Electrostriction, Ion Solvation, and Solvent Release on Ion Pairing

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The theoretical mean molar electrostriction volume of electrolytic solvents, $\Delta V_{el}(\text{solvent})$, was calculated from their properties: the relative pressure derivatives of the density (the compressibility) and permittivity and their second pressure derivatives. The molar electrostriction caused by ions at infinite dilution was taken as the differences of their standard partial molar volumes in the solution and their intrinsic volumes: $\Delta V_{el}(\text{ion}) = V^{\infty}(\text{ion}) - V_{in}(\text{ion})$. The ratio $n^{\infty} = \Delta V_{el}(\text{ion})/\Delta V_{el}(\text{solvent})$ then represents the solvation number of the ion in the solvent at infinite dilution. Similarly, from the molar volume change on ion pair formation, ΔV_{ip}, the ratio $\Delta n_{ip} = \Delta V_{ip}/\Delta V_{el}(\text{solvent})$ represents the number of solvent molecules released thereby. These values were tabulated for those solvents, ions, and ion pairs for which the relevant information could be found, the extension to nonaqueous solvents not having been attempted previously.

Introduction

Various approaches have been suggested over the years for ascertaining the number of solvent molecules closely associated with ions, that is, solvating them, and the number of those solvent molecules released from the solvation shells of ions to the bulk on ion pair formation. It became clear that these numbers must be defined and calculated operationally in terms of the methods employed to obtain them. This point cannot be overemphasized, and the present approach is no exception: it leads to internally consistent results, but for comparison with those of other approaches the limitations of each method must be considered. A reviewer has pointed out that this caution is particularly appropriate in the case of hydration numbers in aqueous solutions. Certain ions, such as transition metal cations, have geometrically well-defined first solvation shells, but they are further solvated in a second concentric solvation shell, with much less well-defined geometries and solvation numbers. Most ions, however, are solvated in a not clearly defined manner, mainly in the closest vicinity of the ions but also beyond that, due to nondirectional electrostatic ion–dipole or ion-induced dipole interactions.

The solvent in the solvation shell(s) of an ion is affected by its strong electric field that is expressed as a compressive force, so that the volume of the solvent in the shell(s) is smaller than that in the bulk. This so-called electrostriction[1–3] depends on the charge and size of the ion and on certain properties of the solvent: its compressibility and the pressure derivative of its electric permittivity.

The solvation is dynamic; that is, solvent molecules enter the close association with an ion and leave it again at rates characteristic of the ion (possibly also of the solvent), but an average number of solvent molecules are attached to the ion at any given instant. This number, n, depends not only on the particular ion and the solvent involved but also on the concentration via the interactions of this ion with other ions, e.g., with the counterion forming an ion pair with it. It also necessarily diminishes when the ratio of solvent molecules to ions decreases substantially with increasing concentrations of the ions. At infinite dilution, though, for a given operational

definition, the value n^{∞} depends on the particular ion and solvent only, independent of the counterion in the solution.

When two ions of opposite charge form an ion pair then some of their solvation shells is lost, since the reduced charge of the pair (for a symmetrical electrolyte the ion pair is neutral altogether) does not permit this moiety to hold and translationally immobilize (by ion/dipole–dipole force) the entire solvation shells of the individual partners. The extra solvent, numbering on the average Δn_{ip}, is then released to the bulk of the solvent. The experimentally available standard molar entropy change on ion pairing is closely related to the number of solvent molecules so released[4,5] and comparable information can be obtained from the experimentally available standard molar volume change on ion pairing, ΔV_{ip}. A few such estimates have been made in the past,[5–8] but they were mostly dependent on superseded data required for relating the volume change to the number of solvent molecules released.

It is the purpose of this paper to calculate the mean molar electrostriction volume, $\Delta V_{el}(\text{solvent})$, of electrolytic solvents, i.e., solvents in which electrolytes are readily soluble, from their properties. The molar electrostriction caused by an ion at infinite dilution is taken to be expressed by the electrostrictive volume decrease, $\Delta V_{el}(\text{ion})$, i.e., by the differences of its standard partial molar volume in the solution and its intrinsic volume: $\Delta V_{el}(\text{ion}) = V_{in}(\text{ion}) - V^{\infty}(\text{ion})$. Then the ratio $n^{\infty} = \Delta V_{el}(\text{ion})/\Delta V_{el}(\text{solvent})$ represents the number of solvent molecules affected by electrostriction, that is, the solvation number of the ion in the solvent at infinite dilution. Similarly, the ratio $\Delta n_{ip} = \Delta V_{ip}/\Delta V_{el}(\text{solvent})$ represents the number of solvent molecules released on ion pairing. These values are tabulated here for those solvents, ions, and ion pairs for which the relevant information could be found.

Theory

The following derivation was published long ago in a rather obscure manner by Padova;[9] hence, it is repeated here more clearly. It is based on the primitive model of ion–solvent interactions. This model involves spherical hard ions in a solvent regarded as a continuum characterized solely by its permittivity

ϵ and bulk compressibility. The molar volume of a solvated salt, V_{sl}, is given by the sum of its apparent molar volume $^{\varphi}V$ and the number n of solvent molecules in the solvation shells of all of its ions times the molar volume of the pure solvent V^*:

$$V_{sl} = {}^{\varphi}V + nV^* \tag{1}$$

Alternatively it is given by the sum of the intrinsic molar volume of the salt (the sum of the intrinsic molar volumes of the ions) and n times the molar volume of the electrosticted solvent $V_{el} \equiv V_{el}(\text{solvent})$ in the solvation shells.

$$V_{sl} = V_{in} + nV_{el} \tag{2}$$

The total electrostriction, i.e., the volume diminution caused by the electrical field of the ions is the difference between the intrinsic volumes of the ions of the salt and the apparent molar volume:

$$-\Delta V_{el}(\text{salt}) = -({}^{\varphi}V - V_{in}) = n(V^* - V_{el}) = n\Delta V_{el} \tag{3}$$

where $\Delta V_{el}(\text{solvent})$ is written for short as ΔV_{el}. The electrostriction is thus related by means of eqs 1 and 2 to the diminution of the volume of the solvent per mole of solvent, ΔV_{el}, and the total solvation number of the ions, n.

