Solvation of Ions. XXIV.[1] Entropies of Transfer of Some Divalent Metal Ions from Water to Nonaqueous Solvents

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Abstract: Standard free energies (molar scale) for the transfer of Cd^{2+}, Zn^{2+}, and Ba^{2+} from water to methanol, hexamethylphosphoramide, acetonitrile, dimethylformamide, and dimethyl sulfoxide have been obtained by means of extrathermodynamic assumptions. Corresponding standard entropies of transfer have also been obtained using enthalpies of transfer from an earlier paper. There is a much larger decrease of entropy when divalent rather than monovalent cations are transferred from water to these nonaqueous solvents. Results are discussed in terms of current models of ion solvation. Divalent cations have more than one layer of solvent molecules in their solvation shells in most of the solvents studied. HMPT has particularly strong enthalpic and entropic interactions with cations.

Significant progress has been made recently toward the thermodynamic characterization of nonaqueous electrolyte solutions,[2] and within the framework of plausible extrathermodynamic assumptions, values of thermodynamic variables for the individual ionic components of some such solutions have been determined.[3-6] The parameters $\Delta G_{tr}(\text{ion})$, $\Delta H_{tr}(\text{ion})$, and $\Delta S_{tr}(\text{ion})$, the respective change in the standard free energy, enthalpy, and entropy of an ion upon transfer from one solvent to another, are widely used in discussing aspects of ion solvation in various solvents. Most of the existing data and models of ion solvation are based upon studies of monovalent ions, however.[7] The importance of extending the data to multivalent ions, having much greater ionic potentials, is evident, especially in testing the general applicability of ion solvation models.[8]

The standard free energies of solvation (gas phase to solution) of divalent cations in polar solvents are usually much more negative than those for the monovalent cations ($\Delta G_{\text{solvation}}(M^{2+})$ typically −1000 to −2000 kJ/g-ion; $\Delta G_{\text{solvation}}(M^{+})$ typically −250 to −500 kJ/g-ion).[9] Compared with monovalent cations, divalent cations generally are smaller and have a greater charge density. They are thus expected to interact more strongly with and to cause more extensive structuring of polar solvents within ion-centered solvation shells than do monovalent cations.

This paper follows our measurement of $\Delta H_{tr}(M^{2+})$ and reports values of $\Delta G_{tr}(M^{2+})$ and thus $\Delta S_{tr}(M^{2+})$ based upon the extrathermodynamic assumptions that $\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$, $\Delta H_{tr}(Ph_4As^+) = \Delta H_{tr}(Ph_4B^-)$, and $\Delta S_{tr}(Ph_4As^+) = \Delta S_{tr}(Ph_4B^-)$ (collectively called the TATB assumption).[10]

Experimental Section

The preparation of salts[11] and the purification of solvents have been described previously.[12] HMPT contained only 15–25 ppm water by Karl Fischer titration. Anhydrous trifluoromethanesulfonates of the divalent cations were used. These can be treated as strong electrolytes in the solvents studied[11] and where comparisons were made gave similar values to those of the corresponding perchlorates. Enthalpies of solution in hexamethylphosphoramide were measured as described for other solvents in part XXIII.[11] Rates of dissolution were often very slow and the uncertainty is greater than for other solvents.[11] Measurements were in the range 6–15 × 10^{-4} *M* and no concentration dependence was observed. Data are in Table V.

The apparatus and methods for potentiometrically determining the free energies of transfer of monovalent cations from water to other solvents using the EMF of cell A have been described in an earlier paper in this series.[12] The method was altered for the divalent metal cations only insofar as a stationary amalgam pool rather than a streaming amalgam electrode was used in cell A at 298°K.

$$\begin{array}{c|l||l|l|c}
\text{M(Hg)} & 10^{-3}\,M\ \text{M(CF}_3\text{SO}_3)_2 & & 10^{-2}\,M\ \text{AgClO}_4 & \text{Ag} \\
0.0289\ \text{mol}\ \% & 10^{-2}\,M\ \text{TEAP} & 10^{-2}\,M\ \text{TEAPic} & 10^{-2}\,M\ \text{TEAP} & \text{wire} \\
\text{pool} & \text{solvent s} & \text{solvent s} & \text{solvent s} &
\end{array}$$

cell A

(M represents barium, cadmium, or zinc; TEAP represents tetraethylammonium perchlorate; TEAPic represents tetraethylammonium picrate.) A stationary configuration was chosen for the amalgam electrode in light of recent evidence indicating that Zn^{2+} and Ba^{2+} reductions,[13] as well as that of Cd^{2+},[14] on mercury in dimethyl sulfoxide are relatively slow processes. Reversible behavior of the amalgam electrode requires that the ratio of the exchange current density to the limiting diffusion current density be at least ten.[15,16] As this ratio varies directly with the thickness of the diffusion layer, all other variables remaining constant, it is obviously desirable to maximize the extent of this layer. At ambient laboratory temperature the thickness of the diffusion layer in solution around the electrode can typically be increased 50-fold (from 10^{-3} cm to 5×10^{-2} cm) by changing from a stirred to a still solution.[17] Thus, to avoid the stirring effect of streaming electrodes, stationary amalgam electrodes were employed throughout the present study. At least four independent measurements were made for each salt with agreement to within 2% and Nernstian behavior was observed in the range studied, *i.e.*, 10^{-3} to 3×10^{-3} *M* electrolyte solution. Cell A had an EMF of −1.840 V in HMPT as solvent and −2.330 V in water with M as barium. This leads to $\Delta G_{tr}(Ba^{2+}W \rightarrow HMPT)$ of +18.6 kJ/g-ion which is completely anomalous. Cyclic voltammetry suggested that the Ba(Hg) $Ba(CF_3SO_3)_2$ half-cell was irreversible. Electron transfer is likely to be very slow with this strongly solvated ion in HMPT, by analogy with Ba^{2+} in DMSO.[13]

