model electrolyte systems.

Alkali metal fluorides are quintessential ionic salts but their solvation behaviour has been relatively little studied [10, 11]. In part this is because it is rather more difficult to obtain reliable data for them than is the case for most simple salts. Problems include their sparing (or in some cases excessive) solubility and their tendency to ion pair formation [10–12]. Even so, a reasonable body of reliable information on the *Gibbs* transfer energies of the alkali metal fluorides from water to various alcohol–water mixtures has been established in recent years, mostly derived from high quality solubility measurements [10–14].

This paper examines these data in terms of the *Born* equation in order to investigate to what extent they are consistent with this purely electrostatic model. Only the (measurable) whole salt quantities, $\Delta_t G^\circ$(MF), will be used to avoid the uncertainties associated with the use of an extrathermodynamic assumption that is necessarily [1, 5] required for estimating single ion quantities. As noted recently by *Conway* [4], despite its advantages this approach has rarely been used.

Database

The database for the present purpose (Table 1) was restricted to those low molecular weight alcohols that are fully miscible with water. The data were either critically-reviewed values [10] or were taken from recent published [12, 13] or, in a few instances, unpublished [14] sources. The data were restricted to LiF and NaF because there are relatively few $\Delta_t G^\circ$ values for other fluoride salts in the solvent mixtures of interest [10].

Table 2 lists the relevant properties of the neat solvents, taken from standard sources [1, 5, 15]. Two key properties of their mixtures with water, relative permittivity and acceptor strength ($E_T{}^N$, see below), are plotted in Figs. 1 and 2.

Table 1. Standard *Gibbs* energy of transfer ($\Delta_t G^\circ$/kJ mol^{-1}) of LiF and NaF from water to aqueous alcohol mixtures at 25°C[a]

100 x_s	$\Delta_t G^o$/kJ mol^{-1}											
	*Me*OH[b]		*Et*OH[b]		1-*Pr*OH[c]		2-*Pr*OH[c]		t-*Bu*OH[d]		*EG*[b,e]	
	LiF	NaF	LiF	NaF	LiF	NaF	LiF	NaF	LiF	NaF	LiF	NaF
10	3.0	3.7	5.1	5.8	4.7		5.5		6.3		2.7	3.3
20	5.5	7.0	9.4	11	9.0		11		13		5.3	5.5
30	7.6	9.9	13	15	13		16		19		7.5	7.9
40	9.4	12	16	18	18		21		25		9.4	9.4
50	11	15	19	22	22	24	26	29	32	30	11	11
60	13	17	22	25		29	31	35		40	12	12
70	14	19	24	28		34		41		51	13	12
80	17	21	27	30		39		47		63	14	13
90	19	24	31	33		44		53		76	16	15
95	21	25	33	35		46		56		83	16	16
100	22	27	37	42							18	15

[a] $\Delta_t G^\circ$ calculated from solubilities measured on the mol dm^{-3} scale; solvent composition is given on the mol percent ($100x_S$) scale; [b] Ref. [12]; [c] Ref. [14]; [d] Ref. [13]; [e] *EG* = ethylene glycol (ethane-1,2-diol)

Table 2. Selected solvent properties (from *Marcus* [1, 15])

Solvent	ε	$E_T{}^N$	*DN*
H_2O	78.39	1.000	33[a]
EG	37.70	0.790	20.0
*Me*OH	32.66	0.762	30.0
*Et*OH	24.55	0.654	32.0
1-*Pr*OH	20.33	0.617	30.0
2-*Pr*OH	19.92	0.546	36.0
*t-Bu*OH	17.51	0.389	38.0

