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Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution. IX. Equilibrium and Enthalpy Measurements on the Mercury(II) Chloride, Bromide, Iodide and Thiocyanate Systems

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The thermodynamics of the formation of mercury(II) halide and thiocyanate complexes in dimethylsulfoxide (DMSO) has been investigated. The order of stability between the halide complexes follows a (*b*)-sequence, $Cl^- < Br^- < I^-$, though much less marked than in water. The levelling between the protic water and the aprotic DMSO is due to characteristic changes in both the enthalpy and the entropy contributions to the overall stabilities. In water, the values of both ΔH_j° and ΔS_j° differ considerably between the systems; in DMSO these differences are largely smoothed out. As to ΔH_j°, a marked levelling also takes place between the consecutive steps of each system while the contrary is true for ΔS_j°. Especially the values of ΔS_1° are very large in DMSO. The thiocyanate ion behaves in many respects as the iodide ion but also has several traits of its own.

In water, hydrogen bonds are responsible both for an ordered solvent structure and a preferential solvation of ligands prone to hydrogen bonding, such as Cl^-. In DMSO, where no hydrogen bonds can be formed, these possibilities do not exist. The differences found between the two solvents for the systems investigated have been rationalized on this basis.

The complex formation of the divalent d^{10} acceptors Zn^{2+}, Cd^{2+} and Hg^{2+} with halide and thiocyanate ions reflects very different acceptor properties. In water, the halide complexes of Hg^{2+} are very stable and their stabilities moreover follow a very marked (*b*)-sequence: $Cl^- < Br^- < I^-$.[1-3] With Cd^{2+}, much less stable complexes are formed, and the (*b*)-sequence is also much less marked.[3,4]. With Zn^{2+}, only very weak complexes are formed, and their stabilities moreover follow an (*a*)-sequence: $Cl^- > Br^- > I^-$.[3,5]

In the aprotic solvent dimethylsulfoxide, (DMSO), the (*a*)-sequence of the Zn^{2+} complexes becomes much more marked,[6] while the mild (*b*)-sequence of the Cd^{2+} complexes turns into an (*a*)-sequence.[7] The complexes also become more stable than in water. These stability changes between the protic water and the aprotic DMSO are no doubt brought about mainly by two factors: the changes of the solvation of the ligands between the two solvents, and the less ordered structure of DMSO relative to water.[7-9] The former factor is the main cause of the change in the relative stabilities of the halide complexes. The latter is the main cause of the general increase of the stabilities. Both effects are, in the end, due to the hydrogen bonding properties of the water molecules, a mode of bonding which has no counterpart in the aprotic DMSO. The conclusions drawn from the halide complex formation are further strengthened by the behaviour of the thiocyanate ion. For this ligand, the changes in the stabilities of the complexes between water and DMSO sre reminiscent of those found for the iodide ion.[8,9] This is to be expected, as both ligands have little capacity for hydrogen bonding.

These conclusions are founded on a scrutiny of all the thermodynamic functions ΔG_j°, ΔH_j° and ΔS_j° of the consecutive complex formation reactions. For each system, not only the stabilities but also the heats of reaction have been measured. The stepwise stability constants K_j yield the free energy changes ΔG_j°, and by combining these with the enthalpy changes ΔH_j° the entropy changes ΔS_j° are finally

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found.

For Hg^{2+}, no complete investigation of the halide and thiocyanate complex formation has so far been done. The existing data indicate, however, that the (*b*)-sequence persists in DMSO, though much less marked than in water.[10-12] From calorimertric data referring to the two later steps in the bromide and iodide systems it is also clear that an extensive levelling occurs between the values of ΔH_j° of the different halides.[13]

In the present study, all the thermodynamic functions pertaining to the Hg^{2+} complexes have been determined under the same conditions as used before for the Zn^{2+} and Cd^{2+} complexes, *viz.* in 1 M ammonium perchlorate, at 25 °C. This ionic medium allows a potentiometric determination of the stability constants by means of the mercury electrode while this electrode is attacked in water-free lithium sodium and tetraethylammonium perchlorate media.[14] The heats of reaction have been determined in separate calorimetric measurements.

EXPERIMENTAL

Chemicals. The source of Hg^{2+} was the solid $Hg(ClO_4)_2.4DMSO$, prepared and analyzed as described previously.[15] The dimethylsulfoxide was purified, stored and analyzed as before.[16] In the later experiments a volatile impurity still present was removed by a stream of dry nitrogen gas before the solvent was used. The mercury(II) perchlorate solutions were always prepared immediately before use, as their concentration decreases with time. For a 10 mM solution a decrease of 1 % was found after 48 h, independent of whether the solutions had been stored in darkness or in diffuse daylight. Other solutions were prepared as before.[16] Double destilled mercury was used without further purification. The cadmium amalgam contained 6.5 % Cd, and was prepared and stored as described previously.[17]

Potentiometric measurements. Metallic mercury reduces the solvated mercury(II) ion according to $Hg(l)+Hg^{2+} \rightleftharpoons Hg_2^{2+}$. In the present medium,[18] the reproportionation constant $K_R=[Hg_2^{2+}]/[Hg^{2+}]=24.5\pm2.0$ This value is considerably smaller than in aqueous media,[19,20] but also in DMSO Hg_2^{2+} evidently predominates strongly over Hg^{2+} at equilibrium in solutions of the pure solvates. The mercury electrode can therefore only be used in the presence of ligands that prefer mercury(II) to mercury(I) so markedly that the divalent state is sufficiently stabilized. Fortunately, this is the case in the systems investigated here, where no appreciable reproportionation is found for ligand numbers $\bar{n} \gtrsim 1.5$. This implies that all the constants K_j can be determined.