Results

Measurement of the potential of cell A in a solvent leads *via* the Nernst equation to a value of $\bar{G}°(M^{2+}) - 2\bar{G}°(Ag^+) = 2F\Delta E°$ for each solvent being studied (assuming negligible salt effects and defining unit activity of the metal in the amalgam), $\bar{G}°(M^{2+}) - 2\bar{G}°(Ag^+)$ representing the difference in the standard partial molar free energies of M^{2+} (M(Hg) unit activity) and Ag^+ in the solvent under consideration. If this difference in some solvent S be compared with the difference in water, one obtains $\Delta G_{tr}(M^{2+}) - 2\Delta G_{tr}(Ag^+) = 2F\Delta E_{tr}°$, *i.e.*, the difference in the potentials of cell A and in the standard partial molar free energies of each ion on transfer from water to solvent S. Since values of $\Delta G_{tr}(Ag^+)$ for transfer of Ag^+ from water to various other solvents S are known in terms of the TATB assumption,[18] one can determine corresponding quantities for $\Delta G_{tr}(M^{2+})$. Table I lists values of $\Delta G_{tr}(M^{2+})$

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Table I. Free Energies of Transfer of Cations from Water to Nonaqueous Solvents[a] at 298°K (TATB Assumption) (Units kJ/g-ion on Molar Scale)

		$\Delta G_{tr}(W \rightarrow S)^d \pm 1.5$ kJ/g-ion[f] in solvent S =					
		W	DMF	DMSO	AN	MeOH	HMPT
				Dielectric constant[c]			
Cation	$\Delta G_{\text{aquation}}{}^b$	78.5	37.8	48.9	37.5	32.6	28.3
Li^+	−510.9	0.0	−9.6	−14.6		+3.8	
Na^+	−410.9	0.0	−10.5	−13.8	+13.8	+8.4	
K^+	−337.2	0.0	−9.6	−12.1	+7.9	+10.0	−16.7
Rb^+	−315.9	0.0	−10.0	−10.9	+6.7	+10.0	
Cs^+	−283.7	0.0	−9.2	−12.6		+9.6	
Ag^+	−479.1	0.0	−17.2	−33.5	−21.8	+7.5	−39.3
Ba^{2+}	−1318.4	0.0	−21.3	−25.1	+57.3	+18.4	(+18.6)[e]
Cd^{2+}	−1801.2	0.0	−33.5	−53.6	+42.3	+32.6	−41.8
Zn^{2+}	−2027.6	0.0	−29.7	−49.0	+68.6	+27.6	−43.6

[a] Abbreviations: W = water, DMF = dimethylformamide, DMSO = dimethyl sulfoxide, AN = acetonitrile, MeOH = methanol, HMPT = hexamethylphosphorotriamide. [b] Reference 9. [c] Reference 4a. [d] Data for monovalent cations taken from ref 7; data for divalent cations are this work and are calculated as described in the text from the EMF of cell A, using $\Delta G_{tr}(Ag^+)$ values from ref 18. [e] Thought to be anomalous due to nonreversible electrode (see text). [f] Estimated maximum uncertainty.

Table II. Enthalpies of Transfer of Cations from Water to Nonaqueous Solvents[a] at 298°K (TATB Assumption) (Units kJ/g-ion on Molar Scale)

		$\Delta H_{tr}(W \rightarrow S)^c \pm 0.5$ kJ/g-ion[d] in solvent S =					
Cation	$\Delta H_{\text{aquation}}{}^b$	W	DMF	DMSO	AN	MeOH	HMPT
Li^+	−527.2	0.0	−32.2	−26.4		−22.2	
Na^+	−418.0	0.0	−33.1	−27.6	−13.0	−20.5	
K^+	−333.5	0.0	−39.3	−34.7	−22.6	−18.4	−57.9
Rb^+	−308.4	0.0	−37.7	−33.5	−23.0	−15.5	
Cs^+	−275.7	0.0	−36.8	−32.2		−13.8	
Ag^+	−487.9	0.0	−38.5	−54.8	−52.7	−20.9	
Ba^{2+}	−1327.6	0.0	−85.5	−78.5	−8.5	−59.2	−144.6
Cd^{2+}	−1830.9	0.0	−63.3	−70.8	+8.2	−40.4	−116.1
Zn^{2+}	−2069.4	0.0	−62.7	−62.2	+20.1	−45.6	−97.4

[a] Abbreviations as in footnote *a*, Table I. [b] Calculated from the conventional standard enthalpies of hydration in ref 9 using $\Delta H_{\text{hydration}}(H^+) = -1103.3$ kJ/g-ion as reported by D. F. C. Morris in "Structure and Bonding", Vol. 4, Springer-Verlag, Berlin, 1968. See also ref 11. [c] Data for monovalent cations taken from ref 7; data for divalent cations taken from ref 11, except for HMPT which is this work (cf. Table V). [d] Estimated maximum uncertainty, except for HMPT (cf. Table V).

for M^{2+} as Zn^{2+}, Cd^{2+}, and Ba^{2+} along with $\Delta G_{tr}(M^+)$ for Ag^+ and for the alkali metal monovalent cations, transfer being from water to solvent S at 298°K. All values are based upon the TATB assumption, the assumption that the free energies of transfer of tetraphenylarsonium cation and tetraphenylboride anion are the same for transfer from water to solvent S ($\Delta G_{tr}(Ph_4As^+) = \Delta G_{tr}(Ph_4B^-)$). Ion association is not expected to be a significant factor for 10^{-3} *M* solutions of $M(CF_3SO_3)_2$ in these solvents[11,19] and at the ionic strength corresponding to 10^{-2} *M*, salt effects are expected to be small and to cancel in cell A.

