

Solvation of Ions. XXIII.¹ Enthalpies of Transfer of Some Divalent Metal Ions from Water to Nonaqueous Solvents

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Abstract: The enthalpies of solution of the anhydrous trifluoromethanesulfonates of barium, zinc, and cadmium are strongly exothermic and decrease in their degree of exothermicity in the order of solvents, DMF > DMSO > MeOH > HCONH₂ > H₂O > MeCN. Some enthalpies of solution of other salts in these solvents are reported. Single ion enthalpies of transfer from water to the nonaqueous solvents, based on the extrathermodynamic assumption that $\Delta H_{tr}(\text{Ph}_4\text{As}^+) = \Delta H_{tr}(\text{Ph}_4\text{B}^-)$, are discussed in terms of the properties of the ions and of the solvents. Transfer of the divalent cations from water to methanol, dimethylformamide, or dimethyl sulfoxide is a strongly exothermic process but the transfer of many anions is endothermic.

Over the past few years there has been increasing interest in the thermodynamics of solvation of electrolytes in nonaqueous solvents. To date, most of the studies have dealt with solvation of the silver cation, the monovalent alkali metal cations, alkylammonium ions, and the halide anions.²⁻⁴ Few studies on the solvation of divalent ions in nonaqueous solvents have been reported. Entropies of transfer of single ions from an ideal solution in an ideal solvent to aqueous solution indicate that the higher ionic potential of the divalent metal cations relative to monovalent ions causes more extensive "structure making" in water,⁵ but the situation in nonaqueous solvents was not clear before this work. Most of our ideas about solvation of ions are based on data for monovalent ions, so that it is important to consider the solvation of multivalent ions, before developing a general theory for solvation.

The enthalpies of solution have been reported^{6,7} of some alkaline earth halates and halides in the amide solvents formamide, *N*-methylformamide, and dimethylformamide and of some alkaline earth perchlorates in methanol,⁸ but problems with ion association, salt activity effects, and the difficulty of preparing anhydrous diunivalent salts have discouraged extensive studies of diunivalent salts.

In this paper, we report the enthalpies of solution of anhydrous Ba(ClO₄)₂ and the anhydrous trifluoromethanesulfonates of zinc, barium, and cadmium in the solvents water, methanol, formamide, dimethylformamide, dimethyl sulfoxide, and acetonitrile. We have been particularly careful to prepare anhydrous salts and by using perchlorate and trifluoromethanesulfonates at the lowest practicable concentrations (10⁻³ *M*) in an LKB calorimeter we have tried to minimize effects due to ion association and salt concentrations. We prefer trifluoromethanesulfonates to perchlorates.

Single ion enthalpies of transfer, ΔH_{tr} , of the ions from water to the nonaqueous solvents are reported. These values are based on an extrathermodynamic assumption, which has been justified elsewhere,⁹ that $\Delta H_{tr}(\text{Ph}_4\text{As}^+) = \Delta H_{tr}(\text{BPh}_4^-)$. The results are discussed in terms of the properties of the ions and solvents.

Experimental Section

Materials. (a) **Solvents.** Water was distilled from an all-glass system. The purification has been described¹⁰ of the solvents dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetonitrile (CH₃CN), and methanol (CH₃OH). The specific conductance of each solvent at 23° and its water content, as determined by Karl Fischer titrations, were used to judge the solvent purity. The values obtained for each solvent were as follows: DMSO, 1.4×10^{-7} ohm⁻¹ cm⁻¹, 40 ppm; DMF, 3.4×10^{-7} ohm⁻¹ cm⁻¹, 65 ppm; CH₃CN, 2.4×10^{-7} ohm⁻¹ cm⁻¹, 30 ppm; CH₃OH, 1.4×10^{-6} ohm⁻¹ cm⁻¹, 50 ppm. Formamide (Merck, AR grade) was dried over freshly activated 4A molecular sieves, once distilled at 0.1–0.2 Torr then subjected to several fractional crystallization cycles. The specific conductance and water content were 6×10^{-5} ohm⁻¹ cm⁻¹ and 60 ppm, respectively.