It is then assumed that the solvated electrolyte, of volume V_{sl} made up from the intrinsic volume of the salt as well as the already electrostricted solvent, eq 2, is not further compressible by externally applied pressure. Only the bulk solvent in the solution is compressible; hence, the fraction of the c molar (c, mol dm^{-3}) solution that is not compressible is

$$1 - \kappa_T/\kappa_{T0} = (c/1000)(V_{sl}/\text{cm}^3\,\text{mol}^{-1}) \tag{4}$$

where κ_T is the isothermal compressibility of the solution and κ_{T0} is that of the solvent. The apparent molar compressibility is related to the compressibilities of the solution and the solvent, in a manner similar to the dependence of the apparent molar volume on the density, as[10]

$$^{\varphi}K = (1000/c)(\kappa_T - \kappa_{T0}) + \kappa_{T0}{}^{\varphi}V \tag{5}$$

The value for n then follows from eqs 1, 4, and 5:

$$n = (V_{sl} - {}^{\varphi}V)/V^* = -{}^{\varphi}K/\kappa_{T0}\,V^* \tag{6}$$

A similar expression can be written for the number of solvent molecules in the solvation shells of the ions at infinite dilution:

$$n^{\infty} = (V_{sl}^{\infty} - {}^{\varphi}V^{\infty})/V^* = -{}^{\varphi}K^{\infty}/\kappa_{T0}\,V^* \tag{7}$$

The two analogous limiting expressions for the apparent molar volume

$$^{\varphi}V = {}^{\varphi}V^{\infty} + S_V c^{1/2} \tag{8}$$

and the apparent molar compressibility

$$^{\varphi}K = {}^{\varphi}K^{\infty} + S_K c^{1/2} \tag{9}$$

involve the infinite dilution values, $^{\varphi}V^{\infty} = V^{\infty}(\text{salt})$, i.e., the standard partial molar volume, and $^{\varphi}K^{\infty}$ and the slopes S_V and S_K, given by the Debye−Hückel theory. Padova[9] then eliminated V_{in} from eq 2 using the analogous expression for infinite

dilution and arrived at the expression

$$(n - n^{\infty})V_{el} = ({}^{\varphi}V - {}^{\varphi}V^{\infty}) + (n - n^{\infty})V^* \tag{10}$$

and from eqs 5 and 6

$$n - n^{\infty} = -(({}^{\varphi}K - {}^{\varphi}K^{\infty})/\kappa_{T0}\,V^* \tag{11}$$

So far, the expressions relate to the entire electrolyte, but they should also be valid for the individual ions, provided that values of such quantities as $^{\varphi}V^{\infty}(\text{ion})$ can be estimated. Independently from this issue, the final expression for the volume of the compressed (electrostricted) solvent in the solvation shells of the ions results by elimination of the solvation numbers from eqs 8−11:

$$V_{el} = V^*[1 - (S_V/S_K)\kappa_{T0}] \tag{12}$$

The Debye−Hückel limiting slopes are given by the expressions[11]

$$S_V = 0.5\nu RTS_f[3(\partial(\ln\epsilon)/\partial P)_T - \kappa_{T0}] = 0.5\nu RTS_f X \tag{13}$$

$$S_K = 0.25\nu RTS_f[\kappa_{T0}{}^2 + 2(\partial\kappa_{T0}/\partial P)_T -$$
$$6\kappa_{T0}(\partial(\ln\epsilon)/\partial P)_T + 15(\partial(\ln\epsilon)/\partial P)_T{}^2 - (6/\epsilon)(\partial^2\epsilon/\partial P^2)_T]$$
$$= 0.25\nu RTS_f[X^2 - 2(\partial X/\partial P)_T] \tag{14}$$

where ν is the number of ions into which the salt dissociates, S_f is the Debye−Hückel limiting slope for activity coefficients, ϵ is the permittivity of the solvent, and $X = 3(\partial(\ln\epsilon)/\partial P)_T - \kappa_{T0}$ is defined in eq 13. Since only the ratio S_V/S_K is required for eq 12 the slope S_f and the coefficient ν cancel out and are not needed for further calculations. The quantity of interest, ΔV_{el}, the average decrease of the solvent volume by electrostriction per mole of solvent, is obtained from eqs 12−14:

$$\Delta V_{el} = V^* - V_{el} = (S_V/S_K)\kappa_{T0}V^* =$$
$$\{2X/[X^2 - 2(\partial X/\partial P)_T]\}\kappa_{T0}V^* \tag{15}$$

This quantity is characteristic of the solvent, measuring its ability to shrink when exposed to the field of an ion, but is independent of the nature of the ion. The latter is manifested in the final reckoning by means of the solvation number, n^{∞}.

Results

The key quantity for obtaining solvation numbers of ions and changes in them on ion pairing is, thus, the average decrease of the solvent volume by electrostriction per mole of solvent, ΔV_{el}, obtained from eq 15. The values of X and its pressure derivative can be obtained from published values for several solvents, and those pertinent for electrolyte solutions and ion pairing are dealt with here, limited to 298.15 K and ambient pressure unless otherwise noted.

For water, the most recent and detailed values of the pressure (and temperature) dependence of the permittivity were reported by Fernandez et al.[12] and at 298.15 K and 0.1 MPa the needed values are $(\partial(\ln\epsilon)/\partial P)_T = 0.4757$ GPa^{-1} and $(\partial^2(\ln\epsilon)/\partial P^2)_T = -0.7935$ GPa^{-2}. Earlier work by Owen et al.[13a] and Dunn and Stokes[13b] yielded somewhat different values $(\partial(\ln\epsilon)/\partial P)_T = 0.4711$ and 0.4547 GPa^{-1} and $(\partial^2(\ln\epsilon)/\partial P^2)_T = -0.7153$ and -0.5486 GPa^{-2}, respectively. The compressibility of water and its pressure derivative are taken from Fine and Millero;[14] at 298.15 K and 0.1 MPa the required values are $\kappa_{T0} = 0.4523$ GPa^{-1} and $(\partial\kappa_{T0}/\partial P)_T = -0.1152$ GPa^{-2}. The values of

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TABLE 1: First and Second Relative Pressure Derivatives at 298.15 K of the Density (Compressibility) and Permittivity of Solvents and Their Molar Electrostriction Volumes