Table II lists single ion enthalpies of transfer (TATB assumption) from water to several nonaqueous solvents of Ba^{2+}, Cd^{2+}, Zn^{2+}, and selected monovalent cations.[11]

Single ion entropies of transfer (TATB assumption) from water to solvent S are calculated from the expression $\Delta S_{tr} = (\Delta H_{tr} - \Delta G_{tr})T^{-1}$ and are listed in Table III. Standard ionic entropies of solution ΔS_s in water (crystal to aqueous solution TATB assumption) are known[8] and when combined with the ionic entropies of transfer, ΔS_{tr} (solvent to solvent) as defined above, yield standard ionic entropies of solution in solvents S. Such values are listed in Table III which also contains data on a concept developed by Cox and Parker,[8] *i.e.*, entropies of transfer of ions from each ideal solvent to its corresponding real solvent as calculated from eq 1.[7]

$$\Delta S_{tr}(\text{ion})(\text{ideal} \longrightarrow \text{real}) = \Delta S_s(\text{ion}) - 12.6 - R \ln \frac{1000\rho}{\text{MW}} \qquad (1)$$

The entropy of solution ΔS_s in (1) is the entropy change associated with the transfer of single ions (TATB assumption) from a real solid ionic lattice to a real solvent to make a unimolar solution in that solvent. The final two terms on the right-hand side of eq 1 reflect the entropy change (12.6 J/°K g-ion) for the change of state of forming a unit mole fraction melt of ions from a hypothetical solid ionic lattice of single ions and the entropy change ($R \ln (1000\rho/\text{MW})$ expressed in units of J/°K g-ion) accompanying the dilution of this melt to 1 l. with a hypothetical noninteracting liquid of the same density (ρ), the same solvent–solvent interaction, and the same molecular weight (MW) as the real solvent under consideration. Thus, taken together, the terms on the right-hand side of eq 1 represent the entropy change associated with transferring 1 mol of single ions from an ideal solution to a corresponding real solution of the same density and molecular weight. The solution taken to be ideal is defined as having no ion–ion or ion–solvent interactions, but has the same solvent structure as pure real solvent and hence the entropy decrease (or increase) upon transferring an ion from an ideal to a real solvent must be attributable to ion-imposed structural changes in the real solution. Implicit in the application of eq 1 is the assumption[8] that $\Delta S_s(Ph_4As^+) = \Delta S_s(Ph_4B^-)$ and the Latimer assumption[20] that the entropy of an ion in a real ionic lattice is independent of the counter ion in the lattice. The full significance of the parameter $\Delta S_{tr}(\text{ion})(\text{ideal} \rightarrow \text{real})$ as defined by eq 1 has been discussed for univalent ions both in water[8] and nonaqueous solvents;[7] this paper simply extends the concept to divalent ions.

Table III. Single Ion Entropies of Transfer $\Delta S_{tr}(W \rightarrow S)$ from Water to Nonaqueous Solvents[a,b] and $\Delta S_{tr}(I \rightarrow R)$ from an Ideal to the Corresponding Real Solvent[d] at 298°K (TATB Assumption) (Units J/°K g-ion on Molar Scale)

		ΔS_{tr} ± 7 J/°K g-ion[f]					
Cation	Transfer	W[g]	DMF	DMSO	AN	MeOH	HMPT
Li^+	W → S	0.0 (−19.7)	−75.7	−39.3		−87.0	
	I → R	−65.7	−129.3	−93.7		−146.0	
Na^+	W → S	0.0 (+14.2)	−75,7	−46,4	−90.0	−97.1	
	I → R	−31.8	−95.4	−66.9	−113.0	−122.2	
K^+	W → S	0.0 (+44.8)	−99.6	−75.7	−102.5	−95.4	−138.2
	I → R	−1.3	−88.7	−65.7	−95.0	−90,0	−120.5
Rb^+	W → S	0.0 (+57.7)	−92.5	−75,7	−99.6	−85.8	
	I → R	+11.7	−68.6	−52.7	−79.1	−67.4	
Cs^+	W → S	0.0 (+60.2)	−92.5	−66.1		−71.5	
	I → R	+14.2	−66.1	−40.6		−50,6	
Ag^+	W → S	0.0 (+7.1)	−71.5	−71.5	−103.8	−95.4	
	I → R	−38.9	−98.3	−99.2	−133.9	−127.6	
Ba^{2+}	W → S	0.0 (−59.0)	−215.3	−179.1	−220.7	−260.3	
	I → R	−105.1	−308.2	−272.9	−317.0	−358.7	
Cd^{2+}	W → S	0.0 (−131,8)	−99.9	−57.7	−114.4	−244,8	−249.2
	I → R	−177.9	−265.6	−224.3	−283.5	−416,0	−408,1
Zn^{2+}	W → S	0.0 (−164,4)	−110.7	−44.3	−162.7	−245.5	−146.2
	I → R	−210.5	−309.0	−243.5	−364.4	−449.3	−337.7

