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On the Heats of Solvation of the Zinc(II), Cadmium(II) and Mercury(II) Ions, and of their Neutral Halide Complexes, in Water and Dimethyl Sulfoxide at 25 °C

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Heats of solution have been determined for the zinc(II), cadmium(II) and mercury(II) halides in dimethyl sulfoxide (DMSO), and for the cadmium(II) halides also in water. Combined with data from the literature, the values measured yield the solvation enthalpies of the neutral complexes ML_2. These are much larger for zinc(II) and cadmium(II) than for mercury(II), indicating that the solvent molecules are much more loosely bound in the latter case. Evidently, in the nearly linear complexes HgL_2 no solvent molecules are really close to the metal ion which they certainly are in the complexes ZnL_2 and CdL_2.

From the heats of solvation, the complex formation enthalpies and the lattice enthalpies, the sums of the solvation enthalpies of the ions present in each compound ML_2 can be calculated. If two reasonable extrathermodynamic assumptions are introduced, the solvation enthalpies of the ions Zn^{2+}, Cd^{2+} and Hg^{2+} in both water and DMSO can also be found. In both solvents, Zn^{2+} is more strongly solvated than Cd^{2+} which, however, is somewhat less strongly solvated than Hg^{2+}. The difference between Zn^{2+} and Cd^{2+} is larger in water than in DMSO, while the difference between Cd^{2+} and Hg^{2+} is smaller in water than in DMSO. These trends reflect the different character of the bonds formed by the various acceptors.

For the past few years the thermodynamics of metal complex formation in dimethyl sulfoxide, DMSO, have been studied in this laboratory and the results compared to those found previously for analogous reactions in aqueous solutions. Particularly the complexes formed between the divalent d^{10} ions of the zinc group and the heavy halides Cl^-, Br^- and I^- have been thoroughly investigated. These metal ions vary greatly in their bonding properties, from the distinctly hard Zn^{2+} *via* the mildly soft Cd^{2+} to the very soft Hg^{2+}. Also the bonding character of the ligands spans a wide range, from the mildly soft Cl^- *via* the softer Br^- to the very soft I^-. This means that in these systems complexes of widely different bonding characteristics are formed.

Both in water and DMSO the three metal ions mentioned are certainly all surrounded by six solvent molecules in a regular octahedral arrangement.[1-4] Their halide complexes are formed according to different patterns, however.[3,5-9] The final complex formed is without exception the tetrahedral ML_4^{2-}. For mercury(II) the neutral complexes HgL_2 generally have a linear structure which has no counterpart for cadmium(II) or zinc(II). The linear HgL_2 complexes have long been known both in crystalline and gaseous phases.[10] By recent X-ray diffraction measurements, linear or nearly linear complexes have been proved to exist also in solutions.[8,9] For cadmium(II) and zinc(II), thermodynamic data also strongly suggest that the switch is directly from octahedral to tetrahedral coordination.[11,12] They indicate, moreover, that the change of coordination generally occurs at an earlier step for Zn^{2+} than for Cd^{2+}. This happens earlier in DMSO than in water. For the zinc chloride and bromide systems, the switch seems mainly to take place already at the first step in DMSO but at the second step in water. On account

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of the weak complex formation, no definite conclusions can be drawn for the zinc iodide system in water. In DMSO, however, it seems that the change occurs mainly at the second step. For the cadmium halide systems, the change of coordination takes place at the second step in DMSO but at the third step in water.

Complex formation equilibria in solution depend very much upon the solvation of the various species involved. This is why a knowledge of such parameters as the free energy, enthalpy and entropy of solvation is likely to shed light on the thermodynamic parameters of the complex formation reactions.

The free energy and heat of solvation should increase with the number of solvent molecules entering into close contact with the acceptor. Other factors will of course also influence the solvation parameters. The charge and size of acceptor and ligand, their capacities for covalent bonding, and the donor properties of the solvent all intricately contribute to the final outcome.