solvent	κ_T, GPa^{-1}	$(\partial \ln\epsilon/\partial P)_T$, GPa^{-1}	$(\partial \kappa_T/\partial P)_T$, GPa^{-2}	$(\partial^2 \ln\epsilon/\partial P^2)_T$, GPa^{-2}	$-\Delta V_{el}/V^*$	$-\Delta V_{el}$, cm^3/mol
water	0.4523[a]	.4757[b]	−0.1152	−0.7935	0.161	2.91[a,b]
methanol	1.195[d]	1.220[f]	−8.940	−8.81[f]	0.147	5.99[d,f]
	1.225[e]	0.932[g]	−9.136	−2.310[g]	>1[e,g]	5.84[e,f]
ethanol	1.115[d]	0.879[d]	−8.485	−2.134	<0[d]	
		0.934[f]		−2.649	>1[d,f]	
1-propanol	0.614[q]	0.759[f]	−1.430	−1.789	0.192	14.41[q,f]
2-propanol	0.770[bb]	0.725[bb]	−2.081	−1.404	0.347	26.67[bb]
1,2-ethanediol	0.337[q]	0.541[r]	−0.572	−0.769	0.169	9.46[q,r]
diethyl ether(303.15 K)	1.009[s]	1.383[t]	−2.575	−2.531	0.318	33.61[s,t]
1,2-dimethoxyethane	0.798[u]	1.784[k]	−2.146	−9.2	0.101	10.60[u,k]
acetone	1.241[v]	1.115[o]	−8.252	−3.053	0.836	25.50[v,aa]
	1.310[z]	1.262[aa]	−8.509	−4.724	0.345	
propylene carbonate	0.514[l]	0.500[k]	+0.222	−1.78	0.0837	7.12[k,l]
4-butyrolactone	0.484[cc]	0.427[k]	−2.231	−1.7	0.121	9.26[k,cc]
acetonitrile	1.093[j]	1.163[k]	−7.761	−11.0	0.0931	4.93[j,k]
	1.048[w]	1.063[w]	−3.086	−2.690	0.308	16.29[w]
formamide	0.399[h]	0.447[c]	−1.120	−0.330	>1	
	0.402[i]		−1.172		>1	
N-methylpyrrolidone	0.518[i]	0.645[m]	−2.069	−1.459	0.222	21.40[i,m]
dinethyl sulfoxide	0.501[n]	0.300[o]	−1.715	−1.498	0.0700	4.98[n,o]
benzene	0.757[p]	0.511[g]	−2.060	−1.367	0.251	22.43[p,g]
dichloromethane (303.15 K)	0.7544[x]	0.913[x]	−1.324	−1.425	0.304	19.76[x]
	0.8856[y]	1.009[y]	−3.283	−3.267	0.215	13.87[y]

[a] Reference 12. [b] Reference 12. [c] Reference 13. [d] Reference 20. [e] Reference 17. [f] Reference 16. [g] Reference 15. [h] Reference 21. [i] Reference 22. [j] Reference 23. [k] Reference 24. [l] Reference 25. [m] Reference 26. [n] Reference 27. [o] Reference 28. [p] Reference 29. [q] Reference 30. [r] Reference 31. [s] Reference 32. [t] Reference 33. [u] Reference 34. [v] Reference 35. [w] Reference 36. [x] Reference 37. [y] Reference 38. [z] Reference 39. [aa] Reference 59. [bb] Reference 41. [cc] Reference 94.

$X = 0.9747$ GPa^{-1} and $(\partial X/\partial P)_T = -2.2653$ GPa^{-2} follow from the more recent quantities. Their insertion into eq 15 yields with $V^* = 18.07$ cm^3 mol^{-1} the final results $\Delta V_{el} = 2.91$ cm^3 mol^{-1}. This value is higher than that, 2.1 cm^3 mol^{-1}, obtained by Padova[9] from values of S_V and S_K listed by Harned and Owen,[10] based on earlier, less accurate pressure derivatives of the permittivity and compressibility.

The problematic quantity required for the evaluation of eq 15 is $(\partial X/\partial P)_T$, since it involves second pressure derivatives of the measurable quantities, density and permittivity, not directly available from the literature. Contrary to the expectation expressed by Marcus[4] that the pressure derivative of the compressibility and thrice the second derivative of the permittivity required for the calculation of $(\partial X/\partial P)_T$ mutually cancel, it is found that for water $(\partial X/\partial P)_T$ is algebraically larger than X^2, so that eq 15 cannot be further simplified. Fortunately, data for the evaluation of $(\partial X/\partial P)_T$ could be found for several solvents other than water, so that both their S_V and S_K could be evaluated, and ΔV_{el} could be estimated for them from eq 15.

For methanol there are the parameters for the Tait-type expression for ϵ at 20, 35, and 50 °C reported by Hartmann et al.[15] These can be evaluated and interpolated to 298.15 K, giving $(\partial(\ln\epsilon)/\partial P)_T = 1.22$ GPa^{-1} and $(\partial^2(\ln\epsilon)/\partial P^2)_T = -8.81$ GPa^{-2}. However, the more recent measurements by Srinivasan and Kay[16] yielded lower values: $(\partial(\ln\epsilon)/\partial P)_T = 0.932$ GPa^{-1} and $(\partial^2(\ln\epsilon)/\partial P^2)_T = -2.310$ GPa^{-2}. These can be combined with the compressibility data of Hruby, Klomfar, and Šifner,[17] $\kappa_T = 1.2250$ GPa^{-1} and $(\partial\kappa_T/\partial P)_T = -9.136$ GPa^{-2} to yield X and $(\partial X/\partial P)_T$ required for the evaluation of ΔV_{el} from eq 15. It turns out, however, that using the pressure derivative of the permittivity values derived from the Srinivasan and Kay[16] data leads to a value of $\Delta V_{el} > V^*$ that is obviously impossible, whereas the values derived from the Hartmann et al.[15] data leads to the reasonable value $\Delta V_{el} = 5.99$ cm^3 mol^{-1}. The compressibility data of Moriyoshi and Inubushi[18] lead to an only slightly different value, 5.84 cm^3 mol^{-1}, with the Hartmann et al.[15]

permittivity data. Padova[19] estimated for the electrostriction in methanol $\Delta V_{el} = 7.54$ cm^3 mol^{-1}, but reported only a value for S_V but not for S_K, so that it is not clear how he arrived at his estimate. Water and methanol were the only solvents for which estimates of ΔV_{el} were previously reported.

The problem noted with the Srinavasan and Kay[16] data for methanol would be repeated for ethanol, the second pressure derivative of the permittivity being insufficiently negative compared with the pressure derivative of the compressibility. The same problem arises with the Dunn and Stokes[13b] data for formamide and there is no other source for evaluation of $(\partial^2(\ln\epsilon)/\partial P^2)_T$ for this solvent.

This, however, is not the case for some dipolar aprotic solvents for which the relevant data were found. Reasonable fractions $\Delta V_{el}/V^*$ were obtained, leading to definite electrostriction volumes of the solvents: diethyl ether, acetone, 1,2-dimethoxyethane, propylene carbonate, acetonitrile, N-methylpyrrolidin-2-one, dimethyl sulfoxide, and dichloromethane, see Table 1. The nonpolar benzene is also included, in view of the reported volume change on ion pairing in this solvent, as is the case for diethyl ether. For three protic solvents, 1-propanol, 2-propanol, and 1,2-ethanediol, the relative values of the compressibility and pressure derivative of the permittivity do permit the calculation of ΔV_{el} values, also shown in Table 1.

