

Thermodynamics and Structures of Complexes in Solvents Coordinating through Nitrogen. II. Equilibrium and Enthalpy Measurements on the Mercury(II) Chloride, Bromide, Iodide and Thiocyanate Systems in Pyridine

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The stabilities and heats of formation of mercury(II) halide and thiocyanate complexes have been determined in pyridine, by means of potentiometric and calorimetric measurements. Potentiometric measurements with the mercury electrode turned out to be quite feasible in this solvent, in spite of its low dielectric constant, $\epsilon=12.3$.

The thermodynamics of the complex formation differs very much from that previously found in DMSO. For all the complexes formed, the entropy terms are much more favourable in pyridine, *i.e.* in the more strongly solvating and less structured solvent. The enthalpy terms are, on the other hand, much less favourable in pyridine than in DMSO. The changes of ΔH_f° and ΔS_f° thus compensate each other so the differences in ΔG_f° between the two solvents are generally not very large. The difference in thermodynamics between pyridine and water is even more marked. In the well-structured water, the desolvation of the mercury(II) ion, and the ligand, results only in small increases of entropy. On the other hand, the weaker solvation of Hg^{2+} means more favourable enthalpy changes, especially for the initial steps. Therefore, while the complex formation is largely entropy controlled in pyridine, it is largely enthalpy controlled in water. In DMSO, the conditions are between these two extremes.

In all complex formation reactions in solution, the solvation of the species involved plays a prominent part. A strong solvation of a metal ion, or a ligand, means that their ability to form complexes will be hampered. This applies even if the complexes formed are also fairly strongly solvated; this counteracting influence is never strong enough to reverse the net result.^{1,2}

For soft metal ions, possessing marked electron acceptor properties, the solvation depends very much upon the donor properties of the solvent molecules, *i.e.* on the formation of a bond of a more or less covalent character. For hard metal ions, on the other hand, the dipole properties of the solvent become of paramount importance. The latter also applies to the solvation of ligands.

For such ligands, however, that are able to form hydrogen bonds, *e.g.* Cl^- , the solvation is especially strong in protic solvents where such bonds can be formed. The difference

between the solvation enthalpies of the chloride and iodide ions, $\Delta H_{sv}^{\circ}(\text{Cl}^-) - \Delta H_{sv}^{\circ}(\text{I}^-)$, is therefore much larger in protic than in aprotic solvents.¹⁻³ Consequently, chloride complexes are much more stable relative to iodide complexes in aprotic solvents than they are in protic ones. To a less degree, this also applies to bromide relative to iodide complexes.^{2,4-6}

Between various aprotic solvents, on the other hand, the difference $\Delta H_{sv}^{\circ}(\text{Cl}^-) - \Delta H_{sv}^{\circ}(\text{I}^-)$ should not differ very much as these solvents do not especially favour anyone of the ligands. That this really applies has been proved by comparisons between the values of $\Delta H_{sv}^{\circ}(\text{L}^-)$ in aprotic solvents which differ greatly in their donor and dielectric properties, *viz.* dimethylsulfoxide (DMSO), propylene carbonate (PC), acetonitrile (AN), and pyridine (PY).¹⁻³

Nor do the values of ΔH_{sv}° for a certain halide ion differ very much between various aprotic solvents.^{1,3} The enthalpies of transfer between any pair of solvents, S_1 and S_2 ,

$$\Delta H_{tr}^{\circ}(S_1 \rightarrow S_2) = \Delta H_{sv}^{\circ}(S_2) - \Delta H_{sv}^{\circ}(S_1) \quad (1)$$

are all small, at most 10 kJ/mol. The halide ions ought to interact stronger with the solvent the higher its dipole moment; on the other hand, a high dipole moment means a more ordered structure which impedes the solvate formation. These, and other terms of interaction, actually balance each other rather neatly.