The heat of solvation of neutral complexes can be determined without any extrathermodynamic assumptions, by combining the heat of sublimation and the heat of solution which can both be experimentally determined. In this investigation, the heats of solvation of the neutral chloride, bromide, and iodide complexes of the zinc group metals in water and DMSO have been determined. Heats of sublimation have been obtained from literature data and heats of solution have been measured calorimetrically.

From the results obtained, heats of solvation of the free ions have also been derived. The heat of solvation of individual ions cannot be found without an extrathermodynamic assumption. Any evaluation from experimental data always gives the sum of the heats of solvation of the positive and negative ions of the electrolyte involved. In the present study, the quantities primarily obtained are therefore the sum of the heats of solvation of $M^{2+}(=Zn^{2+}, Cd^{2+}$ or $Hg^{2+})$ and $2L^-(=Cl^-, Br^-$ or $I^-)$. These are found by combining the heats of reaction measured, the lattice enthalpies found by means of a Born-Haber cycle and the enthalpy changes for the complex formation reactions which have been obtained previously. By means of extrathermodynamic assumptions that we consider reasonable, the individual heats of solvation for the halide ions have been calculated both in water and in DMSO. From these, we have been able to calculate the heats of solvation of Zn^{2+}, Cd^{2+} and Hg^{2+} in both solvents.

CALCULATIONS AND NOTATIONS

The heat of solvation of the neutral complex ML_2, $\Delta H^\circ_{sv}(ML_2)$, pertaining to the reaction

$$ML_2(g) \rightarrow ML_2(solv)$$

is obtained from the heat of sublimation, $\Delta H^\circ_{sub}(ML_2)$, pertaining to

$$ML_2(s) \rightarrow ML_2(g)$$

and the heat of solution, $\Delta H^\circ_s(ML_2)$, pertaining to

$$ML_2(s) \rightarrow ML_2(solv)$$

through the relation

$$\Delta H^\circ_{sv}(ML_2) = \Delta H^\circ_s(ML_2) - \Delta H^\circ_{sub}(ML_2) \quad (1)$$

If the complex ML_2 is not very stable in solution, a more or less extensive dissociation will take place when the salt is dissolved. In many systems reactions involving a disproportionation of the complex also occur. The heats actually measured have to be corrected for effects due to such reactions, in order to provide the quantity $\Delta H^\circ_s(ML_2)$. This requires not only that the compositions of the equilibrium solutions can be calculated from the pertinent stability constants, but also that the enthalpy changes of all the dissociation and disproportionation reactions involved are known. As regards the present systems, extensive dissociation and/or disproportionation takes place for the zinc and cadmium halides, while the mercury ones remain virtually unchanged. The stability constants and enthalpy changes necessary for the calculation of $\Delta H^\circ_s(ML_2)$ for the zinc and cadmium complexes have all been measured,[11-13] though the values determined for the very weak zinc complexes formed in aqueous solution are not sufficiently precise for the present purpose.[13] These measurements all refer to a temperature of 25 °C and to ionic media of 1 M $NaClO_4$ in water and 1 M NH_4ClO_4 in DMSO. Consequently, the same conditions have been chosen for the present study.

For the ion solvation reaction

$$M^{2+}(g) + 2L^-(g) \rightarrow M^{2+}(solv) + 2L^-(solv)$$

the enthalpy change is

$$\Delta H^\circ_{sv}(\mathrm{M,2L}) = \Delta H^\circ_{sv}(\mathrm{M}) + 2\,\Delta H^\circ_{sv}(\mathrm{L}) \qquad (2)$$

where $\Delta H^\circ_{sv}(\mathrm{M})$ and $\Delta H^\circ_{sv}(\mathrm{L})$ are the heats of solvation of M^{2+} and L^-, respectively. The quantity $\Delta H^\circ_{sv}(\mathrm{M,2L})$ is related to the enthalpy change $\Delta H^\circ_{s}(\mathrm{M,2L})$ of the solution reaction

$$\mathrm{ML_2(s)} \rightarrow \mathrm{M^{2+}(solv)} + 2\,\mathrm{L^-(solv)}$$

according to

$$\Delta H^\circ_{sv}(\mathrm{M,2L}) = \Delta H^\circ_{s}(\mathrm{M,2L}) + \Delta H^\circ_{lat} \qquad (3)$$