[a] Abbreviations are as in Table I. [b] For water the entropies of solvation ΔS_s are taken from ref 8. Values of ΔS_s for other solvents can be calculated from $\Delta S_s = \Delta S_s(H_2O) + \Delta S_{tr}(W \rightarrow S)$. [c] Entropies of transfer from water to nonaqueous solvents are calculated from the expression $\Delta S_{tr}(W \rightarrow S) = (\Delta H_{tr} - \Delta G_{tr})T^{-1}$ using ΔG_{tr} values from Table I and ΔH_{tr} values from Table II. [d] Entropies (J/°K g-ion) of transfer from an ideal (as defined in the text) to a corresponding real solvent are calculated by the expression $\Delta S_{tr}(I \rightarrow R) = \Delta S_s - 12.6 - R \ln (1000\rho/MW)$. See also ref 7 and 8. [e] Values of $R \ln (1000\rho/MW)$ in eq 1 are: water, 33.5; HMPT, 14.5; DMF, 21.3; DMSO, 22.2; AN, 24.7; MeOH, 26.8 J/°K g-ion. [f] Estimated uncertainty. [g] Values ΔS_s(crystal to water)[c] are in parentheses.[e]

Discussion

Free Energies of Transfer. The data listed in Table I reveal the general order of solvation for divalent cations of DMSO > HMPT > DMF ≫ H_2O > MeOH > AN and for the monovalent alkali metal cations of HMPT > DMSO > DMF ≫ H_2O > AN > MeOH. This order is somewhat surprising if simple electrostatic solvation effects alone are considered (the so-called Born type solvation) since all of these nonaqueous solvents have lower bulk dielectric constants than does water. However, the apparent anomalies are readily explicable in terms of the chemical properties of solvents,[21-25] *e.g.*, their basicities, solvent-solvent interactions, and donor abilities.

The divalent cations in Table I, being stronger Lewis acids than the monovalent cations[26] and of much higher ionic potential, are considerably more sensitive to solvent transfer. Thus $\Delta G_{tr}(M^+)$ for transfer between any two solvents listed in Table I ranges over no more than 40 kJ/g-ion while for $\Delta G_{tr}(M^{2+})$ the range is 120 kJ/g-ion.

Perhaps most remarkable is the fact that in spite of widely differing molecular structures, all of the solvents of Table I solvate any particular gaseous cation to much the same extent. The difference between the ionic free energy of aquation (*i.e.*, gas phase to water) and the ionic free energy of solvation of any one ion in any of the solvents (*i.e.*, covering a range of dielectric constants of 28 to 78) is only about ±5%. The Born equation would predict such a small variation over this range of dielectric constant, so it seems that electrostatic interactions of the Born type *do* constitute the *major* part of solvation energies.[27-29] Despite this, the much smaller free energies of *transfer* are still sufficient to create enormous differences in the chemical behavior[4] (*e.g.*, reaction rates, equilibria, redox potentials) of ions in different solutions.

The specific back-bonding interaction of the d^{10} Ag^+ ion and Cu^+ ion with the π-bond system of acetonitrile is responsible for an unusual (relative to Na^+) and highly exoenergetic transfer of Ag^+ and Cu^+ from water to acetonitrile.[7,30,31] However, the effects of such an interaction are less apparent in ΔG_{tr} of the divalent d^{10} Zn^{2+} and Cd^{2+} ions from water to acetonitrile. $\Delta G_{tr}(M^{2+})$ values to acetonitrile are endoenergetic for Zn^{2+} and Cd^{2+} as in the case of Ba;$^{2+}$ however, $\Delta G_{tr}(Cd^{2+})$ to acetonitrile is less endoenergetic relative to $\Delta G_{tr}(Ba^{2+})$ than expected from the behavior of these two ions in other solvents. The increased ionic potential of these divalent cations is thought to decrease greatly the tendency for their back bonding,[32] so that acetonitrile occupies no special position as a solvator of Zn^{2+} but it does seem to have a weak specific interaction with Cd^{2+}.

Enthalpies of Transfer. The enthalpy data included in Table II have been discussed in detail elsewhere[11] except for HMPT, which is an extraordinarily fine cation solvator, in an enthalpic sense. Enthalpies of transfer of divalent cations from water to the nonaqueous solvents are most exothermic for the largest cation Ba^{2+} and decrease in exothermicity in the order $Ba^{2+} > Cd^{2+} > Zn^{2+}$ for a given transfer, in accord with decreasing ionic size. For a given gaseous divalent cation, solvation enthalpies decrease in exothermicity in the order HMPT ≫ DMSO ≈ DMF > MeOH > H_2O > AN, which contrasts with the order HMPT > DMF > DMSO > AN > MeOH > H_2O for potassium cation.

Entropies of Transfer. (i) From Water to Solvent S. The substantial decreases of entropy accompanying the transfer of cations from water to all the nonaqueous solvents included in this study indicate that water is a uniquely favorable solvent for cations in an entropic sense. As seen from the data listed in Table III, the entropy decreases for transferring divalent cations from water (typically −100 to −250 J/°K g-ion) are generally greater than for monovalent cations (typically −50 to −100 J/°K g-ion). It is important to note that there is no simple correlation between the entropy decrease (Table III) and, as judged by ΔH_{tr} (Table II), the relative strength of solvation, on transfer of cations between two solvents. Apparently, if a particular number of solvent molecules are structured in a solvent shell, it makes only a very small contribution to the entropy change whether they are strongly or weakly held in that structure. We believe that if there is a difference in the *number* of solvent molecules influenced by the ion, as distinct from the strength of their interaction with the ion, the entropy change will be significantly different. The important point to note is merely that translational entropy is lost in the first solvation sphere; once this entropy is lost, the strength of binding is not entropically important on the scale considered here. Other types of entropy change, *e.g.*, rotational, are sufficiently small to be ignored.