[a] Bulk solvent value

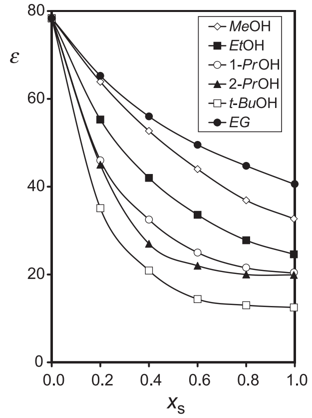


Fig. 1. Relative permittivities of aqueous alcohol mixtures as a function of solvent composition at 25°C [1]

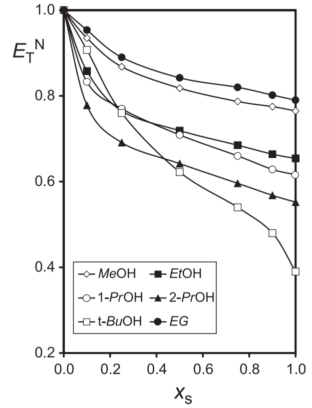


Fig. 2. Acceptor strength (expressed as the normalized *Dimroth-Reichardt* parameter $E_T{}^N$) of aqueous alcohol mixtures as a function of solvent composition at 25°C [1]

Discussion

The standard *Gibbs* energy of transfer of the whole salt MF can be considered as the sum of the *Gibbs* energies of transfer of its constituent ions:

$$\Delta_t G^\circ(\mathrm{MF}) = \Delta_t G^o(\mathrm{M}^+) + \Delta_t G^o(\mathrm{F}^-) \qquad (2)$$

Combination of Eqs. (1) and (2) and insertion of the numerical values for the constants gives, remembering $Z_+ = Z_- = 1$:

$$\Delta_t G^\circ(\mathrm{MF, w \rightarrow s}) = 69.25(\varepsilon_s{}^{-1} - \varepsilon_w{}^{-1})(r_+{}^{-1} + r_-{}^{-1}) \qquad (3)$$

with $\Delta_t G^\circ$ in kJ mol^{-1} when the radii are in nm.

Plots of the experimental values of $\Delta_t G^\circ$ (MF, w → w + s) against those calculated from Eq. (3), using the relevant data from Table 2 and Fig. 1 and assuming ionic radii of 0.069 nm (Li^+), 0.102 nm (Na^+), and 0.133 nm (F^-), are shown in Fig. 3 for LiF and in Fig. 4 for NaF. In both Figs. 3 and 4 the straight line, with a slope of unity, indicates the prediction of the *Born* model, Eq. (3).

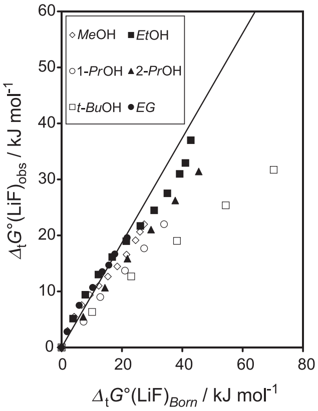


Fig. 3. Observed *Gibbs* energies of transfer of LiF from water to aqueous alcohol mixtures compared with those calculated from the *Born* equation (heavy line) at 25°C

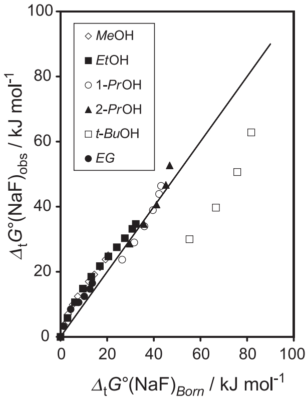


Fig. 4. Observed *Gibbs* energies of transfer of NaF from water to aqueous alcohol mixtures compared with those calculated from the *Born* equation (heavy line) at 25°C

It is readily apparent that the *Born* equation provides a reasonable estimation of $\Delta_t G^\circ$(NaF) and, to a lesser extent, $\Delta_t G^\circ$(LiF). Interestingly, the $\Delta_t G^\circ$ values for NaF are, with the exception of *t-Bu*OH, mostly under-predicted ($\Delta_t G^\circ_{\text{Born}} < \Delta_t G^\circ_{\text{obs}}$) whereas those of LiF are mostly over-predicted. More importantly, the deviations between the experimental and *Born* values are systematic. This can be seen more clearly in Figs. 5 and 6, which plot the difference between the observed and *Born* values as a function of the solvent composition. Similar, but much larger, differences (both in percentage and, of course, absolute terms) were noted by *Conway* [4] for hydration energies.