It must be realized that ΔV_{el} is an average value (per mole of electrostricted solvent) obtained solely from the properties of the solvent itself. It does pertain to the ions of a completely dissociated salt, over both primary and further solvation shells, and is defined only in connection with the value of n^∞. It is, therefore, of interest to obtain the value of n^∞ from the known values of the standard partial molar volumes of ions in solutions, $V^\infty(\text{ion})$. The latter quantities require an extra-thermodynamic assumption for their evaluation from the experimental $V^\infty(\text{salt})$ values. Those obtained for aqueous solutions using $V^\infty(\text{H}^+,\text{aq}) = -5.5$ cm^3 mol^{-1} at 298.15 K have been tabulated.[4,42,43] Values of $V^\infty(\text{ion})$ in nonaqueous solvents have been recently tabulated

by Marcus and Hefter,[44] generally based on the assumption that $V^\infty(Ph_4P^+,S) = V^\infty(BPh_4^-,S) + 2$ cm^3 mol^{-1} in a solvent S. Intrinsic volumes of many ions, $V_{in}(ion)$, have also been tabulated,[45] so that

$$n^\infty = [V_{in} - V^\infty(ion)]/\Delta V_{el} \qquad (16)$$

resulting from eq 3 can be calculated.

It turns out that the solvation numbers depend mainly on the charges of the ions but only slightly on their sizes and not on the signs of the charges. Therefore, for a given charge, an average solvation number can be deduced within fairly small limits. In aqueous solutions, using $\Delta V_{el} = 2.91$ cm^3 mol^{-1}, the average resulting hydration number is for 5 univalent cations (Li, Na, K, Ag, Tl), for which both $V^\infty(ion)$ and $V_{in}(ion)$ values are available, $n^\infty = 2.2 \pm 1.1$, for 13 divalent cations (Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, Pb) it is $n^\infty = 11.8 \pm 1.1$ and for 22 trivalent cations (Al, Sc, Cr, Fe, Ga, Y, In, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl) the corresponding value is 21.1 ± 0.7 and it is 27.1 for Th^{4+}. These values are larger than the primary hydration numbers (e.g., 6 for the divalent and 9 for the trivalent ions) indicating that the electrostriction extends also to water molecules in the secondary hydration shell. Similarly, for 12 univalent anions (Cl, Br, I, SH, SCN, N$_3$, NO$_2$, NO$_3$, ClO$_3$, BrO$_3$, MnO$_4$, ReO$_4$) $n^\infty = 1.2 \pm 0.6$, for 6 divalent anions (S, CO$_3$, SO$_3$, SO$_4$, CrO$_4$, S$_2$O$_3$) $n^\infty = 10.9 \pm 1.6$, and the average for PO$_4^{3-}$ and AsO$_4^{3-}$ is $n^\infty = 20.7$. Some of the ionic volume data cannot be analyzed in these terms, since in such cases $V^\infty(ion) > V_{in}(ion)$, leading to negative n^∞ values (Rb$^+$, Cs$^+$, CN$^-$, ClO$_4^-$, BF$_4^-$, these being also so-called "negatively hydrated" structure breaking ions) and some others are outliers as regards the average values (Be^{2+}, Eu^{2+}, F$^-$, OH$^-$, IO$_3^-$, Cr$_2$O$_7^{2-}$). It is clear, however, that differences in the sizes of the bare (unhydrated) multivalent ions of a given charge play only a minor role in determining the number of water molecules in the hydration shells that undergo electrostrictive compression. For univalent ions, where the hydration numbers are low, the variation with the size of the ion is, of course, noticeable.

There are only few systematic values of $V^\infty(ion)$ for multi-charged ions in nonaqueous solvents,[44] but far more are available for singly charged ones. The corresponding n^∞ values are tabulated in Table 2, necessarily only for those solvents for which $V^\infty(ion)$ and ΔV_{el} are available. Note that $V_{in}(ion)$ is taken to be independent of the solvent. The n^∞ values for aqueous ions are comparable with those obtained from other approaches, such as from compressibility or a simple model related to the ionic charge and radius.[42] Hardly any comparable systematic values of n^∞ of ions in nonaqueous solvents have been reported, based on alternative approaches.

Another use of the ΔV_{el} values obtained in the present study can be made for the calculation of the number of solvent molecules released to the bulk solvent from the solvation shells of ions when they form ion pairs. More specifically, the number released when a solvent separated ion pair forms a contact ion pair. The former kind of pair can be taken to result from long-range electrostatic forces as indicated by the Bjerrum theory of ion pairing.[46] The latter arises when, at higher concentrations, the ions are forced into close contact by elimination of the solvent molecules in the space between the oppositely charged partners of the ion pair, while the latter may still be solvated in its periphery. Experimental values of the volume change occurring on ion pairing, ΔV_{ip}, the difference between the sum $V^\infty(salt) = V_+^\infty + V_-^\infty$ (for a symmetrical electrolyte) and the standard molar volume of the ion pair, V_{ip}^∞ (hypothetical, since

TABLE 2: Solvation Numbers, n^∞, from Electrostriction

ion	water	MeOH[a]	EG[b]	PC[c]	MeCN[d]	DMSO[e]	CH$_2$Cl$_2$
Li$^+$	2.5	3.3	1.0	1.4	4.3	1.0	
Na$^+$	3.2	3.7	0.6	0.7	4.1	0	
K$^+$	0.9	2.5	0.1	0	3.3		
Rb$^+$	0.9	2.5	0	0	3.5		
Cs$^+$		3.2	0		3.1		
Ag$^+$	3.5			1.7	4.9	2.0	
average	2.2	3.0		0.7	3.9		
F$^-$	3.7	1.5	0.3			2.0	
Cl$^-$	1.7	1.8	0.2	1.4	4.7	3.4	1.7
Br$^-$	1.2	1.5	0.1	0.8	4.5	3.0	1.5
I$^-$	0.5	2.2	0.2	1.4	3.7	2.4	1.3
SCN$^-$	0.5	1.2			2.9		1.1
NO$_3^-$	1.4	1.0			4.3	2.2	
ClO$_4^-$		1.5		0.7	3.1	1.0	1.1
average	1.2[f]	1.5	0.2	1.1	3.9	2.3	1.3
Mg^{2+}	11.4			4.5		5.6	
Ca^{2+}	10.0			3.7			
Sr^{2+}	11.8			3.8			
Ba^{2+}	10.6			3.1			
Mn^{2+}	10.5					5.6	
Co^{2+}	13.0					6.4	
Ni^{2+}	14.2					7.0	
Cu^{2+}	13.6					6.6	
Zn^{2+}	11.6					6.0	
Pb^{2+}	11.1			3.4			
average	11.8[f]			3.7		6.2	

[a] Methanol. [b] 1,2-Ethanediol. [c] Propylene carbonate. [d] Acetonitrile. [e] Dimethyl sulfoxide. [f] The average includes also ions not listed in Table 2, for which V^∞ and V_{intr} data are available.

at infinite dilution complete dissociation takes place), are obtained from the pressure derivative of the thermodynamic association constant, K_A.