(b) **Solutes.** Anhydrous Ba(ClO₄)₂ was obtained by drying AR Fluka Ba(ClO₄)₂·3H₂O over concentrated sulfuric acid to form the monohydrate¹¹ then heating at 120° and 0.3 Torr for 30 hr. Analysis for barium by titration with standard EDTA¹² gave 40.8 ± 0.1% (calcd for Ba(ClO₄)₂, 40.8%). The ir spectrum of the salt showed no absorptions characteristic of an OH group (<0.01 mol H₂O).

Barium trifluoromethanesulfonate, Ba(CF₃SO₃)₂, was prepared by the reaction of BDH AR barium carbonate with an aqueous solution of CF₃SO₃H. (Reagent grade 3M Company, Saint Paul, Minn.). The product was recrystallized three times from hot water and then dehydrated by heating under vacuum (90° and 0.1 Torr) for 40 hr. The ir spectrum indicated the absence of water. Analysis for barium EDTA titration gave 31.5% (calcd for Ba(CF₃SO₃)₂, 31.5%).

Anhydrous zinc trifluoromethanesulfonate, Zn(CF₃SO₃)₂, was obtained by dehydration, at 120° and 0.2 Torr, of the twice recrystallized product prepared from the reaction of BDH basic zinc carbonate and an aqueous solution of CF₃SO₃H. Metal ion analysis for Zn²⁺ by EDTA titration gave 17.93 ± 0.05% Zn (calcd for Zn(CF₃SO₃)₂, 17.98%). The ir spectrum indicated no OH absorptions.

Anhydrous Cd(CF₃SO₃)₂ was prepared by the same procedure as for the zinc compound. Analysis for Cd²⁺ by EDTA titration gave 27.33 ± 0.06% Cd (calcd for Cd(CF₃SO₃)₂, 27.38%). The ir spectrum also showed no characteristic OH absorptions.

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Table I. Enthalpies of Solution, ΔH_s^0 (kJ mol⁻¹), of Electrolytes at 25.0 \pm 0.05°

Solute	Solvents					
	H ₂ O	CH ₃ OH	HCONH ₂	DMF ^b	DMSO ^b	CH ₃ CN
Ba(ClO ₄) ₂	+3.85 \pm 0.02	-60.3 \pm 0.3	-60.3 \pm 0.2	-126.8 \pm 0.2	-113.0 \pm 0.3	-41.4 \pm 0.4
Zn(CF ₃ SO ₃) ₂	-79.9 \pm 0.2	-116.7 \pm 1	-100.8 \pm 0.9	-149.4 \pm 0.4	-139.7 \pm 2	-54.8 \pm 0.4
Cd(CF ₃ SO ₃) ₂	-61.3 \pm 0.3	-92.9 \pm 0.4	-85.8 \pm 0.3	-131.4 \pm 0.3	-129.7 \pm 0.6	-48.1 \pm 0.4
KCF ₃ SO ₃	+17.2 \pm 0.1	+3.2 \pm 0.2	+2.0 \pm 0.2	-25.5 \pm 0.1	-16.3 \pm 0.2	-2.9 \pm 0.3
Ba(CF ₃ SO ₃) ₂	-9.8 \pm 0.2			-98.4 \pm 0.3	-87.3 \pm 0.3	
NaClO ₃	+21.9 \pm 0.2		+2.6 \pm 0.06	-8.8 \pm 0.1		

^a Errors are expressed as the standard deviation from the mean of a number of independent determinations. ^b DMF is dimethylformamide, DMSO is dimethyl sulfoxide.

All the divalent ion salts were handled and stored under a dry atmosphere in a glove box. The ir spectra of samples stored under these conditions indicated no water absorption over a period of many months.