For LiF in *EG*-water mixtures the deviation between the experimental and *Born* values is $<2\,\text{kJ mol}^{-1}$ even though $\Delta_t G^\circ(\text{LiF, w} \rightarrow \text{w} + EG)$ varies by up to $20\,\text{kJ mol}^{-1}$ [12]. The magnitude of the negative deviations for LiF increases with increasing co-solvent concentration and in the order: $EG < Me\text{OH} < Et\text{OH} < 2\text{-}Pr\text{OH} \approx 1\text{-}Pr\text{OH} \ll t\text{-}Bu\text{OH}$ (Fig. 5). As noted, the deviations between the experimental and *Born* values of $\Delta_t G^\circ$(NaF) are much smaller than for LiF. Nevertheless,

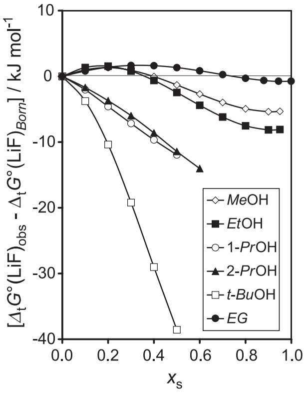


Fig. 5. Difference between observed and calculated (*Born*) *Gibbs* energies of transfer of LiF from water to aqueous alcohol mixtures as a function of solvent composition at 25°C

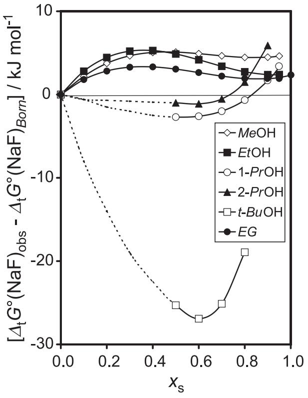


Fig. 6. Difference between observed and calculated (*Born*) *Gibbs* energies of transfer of NaF from water to aqueous alcohol mixtures as a function of solvent composition at 25°C

the order of the (negative) deviations is almost identical, albeit with some subtle differences: *Me*OH ≈ *Et*OH < *EG* < 2-*Pr*OH < 1-*Pr*OH ≪ *t*-*Bu*OH (Fig. 6).

Given the well-known deficiencies of the *Born* equation the level of agreement between the observed and calculated values, modest as it is, is better than might be expected. As with many other simple electrostatic models this probably arises from a cancellation of errors, nevertheless, further insight can be gained by a closer consideration of the deviations between experiment and theory. It is particularly noteworthy that differences between the observed values of $\Delta_tG°$(MF) and those calculated from the *Born* equation correlate with a number of properties of the solvents (Table 2) and hence their mixtures with water (Figs. 1 and 2).

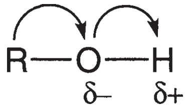
The first of these correlations is with relative permittivity. This seems surprising at first glance as the *Born* equation explicitly includes this quantity. However, as outlined by *Gutmann* [9], the major role of ε in the dissolution of salts is not in the solvation of the ions but is rather in governing their degree of association once dissolved (solvated). Thus the deviations in Figs. 5 and 6 may be a reflection, at least in part, of (unallowed for) ion pairing. The lower the value of ε the greater the ion pairing and hence the higher the salt solubility. This means that the experimental $\Delta_t G^\circ(\mathrm{MF})$ data will be less positive than the "true" values for the fully dissociated salt, thereby producing the negative values of $\Delta_t G^\circ(\mathrm{MF})_{\mathrm{obs}} - \Delta_t G^\circ(\mathrm{MF})_{Born}$ apparent in Figs. 5 and 6. This notion is consistent with the present observations with respect to the effects of both co-solvent character and composition. It also accounts for the differences between LiF and NaF. Thus, although the solubility of LiF is relatively low in these mixtures [10–14] its tendency to form ion-pairs is considerably greater than NaF, even in neat water [16]. Consistent with the *Bjerrum* equation for ion-pair formation [5], this difference is likely to be enhanced with decreasing ε. The existence of this effect has previously been noted [10] for transfers of MF salts between water and neat solvents, $\Delta_t G^\circ(\mathrm{MF}, \mathrm{w} \rightarrow \mathrm{s})$, and for some aqueous organic mixtures [12].