where ΔH°_{lat} is the lattice enthalpy of the salt ML_2, *i.e.* the enthalpy change of the reaction

$$\mathrm{M^{2+}(g)} + 2\,\mathrm{L^-(g)} \rightarrow \mathrm{ML_2(s)}$$

The heats of solution pertaining to the ions and to the neutral complex are related according to

$$\Delta H^\circ_{s}(\mathrm{M,2L}) = \Delta H^\circ_{s}(\mathrm{ML_2}) - \Delta H^\circ_{\beta 2} \qquad (4)$$

where $\Delta H^\circ_{\beta 2}$ is the enthalpy change of the reaction

$$\mathrm{M^{2+}(solv)} + 2\,\mathrm{L^-(solv)} \rightarrow \mathrm{ML_2(solv)}$$

For the calculation of $\Delta H^\circ_{sv}(\mathrm{M,2L})$, the values of $\Delta H^\circ_{\beta 2}$ have thus to be known not only for the zinc and cadmium, but also for the mercury(II) systems.

EXPERIMENTAL

Materials. The salts used were all of analytical grade. Dry zinc chloride and bromide were prepared by heating the pure "anhydrous" salts in a stream of dry hydrogen chloride and bromide gas, respectively. Traces of these gases were afterwards removed by a stream of dry nitrogen. The zinc iodide was recrystallized from water and then dried by heating in a dry nitrogen atmosphere. The dry salts are extremely hygroscopic and have to be very carefully protected from moisture.

The cadmium halides were dehydrated by heating to 80 °C overnight.

The mercury(II) chloride, bromide, and iodide (red) were recrystallized from hot water, alcohol, and acetone, respectively, and dried over silica gel.

The sodium and ammonium perchlorates and the DMSO were purified and analyzed as described before.[14-15]

The calorimetric apparatus and procedure have been described previously.[16] Varying amounts of the salts (0.05 – 0.5 g) were transferred into ampoules in a dry-box. The ampoules were sealed in the box and then weighed. The salts were dissolved in 80.0 ml of solution which in no case took more than 10 min. At least six separate experiments were performed for each salt and solvent. All the measurements were performed at 25 °C.

Table 1. Solvation enthalpies for neutral complexes, ML_2, in water and DMSO, *i.e.* $\Delta H^\circ_{sv}(\mathrm{ML_2})$ for the reactions $\mathrm{ML_2(g)} \rightarrow \mathrm{ML_2(solv)}$, calculated from the dissolution and sublimation enthalpies of the solid compounds according to eqn. (1). Values in kJ mol^{-1}; 25 °C.

ML_2	ΔH°_{sub}	Water		DMSO	
		ΔH°_s	ΔH°_{sv}	ΔH°_s	ΔH°_{sv}
$ZnCl_2$	149.0[a]			−70.0	−219
$ZnBr_2$	145.0[a]			−75.9	−221
ZnI_2	140.4[a]			−84.1	−224.5
$CdCl_2$	180[b]	−13.7	−194	−41.2	−221
$CdBr_2$	163[b]	−7.3	−170	−46.2	−209
CdI_2	146[b]	4.9	−141	−45.2	−191
$HgCl_2$	83.1[c]	14.0[d]	−69	−21.2	−104
$HgBr_2$	83.7[b]	20[e]	−64	−17.0	−101
HgI_2	91.2[b]	28.9[f]	−62	−4.3	−95.5

[a] From Ref. 20. [b] From Ref. 21. [c] From Ref. 22. [d] From Ref. 19; in 1 M $HClO_4$. [e] From Ref. 18; at variable ionic strength. [f] From Ref. 17; in 0.5 M $(Na,H)ClO_4$.