To ensure that no solutions containing mercury(I) were included in the calculations, the mercury electrode compartment initially contained a ligand solution of a concentrations, C_L', high enough to bring about a value of $\bar{n}$ close to the upper limit of 4. In most cases, the solution initially also contained mercury(II), of the concentration $C_M'=10$ or 20 mM; corresponding values of C_L' were 60 and 100 mM, respectively. To these solutions, aliquots of solutions of the same mercury(II) concentration C_M', but containing no ligand, were added. During the titrations, the mercury(II) concentration thus stayed constant $=C_M'$ while the ligand concentration, and hence $\bar{n}$, decreased. In some series, however, the initial ligand solutions, of $C_L'=15.35$ or 70 mM, contained no mercury(II). During the titrations with solutions of $C_M'=5$, 10 and 20 mM, respectively, the mercury concentration therefore increased while the concentration of ligand decreased. This procedure implies a more rapid decrease of the free ligand concentration [L], and hence of $\bar{n}$. A cadmium amalgam electrode, with a cadmium(II) concentration of 20 mM and working in the same medium as the mercury electrode, was used as a reference. The emfs measured attained their final values within $\simeq$20 min. They were generally reproducible within 0.3 mV and stayed constant within 0.5 mV for at least 15 hours. To exclude moisture, the titrations were performed in dry atmosphere in a glove box. In addition, dry nitrogen saturated with DMSO was bubbled through the solutions during the measurements.

The emfs of the cells are given by $E=E^\circ+(RT/2F)\ln[Hg^{2+}]$ where E° is the potential of a standard mercury half-cell $Hg(l)/Hg^{2+}$ relative to the cadmium reference cell used here. To relate the emfs measured with the concentrations $[Hg^{2+}]$ it is necessary to know E°. On account of the reproportionation reaction, this quantity cannot be directly measured but can be found from measurements of the $Hg(l)/Hg_2^{2+}$ and Hg_2^{2+}/Hg^{2+} couples. Under the present conditions, $E^\circ=1190.65$ mV.[18]

The numerical calculations were performed by means of the computer program EMK.[21a] The program had to be slightly modified, however, as the emfs $E-E^\circ$ of the present measurements always refer to galvanic cells with one hypothetical half-cell containing 1 M $[Hg^{2+}]$ while in the previous measurement the input values E_M referred to differences that were actually measured in each series.

Calorimetric measurements. The calorimeter and the procedure of measurements have been described previously.[7,22,23] The calibration constant ε_v was redetermined and found to depend upon the total volume, V ml, according to $\varepsilon_v=a+b(V-80)$, where $a=0.9501\pm0.0025$ J^{-1} and $b=1.3361\pm$ 0.0028

$J^{-1}ml^{-1}$. For the halide systems, gold could still be used as material for calorimeter parts (inner vessel, *etc.*) in contact with mercury(II) complex solutions, but this was not possible for the thiocyanate system. In the presence of this ligand, metallic gold is very rapidly oxidized by mercury(II), as is evident from the almost instantaneous formation of gold amalgam. Most probably, the formation of very strong gold(I) thiocyanate complexes brings down the oxidation potential of gold in DMSO to such a low value that the oxidation by mercury(II) becomes feasible, in spite of the fact that also mercury(II) is considerably stabilized by thiocyanate complex formation. An analogous reaction is brought about by triphenylphospine in DMSO.[24] In this case, rhodium coating of the gold parts has been found to prevent the reduction of mercury(II). Also the thiocyanate system could be measured in this modified calorimeter. One reason why rhodium is not at all attacked might be that this metal, contrary to gold, does not form an amalgam.

For each halide system, twelwe titration series were performed. In six of these, the calorimeter vessel initially contained mercury(II) perchlorate solutions and in the other ones solutions of the dihalide complex HgX_2 With thiocyanate, seven titrations were performed, all starting with perchlorate solutions in the calorimeter. The initial solutions, of 80 ml volume, had mercury(II) concentrations C'_M ranging from 4.0 to 16.0 mM. To these solutions, aliquots of ligand solution, of $C'_L =$ 100 mM, were added, until a total solution volume of 100 ml was reached. A volume of 20 ml was then withdrawn, and another titration with 20 ml ligand solution then performed. The procedure was repeated until a value of $\bar{n}$ close to 4 had been reached.

Heats of dilution were measured not only for Hg^{2+}, but also for the complexes HgX^+, HgX_2 and HgX_3^-. Such measurements are feasible in the present systems where each complex HgX_j^{2-j} predominates completely $\bar{n}=j$. The heats were determined by titrating 16 mM solutions of each species with 1 M ammonium perchlorate. For Hg^{2+}, the heat of dilution was exothermic and relatively large, 0.08 J per ml solution added. For the complexes, the effects were quite small. The heats of dilution of the ligands were determined analogously.[7]

From the calorimetric data, the enthalpy changes have been calculated by the least squares program KALORI,[21b] with the values of β_j found in the potentiometric measurements as fixed parameters. In all the systems investigated, the complexes formed are too stable to allow an independent determination of β_j from the calorimetric data.[25]

Warning. Great caution must be exercised when handling DMSO solutions of mercury(II), mainly because of the skin-penetrating properties of the solution.[26,27].