$$\Delta V_{ip} = -RT(\partial \ln K_{A(m)}/\partial P)_T = -RT[(\partial \ln K_{A(c)}/\partial P)_T - \kappa_T] \qquad (17)$$

Whereas $\ln K_{A(m)}$ is on the molal scale (mol (kg solvent)$^{-1}$), the solvent compressibility is required in the second equality of eq 17 since $K_{A(c)}$ is on the molar scale (mol dm^{-3})$^{-1}$. Another way to obtain ΔV_{ip} is to follow the partial molar volume of the electrolyte to such high concentrations as needed for the ion pair to represent the major fraction of the ions in the solution:

$$^\varphi V(salt) = \alpha[V^\infty(salt) + S_V c^{1/2}] + (1 - \alpha)V_{ip}^\infty + bc \qquad (18)$$

Here α is the fraction dissociated, obtained independently, and bc is an empirical linear correction term. From both approaches, then, $\Delta V_{ip} = V_{ip}^\infty - V^\infty(salt)$ and $\Delta n_{ip}^\infty = \Delta V_{ip}/\Delta V_{el}$. A collection of ΔV_{ip} values was presented some time ago[4] and augmented by values published since then, as shown in Table 3. Necessarily, $\Delta n_{ip}^\infty \leq (n^\infty_+ + n^\infty_-)$ and this constraint is kept as far as the data for the comparison are available with very few exceptions.

Discussion

The present approach, as noted in the Introduction, is based on the widely used primitive model of electrolyte solutions, and its restrictions should be recognized. Furthermore, for aqueous solutions many other approaches to obtaining solvation (hydration) numbers have been employed, for instance using compressibilities of the salt solutions. Hydration numbers of ions of various charges have, therefore, been published before,[4,95,96] and it is not the purpose of this paper to judge the merits of the various approaches, nor to disentangle any discrepancies between hydration numbers obtained by these approaches and

TABLE 3: Volume Changes on Ion Pairing, ΔV_{ip}^{∞}, and the Number of Solvent Molecules Released Thereby, Δn_{ip}^{∞} Compared with the Combined Solvation Number of the Ions, $n_{+}^{\infty} + n_{-}^{\infty}$

solvent (ΔV_{el})	ion pair	ΔV_{ip}^{∞}, cm^3 mol^{-1}	Δn_{ip}^{∞} (from ΔV_{ip}^{∞})	Δn_{ip}^{∞} (from ΔS_{ip}^{∞})[ff]	$n_{+}^{\infty} + n_{-}^{\infty}$
water (2.91)	LiF	7.9[a]	2.7		6.2
	NaF	4.6[a]	1.6		6.8
	KF	3.4[a]	1.2		4.5
	RbF	4.0[a]	1.4		4.5
	CsF	4.2[a]	1.4		
	LiB(OH)$_4$	9.1[a]	3.1		10.6
	NaB(OH)$_4$	8.4[a]	2.9		11.3
	KB(OH)$_4$	6.5[a]	2.3		9.0
	RbB(OH)$_4$	7.6[a]	2.6		9.0
	CsB(OH)$_4$	6.9[a]	2.4		
	LiSO$_4^-$	5.8[b−d]	1.9		12.8
	NaSO$_4^-$	7.3[b,c] (8.3[d])	2.5		13.4
	KSO$_4^-$	5.9[b,c]	2.1		11.1
	NH$_4$SO$_4^-$	3.4[b]	1.2		10.4
	RbSO$_4^-$	3.3[b]	1.1		11.1
	CsSO$_4^-$	6.2[b]	2.2		
	MgSO$_4$	7.4[e] (9.0,[f] 7.8,[f] 7.2−8.5[g])	2.5	4.9	21.6
	CaSO$_4$	11.7[h] (10.1[g])	4.0	5.1	20.2
	MnSO$_4$	7.4[e] (9[i])	2.5	5.4	20.8
	CoSO$_4$	10.9[j] (11.5[h])	3.8	5.1	23.3
	NiSO$_4$	11.4[j] (11.6,[h] 8.6[k])	4.1	5.1	24.5
	CuSO$_4$	11.3[j] (10.0,[l] 11.4[m])	3.9	5.3	23.9
	ZnSO$_4$	10.0[i] (8.0[n])	3.5	5.1	22.0
	CdSO$_4$	9.3[o] (3.4,[i] 20.6[p])	3.3	5.5	21.9
	UO$_2$SO$_4$	20.6[q]	7.0	7.8	
	LaSO$_4^+$	21[r] (26[s])	6.8	6.3	31.0
	EuSO$_4^+$	25.6[r]	8.8		32.3
	RbNO$_3$	6[t]	2.2		2.3
	TlNO$_3$	15[t]	5.2		2.6
	MgCl$^+$	4.0[b,c] (8.2[u,hh])	1.4		13.1
	LaFe(CN)$_6$	8.0[v]	2.7		32.3
	Co(en)$_3$Cl^{2+}	5.4[w]	1.8		
	Co(en)$_3$Br^{2+}	5.2[w]	1.8		
	Co(en)$_3$I^{2+}	5.0[w]	1.7		
	Co(en)$_3$NO$_3^{2+}$	5.0[w]	1.7		
	Co(en)$_3$ClO$_4^{2+}$	4.7[w]	1.7		
	Co(en)$_3$SO$_4^+$	23.3[w]	8.0		
	Co(en)$_3$C$_2$O$_4^+$	30.3[w]	10.4		
	Co(en)$_3$Cit	59.2[w]	20.4		
methanol (5.99)	LiCl	18[x]	3.0		5.1
	LiBr	17[x]	2.8		4.8
	KCl	29[y]	4.8		4.3
ethanol	LiCl	17[x]			
1-propanol (14.41)	LiCl	16[x]	1.1		
	NaBr			2.8	4.5[ff]
	NaI			2.5	4.2[ff]
	NaClO$_4$			3.7	4.5[ff]
	KI			2.7	3.8[ff]
	RbI			2.7	3.5[ff]
2-propanol (26.67)	LiCl	17.4[z] (19,[x] 21.8[aa])	0.7		
	NaI	15[bb]	0.4		
	Bu$_4$NCl	11.7[z]	0.3		
	Bu$_4$NBr	8.8[z]	0.3		
	Bu$_4$NI	8.7[z]	0.3		
	Bu$_4$NClO$_4$	7.8[z]	0.3		
acetone (25.50)	LiI	21[p]	0.8		
	NaI	25[p] (31.2[cc])	1.0 (1.2)	1.9	4.9[gg]
	NaClO$_4$			2.0	6.5[gg]
	KI	23[p] (30.7[cc])	0.9 (1.2)		
	CsI	24[p] (30.4[cc])	0.9 (1.2)		
diethyl ether (33.61)	Bu$_4$NPic	115[dd]	3.4		
benzene (22.43)	Bu$_4$NPic	62[dd] (59[p])	2.8		
dichloromethane	R$_4$NX[ii]	negligible[ee]	~0		~0