Potassium trifluoromethanesulfonate, KCF₃SO₃, was prepared by the neutralization of an aqueous solution of CF₃SO₃H with BDH AR K₂CO₃. The product obtained by evaporation of this solution almost to dryness was then recrystallized three times from distilled water. The sample was dried at 110–120° and ca. 0.02 Torr for 48 hr and stored over silica gel in a desiccator. The ir spectrum indicated the absence of OH absorptions. (Calcd for KCF₃SO₃: K, 20.78; C, 6.38. Found: K, 20.8; C, 6.53.) BDH sodium chlorate (NaClO₃) was recrystallized three times from hot water.

The preparation of anhydrous Cd(ClO₄)₂ was attempted using a reported method and although the analysis for Cd²⁺ indicated satisfactory purity to within the experimental error, the ir spectrum indicated slight water absorption. For this reason, the sample was not used in the heat of solution measurements. Attempts to dehydrate Zn(ClO₄)₂·6H₂O by heating under vacuum were not successful. Careful desolvation of Zn(dioxan)₆·(ClO₄)₂ by heating under vacuum¹³ also did not yield a sample of sufficient purity for calorimetric measurements. (NB: although the authors had no problems with this procedure the process has been reported¹⁴ as explosive under certain conditions.)

Heats of Solution. Heats of solution measurements were made with an LKB-Produkt AB (Stockholm, Sweden) Model 8700-1 precision calorimetry system using a 100-cm³ reaction vessel. The calorimeter is essentially based on the design described by Sunner and Wadso.¹⁵

As the dissolution times in the solution experiments were all less than 4 min, the corrected resistance change was calculated using the Dickinson extrapolation method.¹⁶ For the dissolution of the divalent electrolytes, the sample ampoules were filled under a dry atmosphere in a glove box and sealed using an oxy-propane flame.

The precision of the calorimetry system with water in the calorimeter, determined from electrical calibrations, was to $\pm 0.2\%$ for heat changes of ca. 10 J. For the aprotic solvents the precision for similar heat inputs was generally within $\pm 0.4\%$. The accuracy of the instrument was checked by determining the heat of solution of TRIS (tris(hydroxymethyl)aminomethane) in 0.1 M aqueous hydrochloric acid.¹⁷ The mean of five determinations with heat inputs in the range 5–10 J was -29.66 ± 0.02 kJ mol⁻¹ which is 0.3% lower than accepted literature values.^{17–19} All heats of solution were determined at 25.00 \pm 0.05°.

Results

For all the electrolytes, the enthalpies of solution, ΔH_s , were determined in the concentration range of ca. 0.7–3.0 $\times 10^{-3}$ M. In this range, the concentration dependence of ΔH_s is small and masked by experimental errors. For each electrolyte the mean ΔH_s of a number (at least three) of determinations was taken as the enthalpy of solution at infinite dilution, ΔH_s^0 . The

results are shown in Table I. In the limit of infinite dilution

$$\Delta H_s = \Delta H_s^0 + kc^{1/2}$$

where c is the molar concentration and k is readily calculated.²⁰ Using literature data from the references indicated, the calculated values of k for the dissolution of biunivalent electrolytes in the solvents H₂O,²⁰ CH₃OH,^{21,22} formamide,^{21,23} DMSO^{21,24} DMF,^{21,23} and CH₃CN^{21,25} are +10.3, +61.9, +0.3, +9.4, +33.0, and +15.5 kJ mol^{-3/2} l.^{1/2}, respectively. For the solvents H₂O, formamide, DMSO, and acetonitrile and at an electrolyte concentration of 1 $\times 10^{-3}$ M, the $kc^{1/2}$ values are less than 0.5 kJ mol⁻¹. For DMF, the $kc^{1/2}$ value is 1.0 kJ mol⁻¹.

For methanol, even though the $kc^{1/2}$ value is slightly larger than for the other solvents, no corrections were applied to the ΔH_s results in Table I. For the dissolution of 1:1 electrolytes the coefficient k is three times smaller²⁰ than for the 2:1 case, so no corrections were made to the ΔH_s data for uni-univalent electrolytes.