RESULTS

For all the halide systems, the potentiometric titrations show extended regions of low buffer capacity around the molar ratios 3 and 2 of ligand to mercury(II). This indicates that each consecutive complex HgX_j^{2-j} loses one ligand almost completely before a further ligand starts to dissociate from the complex formed. Consequently, each complex predominates in the solutions over a fairly wide range of $[X^-]$, characterized by a practically constant ligand number $\bar{n}\simeq j$. As already mentioned, this circumstance allows the separate determination of the heat of dilution for each species. Moreover, the amount of ligand added between the equivalence points provides a check of the concentration of mercury(II) present. The values of C'_M found in this way were throughout somewhat lower than those calculated from the analysis of the solid solvate used. As the difference was independent of C'_M, it could hardly be due to a reproportionation involving the formation of complexes of mercury(I). This conclusion was confirmed beyond doubt by the calorimetric measurements, where no repro-

Table 1. Overall stability constants (β_j/M^{-j}) of the mercury(II) halide and thiocyanate complexes in DMSO at 25 °C. Medium 1 M NH_4ClO_4. The limits of error refer to three standard deviations; NP denotes the number of observations (emfs measured) for each system.

Ligand	Cl^-	Br^-	I^-	SCN^-
β_1	$(7.41\pm0.53)\times10^{10}$	$(1.38\pm0.16)\times10^{12}$	$(3.31\pm0.29)\times10^{13}$	$(2.14\pm0.17)\times10^{9}$
β_2	$(9.26\pm0.77)\times10^{17}$	$(1.57\pm0.21)\times10^{20}$	$(1.88\pm0.13)\times10^{23}$	$(9.85\pm1.05)\times10^{14}$
β_3	$(9.13\pm1.03)\times10^{21}$	$(2.16\pm0.40)\times10^{25}$	$(1.92\pm0.14)\times10^{29}$	$(8.93\pm1.31)\times10^{17}$
β_4	$(1.09\pm0.24)\times10^{24}$	$(7.42\pm2.16)\times10^{27}$	$(8.12\pm0.49)\times10^{31}$	$(1.84\pm0.51)\times10^{20}$
NP	323	372	346	317

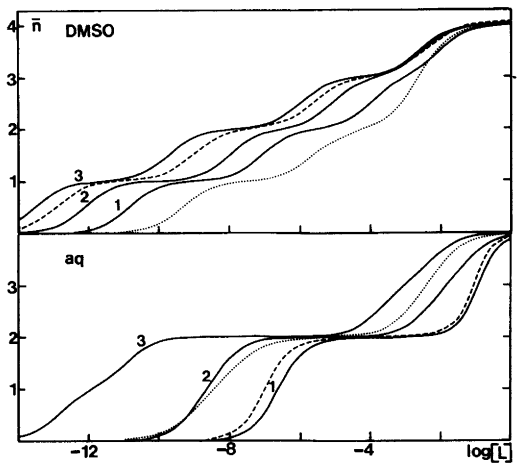

Fig. 1. The complex formation curves of the mercury(II) halide and thiocyanate systems in DMSO and aqueous solutions, at 25 °C. DMSO; fulldrawn curves: chloride (1), bromide (2) and iodide (3); dotted curve: thiocyanate; all in 1 M NH_4ClO_4; dashed curve: bromide in 0.1 M NH_4ClO_4. Aq; fulldrawn curves: chloride (1), bromide (2) and iodide (3), in 0.5 M $NaClO_4$; dotted curve: thiocyanate, in 1 M $NaClO_4$; dashed curve: chloride, in 3 M $NaClO_4$.

portionation is possible. The values of ΔH_j° of the consecutive steps are different enough to produce fairly well-defined equivalence points. The values of C_M' calculated from these agree with the ones found potentiometrically. Most likely, the discrepancy is due to an impurity in the DMSO, with a strong affinity for mercury(II). The presence of dimethylsulfide might be suspected. As this compound is quite volatile (*b.p.* 37.3 °C), it should be largely removed by a stream of nitrogen passing through the solvent. In the later series of measurements, this expedient was successfully tried. While the discrepancies amounted to 0.3 or 0.4 mM when ordinary DMSO was used, they were suppressed to at most 0.1 mM when the DMSO had been treated with nitrogen for 1 h. The values determined by the equivalence points were always used in the calculations which gave consistent results.

In the thiocyanate system, the concentration of the complex $Hg(SCN)_3^-$ never exceeds $\simeq 50\,\%$ of the total mercury(II) concentration. Consequently, no equivalence point develops at $\bar{n}=3$. The value of C_M' to be used cannot, therefore, be determined directly from the potentiometric measurements. The calorimetric measurements provide, however, a precise value of the correction, *viz.* 0.4 mM, from

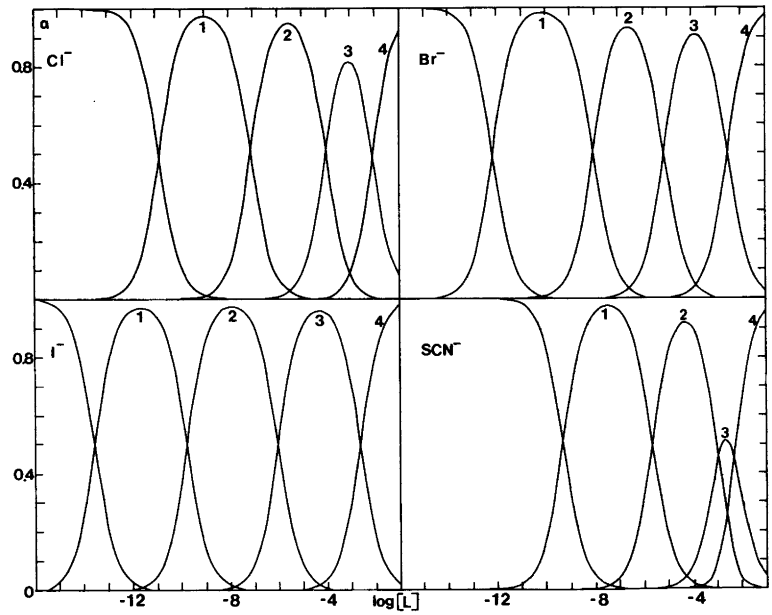

Fig. 2. Distribution in DMSO of the species present in the mercury(II) halide and thiocyanate systems, as a function of the free ligand concentration. Medium 1 M NH_4ClO_4; 25 °C.