^{a} Reference 43. ^{b} Reference 48. ^{c} Reference 49. ^{d} Reference 50. ^{e} Reference 51. ^{f} Reference 6. ^{g} Reference 52. ^{h} Reference 53. ^{i} Reference 54. ^{j} Reference 7. ^{k} Reference 93. ^{l} Reference 55. ^{m} Reference 56. ^{n} Reference 57. ^{o} Reference 58. ^{p} Reference 59. ^{q} Reference 60. ^{r} Reference 61. ^{s} Reference 62. ^{t} Reference 63. ^{u} Reference 64. ^{v} Reference 65. ^{w} Reference 66. ^{x} Reference 67. ^{y} Reference 68. ^{z} Reference 41. ^{aa} Reference 69. ^{bb} Reference 70. ^{cc} Reference 71. ^{dd} Reference 72. ^{ee} Reference 73. ^{ff} Reference 5. ^{gg} Reference 4. ^{hh} At 369.36 K and 10.22 MPa. ^{ii} R = ethyl to butyl, X = halide, SCN$^-$, ClO$_4^-$.

the present one. However, compressibilities of the salt solutions are rarely available for nonaqueous solvents, nor are reliable methods for apportioning them between the ions. The present paper is oriented in particular toward dealing with ion solutions in such solvents.

The calculation of ΔV_{el} by the present approach (traceable to Padova[9]) has as its main problem the obtaining of reliable values of $(\partial X/\partial P)_T$ that depend on the second pressure derivative of the permittivity and density of the solvent. Optimally, these quantities should be determined simultaneously in the same

experiment, or at least by the same authors, but such cases are exceptions,[36−38,41] and they need not of themselves yield reliable values. Efforts were made to take the most reliable values of $(\partial \kappa_T/\partial P)_T$ and $(\partial^2(\ln\epsilon)/\partial P^2)_T$ from the literature for presentation in Table 1, but even so different values of ΔV_{el} result in some cases. For instance, the compressibility and permittivity second derivatives reported by Lührs and Schwitzgebel[36] for acetonitrile lead to a much larger electrostriction volume than the combination of the values reported by Easteal and Woolf[23] and Côté et al.[24] The pressure derivatives of the isothermal compressibility calculated from data reported by Richard[74] for acetone or by Optushchennikov et al.[75] for benzene could not be employed, since they lead to values of $\Delta V_{el} > V^*$. Similarly, the pressure derivative of the compressibility calculated from data reported by Egorov et al.[35] or the second pressure derivative of the permittivity reported by Schadow and Steiner[40] for acetone lead to an unreasonably large fraction $\Delta V_{el}/V^*$.

No forcing explanation could be found for the difference between some protic solvents (methanol, ethanol, and formamide) and the dipolar aprotic solvents and water with respect to obtaining $0 < \Delta V_{el}/V^* < 1$ values. It should be noted, however, in this connection that Côté et al.[24] showed that plots of $\epsilon(\epsilon - 1)^{-1}(\partial(\ln\epsilon)/\partial P)_T$ vs κ_T were straight lines with slopes of 1.21 for several aprotic solvents but of only 0.62 for protic ones, with water being common to both lines. The hydrogen bonding characterizing the protic solvents seems to play a role in the difference between the compression behavior of the solvent and the change in the orientation ability of its molecules in an electric field as the pressure increases. However, propanol and 1,2-ethanediol do not conform to such a generalization, again, without an obvious explanation.

Estimates of of ΔV_{el} of water ranging from 2.0 to 7.0 cm^3 mol^{-1} were mentioned by Millero,[76] referring to an earlier review by him,[77] where however, these estimates and their sources were *not* mentioned at all. An estimate of ΔV_{el} of water of 4.94 cm^3 mol^{-1} is derivable from the much earlier pressure derivatives (at 293.15 K) available to Gucker.[78] Another estimate is 3.4 ± 0.5 cm^3 mol^{-1} reported by LoSurdo and Millero,[7] based the ratio $k = \Delta V_{ip}^\infty/\Delta K_{ip}^\infty$ of the volume and compressibility changes on the formation of divalent metal sulfate ion pairs, having the value $k = 420 \pm 60$ MPa. A theoretical value of $k = 360$ MPa ascribed[7] to Millero[76] yields $\Delta V_{el} = 2.9$ cm^3 mol^{-1}, in agreement with the present value, whereas $k = 500$ MPa given by Millero et al.[79] leads to $\Delta V_{el} = 4.09$ cm^3 mol^{-1}. Other estimates by Millero et al.[79] range from 2.5 at 273 K to 2.8 at 318 K, based on hydration numbers calculated from the compressibilities of electrolyte solutions.

Desnoyer, Verrall, and Conway[3] used a completely different approach for the estimation of ΔV_{el} of water. They calculated the pressure effect of the electric field of the ions and arrived at the expression:

$$\log(1 + \Delta V_{el}/V^*) = -0.1469 \log(1 + 1.225 \times 10^{-20}\{E/(\text{V m}^{-1})\}^2) \quad (19)$$

The numerical coefficients pertain specifically to water as the solvent. Since the field E depends on the ionic charge, the distance from the ion and the effective permittivity of the water in its hydration shell,[2] no unique value for ΔV_{el} can result from this expression. For ions such as Na$^+$ and F$^-$, at a distance of 0.255 nm from the centers of the ions and an estimated relative permittivity of 1.78 (the square of the refractive index) the electric field is ∼1.24×10^{10} V m^{-1}, and the resulting $\Delta V_{el} \approx 3.1$ cm^3 mol^{-1}.[3] For a divalent ion of typical radius 0.08 nm, at

the distance of the middle of the first hydration shell (that is larger than the ionic radius by the radius of a water molecule, 0.14 nm), i.e., a distance of 0.22 nm, and a more realistic estimate of the relative permittivity of 2.5 in the dielectrically saturated region,[2,44,80] the field is $E \approx 2.4 \times 10^{10}$ V m^{-1}; hence, $\Delta V_{el} \approx 4.8$ cm^3 mol^{-1}. These values depend strongly on the estimated relative permittivity in the region of interest and less so on the charge and radius of the ion. Hence, they cannot be valid beyond such estimates, although they are of a reasonable magnitude. Desnoyer et al.[3] did not extend their approach to solvents other than water.