Possible ion pairing effects have been neglected in the analysis of the heat of solution measurements. No effects were detected over the range of concentrations studied. The use of the weakly coordinating ClO₄⁻ anion of low ionic potential should minimize ion pairing. The CF₃SO₃⁻ anion is also a very weak nucleophile, although there is evidence to suggest that it is a slightly stronger coordinator than ClO₄⁻.²⁶ Ion association constants for di-univalent electrolytes in the dipolar aprotic solvents are scarce but perchlorates are strong electrolytes at 10⁻³ M whenever studied.²⁷ The K_A of LiClO₄ in CH₃CN,²⁸ a solvent in which ion association is likely to be more significant than others, is only 4, suggesting that K_A for the di-univalent electrolytes studied is less than 50 and thus that ion-association effects are not significant at $<3 \times 10^{-3}$ M.

The internal consistency of $\Delta H_{tr}(\text{Ba}^{2+})$, derived from measurements on Ba(CF₃SO₃)₂, Ba(ClO₄)₂, and Ba(ClO₃)₂ (*vide infra*), gives strong support to our con-

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clusion that ion association and salt effects are not significant for the salts, solvents, and concentrations used.

The enthalpies of solution have been reported⁸ of anhydrous $\text{Ba}(\text{ClO}_4)_2$ in water and methanol. The values of $+4 \text{ kJ mol}^{-1}$ (water) and -60 kJ mol^{-1} (methanol) are in excellent agreement with those in Table I.

Enthalpies of transfer from water to each nonaqueous solvent, S, of the electrolyte MX_2 ($\Delta H_{\text{tr}}(\text{MX}_2) = \Delta H_s^0(\text{MX}_2 \text{ in S}) - \Delta H_s^0(\text{MX}_2 \text{ in H}_2\text{O})$) have been split into single ion values using the extrathermodynamic assumption (TATB assumption)⁹ that $\Delta H_{\text{tr}}(\text{BPh}_4^-) = \Delta H_{\text{tr}}(\text{Ph}_4\text{As}^+)$. Values are in Table II.

Table II. Single Ion Enthalpies of Transfer (kJ mol^{-1}) from Water to Nonaqueous Solvents of Some Cations and Anions (Assumption $\Delta H_{\text{tr}}(\text{Ph}_4\text{As}^+) = \Delta H_{\text{tr}}(\text{Ph}_4\text{B}^-)$)

Ion	Solvents					
	H_2O	CH_3OH	HCONH_2	DMF	DMSO	CH_3CN
ΔH_{tr}						
Ba^{2+}	0	-59.2	-40.2	-85.5	-78.5	-8.5
Zn^{2+}	0	-45.6	-23.9	-62.7	-62.2	+20.1
Cd^{2+}	0	-40.4	-27.5	-63.3	-70.8	+8.2
$\text{Na}^+{}^a$	0	-20.5	-16.3	-33.1	-27.6	-13.0
$\text{K}^+{}^a$	0	-18.4	-16.7	-39.3	-34.7	-22.6
$\text{Ag}^+{}^a$	0	-20.9	-22.6	-38.5	-54.8	-52.7
CF_3SO_3^-	0	+4.4	+1.5	-3.4	+1.2	+2.5
ClO_3^-	0		-2.9	+2.5		
$\text{ClO}_4^-{}^a$	0	-2.5	-12.0	-22.6	-19.2	-18.4
$\text{Cl}^-{}^a$	0	+8.4	+3.3	+21.3	+18.8	
$\text{Ph}_4\text{B}^-{}^b$	0	-1.7	-0.4	-19.7	-11.7	-10.5

^a Data from ref 2. ^b Value for Ph_4As^+ is the same.