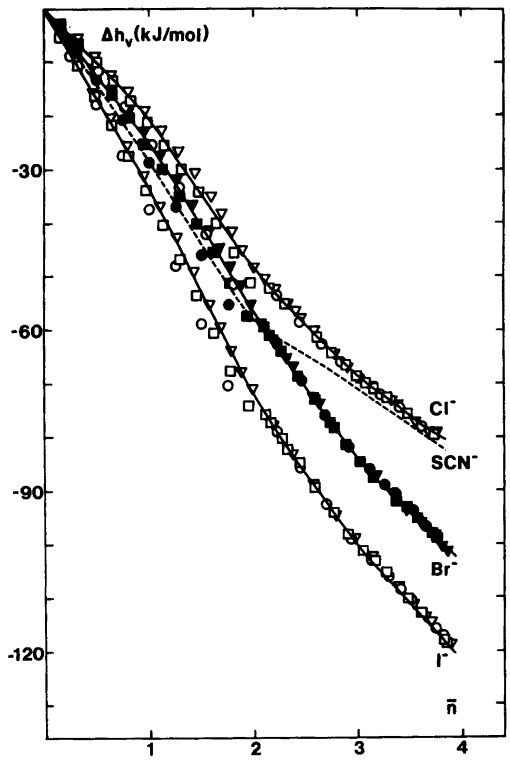

Fig. 3. The total molar enthalpy change Δh_v as a function of the ligand number $\bar{n}$ for the mercury(II) halide systems in DMSO. The points refer to the values actually measured in the series of $C_M'=4$, 8 and 16 mM (circles, squares and triangles, respectively; for the sake of clarity, those referring to the bromide system are filled). The fulldrawn curves have been calculated from the values of β_j and $\Delta H^\circ_{\beta j}$ determined (Tables 1 and 2). The curve of the thiocyanate system (from Fig. 4) has been included for comparison (dashed). Medium 1 M NH_4ClO_4; 25 °C.

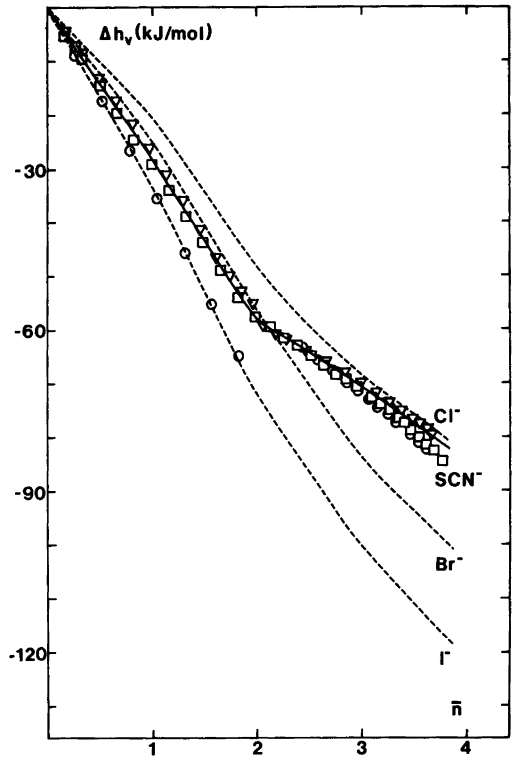

Fig. 4. The total molar enthalpy change Δh_v as a function of the ligand number $\bar{n}$ for the mercury(II) thiocyanate system in DMSO, measured under the same condirions as for the halide systems (*cf.* Fig. 3). The curves of those systems have moreover been included for comparison.

the well-defined equivalence point $\bar{n}=2$. With this correction applied, also the potentiometric data yield a consistent result.

For all the systems, the potentiometric data can be interpreted by the formation of the four mono-

Table 2. Overall enthalpy changes ($\Delta H^\circ_{\beta j}$/kJ mol^{-1}) for the formation of the mercury(II) halide and thiocyanate complexes in DMSO, at 25 °C. Medium 1 M NH_4ClO_4. The limits of error refer to three standard deviations; NP denotes the number of observations (aliquots added) for each system.

Ligand	Cl^-	Br^-	I^-	SCN^-
$-\Delta H^\circ_{\beta 1}$	20.3±0.8	24.7±0.8	33.2±0.8	28.1±0.9
$-\Delta H^\circ_{\beta 2}$	48.8±1.2	56.6±1.2	72.6±1.2	59.1±1.3
$-\Delta H^\circ_{\beta 3}$	68.9±1.4	84.4±1.3	100.7±1.4	68.9±2.3
$-\Delta H^\circ_{\beta 4}$	82.9±1.9	103.5±1.6	121.8±1.7	85.6±2.6
NP	255	253	260	180

nuclear complexes HgX_j^{2-j}, $j=1-4$, provided that the value of $\bar{n}>1.45$. The emfs measured below this limit become increasingly ill-fitted to this scheme as the value of $\bar{n}$ decreases which evidently reflects the growing reproportionation.

The overall stability constants calculated are listed, with their limits of error, in Table 1. The complex formation functions found from these constants are presented in the upper part of Fig. 1. The predominance of each consecutive complex Hg_j^{2-j} (with the sole exception of $Hg(SCN)_3^-$) at the value of $\bar{n}=j$ is immediately evident. The conditions are even more strikingly illustrated by the distribution curves presented in Fig. 2. The maximum share of the total mercury(II) concentration (attained at $\bar{n}=j$) is for most of the complexes well over 90 %. The third complex is throughout the least stable relative to its neighbours; as already pointed out, this applies especially to $Hg(SCN)_3^-$.