Several publications have dealt quantitatively with the solvent electrostriction in the solvation shells of ions, but practically exclusively for aqueous solutions. An exception is the paper by Walden of almost a century ago,[81] in which the author calculated the electrostriction of completely dissociated salts in several nonaqueous solvents. He assumed that the ratio of the difference of the partial molar volumes of a salt at two dilutions to the difference in the corresponding degrees of dissociation (obtained as the ratio of the conductivity at a given dilution (concentration) to that at infinite dilution) represents the electrostriction of the solvent per mole of salt. The resulting values, averaging at 13 cm^3 mol^{-1}, are similar to those, 8−11 cm^3 mol^{-1}, deduced by Drude and Nernst[1] for aqueous solutions in an even earlier paper on a similar premise. They are only of historical interest, since the premise, depending on assumed degrees of dissociation, is not valid. Of the publications dealing with aqueous solutions, that of Goto[82] is questionable. The expression he gave for the volume of an *m* molal solution containing 1 kg of water was $V_m = m\upsilon_m + 1000/d_0 - V_m^e$. However, no means were disclosed how the author uncoupled the "effective molar volume" of the salt υ_m and the solvent electrostriction V_m^e. The hydration numbers deduced ranged from 22 for NaCl to 96 for CsI, which do not seem physically reasonable.

A modern relationship between the electrostriction volume and hydration numbers was presented by LoSurdo and Millero[83] for divalent cations. The molar electrostriction, V_{el}, caused by the ions was calculated from the standard partial molar volumes (apparent molar volumes at infinite dilution) and eq 3 on the same assumption for obtaining absolute ionic molar volumes employed here, $V^\infty(\text{H}^+,\text{aq}) = -5.5$ cm^3 mol^{-1}, see above, and reasonable values of the intrinsic volumes (based on crystal ionic radii and packing effects, but anyway, these are small for the divalent cations). The hydration numbers of these divalent ions followed from eq 3 and $\Delta V_{el} = 3.2$ cm^3 mol^{-1} used,[83] that is similar to the value used in Table 2 here, and arrived as expected at an average value 11.1 ± 1.5 cm^3 mol^{-1}. This treatment was not extended, however, to other cations, to anions, or to other solvents.

The approach taken by Danielewicz-Ferchmin and Ferchmin[84] is akin to that of Desnoyers et al.[3] in that it equates the electrical work of the orientation of the water dipoles by the ion and the pressure work compressing the solvent. The calculated electrostrictive pressures in the hydration shells range down from 49 GPa for Al^{3+} to 23 GPa for In^{3+} to 8 GPa for La^{3+} and M^{2+} (first row divalent transition metal cations), to 3.2 GPa for Ca^{2+}, 0.9 GPa for Li$^+$, and down to 0.03 GPa for Cs$^+$ as representative ions among many others for which values were reported. These pressures lead to densities of the water in the hydration shells considerably higher than of ambient bulk water for multivalent cations: $\rho_{el}/\text{g cm}^{-3} = 2.7$ for Al^{3+}, 2.2 for In^{3+}, 1.8 for La^{3+} and M^{2+}, 1.35 for Ca^{2+}, 1.2 for Li$^+$, but not differing from the bulk density, ρ^*, for the larger univalent cations. Hence, values

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of $\Delta V_{el} = V^*(1 - \rho^*/\rho_{el})$ dependent on the ion charge and size result: $\Delta V_{el}/cm^3 \ mol^{-1} = 11.4, 9.9, 8.0, 4.7, 3.0,$ and 0.0 for these representative ions. These authors[84] proceeded to calculate hydration numbers of the cations, based on experimental values of the volumes of the hydrated ions, V_{sl} (from neutron diffraction data of Hahn[85]): $n = V_{sl}\rho_{el}/V^*\rho^*$, that are 7.4, 7.9, 10.9, 7.4 ± 0.3, 5.3, and 6.0 ± 0.7 for the set of ions mentioned above. Since these values are directly proportional to V_{sl}, they do not reflect directly the number of water molecules subjected to electrostriction, hence they are much larger for the univalent cations than expected from their relatively weak electric field (cf. the pressures listed above). No extension of the treatment to anions and solvents other than water was made by Danielewicz-Ferchmin and Ferchmin.[84]

David, Vokhmin, and Ionova[86] started from experimental values of the coordination number and ion−water molecule distances from radial distribution functions obtained by X-ray and neutron diffraction and EXAFS measurements and concluded that the radius of a water molecule in the hydration shells of ions is not constant but is diminished by the electrostriction. Whereas r_W is 0.142 ± 0.002 nm for the alkali metal cations, it is 0.138 ± 0.003 nm for the alkaline earth cations (Be^{2+} was not considered), 0.135 ± 0.003 nm for the lanthanide cations and for the halide anions (I^- was not considered), compared with $r_W^* = 0.138$ nm for bulk water (the alkali metal cations are, thus, negatively hydrated, see above). An iterative calculation involving the distance, permittivity, field strength, electrostrictive pressure, and coordination number was then used[87,88] to obtain the average packing fractions r_W/r_{el} (accounting for void space between the water molecules). The r_W/r_{el} values 0.736 for the halide anions, 0.777 for the alkali metal cations, 0.797 for the alkaline earth cations, and 0.804 for the lanthanide cations[86] were reported. From these one can derive the average volumes of the water molecules, $V_{el} = (4\pi/3)N_A r_{el}^3$ in the first hydration shell (and subsequently also the second shell) and the values of $\Delta V_{el} = V^* - V_{el}$. These are, on the average, 2.7 ± 0.4 for the alkali metal cations (except Li^+, 4.0), 4.8 ± 0.8 for the alkaline earth cations, and 6.0 ± 0.3 for the lanthanide cations, 2.9 for F^-, 2.2 for Cl^-, and 2.1 for Br^-, in $cm^3 \ mol^{-1}$, to be compared with the average value 2.9 $cm^3 \ mol^{-1}$ irrespective of the nature of the ions, obtained in the present work from the properties of the solvent water alone.

It remains to discuss the volume change on ion pairing and the number of solvent molecules released thereby in relation to theories of ion pairing and in particular also the use of these data as a diagnostic tool for distinguishing inner- and outer sphere association and solvent separated (or shared) and contact ion pairs. Unfortunately, most available experimental data concerning this volume change pertain to aqueous solutions, see Table 3, where as pointed out by a reviewer, the concept of hydration numbers may be questionable. Furthermore, discussions of the subject have devolved almost exclusively about aqueous solutions. Hemmes[89] was among the first to deal with this issue in detail. He derived the volume changes expected, given the validities of the Bjerrum theory,[46] ΔV_{ip}^B, pertaining to ion pairing not distinguishing between contact and solvent separated (or shared) species, and of the Fuoss theory,[90] ΔV_{ip}^F, pertaining to contact ion pairs only. The latter is

$$\Delta V_{ip}^F = RT[b(\partial(\ln\epsilon)/\partial P)_T - \kappa_T] \qquad (20)$$

where $b = |z_+ z_-|e^2/4\pi\epsilon_0\epsilon a k_B T$ and a is the distance of closest approach and the other symbols have their usual meaning.