Published heats of solution of the alkali metal perchlorates in water and formamide²⁹ do not yield a satisfactorily consistent value of $\Delta H_{\text{tr}}(\text{ClO}_4^-)$ based on the TATB assumption. The value in Table II was obtained by determining ΔH_s of Et_4NClO_4 in water and formamide ($\Delta H_s(\text{H}_2\text{O}) = +30.5 \text{ kJ mol}^{-1}$, $\Delta H_s(\text{formamide}) = +25.7 \text{ kJ mol}^{-1}$) and using $\Delta H_{\text{tr}}(\text{Et}_4\text{N}^+)$ calculated from the ΔH_s data for the Et_4NBr salt³⁰ and the single ion $\Delta H_{\text{tr}}(\text{Br}^-)$ based on the TATB assumption.²

The enthalpies of solution have been reported of anhydrous $\text{Ba}(\text{ClO}_4)_2$ in formamide and DMF.⁶ Using these data and the single ion enthalpies of transfer of the ClO_3^- anion, as calculated from the ΔH_s of NaClO_3 in Table I, the single ion enthalpies of transfer of the barium cation from water to formamide and DMF are -38.5 and $-82.0 \text{ kJ mol}^{-1}$, respectively. These are in fair agreement with the values in Table II. To check consistency, the enthalpies of solution were determined of $\text{Ba}(\text{CF}_3\text{SO}_3)_2$ in the three solvents H_2O , DMSO, and DMF. Using the single ion $\Delta H_{\text{tr}}(\text{CF}_3\text{SO}_3^-)$ values from Table II, the enthalpies of transfer of Ba^{2+} from water to DMSO and to DMF are -79.9 and $-81.8 \text{ kJ mol}^{-1}$, respectively. These are in reasonable agreement with the values calculated from the ClO_4^- data (Table II).

Discussion

The enthalpies of solution, ΔH_s^0 , of the anhydrous trifluoromethanesulfonates of barium, zinc, and cadmium

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are strongly exothermic and decrease in their degrees of exothermicity in the order of solvents: $\text{DMF} > \text{DMSO} > \text{MeOH} > \text{HCONH}_2 > \text{H}_2\text{O} > \text{MeCN}$. Thus enthalpies of transfer from water are exothermic except when transfer is to acetonitrile. The enthalpies of solution of the corresponding uni-univalent potassium trifluoromethanesulfonates are much less exothermic; indeed in some solvents they are endothermic. In an enthalpic sense, water is a relatively poor solvent when considering the electrolytes and solvents in Table I. Water is especially poor for the di-univalent electrolytes, compared to uni-univalent electrolytes. Dimethylformamide and dimethyl sulfoxide are excellent solvents, in an enthalpic sense, for these di-univalent electrolytes.

Further consideration of the data in Table I is much more profitable if we estimate enthalpies of transfer of single ions from water to other solvents. Values based on the TATB assumption⁹ are in Table II. We agree³¹⁻³³ that electrostatic interactions, whose magnitude can be estimated by Born-type calculations of the work required to charge a sphere in a vacuum and in a continuous dielectric, are the major contributor (90-95%) to the *solvation enthalpies* of ions (*i.e.*, transfer from vacuum to solvent) as recorded in Table III. Each gaseous ion is solvated to much the same extent, in terms of enthalpy, in water, methanol, acetonitrile, formamide, DMSO, and DMF. However, enthalpies of *transfer* (Table II) between a series of solvents of relatively high and similar dielectric constant require more subtle considerations of considerable importance to the solution chemistry of ions. Our discussion is in terms of changes in three types of interaction, with transfer of ions. Solvent-solvent interactions, ion-solvent interactions, and interactions between solvent and the ion plus its first solvation shell are all important.

As well as electrostatic interactions, many ions, such as the IB and IIB cations, Ag^+ , Zn^{2+} and Cd^{2+} , and other class b cations,³⁴ have covalent ion-solvent interactions with suitable donor solvents. These are the soft cations in the Pearson terminology,³⁵ and suitable donor solvents are soft bases. The Ag^+ and Cd^{2+} ions are very typical soft and class b ions, whereas Zn^{2+} is intermediate between these cations and the hard and class a cations of Table II, like K^+ , Na^+ , and Ba^{2+} . The concept of a transition from predominantly electrostatic to covalent cation-ligand interactions as the cation and ligand change is well established in inorganic chemistry.³⁴ However, chemical intuition about cation-ligand interactions does not provide a complete understanding of solvation, because most ideas about cation-ligand interactions come from studies of *aqueous* solutions, dilute in cation and ligand.