The decrease of entropy upon transfer of a cation from water to a nonaqueous solvent S is interpretable in terms of solvent structure.[33-36] It is helpful to relate transfer to the following steps: water → ideal water → ideal S → S. We will first consider water → ideal water. As shown in Table III, either an entropy increase or decrease accompanies transfer of a cation from water to ideal water (negative of $\Delta S_{tr}(I \rightarrow R)$ in Table III). Ions of low ionic potential, *e.g.*, Cs^+, show a decrease of entropy on transfer from water to ideal water. Ions of high ionic potential show a gain of entropy. All of the water molecules of lower entropy than bulk water heretofore in the cation's solvation shell(s) and those of higher entropy in the disordered region, *i.e.*, partly within the hydration shell and partly between the hydrated ion and bulk water, are incorporated into the highly developed, low entropy, bulk water structure[37-40] when the ion is removed from water. Whether this entropy change represents a net decrease or increase depends upon the relative *number* of water molecules, both in the structured solvation shell(s) and in the disordered region, whose structural environment returns to that of bulk water when the ion is removed and transferred to ideal water. A large cation of low ionic potential (*e.g.*, Cs^+) in water is surrounded by many disordered water molecules but has few molecules in its solvation shell; a small cation of high ionic potential (*e.g.*, Zn^{2+}) has a very large number of water molecules in its solvation shell but fewer disordered water molecules.[6,41,42] The entropy change from ideal water to ideal nonaqueous is largely a mathematical device related to the density and molecular weight of the solvent and will not be discussed.

The entropy change upon transferring the ion from ideal nonaqueous into a real nonaqueous solvent (Table III, $\Delta S_{tr}(I \rightarrow R)$) is somewhat simpler to interpret qualitatively than is the water transfer. The entropy increases slightly due to the disruptive process of fitting the solvated cation into the real nonaqueous solvent, but the entropy strongly decreases due to the process of forming an ion-centered solvation shell. The latter decrease of entropy strongly predominates in terms of net entropic effects, in nonaqueous solvents, because the nonaqueous solvents have rather poorly developed bulk structures[34] of high entropy relative to water, due to weaker solvent-solvent interactions, when compared with water.

It must be remembered, however, that "poorly developed bulk solvent structure" does not imply the *absence* of bulk solvent structure in these nonaqueous solvents. Indeed, methanol is known to exhibit hydrogen bonding solvent-solvent interactions in the liquid state,[43] possibly to form dimers or trimers,[11] and there is evidence that dimethyl sulfoxide is more highly associated in the liquid state, perhaps owing to stronger dipole-dipole interactions,[34] than are many of the other nonaqueous solvents. However, water is a uniquely low entropy solvent in that its extensive three-dimensional structure greatly decreases the inherent translational entropy of water. Formamide is one of the few solvents which approaches water in its degree of developed structure, *i.e.*, it has low inherent translational entropy.[43]

Let us summarize the processes real to ideal water to ideal nonaqueous to real nonaqueous solvent. The transfer real to ideal water always produces a relatively smaller increase of entropy than similar transfers in other solvent systems, because of the relatively low entropy of bulk water and the existence of disordered regions about ions in water. The transfer ideal to real nonaqueous always produces a large decrease of entropy for reasons just presented. Thus the transfer of cations from real water to real nonaqueous solvents involves a substantial decrease of entropy, as observed in Table III.

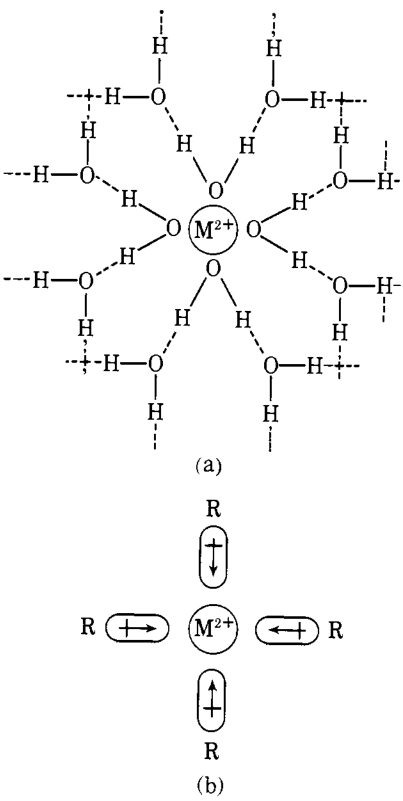

Figure 1. Solvation shells about M^{2+} in water (a) and dipolar aprotic solvents (b). R is generally a methyl group.

As noted, the entropies of transfer of divalent cations from water to the nonaqueous solvents of Table III are generally somewhat more negative than are those of monovalent cations, especially of Li^+. This was unexpected, following the reasoning in part XIX,[7] which was based on the observation (Table III) that $\Delta S_{tr}(Li^+)$ or $\Delta S_{tr}(Na^+)$ was usually *less* negative than ΔS_{tr} for Cs^+ or Rb^+. Because of their even greater charge density than Li^+, divalent cations were expected to continue the trend, *i.e.*, less negative ΔS_{tr} from Cs^+ to Li^+ to M^{2+}. The reasoning followed from the expectation that divalent cations cause much more extensive structuring of water about themselves than do univalent cations. Divalent cations are likely to encourage structured ion-centered hydration shells which have water hydrogen bonded to the first shell.[44-46] This mechanism for extension of the hydration shell is feasible because of the enhanced acidity of the water molecules in the first solvation shell. In dipolar aprotic solvents extension of the solvation shell by means of hydrogen bonding is clearly impossible because the solvent usually "sees" groups like methyl, not acidic hydrogens, about the first shell of the cation. Extension to other shells is possible only through alternative and weaker mechanisms, such as enhancement of the induced dipoles in the first solvation shell.[46] A pictorial representation of these two schemes for divalent cation solvation is in Figure 1.