The ratio of the two values is

$$\Delta V_{ip}^B/\Delta V_{ip}^F \approx (3/b) + \exp(b)/b^4 Q(b) \qquad (21)$$

where $Q(b)$ is the Bjerrum integral,[46] and when b is large $Q(b) \approx \exp(b)/b^4$ so that the ratio becomes $\approx (3/b) + 1$. Hemmes[89] applied the two approaches to the association of $La^{3+}Fe(CN)_6^{3-}$ in aqueous solutions and found them to yield values of $\Delta V_{ip}/cm^3 \ mol^{-1}$, 9.0 and 6.9, in fair agreement with the experimental value[65] of 8.0. However, for $Mn^{2+}SO_4^{2-}$ in water a larger difference is noted: $\Delta V_{ip}^F = 8.3$, $\Delta V_{ip}^B = 5.0$, and the experimental value is 7.4 $cm^3 \ mol^{-1}$.[51] All these values depend, however, on the rather arbitrary choice of the value of a made to fit the association constant according to these two theories, hence no fair choice between these approaches can be made on this basis.

Other authors also compared values of ΔV_{ip} expected from these theories with experimental values. Masterton et al.[63] calculated $\Delta V_{ip}^F \approx 1.3 \ cm^3 \ mol^{-1}$ compared with the experimental $\Delta V_{ip}^\infty/cm^3 \ mol^{-1} \approx 6$ for $Rb^+NO_3^-$ and ≈ 15 for $Tl^+NO_3^-$ in aqueous solutions. However, the latter value appears to be too high, since it corresponds to the release of more water molecules on ion pairing than are bound to the free ions. Eigen and Tamm[91] in their interpretation of the ultrasonic relaxation in aqueous $Mg^{2+}SO_4^{2-}$ solutions suggested that the formation of the solvent separated ion pair (the first of a three stage process) involves a negligible volume change, hence no solvent release. The major volume change takes place when solvent is released (some 4−5 mol per mole ion pair) to form the solvent shared ion pair, and a modest volume change occurs (corresponding to the release of a further 1−2 mol of solvent) when this forms the contact ion pair. Similar conclusions were drawn by Jackopin and Yeager[54] who preferred a two step process to interpret their ultrasonic relaxation data of the analogous aqueous $Mn^{2+}SO_4^{2-}$ system, where the volume changes correspond to 3 and 1 water molecules being released in the steps involved. Millero and co-workers[6,79] estimated the electrostriction of the water caused by the $Mg^{2+}SO_4^{2-}$ contact ion pair as $-16.6 \ cm^3 \ mol^{-1}$, corresponding (with $\Delta V_{el} = 2.9 \ cm^3 \ mol^{-1}$) to its being still solvated by 5.7 molecules of water (The authors[6] used Padova's[9] too low value of $\Delta V_{el} = 2.1 \ cm^3 \ mol^{-1}$ and arrived at 8 molecules still solvating the ion pair). For the contact ion pair, the 5.7 molecules are probably the remainder of the primary hydration shell of the magnesium cation into which the sulfate anion intruded. The sulfate anion had shed all of its own hydration shell (some 9 molecules) and released the second hydration shell of the magnesium cation (some 3 molecules), altogether about 12 molecules being released on formation of the contact ion pair. A much smaller value, 2.3 molecules of water released, arises from the experimental ΔV_{ip} (Table 3), showing that only a fraction of the magnesium sulfate is in the form of contact ion pairs, the other kinds of ion pair retaining much of the water of hydration.[7,79] The small relative amount of contact ion pairs explains why ΔV_{ip}^F fails to account for the experimental ΔV_{ip} in this case as also in other cases, such as $Cu^{2+}SO_4^{2-}$,[55] $UO_2^{2+}SO_4^{2-}$,[60] or $La^{3+}SO_4^{2-}$ [61] in water. Nguyen-Trung and Hovey[60] showed that the volume changes for contact ion pairing (inner sphere association) of di- and trivalent metal cations with sulfate anions in aqueous solutions increase with the ion potential, z^2/r as expected.

Few values of ΔV_{ip} for ion pair formation in nonaqueous solvents have been published; see Table 3. The values for the lithium salts in methanol, yielding Δn_{ip} near 3 out of total solvation numbers near 5 appear reasonable. However, the reported ΔV_{ip} value for KCl is too large, being based[68] on an

uncertain analogy with the ion pair volume in acetic acid solutions and of electrostriction of the ions in methanol. For the salts in 2-propanol,[41] reasonable values of ΔV_{ip} lead to rather small values of Δn_{ip} because of the rather large ΔV_{el} of the solvent, 26.7 cm^3 mol^{-1}. Unfortunately, no solvation numbers in 1- and 2-propanol are available from electrostriction volumes, nor ΔV_{ip} data for ion pairing in the analogous 1-propanol with the more reasonable $\Delta V_{el} = 14.4$ cm^3 mol^{-1}. For the latter solvent entropy changes for ion pairing lead to $\Delta n_{ip} \approx 2.7$ for alkali halides.[5] However, in the case of LiCl an estimate of $\Delta V_{ip} \approx 16$ cm^3 mol^{-1} [67] (albeit from apparent molar volumes at concentrations where only 5.1 to 12.6% of the salt was ionized) yields $\Delta n_{ip} \approx 1.1$, but for this salt, no value from the entropy change is available. For the higher alcohols the fractions of LiCl dissociated is even smaller; hence the volume change on ion pairing obtained from the apparent molar volumes is rather uncertain and therefore the reported estimates[67] are not included in Table 3. Nor need the values of ΔV_{ip} estimated by the present author[92] in acetone and acetonitrile be further considered, since these were based on the pressure derivative of the theoretical association constant according to the Bjerrum theory rather than on actually measured values. Finally, for Bu$_4$N$^+$ picrate in the low permittivity solvents diethyl ether and benzene the values of ΔV_{ip} are large but so are those of ΔV_{el}, hence reasonable values of Δn_{ip} result, arising from desolvation of the highly dipolar picrate anion on ion pairing.

The number of solvent molecules liberated from translational confinement near the ion partners on the formation of ion pairs has previously[5] been estimated from the standard molar change of entropy on such a desolvation process, ΔS_{desol}. This quantity is the difference between the observed entropy change on ion pairing, ΔS^{∞}_{obs} and the sum of the theoretically calculated contributions from translation, rotation and electrostatic effects. The number of solvent molecules released was taken[5] to be the ratio of the desolvation entropy and the entropy of fusion of the solvent, ΔS_{fus}, extrapolated from the fusion temperature of the solidified solvent to ambience. The resulting values are shown in Table 3 for the few cases where Δn_{ip} is available from both the volume and the entropy changes on ion pairing. It is seen that the entropy changes lead to larger values than the volume changes, but the total number of comparisons that can be carried out is very limited, so that no conclusions from the differences can be drawn.

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