The solvent structure also strongly influences the entropy terms. In protic solvents, strong hydrogen bonds exist also between the solvent molecules. The break-up of solvate shells accompanying the complex formation therefore means that solvent molecules move from one well-ordered structure to another fairly well-ordered structure, *viz.* that of the bulk solvent. The entropy gain in this process will be small and the total entropy change ΔS_j° of a formation reaction $\text{ML}_{j-1} + \text{L} \rightarrow \text{ML}_j$ may well become negative. Aprotic solvents are less strictly ordered. Consequently, the break-up of a well-ordered solvate means a large loss of order and hence a large gain of entropy. The total change ΔS_j° will therefore be much more favourable than in protic solvents; if the acceptor and ligand involved are at least fairly strongly solvated, the values of ΔS_j° are indeed very positive.^{1,2,4-7}

The aim of this series of investigations is to determine how the complex formation is influenced by the donor and dielectric properties of the solvent. In the present study, the thermodynamic functions for the formation of mercury(II) halide and thiocyanate complexes in pyridine are reported, and compared with previous measurements of these systems in DMSO and water, both acting as oxygen donors.⁸⁻¹⁰ Pyridine has been chosen as a nitrogen donor solvent because Raman spectroscopic data¹¹⁻¹³ referring to the halides HgL_2 indicate that it interacts quite strongly with mercury(II).

The stabilities have been determined potentiometrically, by means of the mercury electrode. To evaluate such measurements, the constant $K_R = [\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$ of the reproporation reaction $\text{Hg}(1) + \text{Hg}^{2+} \rightleftharpoons \text{Hg}_2^{2+}$ has to be determined. In pyridine, mercury(II) is more stable relative to mercury(I) than in DMSO, or water. In equilibrium solutions containing only the solvated species Hg^{2+} and Hg_2^{2+} , the part present as mercury(I) is nevertheless sizable. As the ligands used strongly prefer mercury(II) to mercury(I), however, the concentration of the latter oxidation state is negligible in all solutions where $[\text{Hg}^{2+}]$ is only a minor fraction of the total mercury(II) concentration. By measurements in this range which in practice means that the ligand numbers have to be $\bar{n} \geq 1.4$, the stabilities of the mercury(II) complexes can be determined without interference from mercury(I).

The heats of reaction have been determined calorimetrically. By combining these with the free energy changes calculated from the stability constants, the entropy changes are found. All measurements have been performed at 25 °C.

EXPERIMENTAL

Choice of medium. In the investigations of the mercury(II) halide and thiocyanate complexes in DMSO,^{4,5} 1 M (in the case of bromide also 0.1 M) ammonium perchlorate was used to create an approximately constant ionic medium. In pyridine, NH_4^+ is not a suitable medium ion, however, as both the perchlorate and the halides are only slightly soluble. The tetraethylammonium (Et_4N^+) salts are just sufficiently soluble, however. From the perchlorate, 0.1 M solutions can be obtained, to be used as an ionic medium. The solubilities of the halides are lower; in the presence of 0.1 Et_4N^+ , the highest concentrations of chloride, bromide and iodide possible are 60, 24 and 13 mM, respectively. The complexes are so stable, however, that even within the limits set for the ligand concentrations by these solubilities the final complex is formed in all the halide systems. The tetraethylammonium thiocyanate is very soluble so in this case the upper limit of the ligand concentration is set by the ionic strength chosen.

The lower concentration of perchlorate is also necessary because of the fairly low solubility of the mercury(II) perchlorate in pyridine; only 16 mM in the present medium. Even lower solubilities are found for salts containing the complex ions HgL_4^{2-} finally formed in these systems, as will be further discussed below.

Chemicals. The disolvate $\text{Hg}(\text{Py})_2(\text{ClO}_4)_2$ was used as a source of Hg^{2+} . It was prepared by heating the hexasolvate $\text{Hg}(\text{Py})_6(\text{ClO}_4)_2$ (prepared as described in Ref. 14) at 100 °C for at least 6 h. Analysis of the disolvate: found C 21.51, H 1.79, N 4.91 %; calc. C 21.54, H 1.81, N 5.02 %. The tetraethylammonium perchlorate, chloride, bromide, iodide and thiocyanate (Fluka) were dried at 100 °C under vacuum. The halide and thiocyanate contents were checked titrimetrically. Pyridine *p.a.* was kept water-free by storage over molecular sieves of 3 Å pore size and used without further purification.