The quantity directly obtained from the calorimetrical measurements, *viz.* the heat evolved per mol mercury(II), Δh_v is plotted as a function of $\bar{n}$ for the various systems in Figs. 3 and 4. All the complexes are evidently formed in exothermic reactions. As already mentioned, the differences between the values of ΔH_j° for two consecutive steps are in most instances so large that marked deflections occur at the equivalence points. The values of the overall enthalpy changes $\Delta H_{\beta j}^\circ$ calculated from the values of Δh_v are listed, with their limits of error, in Table 2. In Tables 1 and 2, the number of observations performed for each system (NP) is also reported.

Table 3. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j°, ΔH_j°/kJ mol^{-1}; ΔS_j°/JK^{-1} mol^{-1}) for the stepwise formation of mercury(II) halide and thiocyanate complexes in DMSO and water, at 25 °C.

	DMSO 1 M NH_4ClO_4[a]				Water 0.5 M $NaClO_4$[b]			1 M $NaClO_4$[c]
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-
$\log K_1$	10.87	12.14	13.52	9.33	6.74	9.05	12.87	9.08
$\log K_2$	7.10	8.06	9.76	5.66	6.48	8.28	10.95	7.78
$\log K_3$	3.99	5.14	6.01	2.96	0.85	2.41	3.78	2.84
$\log K_4$	2.08	2.54	2.62	2.31	1.00	1.26	2.23	1.97
K_1/K_2	5930	12100	5810	4660	1.8	5.9	83	20
K_2/K_3	1270	830	5540	510	4×10^5	7×10^5	1.5×10^7	9×10^4
K_3/K_4	82	400	2450	4.4	0.7	14	35	7
$-\Delta G_1^\circ$	62.0	69.3	77.2	53.3	38.5	51.7	73.5	51.8
$-\Delta G_2^\circ$	40.5	46.0	55.7	32.3	37.0	47.3	62.5	44.4
$-\Delta G_3^\circ$	22.8	29.3	34.3	16.9	4.9	13.8	21.6	16.2
$-\Delta G_4^\circ$	11.9	14.5	15.0	13.2	5.7	7.2	12.7	11.2
$-\Delta H_1^\circ$	20.3	24.7	33.2	28.1	24.7	42.2	75.3	49.7
$-\Delta H_2^\circ$	28.5	31.9	39.4	31.1	28.9	44.8	67.8	50.4
$-\Delta H_3^\circ$	20.1	27.8	28.1	9.7	9.2	12.0		20.4
$-\Delta H_4^\circ$	14.0	19.1	21.1	16.8	0.4	17.2		21.0
ΔS_1°	140	149	148	85	46	32	−6	7
ΔS_2°	40	47	54	4	27	8	−18	−20
ΔS_3°	9	5	21	24	−14	6		−14
ΔS_4°	−7	−16	−21	−12	20	−33		−33
$-\Delta H_{\beta4}^\circ$	82.9	103.5	121.8	85.6	62.4	116.2	185	141.5
$\Delta S_{\beta4}^\circ$	182	186	202	100	79	13	−49	−60

[a] This work. The values pertaining to the thiocyanate system differ slightly from a preliminary set published previously[9] which had been calculated without correction for the impurity present in the solvent (*cf.* above). [b] Refs. 2, 39–42. [c] Ref.s. 43, 44.

DISCUSSION

Quantities related to the consecutive steps. From the values of β_j obtained, the stepwise stability constants K_j and the standard free energy changes ΔG_j° are calculated for each consecutive step. From the values of $\Delta H_{\beta j}^\circ$, the stepwise enthalpy changes ΔH_j° are calculated, and by combining these with ΔG_j° the stepwise entropy changes ΔS_j° are obtained. In Table 3, the values found are compared with those previously determined for the same system in aqueous solutions. Here, the most representative results refer to sodium perchlorate media but such a change of medium certainly means little compared to the change of solvent.[3] This is also confirmed by the stability constants found for the present systems in DMSO solutions containing various supporting electrolytes, see Table 4. The ratios K_j/K_{j+1} have also been entered for both solvents.

Stability constants, and their ratios. Also in DMSO, the stabilities of the halide complexes follow a (*b*)-sequence, though much less marked than in water. The present study thus definitely confirms this main result of the previous investigations.[10-12] As these moreover refer to other media, *viz.* 0.1 M Et_4NClO_4 and 1 M $NaClO_4$ or $LiClO_4$, it is evident that the influence of the medium is indeed small compared to that of the solvent. Also measurements of the mercury(II) bromide system performed in 0.1 M NH_4ClO_4 support this conclusion,[28] see Table 4.

Though the main picture is not changed, marked differences nevertheless exist between 1 M NH_4ClO_4 on one hand, and the other media on the other. These are quite substantial for chloride, smaller for bromide and very small for iodide. They are certainly due to hydrogen bond formation between NH_4^+ and the halide ions, strongly decreasing in strength in the order $Cl^- > Br^- > I^-$.[28] At high values of $[NH_4^+]$ this complex formation evidently involves a strong competition for ligands of marked hydrogen bonding properties.

The levelling implies large increases in the overall stabilities of the chloride complexes, and sizable ones in the stabilities of the bromide complexes, while the stabilities of the iodide complexes change very little. The changes are very different for the consecutive steps, however (Table 3). Especially the first and third steps are favoured in DMSO relative to water. The second step, on the other hand, shows only a modest increase of stability even in the chloride system and a decrease in the bromide and, especially, in the iodide system. The thiocyanate complexes behave much like the iodide ones, though they are, on the whole, even less favoured by the transfer to DMSO. Especially the strong suppression of the second complex should be noted.