MEASUREMENTS AND RESULTS

Heats of solvation of neutral complexes. In the present investigation, heats of solution have been measured for all the halides in DMSO, and for the cadmium halides also in water. The values of $\Delta H_s^\circ(ML_2)$ found are collected in Table 1. These values are fairly precise with random errors estimated to 0.5 – 0.8 kJ mol^{-1} in DMSO and even less, <0.2 kJ mol^{-1}, in water. The degree of dissociation and disproportionation of a salt depends on its concentration. We found the same value of $\Delta H_s^\circ(ML_2)$ independent of the amount of salt dissolved so the corrections introduced to account for these reactions are evidently correct.

The mercury(II) bromide is very sparingly soluble in water and the iodide even less. A determination of $\Delta H_s^\circ(ML_2)$ by means of the present calorimetric method is therefore not feasible for these systems. For HgI_2, a value has nevertheless been determined calorimetrically, from measurements including the precipitation reaction.[17] For $HgBr_2$, on the other hand, one has to be content with a value calculated from the temperature coefficient of the solubility.[18] The value given for $HgCl_2$ has been determined calorimetrically, by much the same method as used in the present work.[19] The errors of the chloride and iodide values given in Table 1 are estimated to ± 1 kJ mol^{-1}, while the precision of the bromide value is probably only ± 4 kJ mol^{-1}.

The heats of sublimation listed in Table 1 are claimed to be correct within 2 or 3 kJ mol^{-1}. In all but the $HgBr_2$ case, these errors thus contribute most to the errors of ΔH_{sv}°.

Heats of solvation of individual ions. The total heats of solution, $\Delta H_s^\circ(M,2L)$, of the halide salts, calculated from eqn. (4) by using the values of $\Delta H_s^\circ(ML_2)$ in Table 1, are given in Table 2, where the values of $\Delta H_{\beta 2}^\circ$ are also stated. The values of $\Delta H_s^\circ(M,2L)$ for the zinc halide systems in water have been obtained directly from calorimetric determinations of the heats evolved when the salts are dissolved.[25]

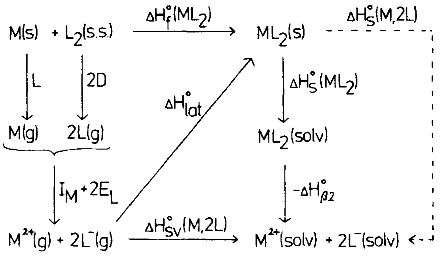
The lattice enthalpies, ΔH_{lat}°, at 25 °C, wanted for the calculation of $\Delta H_{sv}^\circ(M,2L)$ have been obtained by the Born-Haber cycle given in Fig. 1. The data used in these calculations are listed in Table 3. The heat of solvation values, $\Delta H_{sv}^\circ(M,2L)$, obtained from eqn. (3) are given in Table 4.

From the difference $\Delta H_{sv}^\circ(M,2L) - \Delta H_{sv}^\circ(M,2L')$, the difference in the heat of solvation between the two halide ions can be obtained. Values of $\Delta H_{sv}^\circ(Cl-L)$ have been calculated between the chloride ion and the bromide and iodide ions. For each of the two solvents, the three metal ions ought to give the same differences which they do, within the experimental errors, as is demonstrated by the values listed in Table 4. In Fig. 2, the differences are plotted *vs.* the ionic radii of the halide ions. In both solvents, $-\Delta H_{sv}^\circ(L^-)$ decreases in the sequence $Cl^- > Br^- > I^-$, *i.e.* with increasing radius of the halide ion. The decrease is much slower in DMSO than in water, however. From studies involving only alkali halides, Halliwell and Nyburg[31] found

Table 2. Heats of solution, $\Delta H_s^\circ(M,2L)$, in water and DMSO. The values calculated from $\Delta H_s^\circ(ML_2)$, see Table 1, and $\Delta H_{\beta 2}^\circ$ according to eqn. (4). All values in kJ mol^{-1}.