Determination of K_R . In pyridine, K_R can be determined only by chemical analysis of equilibrium solutions. The equilibrium was approached from both sides, either by shaking the metal with a mercury(II) perchlorate solution or by dissolving $\text{Hg}_2(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ in pyridine. The solutions also contained 0.1 M Et_4NClO_4 . The total concentration of mercury at equilibrium was 5 to 10 mM. The extra water added with the mercury(I) hydrate corresponds to a water content of at most ≈ 0.07 %, *i.e.* amounts of the same order of magnitude as generally found in the solvents used. For mercury ions which strongly prefer pyridine to water, this contamination should be of no consequence, as is also confirmed by the fact that the two approaches used yield the same result.

The total concentration of mercury in solution at equilibrium, C_e , is found by EDTA-titration, after oxidation of the mercury(I) present with 5 M nitric acid. If C_{II} and C_{I} denote the initial concentrations of mercury(II) and mercury(I), respectively, the following conditions are valid: $C_e = [\text{Hg}^{2+}]_e + 2[\text{Hg}_2^{2+}]_e$, $C_{\text{II}} = [\text{Hg}^{2+}]_e + [\text{Hg}_2^{2+}]_e$ and $C_{\text{I}} = 2([\text{Hg}^{2+}]_e + [\text{Hg}_2^{2+}]_e)$. Hence the following expressions for K_R are obtained in the two cases: $K_R = (C_e - C_{\text{II}})/(2C_{\text{II}} - C_e)$ and $K_R = (2C_e - C_{\text{I}})/2(C_{\text{I}} - C_e)$.

Potentiometric measurements. In order that no solutions containing mercury(I) would be included in the calculations, the solutions in the mercury electrode compartment initially contained a concentration of ligand, C_L , high enough to ensure that the mercury(II), of concentration C_M , would be predominant in the form of the final complex HgL_4^{2+} , or in the case of SCN^- , HgL_5^- . Generally, an initial ratio $C_L/C_M = 5$ was chosen. The solutions were then titrated with a mercury(II) perchlorate solution, preferably of the same C_M . If possible, series with $C_M = 3, 6$ and 12 mM were performed. In the chloride and iodide systems, however, the complex HgL_4^{2-} precipitated at $C_M = 12$ mM, presumably as the tetramethylammonium salt, so $C_M = 9$ mM was used as the highest metal concentration. The titration was continued down to a ratio $C_L/C_M \approx 1$. An $\text{Ag(s)}/\text{Ag}^+$ -electrode with a silver concentration of 10 mM, in the same medium as the $\text{Hg(1)}/\text{Hg}^{2+}$ electrode, was used as a reference.

The emfs generally reached their final values in about 10 min and then stayed constant

for several hours. They were as a rule reproducible within ± 1 mV, or somewhat worse in the chloride and bromide systems. The titration was performed in a carefully dried glovebox.

The emfs are given by $E = E_{02} + (RT/2F) \ln [\text{Hg}^{2+}]$ where E_{02} is the electrode potential of the couple $\text{Hg}(1)/[\text{Hg}^{2+}]$ relative to the silver reference electrode used here. To relate the values of E measured to the concentration $[\text{Hg}^{2+}]$, it is necessary to know E_{02} . On account of the reproporationation, this potential cannot be directly measured. The same applies to potentials E_{01} involving the couple $\text{Hg}(1)/\text{Hg}_2^{2+}$; in that case Hg_2^{2+} will always disproportionate. The standard potentials E_{02}° and E_{01}° can both be calculated from K_R and the standard potential E_{12}° , however, according to the formulas $E_{01}^\circ = E_{12}^\circ - (RT/F) \ln K_R$ and $E_{02}^\circ = (E_{01}^\circ + E_{12}^\circ)/2$. The value of E_{12}° was determined experimentally in the same manner as in DMSO.⁴ In such a determination, the ratio $[\text{Hg}_2^{2+}]/[\text{Hg}^{2+}]$ must not exceed K_R if disproportionation of Hg_2^{2+} is to be avoided. For pyridine, this means that the ratio has to be kept < 0.171 , cf. below.