However, with solvation in various pure solvents the bulk solvent is not water and one must consider the effect on different solvent-solvent interactions of changing ion-solvent interactions. There will be different interactions of the ion plus its solvation shell with the different bulk solvents. When ions are transferred between some solvents there will be enthalpy changes

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Table III. Enthalpies of Solvation^{a,b} (kJ mol⁻¹) of Some Gaseous Mono- and Divalent Ions at 298°K

Ion	Solvents					
	H ₂ O	CH ₃ OH	HCONH ₂	DMF	DMSO	CH ₃ CN
	ΔH_s					
Na ⁺	-418.0	-438.5	-434.3	-451.1	-445.6	-431.0
K ⁺	-333.5	-351.9	-350.2	-372.8	-368.2	-356.1
Ag ⁺	-487.9	-508.8	-510.5	-526.4	-542.7	-540.6
Ba ²⁺	-1328	-1387	-1368	-1413	-1406	-1336
Zn ²⁺	-2069	-2115	-2093	-2132	-2132	-2049
Cd ²⁺	-1831	-1871	-1858	-1894	-1902	-1823

^a The hydration enthalpies were calculated from the conventional standard enthalpies of hydration using $\Delta H_{\text{hyd}}(\text{H}^+) = -1103.3 \text{ kJ mol}^{-1}$ ($-263.7 \text{ kcal mol}^{-1}$); cf. D. F. C. Morris in "Structure and Bonding," Vol. 4, Springer-Verlag, Berlin, Germany, 1968, and data in D. R. Rosseinsky, *Chem. Rev.*, **65**, 467 (1965). ^b For the nonaqueous solvents, the solvation enthalpies were calculated from the hydration enthalpies and the single ion enthalpies of transfer from Table II, i.e., $\Delta H_s(\text{M}^{n+}) = \Delta H_{\text{hyd}}(\text{M}^{n+}) + \Delta H_{\text{tr}}(\text{M}^{n+})$ from H₂O → S.

associated with the changes in solvent-solvent hydrogen-bond interactions, but with other solvents such changes are absent, because the solvent lacks suitable hydrogens. Thus in considering enthalpies of transfer between pure solvents, we need much more than a knowledge of ion-ligand interactions in a predominantly aqueous solvent.

The enthalpies of transfer of the alkali metal cations from water to the nonaqueous solvents of this study including acetonitrile are all exothermic.² Similarly the enthalpies of transfer of the divalent ions Zn²⁺, Cd²⁺, and Ba²⁺ from water to methanol, formamide, dimethylformamide, and dimethyl sulfoxide are also strongly exothermic. All these solvents are strong donors. However, transfer of Ba²⁺ from water to the weaker base acetonitrile³⁶ is only slightly exothermic and transfer of Zn²⁺ and Cd²⁺ from water to acetonitrile is endothermic.

A major factor tending to produce exothermic transfer from water to other solvents is the enthalpy gained in re-forming the unique three-dimensional hydrogen-bonded structure of water, when ions are desolvated and removed from water and transferred to a less structured solvent in which a new ion-centered solvent shell is formed.² The enthalpy gained in the water is greater than the corresponding enthalpy required to disrupt solvent-solvent interactions in the nonaqueous solvents. One must also consider the enthalpy changes associated with ion-solvent interactions in the first solvation sphere, but transfers from water to most polar solvents tend to be exothermic processes, except where the solvent is a much weaker donor than water, e.g., acetonitrile,³⁶ and the cation is a very strong acceptor, e.g., Zn²⁺. In these cases the effect of ion-solvent interactions prevails and transfer from water is endothermic; however, as noted, exothermic transfers from water to acetonitrile are the rule for monovalent cations even although acetonitrile is the weaker base. Presumably the monovalent cations are not sufficiently acidic to generate ion-solvent interactions whose enthalpic effect outweighs the effect due to changes in solvent-solvent interactions.