ML_2	Water		DMSO	
	$\Delta H_{\beta 2}^\circ$	$\Delta H_s^\circ(M,2L)$	$\Delta H_{\beta 2}^\circ$	$\Delta H_s^\circ(M,2L)$
$ZnCl_2$		−67.2[d]	23.1[e]	−93.1
$ZnBr_2$		−59.4[d]	36.9[e]	−112.8
ZnI_2		−51.0[d]	48.4[e]	−132.5
$CdCl_2$	2.6[a]	−16.3	8.7[f]	−49.9
$CdBr_2$	−6.5[b]	−0.8	13.1[f]	−59.3
CdI_2	−12.3[a]	17.2	29.4[f]	−74.6
$HgCl_2$	−53.6[c]	68	−49.3[g]	28.1
$HgBr_2$	−87.0[c]	107	−57.5[g]	40.5
HgI_2	−143.1[c]	172	−73.1[g]	68.8

[a] From Ref. 23. [b] From Ref. 24; in 3 M $NaClO_4$. [c] From Ref. 17; in 0.5 M ($NaClO_4$, $HClO_4$). [d] From Ref. 25; in 2 M HNO_3 ($ZnCl_2$ and $ZnBr_2$) and in 2 M $HClO_4$ ($ZnBr_2$). [e] From Ref. 12. [f] From Ref. 11. [g] From Ref. 26.



$$\Delta H^\circ_{lat} = \Delta H^\circ_f(ML_2) - L - 2D - I_M - 2E_L$$

$$\Delta H^\circ_{sv}(M,2L) = \Delta H^\circ_{lat} + \Delta H^\circ_s(ML_2) - \Delta H^\circ_{\beta 2}$$

Fig. 1. The Born-Haber cycle used for the calculation of ΔH°_{lat} and $\Delta H^\circ_{sv}(M,2L)$.

differences $-\Delta H^\circ_{sv}(Cl-Br)=27$ kJ mol^{-1} and $-\Delta H^\circ_{sv}(Cl-I)=68$ kJ mol^{-1} while Morris[32] found 31 and 72 kJ mol^{-1}, respectively. Especially the latter values agree nicely with ours; *cf.* Fig. 2 and Table 4.

There is, as has been pointed out above, no purely thermodynamic way to separate $\Delta H^\circ_{sv}(M,2L)$ into its constituent parts $\Delta H^\circ_{sv}(M^{2+})$ and $2\Delta H^\circ_{sv}(L)$, *cf.* eqn. (2). Large efforts have been made to effect a reasonable partition by means of various extrathermodynamic assumptions. Aqueous solutions have naturally attracted the largest interest. The focal point of this discussion has been how to calculate the "best" value of the solvation enthalpy of the proton, $\Delta H^\circ_{aq}(H^+)$. The most satisfactory approach seems to be the semi-empirical one used by Halliwell and Nyburg.[31] By this method Morris[32] found $-\Delta H^\circ_{aq}(H^+)=1103\pm12$ kJ mol^{-1}. With this value as reference Morris determined, *i.a.*, the heats of hydration of the halide ions, Table 4, note *a*. These values have been used in the calculation of heats

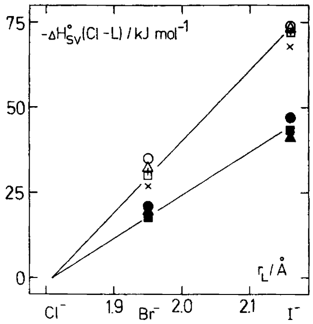


Fig. 2. Differences $\Delta H^\circ_{sv}(Cl-L)$ between halide ions in water and DMSO plotted *vs.* the ionic radii. Circles, squares and triangles refer to values obtained from ZnL_2, CdL_2 and HgL_2, respectively; open signs refer to water, filled signs to DMSO. The signs × and + refer to the values found for water by Halliwell and Nyburg[31] and by Morris,[32] respectively.

Table 3. Calculation of lattice enthalpies, ΔH°_{lat}, for the reactions $M^{2+}(g)+2L^-(g)\rightarrow ML_2(s)$, from the Born-Haber cycle, Fig. 1. All values in kJ mol^{-1}.