The numerical calculations of the stability constants β_j have been performed by means of a modified version of the least squares program EMK.⁴ The modifications are necessary because the emfs $E - E_{02}$ of the present measurement refer to cells with one hypothetical half-cell of $[\text{Hg}^{2+}] = 1$ M while in earlier measurements (*e.g.* on zinc(II) and cadmium(II) halides in DMSO¹⁵) the input values E_M referred to differences actually measured in each series. Most unfortunately, all the relevant changes were not introduced in the program used for the calculations on the mercury halide system in DMSO.^{4,5} As a consequence, the values of K_1 turned out too high by a factor of ≈ 100 . Hence, the values of ΔG_1° reported are ≈ 11 kJ mol⁻¹ too negative, those of $\Delta S_1^\circ = 35$ JK⁻¹ mol⁻¹ too positive. The other constants K_j ($j=2-4$), as well as all the enthalpy changes ΔH_j° ($j=1 \rightarrow 4$) are changed only marginally, however (see below).

Calorimetric measurements. The calorimeter and the procedure were much the same as before.¹⁶ In thiocyanate solutions, the parts made from gold were attacked, though less severely than in DMSO.⁴ For these solutions, a calorimeter where all gold parts had been rhodium plated was therefore employed.

The heat evolved, $Q > 0$, or consumed, $Q < 0$, on the addition of an aliquot of the titrant is calculated from $Q = -\epsilon_v(\Delta R - \Delta R_{\text{dil}})$ where ΔR is the change of thermistor resistance actually observed and ΔR_{dil} the corresponding change due to the heat of dilution of the titrant (*i.e.* $\Delta R > 0$ if the resistance increases). The calibration factor ϵ_v depends upon the volume V of the solution according to $\epsilon_v = a + bV$ where $a = 0.0580$ J ohm⁻¹ and $b = 0.008586$ J ohm⁻¹ ml⁻¹. The heat capacity of pyridine is only ≈ 40 % of that of water. It is also lower than for the other aprotic solvents used, *viz.* 67 % of that of DMSO and 88 % of that of AN. The constants a and b quoted previously⁴ for DMSO solutions have unfortunately wrong dimensions and, in the case of b , also an erroneous value. The correct data are $a = 0.9501$ J ohm⁻¹ and $b = 1.3361 \cdot 10^{-2}$ J ohm⁻¹ ml⁻¹. It should be noted that in the DMSO paper the equation for ϵ_v is differently formulated so that a also includes the heat capacity of 80 ml of solution. The lower heat capacity implies that the method of measurement is rather more sensitive for aprotic solvents than for aqueous solutions.

The calorimeter vessel initially contained a mercury perchlorate solution of a C_M ranging from 3 to 12 mM. To this solution, a saturated halide solution was added, or a thiocyanate solution of $C_L = 100$ mM. The initial volume V_0 was either 80 ml, as before, or 50 ml. The lower volume was preferred in the halide titrations where the titrants had to be fairly dilute. In this way, the measurements could more easily be extended to as high values of C_L as possible, which is necessary in order to determine the enthalpy changes connected with the highest complexes formed.

The heats of dilution were determined for Hg^{2+} by titrating the perchlorate solution with 0.1 M Et_4NClO_4 , and for the ligands by adding the titrants to 0.1 Et_4NClO_4 . These heats were small. The largest correction, still not amounting to more than ≈ 5 % of the total heat evolved, had to be introduced in the chloride titrations.

The enthalpy changes $\Delta H_{\beta_j}^\circ$ of the complex formation reaction were computed by the program KALORI¹⁷ which minimizes the least square sum $U = \sum (Q_{\text{exp}} - Q_{\text{calc}})^2$. The stability constants obtained in the potentiometric measurements are used as fixed parameters. In the present systems the differences between the enthalpy changes of the consecutive steps are not large enough to allow a calculation of both $\Delta H_{\beta_j}^\circ$ and β_j from the calorimetric data; the first two complexes are moreover too stable to allow such a calculation.^{18,19}