Application of this model suggests that entropies of transfer of divalent cations from water to nonaqueous solvents would be no more negative, and could even be less negative, than those for univalent cations like lithium. Once

Table IV. Minimum Solvation Numbers for Divalent Cations in Various Solvents[a] at 298°K (TATB Assumption)

Solvent S	W	DMF	DMSO	AN	MeOH	HMPT
ΔH_m, kJ/mol[c]	6.0078	7.88[e]	13.93	8.167	3.205	16.9
Mp, °K[c]	273.15	212.72	291.69	229.315	175.47	280.3
ΔS_f, J/°K mol[d]	−22.2	−37.0	−47.7	−35.6	−18.4	−60.4
Cation	Minimum solvation number n[b]					
Ba^{2+}	4.7	8.3	5.7	8.9	19.5	
Cd^{2+}	8.0	7.2	4.7	8.0	22.6	6.8
Zn^{2+}	9.5	8.4	5.1	10.2	24.4	5.6
Li^+	3.0	3.5	2.0		7.9	
K^+	0.1	2.4	1.4	2.7	4.9	2.0
Cs^+	−0.64	1.8	0.85	2.2	2.7	

[a] Abbreviations are as in Table I. [b] Calculated from $n = [\Delta S_{tr}(I \rightarrow R)]/[\Delta S_f(\text{solvent S})]$ as described in text. See also ref 7. [c] Heats of fusion taken from J. A. Riddick and W. B. Bunger, "Organic Solvents", 3rd ed, in A. Weissberger, Ed., "Techniques of Chemistry", Vol. 2, Wiley-Interscience, New York, N.Y., 1970, but note that ΔH_m for DMF is in error in this reference, *cf.* footnote *e*. [d] Entropy of freezing calculated from $(-\Delta H_m)(T)^{-1}$. [e] R. R. Dreisbach, *Adv. Chem. Ser.*, No. 29 (1961).

the first solvation shell was filled in nonaqueous solvents (Figure 1b), there would be little further loss of entropy on transfer from ideal nonaqueous to real nonaqueous, no matter how great the ionic potential of the ion. However, as shown in Table III, $\Delta S_{tr}(I \rightarrow R)(M^{2+})$ in all solvents is not constant and is much more negative than $\Delta S_{tr}(I \rightarrow R)(M^+)$ decreasing strongly from Cs^+ to Zn^{2+}. This suggests that there is a substantial and continuous increase in the number of "translationally frozen" nonaqueous solvent molecules as the ionic potential of the cation increases. The increase is illustrated by $\Delta S_{tr}(I \rightarrow R)(Cs^+) = -66.1$ J/°K g-ion, $\Delta S_{tr}(I \rightarrow R)(Li^+) = -95.4$ J/°K g-ion, and $\Delta S_{tr}(I \rightarrow R)(Zn^{2+}) = -309$ J/°K g-ion for transfer from ideal to real DMF. Much of the same type of increase is observed for transfer from ideal to real water, *i.e.*, $\Delta S_{tr}(I \rightarrow R)(Cs^+) = +14.2$, $\Delta S_{tr}(I \rightarrow R)(Li^+) = -65.7$, $\Delta S_{tr}(I \rightarrow R)(Zn^{2+}) = -210.5$ J/°K g-ion. Each value shows less loss of entropy in water than in DMF, but the trend is very similar. The lower values in water are related to the lower loss of translational entropy when bulk water is frozen and to the larger gain of entropy when a region of disordered water is formed between bulk water and hydrated ion, relative to DMF.

The relatively "open" and extensive water structure about a multiply hydrated divalent cation (Figure 1a), the structure being especially "open" in the second shell, allows not only an extensive region of disordered water to be interposed between the hydrated ion and the bulk water structure, but also allows room for disordered water molecules within the hydrogen-bonded water molecules of the second and higher hydration shells. These disordered water molecules interpenetrate the region of the second-hydration shell and occupy the large "voids" between the hydrogen bonded waters in the second hydration shell. In the case of solvation by dipolar aprotic solvents, the disordered region about divalent cations is much less extensive than in water and the solvation shell is well filled (*vide infra*). The net result is that transfer of a divalent cation from water to a dipolar aprotic solvent causes a greater loss of entropy than does transfer of a monovalent cation, as is observed.

(ii) From Ideal Solvent S to Real Solvent S and Minimum Solvation Numbers. The question remains, how many divalent cations have their first solvation shell filled by the nonaqueous solvents studied here?[6,41,42] A reasonable maximum solvation number for a first shell is 6, based on assumed octahedral coordination. A method of determining *minimum* values of solvation numbers has been proposed (cf. ref 47 and 48), and it is interesting to see if these minimum numbers are greater than 6.

Values of $\Delta S_{tr}(I \rightarrow R)$ for transfer of mono- and divalent cations from an ideal to a corresponding real solvent have been calculated using eq 1 and are included in Table III. There are substantial entropy losses accompanying transfer of divalent cations from unstructured ideal to all real solvents, while for monovalent cations the entropy losses are less significant. Indeed for transfer from ideal water to real water many of the monovalent cations experience a gain in entropy.