ML_2	ΔH°_f [a]	D [b]	E [c]	L [d]	I [e]	$-\Delta H^\circ_{lat}$
$ZnCl_2$	−416.7	121.8	−348.5	130.5	2638.0	2731.8
$ZnBr_2$	−328.0	111.7	−324.7	130.5	2638.0	2670.5
ZnI_2	−208.4	106.7	−295.4	130.5	2638.0	2599.5
$CdCl_2$	−389.1	121.8	−348.5	111.9	2497.8	2545.4
$CdBr_2$	−317.1	111.7	−324.7	111.9	2497.8	2500.8
CdI_2	−202.5	106.7	−295.4	111.9	2497.8	2434.8
$HgCl_2$	−223.4	121.8	−348.5	61.3	2815.0	2646.3
$HgBr_2$	−170.3	111.7	−324.7	61.3	2815.0	2620.6
HgI_2	−105.9	106.7	−295.4	61.3	2815.0	2604.8

[a] Standard heats of formation of the crystalline halides, *i.e.* ΔH°_f for the reactions $M(s)+\frac{1}{2}L_2(s,s)\rightarrow ML_2(s)$. The values (at 298 K) from Ref. 27. [b] Heats of atomization of the halogens, *i.e.* D for the reactions $\frac{1}{2}L_2(s,s)\rightarrow L(g)$. The values (at 298 K) from Ref. 28. [c] Electron affinities of the halogen atoms, *i.e.* E for the reactions $e^-+L(g)\rightarrow L^-(g)$. The values (at 0 K) from Ref. 29. [d] Heats of sublimation of the metals, *i.e.* L for the reactions $M(s)\rightarrow M(g)$. The values (at 298 K) from Ref. 27. [e] Ionization potentials of the metal atoms, *i.e.* I for the reactions $M(g)\rightarrow M^{2+}(g)+2e^-$. The values (at 0 K) from Ref. 30.

Table 4. Solvation enthalpies of pairs of ions and determination of single-ion heats of solvation. All values in kJ mol^{-1}.

$M^{2+}+2L^-$	Water			DMSO		
	$-\Delta H^\circ_{sv}(M,2L)$	$-\Delta H^\circ_{sv}(Cl-L)$	$-\Delta H^\circ_{sv}(M^{2+})^a$	$-\Delta H^\circ_{sv}(M,2L)$	$-\Delta H^\circ_{sv}(Cl-L)$	$-\Delta H^\circ_{sv}(M^{2+})^b$
$Zn^{2+}+2Cl^-$	2799	0	2067	2825	0	2131
$Zn^{2+}+2Br^-$	2730	35	2060	2783	21	2121
$Zn^{2+}+2I^-$	2651	74	2063	2732	47	2118
			Av. 2063			Av. 2123
$Cd^{2+}+2Cl^-$	2562	0	1830	2595	0	1901
$Cd^{2+}+2Br^-$	2502	30	1832	2560	18	1898
$Cd^{2+}+2I^-$	2418	72	1830	2509	43	1895
			Av. 1831			Av. 1898
$Hg^{2+}+2Cl^-$	2578	0	1846	2618	0	1923
$Hg^{2+}+2Br^-$	2514	32	1844	2580	19	1917
$Hg^{2+}+2I^-$	2433	73	1845	2536	41	1922
			Av. 1845			Av. 1921

[a] Calculated from heat of hydration values of the halide ions given in Ref. 32: $-\Delta H^\circ_{aq}=366$, 335 and 294 kJ mol^{-1} for Cl^-, Br^- and I^-, respectively. [b] From heats of hydration given in Ref. 32 and heats of transfer given in Ref. 37; the heats of solvation of the halide ions in DMSO have been calculated to be $-\Delta H^\circ_{sv}=347$, 331 and 307 kJ mol^{-1} for Cl^-, Br^- and I^-, respectively.