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

	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Br ⁻
Pyridine, 0.1 M ET ₄ NClO ₄	β_1	$(3.86 \pm 0.40) \cdot 10^{10}$	$(5.39 \pm 0.69) \cdot 10^{10}$	$(5.20 \pm 0.54) \cdot 10^{11}$	$(5.89 \pm 0.98) \cdot 10^6$
	β_2	$(9.61 \pm 1.10) \cdot 10^{18}$	$(2.87 \pm 0.41) \cdot 10^{19}$	$(3.51 \pm 0.44) \cdot 10^{21}$	$(5.25 \pm 2.34) \cdot 10^{11}$
	β_3	$(3.80 \pm 0.61) \cdot 10^{23}$	$(1.48 \pm 0.30) \cdot 10^{24}$	$(2.37 \pm 0.43) \cdot 10^{26}$	$(6.90 \pm 4.75) \cdot 10^{14}$
	β_4	$(1.67 \pm 0.49) \cdot 10^{26}$	$(1.19 \pm 0.63) \cdot 10^{26}$	$(2.09 \pm 1.17) \cdot 10^{28}$	—
	NP	226	190	241	245
DMSO, 1 M NH ₄ ClO ₄ (last column: 0.1 M NH ₄ ClO ₄)	β_1	$(7.83 \pm 0.46) \cdot 10^8$	$(1.02 \pm 0.07) \cdot 10^{10}$	$(3.02 \pm 0.19) \cdot 10^{11}$	$(3.06 \pm 0.13) \cdot 10^7$
	β_2	$(8.89 \pm 0.58) \cdot 10^{13}$	$(1.20 \pm 0.10) \cdot 10^{18}$	$(1.71 \pm 0.12) \cdot 10^{21}$	$(1.20 \pm 0.07) \cdot 10^{13}$
	β_3	$(8.34 \pm 0.73) \cdot 10^{19}$	$(1.63 \pm 0.18) \cdot 10^{23}$	$(1.55 \pm 0.14) \cdot 10^{27}$	$(1.07 \pm 0.08) \cdot 10^{16}$
	β_4	$(7.72 \pm 1.44) \cdot 10^{21}$	$(3.65 \pm 0.74) \cdot 10^{25}$	$(4.52 \pm 0.67) \cdot 10^{29}$	$(1.85 \pm 0.29) \cdot 10^{18}$
	NP	295	274	284	413
					336

RESULTS

Reproportionation constant and standard potentials. A value of $K_R=0.171$ is found by both the approaches to equilibrium described above. For the couple $\text{Hg}_2^{2+}/\text{Hg}^{2+}$, the standard potential $E_{12}^{\circ}=164.7$ mV, was found. Hence $E_{01}^{\circ}=210.2$ mV and, finally, $E_{02}^{\circ}=187.4$ mV, all values of E° referred to the standard silver electrode in pyridine (*i.e.* all species of activity 1 on the molar scale, for the ionic medium actually used).

Stabilities, and heats of complex formation. As in water and DMSO, the potentiometric data of the halide systems fit well to a consecutive formation of four mononuclear complexes, HgL_j^{2-j} , $j=1\rightarrow 4$. The overall constants β_j calculated are listed, with their limits of error, in Table 1, together with the number of emfs (NP) measured for each systems. The distribution of the mercury between the different complexes, as a function of the free ligand ion concentration, $[\text{L}]$, is given in Fig. 1A. Evidently, each intermediate complex predominates quite strongly at its maximum concentration (attained at $\bar{n}=j$). Except for the thiocyanate system, the second complex predominated among the intermediate ones. The thiocyanate complexes are considerably less stable than the halide ones; the formation of a