As noted, the entropy losses associated with orienting dipolar solvent molecules about an ion are due mainly to losses of translational degrees of freedom and apparently depend upon the number of solvent molecules so oriented, rather than upon the strength of the ion-solvent interaction.[7] The number of oriented solvent molecules about a cation is influenced not only by the usual coordination number of the ion, where applicable, but also by the ionic charge, the ionic size, and the steric requirements of solvent molecules. This number can be estimated as a minimum value by using the molar entropy of freezing (ΔS_f) of the solvent to approximate to the maximum loss of entropy associated with transferring 1 mol of solvent from the bulk liquid to the ionic solvation shells of a unimolar cationic solution at 298°K. It is highly desirable for accurate modeling that the solvent's freezing point be near room temperature. However, most dipolar aprotic solvents have entropies of freezing of −35 to −45 J/°K mol despite a variety of melting points.[7] The ratio $\Delta S_{tr}(I \rightarrow R)/\Delta S_f = n$ then gives an estimate of the *minimum* number n of solvent molecules translationally bound in the ion's solvation shells. This is an estimate of a number which is regarded as a minimum for two reasons. First, $\Delta S_{tr}(I \rightarrow R)$ is less than the entropy loss for forming the first solvation shell because we have neglected the entropy gains associated with forming a region of disorder between the bulk solvent molecules and the solvent molecules which are oriented about an ion. In water especially, n will be much less than the number of molecules in the first and subsequent solvation shells. Second, the entropy loss on freezing bulk solvent at 298°K is possibly an overestimation of the entropy change associated with forming an ion-centered solvation shell from bulk liquid. In Table IV are listed minimum solvation numbers n for a variety of cations as estimated from the entropy of transfer (ideal to real) of the ion and the entropy of freezing of the solvent, *i.e.*, $n = \Delta S_{tr}(I \rightarrow R)/\Delta S_f$. It is believed, on steric grounds and following the principles of coordination chemistry, that no more than 6 HMPT, DMF, DMSO, or acetonitrile molecules can fit around a small divalent cation, without forming a second solvent shell.

Of the solvents studied, only water, HMPT, and dimethyl sulfoxide have freezing points in the vicinity of 298°K at atmospheric pressure; the others melt at much lower temperatures. Unfortunately, insufficient solid and liquid heat ca-

Table V. Enthalpies of Solution of Electrolytes, ΔH_S, and Enthalpies of Transfer from Water and Enthalpies of Transfer of Single Ions (TATB assumption) to Hexamethylphosphorotriamide at 298°K (Units kJ/mol on Molar Scale)

Salt	ΔH_S(HMPT)	ΔH_{tr}(W → HMPT)[b]	Ion	ΔH_{tr}(W → HMPT)
Ph_4AsBPh_4	+15.0 ± 1.2	−27.3	Ph_4As^+	−13.7[a] ± 1.5
$KBPh_4$	−32.3 ± 0.7	−71.6	K^+	−57.9 ± 1.5
KCF_3SO_3	−29.9 ± 0.6	−47.1	Ba^{2+}	−144.6 ± 3.5
$Ba(CF_3SO_3)_2$	−132.8 ± 2.2	−123.0	Cd^{2+}	−116.1 ± 3
$Cd(CF_3SO_3)_2$	−155.8 ± 1.9	−94.5	Zn^{2+}	−97.4 ± 5
$Zn(CF_3SO_3)_2$	−155.7 ± 4.1	−75.8	$CF_3SO_3^-$	+10.8 ± 1.5

[a] Value for Ph_4B^- is the same. [b] Water values from ref 7 and 11.

pacity data are available to allow calculation of the entropy change associated with the hypothetical liquid to solid phase transition at 298°K for methanol, dimethylformamide, and acetonitrile, each of which fails to satisfy the proviso that the solvent's freezing point be near room temperature. Hence for each of these latter three solvents the molar entropy of freezing will only qualitatively approximate the maximum entropy loss associated with ordering 1 mol of bulk solvent molecules about ions in a unimolar cationic solution at 298°K. However, since we are confining ourselves to maximum entropy loss and minimum solvation numbers, ΔS_{fr} is probably a reasonable model for behavior at 298°K, because ΔS_{fr} is close to −40 J/°K mol for DMF and acetonitrile, as expected for typical dipolar aprotics at 298°K.

It is interesting to view the minimum solvation numbers in Table IV in terms of the solvation schemes pictured in Figure 1. Minimum solvation numbers, n, for the divalent cations in water are up to 9.5 for zinc and are much less for monovalent ions in water. Remembering that n values for water are estimated as very minimal solvation numbers supports the idea that there is extensive structuring of water beyond a first tetrahedral or octahedral solvation layer about divalent cations; this is consistent with Figure 1a. The pK_a of $Ba(H_2O)_n^{2+}$ is 13.4 while that for $Zn(H_2O)_n^{2+}$ is about 9, so it is not surprising that hydration obviously extends to a second layer for $Zn(H_2O)_n^{2+}$ but less obviously for $Ba(H_2O)_n^{2+}$. For divalent cations in dimethyl sulfoxide, a solvent somewhat more structured than most dipolar aprotics, and in HMPT, which is weakly structured, the minimum solvation number is about 5–6 and it is less than 6 for small Zn^{2+}. The solvation number is much greater than for monovalent cations, however. There may not be extension of the solvation shell about divalent cations into a second layer of DMSO or HMPT molecules which is consistent with the model in Figure 1b; however, for DMSO, but not HMPT, 5 is regarded as a very minimal solvation number about M^{2+}. In any case, fewer DMSO and HMPT than water molecules are in the solvation shells about Cd^{2+} and Zn^{2+} in the respective solvents. As noted above, there is some ambiguity concerning the interpretation of minimum solvation numbers for divalent cations in methanol, dimethylformamide, and acetonitrile, both because of their low melting points and because of uncertainties in methanol data,[7] but the trend is clear. Values in DMF are about 8 for divalent cations but only 3.5 for Li^+ and even less for Cs^+ and K^+. Acetonitrile behaves similarly to DMF toward cations and *the raw numbers are very similar in AN and DMF to those for water.* It is highly likely that there is extension of the first into a second solvation layer about the divalent cations in acetonitrile, DMF, and methanol,[46] because the *minimum* solvation numbers are greater than 6, which is the number for octahedral solvation. A second solvation shell in dipolar aprotics is required by the data in Table IV, but this is not in accord with the model in Figure 1b. It is significant that Ba^{2+} and Zn^{2+} have very similar minimum solvation numbers in the nonaqueous solvents, despite the very much greater ionic potential of the much smaller zinc cation. If our method of using ΔS_f values results in an *underestimate* of the entropy lost in forming the solvation shell, rather than an overestimate as assumed by us, then both the solvation numbers of Ba^{2+} and Zn^{2+} would be less (e.g., 5–6) but still much the same as each other. A lower value of 5–6 would agree with the concept of a single solvation shell, completely filled by the same number of DMF or acetonitrile molecules, about both Ba^{2+} and Zn^{2+}. In water, of course, the solvation number does depend on ionic radius and ionic potential and one can imagine solvation shells extending indefinitely, according to the ionic potential of the cation.