of hydration of Zn^{2+}, Cd^{2+}, and Hg^{2+}, Table 4. For each metal ion the three halides should give the same value of $\Delta H^\circ_{aq}(M^{2+})$. Indeed the values found agree within a few kJ mol^{-1}, Table 4. The values of $\Delta H^\circ_{aq}(M^{2+})$ also agree well with those given by Noyes[33] in a compilation of ion hydration data. Recalculating Noyes' values to the same reference point as ours, *i.e.* $-\Delta H^\circ_{aq}(H^+)=1103$ kJ mol^{-1}, gives $-\Delta H^\circ_{aq}=2071$, 1833, and 1848 kJ mol^{-1} for Zn^{2+}, Cd^{2+}, and Hg^{2+}, respectively. Values of $\Delta H^\circ_{aq}(M^{2+})$ for these ions have also been reported by Ladd and Lee.[34] Their values for Zn^{2+} and Cd^{2+}, *viz.* 2067 and 1837 kJ mol^{-1} are close to ours, while the value quoted for Hg^{2+} is considerably more exothermic. Ladd and Lee calculated their $\Delta H^\circ_{aq}(Hg^{2+})$ value from measurements on $HgCl_2$, $HgBr_2$, and $Hg(CN)_2$. By means of eqn. (3) above, they found from these measurements $-\Delta H^\circ_{aq}(Hg^{2+})=1908$, 1942, and 2042 kJ mol^{-1}, respectively. In their evaluation Ladd and Lee apparently assumed that these mercury(II) salts are all completely dissociated in aqueous solution. In fact, they dissociate very little even at low concentrations. Ladd and Lee's values can be corrected by subtracting the enthalpy changes, $\Delta H^\circ_{\beta 2}$, from the calculated hydration enthalpies; *cf.* eqn. (4). Christensen *et al.*[17,35] have determined the enthalpy changes for the complex formation in the mercury(II) halide and cyanide systems. Using their $\Delta H^\circ_{\beta 2}$-values we find the corrected values $-\Delta H^\circ_{aq}(Hg^{2+})=1854$, 1853, and 1840 kJ mol^{-1} from the $HgCl_2$, $HgBr_2$ and $Hg(CN)_2$ data, respectively. These values agree satisfactorily among themselves and the mean, 1849 kJ mol^{-1}, is indeed very close both to our value and to the modified Noyes value quoted above.

The solvation enthalpies of ions differ relatively little between different solvents. The differences are defined as enthalpies of transfer, ΔH°_{tr}. Values of ΔH°_{tr} for salts are readily determined as differences between the values of ΔH°_s in the solvents concerned. Just as for ΔH°_{sv}, however, the values of the individual ions cannot be calculated except by the introduction of an extrathermodynamic assumption. Again, several such assumptions have been proposed. Of these, the assumption that $\Delta H_{tr}(Ph_4As^+)=\Delta H_{tr}(Ph_4B^-)$ has become most widely used, as being both very reasonable and also easy to apply.[36] Based on that assumption Krishnan and Friedman[37] determined values of ΔH°_{tr} of single ions for the transfer between the three solvents propylene carbonate, DMSO, and water. For the halide ions Cl^-, Br^-, and I^-, ΔH°_{tr} (W → DMSO) were found to be 18.8, 3.5, and −12.8 kJ mol^{-1}, respectively, with errors not exceeding 1 or, at most, 2 kJ (*cf.*

also Ref. 38, p. 19. These values together with the $\Delta H_{aq}^{\circ}(L^-)$-values given by Morris[32] yield the absolute heats of solvation of the halide ions in DMSO, see note *b* of Table 4. From these, the values of the heats of solvation of Zn^{2+}, Cd^{2+}, and Hg^{2+} in DMSO, can be calculated, Table 4. The results show that also in DMSO, the values of $\Delta H_{sv}^{\circ}(M^{2+})$ obtained from the chloride, bromide, and iodide data agree very well for each metal ion.

DISCUSSION

For the metal ions studied the heat of solvation is more exothermic in DMSO than in water, indicating a preference for DMSO. For Zn^{2+}, Cd^{2+}, and Hg^{2+}, ΔH_{tr}° (W → DMSO) is found to be −60, −67, and −76 kJ mol^{-1}, respectively, Table 4. Thus, the softer the metal ion, the stronger its preference for DMSO. In both water and DMSO the heat of solvation decreases considerably from Zn^{2+} to Cd^{2+} but increases a little from Cd^{2+} to Hg^{2+}. The total heat is composed of contributions from electrostatic as well as covalent interactions between the metal ion and the solvent molecules. The electrostatic interaction decreases with increasing radius of the ion, *i.e.* in the order $Zn^{2+} > Cd^{2+} > Hg^{2+}$ (for recent values of the octahedral ionic radii, see Refs. 4 and 39). The covalent interaction, on the other hand, increases as the metal ion becomes softer, *i.e.* in the order $Zn^{2+} < Cd^{2+} < Hg^{2+}$. Evidently the sum of the two contributions might pass through a minimum, as is in fact observed for Cd^{2+}.