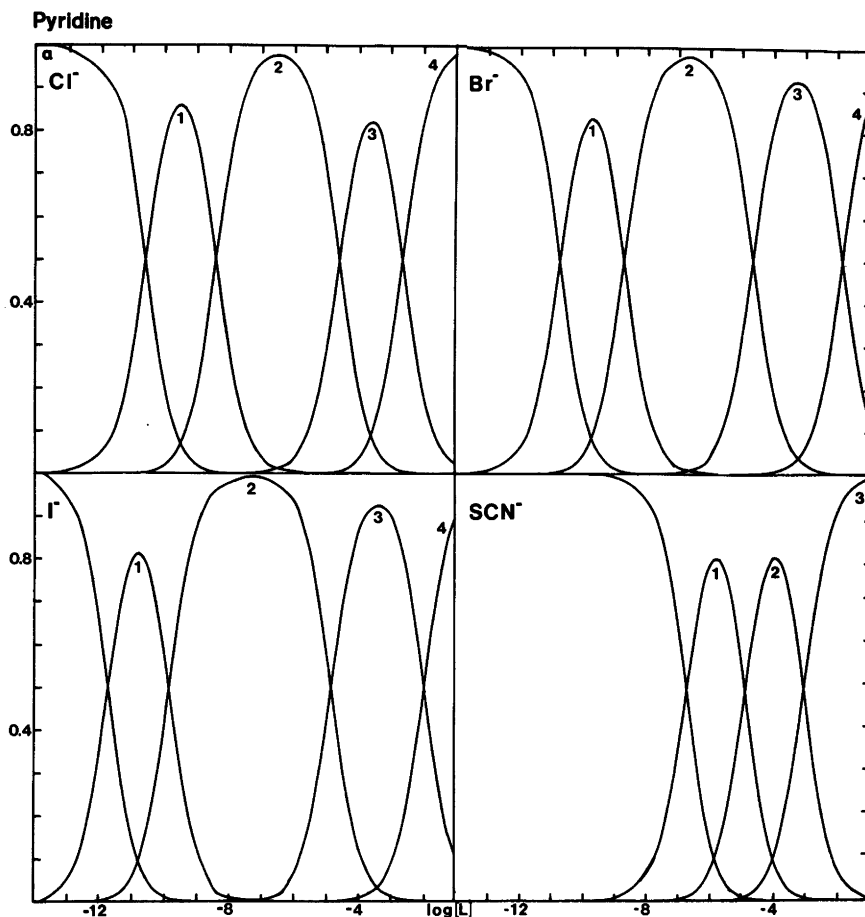


Fig. 1 A. Distribution of mercury(II) halide and thiocyanate species in pyridine.

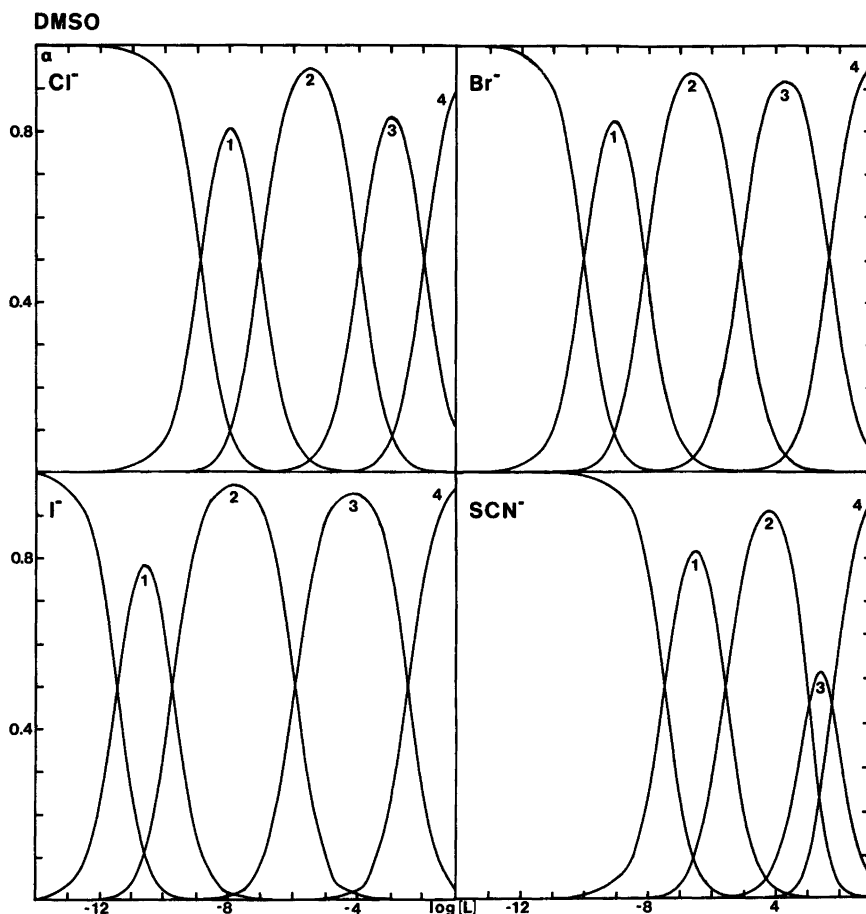


Fig. 1 B. Distribution of mercury(II) halide and thiocyanate species in DMSO.

fourth complex $\text{Hg}(\text{SCN})_4^{2-}$ cannot be proved even at the highest free ligand concentration reached ($[\text{L}] \approx 20 \text{ mM}$).