An important factor which must be considered is the number of solvent molecules which interact with the cation.² This is related to the question of interaction between solvent and the ion plus its solvation shell. Zinc and Cd²⁺ in water polarize the water in their inner coordination shells, as reflected by the much greater acidity of $\text{M}(\text{H}_2\text{O})_n^{2+}$ species *vs.* $\text{M}(\text{H}_2\text{O})_n^+$.³⁷ A hy-

drated divalent cation is a strong hydrogen-bond donor and this provides a mechanism by which these structure making cations can extend their strong interaction with water beyond the water in the first coordination shell. A mechanism whereby the first solvation shell is extended *via* hydrogen bonds to other solvent molecules is not possible in acetonitrile, because acetonitrile is a poor H-bond acceptor and it lacks protons of suitable acidity. Thus more water than acetonitrile strongly coordinates to divalent cations in these respective solvents, and this, coupled with the stronger ion-solvent coordination of water than of acetonitrile in the first solvation sphere, leads to an endothermic transfer of Zn²⁺ and Cd²⁺ from water to acetonitrile. It is appreciated that more solvent-solvent interactions are disrupted as second or higher hydration shells are formed, but the solvent-coordinated ion interaction predominates.

The enthalpy of transfer of Ag⁺ from water to acetonitrile is $-52.7 \text{ kJ mol}^{-1}$. This is a much more exothermic transfer than that of Na⁺ (-13 kJ mol^{-1}) and is attributable primarily to the specific covalent interactions (back-bonding) of the d¹⁰ Ag⁺ ion with acetonitrile. It might seem surprising that Zn²⁺ and Cd²⁺ which are also d¹⁰ cations do not have strongly exothermic transfers from water to acetonitrile. However, the greater formal positive charge on Zn²⁺ and on Cd²⁺, which is isoelectronic with Ag⁺, makes back bonding much less significant³⁸ than with monovalent Ag⁺, so that as noted, $\Delta H_{\text{tr}}(\text{Zn}^{2+})$ and $\Delta H_{\text{tr}}(\text{Cd}^{2+})$ are endothermic, while $\Delta H_{\text{tr}}(\text{Ag}^+)$ is exothermic for transfer to acetonitrile.

The enthalpy of transfer of Cd²⁺ from DMF to DMSO is -7.5 kJ mol^{-1} , while, enthalpywise, DMF is a significantly better solvator than DMSO of Ba²⁺ and the alkali metal cations. Zinc cation is similarly solvated, enthalpywise, in DMF and DMSO. These variations are consistent with the concept of covalent *vs.* electrostatic interactions and with the concept of soft *vs.* hard interactions. DMSO has stronger covalent interactions with electron acceptors than does DMF. It is softer than DMF. Cadmium has stronger covalent interactions with donors than has zinc, which in turn has stronger interactions than has barium ion, whereas electrostatic interactions increase in the opposite sense; i.e., cadmium is the softest cation in the series of increasing softness: $\text{Ba}^{2+} < \text{Zn}^{2+} < \text{Cd}^{2+}$.³⁴

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The enthalpies of transfer of the divalent cations and the alkali metal ions from water to the protic solvents methanol and formamide are exothermic. The endothermic transfer of all cations to methanol and formamide from DMF and DMSO is attributable to ion-solvent interactions which disrupt the hydrogen-bonded solvent-solvent interactions that occur in both CH_3OH and HCONH_2 . In the case of methanol the endothermicity is enhanced by the greater donor power of DMF and DMSO, relative to methanol. Transfer of cations from formamide to dimethylformamide is a strongly exothermic transfer. These solvents use a similar $\text{NC}=\text{O}$ grouping for cation solvation and are of comparable donor strength so that cation-solvent interactions are likely to be comparable. The exothermicity of transfer is a function of the hydrogen-bonded solvent-solvent interactions in formamide which are absent in DMF and which re-form when cations are transferred from formamide to DMF.