The changes of the relative stabilities of the consecutive complexes taking place on the transfer from water to DMSO are reflected in large changes

Table 4. Comparison between stability constants (β_j/M^{-j}) of mercury(II) halide and thiocyanate complexes determined in various DMSO media, at 25 °C.

	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-
0.1 M $(C_2H_5)_4NClO_4$[a]					1 M $LiClO_4$[b]	1 M $NaClO_4$[b]		
log β_2	21.2	22.2	24.2	16.1	21.1			16.1
log β_3	26.9	28	30.4	19.1	26.9	28.3	30.4	19.0
log β_4		30.4	32.6	21.2	28.3	29.2	32.3	20.4
Medium unknown[c]								
log β_1	13.40	14.60	16.00	10.70				
1 M NH_4ClO_4[d]					0.1 M NH_4ClO_4[e]			
log β_1	10.87	12.14	13.52	9.33	12.92			
log β_2	17.97	20.20	23.27	14.99	21.96			
log β_3	21.96	25.33	29.28	17.95	27.62			
log β_4	24.04	27.87	31.91	20.26	30.22			

[a] Ref. 10. [b] Ref. 11. [c] Ref. 12; presumably no supporting salt added. [d] This work. [e] Ref. 28.

of the ratios K_j/K_{j+1}, see Table 3. In water, the ratios K_2/K_3 are very large, as is shown by the very extended horisontal portions of the complex formation curves found at $\bar{n}=2$, *cf.* lower part of Fig. 1. These ratios are much smaller in DMSO, but still large enough to bring about marked plateaus at $\bar{n}=2$, *cf.* upper part of Fig. 1. The ratios K_1/K_2 and K_3/K_4 are generally quite small in water, and therefore no inflexions develop at $\bar{n}=1$ and 3, except for a very slight one at $\bar{n}=1$ in the iodide curve (Fig. 1). In DMSO, on the other hand, the ratios are large enough to bring about marked plateaus, except at $\bar{n}=3$ in the thiocyanate curve. The relative changes of stability between water and DMSO thus result in that predominance of each complex (except $Hg(SCN)_3$) within a certain range of [L] which is such a striking feature of the complex formation in the latter solvent, see Figs. 1 and 2.

Enthalpy changes. The levelling of the stabilities is brought about by a very considerable levelling of the values of ΔH_j° between water and DMSO (Table 3). Especially for the first two steps, the effect is very large. While the differences in water between the chloride and iodide systems are 50.6 for ΔH_1° and 38.9 kJ mol^{-1} for ΔH_2°, respectively, they are only 12.9 and 10.6 kJ mol^{-1} in DMSO. Analogous decreases, though smaller, are found between chloride and bromide. As already mentioned, this levelling must mainly be due to the relative change of solvation of the ligands. While Cl^-, prone to hydrogen bonding, is more strongly solvated in the protic water than in the aprotic DMSO, the contrary is true for I^-, of little hydrogen bonding capacity. This is reflected in the transfer enthalpies between water and DMSO, ΔH_{tr}° (W→DMSO), which for these ions are 18.8 and −12.8 kJ mol^{-1}, respectively.[9,29] Consequently, the difference $-[\Delta H_{sv}^\circ(Cl)-\Delta H_{sv}^\circ(I^-)]$ between the solvation enthalpies is 31.6 kJ mol^{-1} smaller in DMSO than in water. This implies *per se* a decrease by this amount of the differences between the values of ΔH_j° on a transfer of the chloride and iodide systems from water to DMSO. In the case of Br^- ΔH_{tr}°(W→DMSO)=3.5 kJ mol^{-1} which definitely indicates a capacity for hydrogen bonding in water.[29] This is also in compliance with the behaviour of the bromide complexes on their transfer from water to DMSO.

Especially for I^-, but also for Br^-, the values of $-\Delta H_1^\circ$ decrease very much from water to DMSO (Table 3). This must mainly be due to the stronger solvation of Hg^{2+} in DMSO,[30] reflected in the large value of ΔH_{tr}°(W→DMSO)=−76 kJ mol^{-1}. For I^-, the effect is further enhanced by the higher value of $-\Delta H_{sv}^\circ(I^-)$. That the total effect does not amount to more than 42.1 and 17.5 kJ mol^{-1} for I^- and Br^-, respectively, must largely be due to the circumstance that also the values of $-\Delta H_{sv}$ (HgX^+) are certainly higher in DMSO than in water. Moreover, the lower value of the dielectric constant in DMSO, $D=46.4$,[26] must contribute to more exothermic values of ΔH_1°, by increasing the electrostatic interaction between Hg^{2+} and X^-. In the case of Cl^-, the changes between water and DMSO in the terms contributing to ΔH_1° almost compensate each other. The values of ΔH_2° show similar trends, though less marked (Table 3). For I^- and Br^-, the second step is still much less exothermic in DMSO than in water, and the reasons must be analogous to these advanced for the first step.

In contrast to ΔH_1° and ΔH_2°, the values of ΔH_3° and ΔH_4° are generally more exothermic in DMSO than in water. This applies especially to the chloride system. The reason for this difference between the earlier and later steps is certainly that the desolvation has gone very far with the formation of the second complex. In the following steps, the desolvation enthalpies should therefore not be very important and hence not able to bring about a decrease of $-\Delta H_3^\circ$ or $-\Delta H_4^\circ$ when the systems are transferred from water to DMSO. This interpretation also agrees with the magnitude of the entropy changes of the various steps, as will be further discussed below.