On the other hand, the presence of uncompensated ion pairing cannot explain the large differences between *t-Bu*OH and the other solvents since the greatest differences in ε are between the lower alcohols (Fig. 1). Explanation of this phenomenon must be sought elsewhere.

Comparison of the data in Fig. 2 and Table 2 with Figs. 5 and 6 shows that the deviations from the *Born* model also correlate well with the donor and the acceptor properties of the (mixed) solvents, expressed here as their donor number (*DN*) and the normalised *Dimroth-Reichardt* parameter $E_T{}^N$ [1, 15], respectively. It is well established that $\Delta_t G^\circ(\mathrm{M}^+)$ and $\Delta_t G^\circ(\mathrm{X}^-)$ correlate well, respectively, with solvent donor and acceptor abilities [1, 9]. The marked differences of both the *DN* and $E_T{}^N$ values of *t-Bu*OH, and hence its mixtures with water (at least at high co-solvent concentrations), from those of the other alcohols (and their aqueous mixtures) is consistent with the observed differences between the *Born* and experimental values of $\Delta_t G^\circ(\mathrm{MF}, \mathrm{w} \rightarrow \mathrm{w} + \mathrm{ROH})$.

In this context it should be noted that *DN* and $E_T{}^N$ values, expressing contrary properties, should ideally be orthogonal. This is true, to a reasonable degree, for most of the common solvents [15, 17]. However, as is apparent from Table 2, there is a correlation ($R^2 = 0.68$) between *DN* and $E_T{}^N$ for the present solvents. This is because for this group of solvents the variation in the donor and acceptor abilities arises from a common effect.

As presented in detail by *Gutmann* [9], electron donation from one atom (or group of atoms) to another within a molecule has flow-on effects to neighbouring atoms. Thus for alcohols, where the differences in, say, their electron donor abilities towards ions, arise mostly from variations in the electron donation of the alkyl moiety, the shifts in electron density will be:



It follows that any build up of electron density on the O donor site will be accompanied by a decrease in the (partial positive) charge on H acceptor site. This results in the observed, negatively-sloped correlation between the *DN* and $E_T{}^N$ values for the ROH solvents under consideration here.

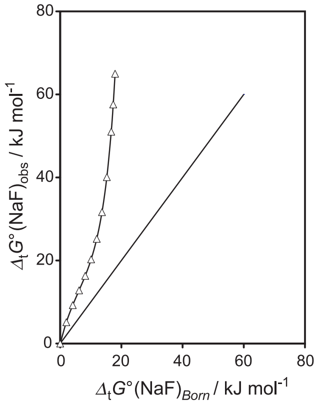


Fig. 7. Observed *Gibbs* energies of transfer of NaF from water to aqueous acetonitrile mixtures compared with those calculated from the *Born* equation (heavy line) at 25°C