The enthalpies of transfer of many small anions, which are strong hydrogen bond acceptors, from water to dipolar aprotic solvent are endothermic. This is be-

cause strong anion-water hydrogen-bonding interactions are lost and this outweighs the gain of water-water H bonds (*vide supra*) when these anions are transferred from water to dipolar aprotic solvents. However, the enthalpies of transfer of ClO_4^- from water to all of the nonaqueous solvents are strongly exothermic. The perchlorate ion is a very weak H-bond acceptor.²

Transfer from water of the ClO_3^- anion, which has a pyramidal structure, is less exothermic than transfer of ClO_4^- . This is consistent with a loss of stronger ClO_3^- -water interactions due to the greater hydrogen-bonding acceptor ability of ClO_3^- and its lower polarizability, relative to ClO_4^- . The small, usually endothermic enthalpies of transfer of the CF_3SO_3^- ion from water indicate that this anion is a stronger hydrogen-bond acceptor than ClO_4^- , a much weaker acceptor than Cl^- , and a slightly weaker acceptor than ClO_3^- .

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The Crystal and Molecular Structure of α -Acetoxy- α ,2-*anti*-diphenylmethylenecyclohexane

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Abstract: The crystal and molecular structure of α -acetoxy- α ,2-*anti*-diphenylmethylenecyclohexane, $\text{C}_{21}\text{H}_{22}\text{O}_2$, has been determined by a single-crystal, three-dimensional, X-ray diffraction study. The compound crystallizes in space group *Pbca* with lattice parameters $a = 24.157 \pm 0.006$, $b = 16.758 \pm 0.004$, and $c = 8.535 \pm 0.002$ Å ($Z = 8$). The intensities of 2929 independent reflections were measured on a Picker automatic diffractometer (Cu K α radiation) and the structure was solved by the symbolic addition method. Full-matrix least-squares refinement of atom positions, hydrogen isotropic temperature factors, and anisotropic thermal parameters for carbons and oxygens converged at a final $R_1 = 6.5\%$ for the 1722 reflections above background. The cyclohexylidene system is found in a flattened chair conformation with the 2-phenyl substituent axial as required by the theory of $\text{A}^{(1,3)}$ strain. Torsion angles in the ring range from 52.9 to 57.1° (average 55.3°), and internal bond angles at sp^3 hybridized carbons average to 110.7° . Except for the $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^3)$ bond distances of 1.503 and 1.515 Å and the $\text{C}(2)\text{--C}(1)\text{--C}(6)$ angle of 114.0° , metric parameters in the saturated ring conform quite closely to values observed in cyclohexanes. The $\text{C}(\text{sp}^2)\text{--O}$ bond lengths in the acetoxy group are 1.427 and 1.358 Å for the bonds to the methylene and carbonyl carbon atoms, respectively. Bond distances and angles in the aromatic rings are in good agreement with literature values.

It has long been recognized that of the two possible conformers of a cyclohexane ring the chair is far more stable than the boat¹⁻³ and that substituents, in all but a few cases, tend to occupy equatorial positions.³ However, the basic structural parameters of the cyclohexane system, which define essentially a flattened chair conformation, have been measured only during the last decade. For cyclohexane itself, electron diffraction analysis has given a value of 111.9° for the internal bond angle,⁴ and X-ray studies of several of its sub-

stituted derivatives⁵⁻⁷ have determined mean ring angles ranging from 110.6 to 112.1° . As a result of minimization of bond angle strain, the internal angle thus appears to lie between the tetrahedral angle and the n -paraffin angle of 112.7° .⁸ In addition, torsional strain is minimized by reducing the torsion angle from an ideal 60° to values ranging from 52.9 to 57.1° .⁵⁻⁷

While there is ample experimental evidence indicating that the chair form is also the predominant ground-state conformation of six-membered rings containing one sp^2

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