The heats of solvation of the neutral complexes, ML_2, should follow the same trend as those of the metal ions, if no special effects intervene. For all halides studied, $-\Delta H_{sv}^{\circ}(ML_2)$ is considerably higher in DMSO than in water, Table 1. This is, as previously noted, also the case for the free metal ions. For the complexes, however, the heat differences between the two solvents are relatively much larger than for the free ions. This is evident from the ratio ΔH_{tr}° (W → DMSO)/ΔH_{aq}° which for the free metal ions is ≈ 0.04, much lower than for any of the complexes. For the complexes HgL_2, the ratio even reaches values as high as ≈ 0.5. The solvents thus interact much more specifically with the complexes ML_2 than with the free metal ions. In fact, the absolute values of $-\Delta H_{tr}^{\circ}$ (W → DMSO) for the complexes, 30 to 50 kJ mol^{-1} are not much smaller than for the free ions, 60 to 76 kJ mol^{-1}; Table 1.

For both water and DMSO the values of $-\Delta H_{sv}^{\circ}(ML_2)$ are much higher for the zinc and cadmium halides than for the mercury halides. The reason is certainly that solvent molecules enter into a much closer contact with the metal ion in the case of ZnL_2 and CdL_2 than in the case of HgL_2. The second zinc and cadmium complexes are in solution either octahedral or tetrahedral,[11,12,38] with solvent molecules coordinated about as closely as the other ligands. In the nearly linear mercury complexes, on the other hand, the solvent to metal bonds are certainly all long[8,9] and the interaction consequently much weaker.

Another very striking fact is that while for HgL_2 and CdL_2 the values of $-\Delta H_{sv}^{\circ}(ML_2)$ in both water and DMSO distinctly decrease in the order $Cl^- > Br^- > I^-$, the values for Zn^{2+} increase slowly in the same order. This is probably due to a combination of the following two effects.

Firstly, in the complexes ZnL_2, where the forces between L^- and the hard acceptor Zn^{2+} are of a mainly electrostatic character, the effective charge on the metal ion will be higher the lower the charge density on the ligand, and the higher the effective charge, the stronger the solvation. As the charge density decreases in the sequence $Cl^- > Br^- > I^-$, the effective charge will increase and the solvation consequently become stronger in the same sequence. On the other hand, in complexes like CdL_2 and HgL_2 where the metal ions are soft, the interactions between the ligands and the central ions are of a rather covalent character. The effective charge on the metal ion will in such cases be lower the more covalent the bonding, *i.e.* the softer the ligand. As the softness increases in the sequence $Cl^- < Br^- < I^-$, the effective charge for these soft metal ions decreases, and the solvation consequently becomes weaker in the same sequence.

Secondly, in the zinc chloride and bromide systems, the switch from octahedral to tetrahedral coordination in DMSO occurs mainly at the first step and is certainly complete at the second, while the process occurs later in the zinc iodide and in all the cadmium halide systems. Consequently, the heats of solvation of $ZnCl_2$ and $ZnBr_2$, forming exclusively tetrahedral complexes, should be expected to be relatively low compared to the other complexes which are more extensively solvated. For $ZnCl_2$, the value of $-\Delta H_{sv}^{\circ}$ is in fact even somewhat lower than that of $CdCl_2$, though the opposite could be expected considering the values of ΔH_{sv}° of the respective metal ions.

The two effects discussed are most likely interwoven. The high effective charge left on zinc iodide complexes permits the coordination of more solvent molecules at a later stage of the complex formation than in the case of the chloride and bromide systems, where the effective charge is lower.

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