That the desolvation is indeed very extensive after the first two steps has been shown by independent thermodynamic measurements. Thus, the solvation enthalpies $\Delta H_{sv}^\circ(HgX_2)$ of the neutral complexes are only $\simeq 5\,\%$ of $\Delta H_{sv}^\circ(Hg^{2+})$.[30] Even more significant, they are less than half of the solvation enthalpies of the formally analogous complexes CdX_2 and ZnX_2, in spite of the fact that $\Delta H_{sv}^\circ(Hg^{2+})$, $\Delta H_{sv}^\circ(Cd^{2+})$ and $\Delta H_{sv}^\circ(Zn^{2+})$ are all of the same order of magnitude.[30]

A direct proof of this desolvation has further been provided by structure determinations of the species present in the solutions, performed by means of X-ray diffraction studies. In solution,[15] Hg^{2+} coordinates octahedrally six DMSO (by their oxygens) at the close distance 2.39 Å (in the corresponding solid solvate[31] the distance is 2.34 Å). In the complexes HgX_2, no Hg−O distances can be discerned. An approximate value can still be determined for the distances Hg to S, however. These are

Table 5. Previously determined stepwise stability constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j°, ΔH_j°/kJ mol^{-1}; ΔS_j°/JK^{-1} mol^{-1}) for the formation of mercury(II) halide and thiocyanate complexes in DMSO, at 25 °C.

1 M $NaClO_4$[a]			Li-medium[b]			Na-medium[c]	
	Br^-	I^-	Cl^-	Br^-	I^-	I^-	SCN^-
$\log K_3$	5.6	6.1					
$\log K_4$	2.65	2.55					
K_3/K_4	890	3310					
$-\Delta G_3^\circ$	32.0	34.8					
$-\Delta G_4^\circ$	15.1	14.7					
$-\Delta H_3^\circ$	26.9	26.8	20.9	23.4	30.9	32.2	
$-\Delta H_4^\circ$	22.7	22.8	13.4	13.8	11.3	11.3	15.4
ΔS_3°	17	27					
ΔS_4°	−25	−27					

[a]Ref. 13. [b]Ref. 34. [c]I^-: Ref. 35; SCN^-: Ref. 34.

≃0.2 Å longer than in $Hg(DMSO)_6^{2+}$, corresponding to Hg−O distances ≃2.6 Å.[32] The considerable lengthening means a much weaker bond. The number of Hg−O bonds in the complexes HgX_2 is difficult to ascertain, but is in any case not higher than four which, of course, also contributes to a weaker overall solvation.

A previous calorimetric determination[13] of ΔH_3° and ΔH_4° for the bromide and iodide systems in 1 M $NaClO_4$ agrees quite well with the present results, see Table 5. Also the values of K_3 and K_4 calculated from these measurements are in fair agreement with those found potentiometrically in the present study. On account of the low solubility of NaCl in DMSO,[33] the chloride system could not be investigated.

In other calorimetric investigations,[34,35] the formation of the complex ML_j has been assumed to be complete when $C_L/C_M = j$ (*i.e.* $[L] \simeq 0$ over the whole range of complex formation). As this is certainly not the case in the last step, the values of $-\Delta H_4^\circ$ calculated are much too low (Table 5). Also the values of $-\Delta H_3^\circ$ differ considerably from those found in the other investigations, however, see Tables 3 and 5.

The changes of ΔH_j° taking place between the two solvents imply that the pattern which is so characteristic for aqueous solutions, with $-\Delta H_1^\circ$ and $-\Delta H_2^\circ$ large and of about the same size, and with $-\Delta H_3^\circ$ and $-\Delta H_4^\circ$ much smaller, is largely smoothed out in DMSO (Table 3). In this solvent, the change of structure[32] taking place between the digonal HgX_2 and the trigonal, or pyramidal, HgX_3^- is therefore not at all as clearly indicated by the ΔH_j° values as it is in water.

A characteristic feature of all the systems in DMSO is, on the other hand, that $-\Delta H_2^\circ > -\Delta H_1^\circ$. Evidently, the desolvation taking place in the first step is so extensive, and the desolvation enthalpy needed consequently so large, that the net enthalpy change becomes less exothermic than for the second step, in spite of the fact that the heat evolved on the formation of the new Hg−X bond is certainly larger in the first step. The latter conclusion rests on the observation that the length of the Hg−X bond generally increases with the number of ligands coordinated, indicating a corresponding decrease in the bond strength.[32,36,37] This decrease should, moreover, be the main cause of the monotonous decrease of $-\Delta H_j^\circ$ found in DMSO between the later steps of all the halide systems (Table 3 and Fig. 5).

In the thiocyanate system, the values of $-\Delta H_1^\circ$ and $-\Delta H_2^\circ$ decrease between water and DMSO in much the same manner as in the halide systems, Table 3. The higher steps behave differently, however. Contrary to what is found for the halides, they become less exothermic in DMSO, and the pattern is moreover different, with $-\Delta H_4^\circ > -\Delta H_3^\circ$. Seemingly, the structures of the complexes in solution are

not wholly analogous to those formed in the halide systems, as is further indicated by the entropy changes discussed below.

For the overall reactions $Hg^{2+} + 4X^- \rightleftharpoons MX_4^{2-}$, the changes between water and DMSO mean a large decrease of enthalpy stabilization for $X^- = I^-$ and SCN^-, a modest decrease for Br^- and a modest increase for Cl^-, *cf.* the values of $\Delta H^\circ_{\beta 4}$ in Table 3.

Entropy changes. Relative to water, the entropy terms are so favourable in the aprotic DMSO that the loss of stabilities due to the less exothermic values of ΔH°_1 and ΔH°_2 are more than compensated. The values of ΔS°_1, are indeed huge in DMSO and also the values of ΔS°_2 are quite considerable, see Table 3. For both ΔS°_1 and ΔS°_2, the differences between water and DMSO grow from Cl^- to I^-. This results in a marked levelling of the values of the different halides, just as has been found also in the case of ΔH°_1 and ΔH°_2.