It appears therefore that the better-than-expected predictions of $\Delta_t G°$(MF, $w \rightarrow w + ROH$) via the *Born* equation result from the fortuitous cancellation of the donor and acceptor contributions in this closely related group of solvents. This can be tested easily by considering the transfer of MF from water to mixtures of water with a non-alcoholic solvent for which this correlation does not exist. Fig. 7 plots the *Born* and experimental values for $\Delta_t G°$(MF, $w \rightarrow w + MeCN$) with $M^+ = Na^+$ (the corresponding data for LiF are complicated by ion-pairing effects [12] but show a similar trend). It is readily apparent from Fig. 7 that the *Born* equation seriously under-estimates $\Delta_t G°$(NaF) in aqueous acetonitrile mixtures, even in solutions with high water content. This is highly unlikely to be due to any inadequacies of the data. Rather it must be seen as a direct failure of the *Born* model. Similar results are obtained if the experimental and *Born* predictions for $\Delta_t G°$(MF, $w \rightarrow w + s$) are plotted for aqueous mixtures with other co-solvents such as *DMSO* or acetone.

Two other phenomena deserve brief mention. A major failing [4, 5] of the *Born* model is that it makes no allowance for dielectric saturation, the drastic reduction in the permittivity of the solvent which occurs in the vicinity of the dissolved ions. This effect is well known but difficult to quantify, especially in mixed solvents [1, 5]. The second is the role of solvent "structuredness" [15]. Alcohol–water mixtures are well known, from a variety of measurements, to undergo considerable structural change as the chemical character and concentration of the co-solvent changes [18]. Indeed, this is a major attraction for their study. Unfortunately however, there is no simple measure of structuredness [15], nor is it clear what is the relationship between this property and thermodynamic quantities such as $\Delta_t G°$. Even so, the reality and complexity of such effects in water–ROH mixtures is well known [18–20]. For the present purposes it is fortunate that the influence of solvent structure appears to be expressed almost entirely through the entropy and enthalpy components of $\Delta_t G°$ (which show dramatic variations with solvent composition [19, 20]) rather than $\Delta_t G°$ itself, which almost invariably changes monotonically with solvent composition because of compensation of the $\Delta_t S°$ and $\Delta_t H°$ contributions [20].

References

[1] Marcus Y (1985) Ion Solvation, Wiley-Interscience, New York

[2] Krestov GA, Novosyolov NP, Perelygin IS, Kolker AM, Safonova LP, Ovchinnikova VD, Trostin VN (1994) Ionic Solvation, Ellis Horwood, Chichester, UK

[3] Born M (1920) Z Phys **21**: 45

[4] Conway BE (2002) In: Conway BE, White RE (eds) Modern Aspects of Electrochemistry, vol 35, Kluwer Academic/Plenum, New York

[5] Popovych O, Tomkins RPT (1981) Nonaqueous Solution Chemistry, Wiley, New York

[6] Davis T, Ricci J (1939) J Amer Chem Soc **61**: 3274

[7] Bax D, DeLigny CL, Alfenaar M (1972) Rec Trav Chim **91**: 452

[8] See for example, Sinha R, Kundu KK (1998) J Phys Chem **102**: 6880 and references cited therein

[9] Gutmann V (1978) The Donor–Acceptor Approach to Molecular Interactions, Plenum, New York

[10] Hefter GT (1989) Rev Inorg Chem **10**: 185

[11] Hefter GT (1991) Pure Appl Chem **63**: 1749

[12] Hefter GT, McLay PJ (1988) J Solution Chem **17**: 535

[13] Hefter GT (1997) J Molec Liq **73/74**: 267

[14] Hefter GT (2002) Unpublished observations

[15] Marcus Y (1998) The Properties of Solvents, Wiley, Chichester

[16] Chan CB, Tioh NH, Hefter GT (1984) Polyhedron **3**: 845

[17] Marcus Y (1993) Chem Soc Rev: 409

[18] Franks F, Desnoyers JE (1985) Water Sci Rev **1**: 171

[19] Hefter GT, McLay PJ (1988) Austral J Chem **41**: 1971

[20] Hefter GT, Marcus Y, Waghorne WE (2002) Chem Rev **102**: 2773