It should also be noted that class A cations (Ba^{2+}) should have less well defined solvation numbers than class B cations (Zn^{2+}, Cd^{2+}) where covalent bonding is more important.[11,32] Zinc often prefers tetrahedral coordination, whereas, despite a weaker interaction, the number of dipolar aprotic solvent molecules about a class A cation will be determined by the ion size and interligand repulsion. This may be the reason why large Ba^{2+} has as high or higher solvation number than does Zn^{2+} or Cd^{2+} in dipolar aprotic solvents. Ionic potential and the acidity of $M(H_2O)_n^{2+}$ are important in water, whereas in dipolar aprotic solvents, class A and class B character, as well as size, are important in deciding the solvation number, as shown in Table IV.

A more quantitative statement awaits the heat capacity data which are required for calculating the entropy change for the hypothetical liquid to solid phase transition at 298°K for DMF, acetonitrile, and methanol. We have reservations about single ion thermodynamic parameters, especially ΔH_{tr}, in methanol as solvent.[7] However, within the framework of the TATB assumption and the model of ΔS_f for estimating entropy losses in the solvation shell, the semiquantitative minimum solvation numbers for acetonitrile and DMF do seem to support the concept that acetonitrile and DMF, like water, form solvation shells containing more than six solvent molecules about some divalent cations. We believe that this requires more than one layer of translationally restricted solvent molecules oriented about these small cations. A reason for the extra layer could be that with highly charged cations in dipolar aprotics, the first layer experiences dielectric saturation due to the high charge density. This gives a very low dielectric constant and most ineffective screening of the second solvation sphere from the intense charge. In the case of HMPT, even if dielectric saturation occurs, a second layer beyond the first six molecules is less likely, because the very large HMPT molecules prevent the potential second layer from coming close enough to interact strongly electrostatically with the charged center.

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Thermochemical Isotope Effects. II. CH_3OH-CH_3OD, C_2H_5OH-C_2H_5OD, and H_2O-D_2O in Selected Solvents

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Abstract: Standard heats of solution at 25° have been determined for the isotopic pairs methanol-methanol-*d*, ethanol-ethanol-*d*, and water-heavy water in a variety of solvents. In every case, the transfer of the deuterated compound from an inert solvent (in the case of water, from the gaseous state) to a hydrogen-bonding solvent is more exothermic than the transfer of the parent compound. The isotope effect on the enthalpy of transfer shows a rough correlation with the difference between the reduced masses of the solvent-solute pair. The isotope effect on the enthalpy of the O-H bond in methanol has also been determined.

As part of a continuing investigation of thermochemical isotope effects,[1-4] we have measured standard heats of solution of the isotopic pairs methanol-methanol-*d*, ethanol-ethanol-*d*, and water-heavy water in a variety of solvents at 25°. In a previous study[1] involving chloroform-chloroform-*d* and acetone-acetone-d_6, isotope effects on the enthalpy of transfer of chloroform from "inert" solvents to "active" solvents were interpreted as evidence that solvent-solute interactions were stronger for the deuterated compound than for the parent compound. Similar effects were observed for acetone, but interpretation in this case was clouded by possible isotope effects on the enolization of acetone in different solvents. This complication was avoided in the present study by the choice of solutes, and the results generally confirm the conclusions advanced for the chloroform-chloroform-*d* study. The trends in isotope effects for alcohols are more similar to those for acetone than for chloroform, but the only important differences between the chloroform and alcohol studies are in the position of alcohols as solvents relative to the basic solvents pyridine, tetrahydrofuran, and *p*-dioxane. This difference is compatible with the fact that alcohol solutes can form multiple hydrogen bonds with alcohol solvents and single hydrogen bonds with basic solvents, while chloroform forms single hydrogen bonds with all of these solvents.

Isotopic exchange is a more important consideration for alcohols and water as solutes than was the case for chloroform, and apparently was a complication in some of these measurements. The enthalpy of the isotopic exchange reaction between water and methanol was used to calculate the isotope effect on the enthalpy of the O-H bond in methanol.

Experimental Section

Materials. Methanol was Matheson Coleman and Bell (MCB) Spectroquality Reagent and was used without further purification. Methanol-*d* was supplied by Stohler Isotope Chemicals (SIC) with a labeled isotopic purity of greater than 99%. Conductivity grade ethanol was prepared by the method of Murr and Shiner.[5] Ethanol-*d* as supplied by SIC with an isotopic purity of greater than 99% contained a significant amount of an unidentified impurity, as detected by gas chromatography. This impurity was reduced to an undetectable level by fractional distillation from CaO on a spinning band column. Conductivity grade water was prepared with a Barnstead conductivity still. Heavy water was obtained from Savannah River Laboratory[6] with a labeled isotopic purity of