The total molar heat changes, Δh_v , obtained directly from the values of Q measured,¹⁶ are plotted in Fig. 2, as functions of \bar{n} . Evidently, the halide complexes are all formed in exothermic reactions, while in the thiocyanate system the heats are all close to zero. With the values of β_j of Table 1, the calorimetric data yield the values of the overall enthalpy changes $\Delta H_{\beta_j}^0$ listed in Table 2. The values of Δh_v calculated from these fit the experimental data very well, Fig. 2. The parameters calculated thus describe the measurements quite satisfactory.

The limits of error in β_j are considerably larger for pyridine than for DMSO, Table 2, indicating the lower precision of potentiometric measurements in solvents of low dielectric constant. The limits of error in $\Delta H_{\beta_j}^0$ are, on the other hand, much the same for the two solvents, Table 2.

Revised values of the stabilities, and heats of complex formation, in DMSO. The new values of β_j are listed in Table 1, and the distribution between the different complexes is

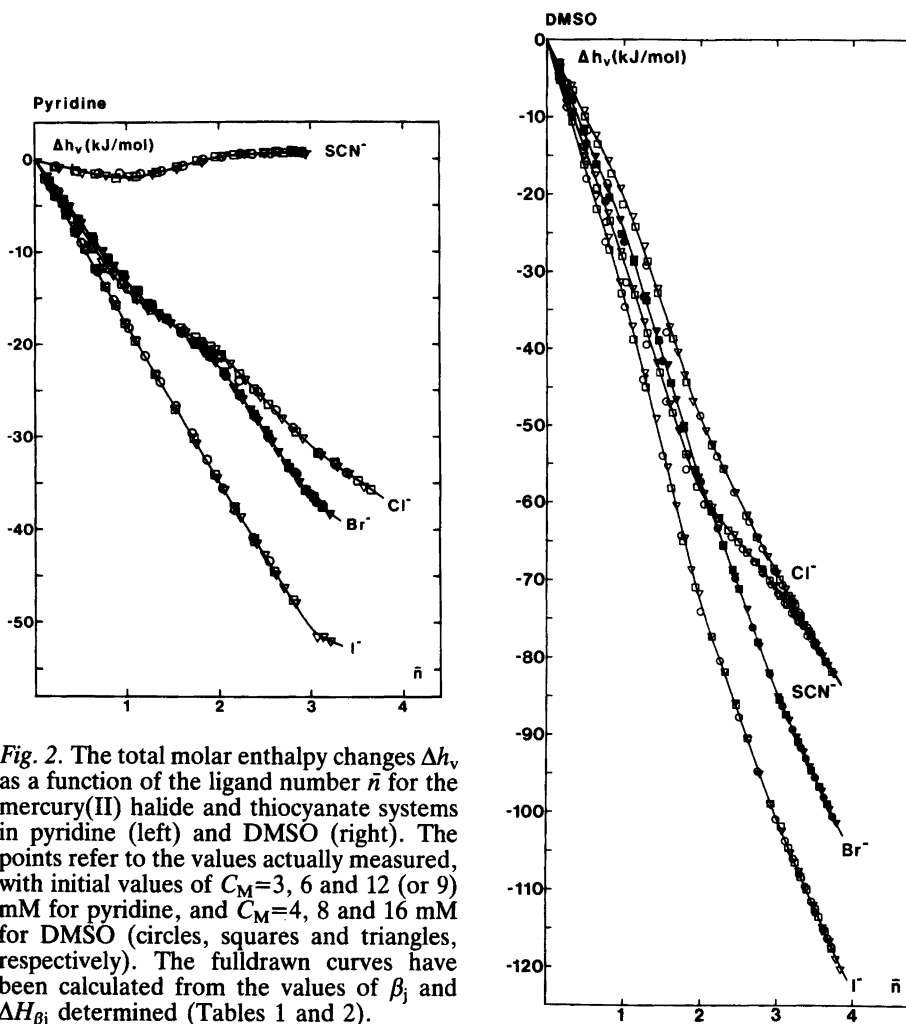


Fig. 2. The total molar enthalpy changes Δh_v as a function of the ligand number \bar{n} for the mercury(II) halide and thiocyanate systems in pyridine (left) and DMSO (right). The points refer to the values actually measured, with initial values of $C_M=3, 6$ and 12 (or 9) mM for pyridine, and $C_M=4, 8$ and 16 mM for DMSO (circles, squares and triangles, respectively). The full-drawn curves have been calculated from the values of β_j and $\Delta H_{\beta_j}^0$ determined (Tables 1 and 2).

given in Fig. 1 B. The overall picture of the complex formation is fairly similar to what is found in pyridine, except for the thiocyanate system where the fourth complex becomes predominant in DMSO at the highest ligand concentrations attained. The third thiocyanate complex is, on the other hand, rather suppressed in DMSO.