The large increases of ΔS°_1 and ΔS°_2 relative to water are no doubt mainly due to the lower degree of order in DMSO. In water, the desolvation reactions imply that water molecules leave the hydrates for the bulk water which, however, has a fairly well-ordered structure brought about by intermolecular hydrogen bonds. Such a process involves, at most, a modest entropy gain. If the formation of the complex *per se* means a sufficiently large increase of the degree of order, as is the case for I^-, a net loss of entropy may even occur. In DMSO, on the other hand, solvent molecules leave the solvates for a fairly unstructured bulk solvent which results in a large entropy gain. A further increase is brought about by the circumstance that the DMSO solvates have to be more strictly ordered than the corresponding hydrates, in order to accomodate the more bulky and less symmetrical DMSO molecules in the preferred arrangements. This is very evident in the case of the hexasolvates,[15,31,38] $Hg(DMSO)_6^{2+}$ and $Hg(H_2O)_6^{2+}$, but presumably applies also to the solvates of the complexes and the ligands.

In concentrated solutions of the mercury(II) halide and thiocyanate systems in DMSO, the entropy stabilization of the first complex breaks down. This is evidently due to the fact that in such solutions a fair amount of order is imposed on the solvent as a whole, *i.e.* the regions of unordered bulk solvent cease to exist. As a consequence, the first complex, so prominent in dilute solutions, will be more or less completely disproportionated.[32,36,45]

The values of ΔS°_3 and ΔS°_4 are, on the other hand, fairly small in DMSO; ΔS°_3 slightly positive, ΔS°_4 slightly negative. This again indicates that the desolvation is much less important in the later steps and especially for the formation of MX_4^{2-}. This is also confirmed by the fact that the values of ΔS°_3 and ΔS°_4 in DMSO are not drastically different from those found in water.

In water, the total entropy change $\Delta S^\circ_{\beta 4}$ for the reaction $Hg^{2+} + 4\ X^- \rightleftharpoons HgX_4^{2-}$ decreases fairly rapidly in the order $Cl^- > Br^- > I^-$, reflecting the

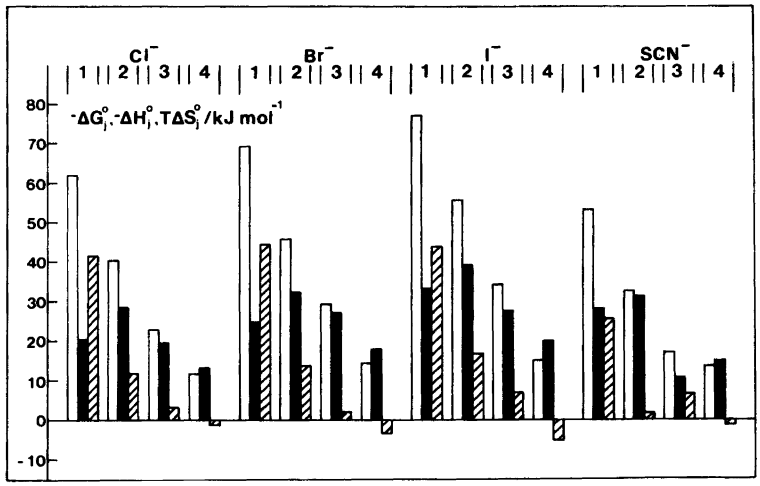

Fig. 5. The changes of free energy (white), enthalpy (black) and entropy (hatched) for the consecutive steps of the mercury(II) halide and thiocyanate systems in DMSO. Medium 1 M NH_4ClO_4, 25 °C.

strong decrease of solvation of these ligands in the same order. In DMSO, however, much the same values of $\Delta S^\circ_{\beta 4}$ are found for all halides. The differences in solvation are much smaller in this solvent and what remains is evidently compensated by other entropy contributions.

For the thiocyanate complexes the entropy changes are throughout less favourable than for the halides, see Table 3. This is evidently due to the loss of conformational entropy accompanying the coordination of a ligand of much lower symmetry than the halide ions. The overall gain $\Delta S^\circ_{\beta 4}$ is hardly larger than half the values found for the halides.

The values of ΔS°_j follow a pattern different from that of the halides, as was also found for the values of ΔH°_j (Table 3). In the thiocyanate system $\Delta S^\circ_3 > \Delta S^\circ_2$, while a monotonous decrease of ΔS°_j takes place in the case of the halides. The solvation of the second complex is evidently relatively stronger in the thiocyanate system, presumably implying a structure appreciably different from that of the formally analogous halide complexes HgX_2.

Contributions from enthalpy and entropy terms to the decrease of free energy. A general view of the relative importance of the enthalpy and entropy contributions to the stabilities of the complexes formed is provided by Fig. 5. The strong entropy stabilization of the first complex in all the systems is evident. For Cl^-, the entropy change contributes twice as much as the heat of reaction to the stability, and even for SCN^- the two terms are of about the same size. For all the halides, the entropy contribution is still important in the second step, providing about one third of the total decrease of free energy, but drops into insignificance in the following steps. These are therefore heavily enthalpy stabilized, in spite of the gradual decrease of ΔH°_j. In the case of SCN^-, however, the trend is reversed relative to the halides both between ΔS°_2 and ΔS°_3, and between ΔH°_3 and ΔH°_4. As a result, the third complex, but not the second one, is appreciably entropy stabilized in this system. Related differences between halide and thiocyanate complexes have also been found for cadmium(II), both in DMSO and water.[7] As already pointed out, they certainly reflect a difference in structure between formally analogous thiocyanate and halide complexes.

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