The new values of the total molar heat changes Δh_v are plotted in Fig. 2, and the overall enthalpy changes $\Delta H_{\beta_j}^0$ listed in Table 2. On account of the high stability of the first complex, even the fairly large changes of $(\beta_1 (=K_1))$ resulting from the recalculation cause only minor changes of the values of $\Delta H_{\beta_1}^0 (= \Delta H_1^0)$. The distribution between the following complexes is determined by the ratios K_2/K_3 and K_3/K_4 which are changed only little (*cf.* the present Table 3 with Tables 3 and 6 of Refs. 3 and 4, respectively). The values of $\Delta H_{\beta_j}^0$ found fit the experimental points well, Fig. 2.

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

		Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Br ⁻
Pyridine, 0.1 M Et ₄ NClO ₄	- $\Delta H^\circ_{\beta 1}$	14.9±0.5	13.6±0.4	18.2±0.6	2.5±0.3	
	- $\Delta H^\circ_{\beta 2}$	20.9±0.6	22.3±0.5	35.0±0.8	-0.6±0.4	
	- $\Delta H^\circ_{\beta 3}$	31.3±0.8	36.7±0.6	51.2±1.0	-0.7±0.5	
	- $\Delta H^\circ_{\beta 4}$	38.0±0.9	44.2±1.8	55.5±4.0	-	
	NP	128	156	148	137	
DMSO, 1 M NH ₄ ClO ₄ (last column: 0.1 M NH ₄ ClO ₄)	- $\Delta H^\circ_{\beta 1}$	19.3±0.8	24.0±0.8	32.4±0.8	27.9±1.0	20.0±0.6
	- $\Delta H^\circ_{\beta 2}$	49.0±1.0	56.8±1.0	72.8±1.1	59.2±1.3	44.1±0.9
	- $\Delta H^\circ_{\beta 3}$	69.1±1.2	84.5±1.2	100.8±1.2	69.0±2.3	68.5±1.1
	- $\Delta H^\circ_{\beta 4}$	85.6±1.8	106.0±1.5	123.8±1.5	86.5±2.7	85.8±1.3
	NP	255	262	260	170	219

Table 3. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/kJ\ mol^{-1}$; $\Delta S_j^\circ/J\ K^{-1}\ mol^{-1}$) for the stepwise formation of mercury(II) halide and thiocyanate complexes in pyridine and DMSO, at 25 °C.

	Pyridine, 0.1 M Et ₄ NClO ₄				DMSO, 1M NH ₄ ClO ₄			
	Cl ⁻	Br ⁻	I ⁻	SCN ⁻	Cl ⁻	Br ⁻	I ⁻	SCN ⁻
log K_1	10.59	10.73	11.72	6.77	8.89	10.01	11.48	7.49
log K_2	8.40	8.73	9.83	5.0	7.05	8.07	9.75	5.59
log K_3	4.60	4.71	4.83	3.1	3.97	5.13	5.96	2.95
log K_4	2.64	1.9	2.0		1.97	2.35	2.47	2.24
K_1/K_2	155	101	77	60	69.0	85.5	53.4	78.1
K_2/K_3	$6.3 \cdot 10^3$	$1.03 \cdot 10^4$	$10.0 \cdot 10^4$	80	1210	878	$6.23 \cdot 10^3$	438
K_3/K_4	90	640	700		101	603	$3.11 \cdot 10^3$	5.2
$-\Delta G_1^\circ$	60.4	61.3	66.9	38.6	50.8	57.1	65.5	42.7
$-\Delta G_2^\circ$	47.9	49.8	56.1	28	40.3	46.1	55.7	31.9
$-\Delta G_3^\circ$	26.2	26.9	27.6	18	22.7	29.3	34.0	16.8
$-\Delta G_4^\circ$	15.1	11	11		11.2	13.4	14.1	12.8
$-\Delta H_1^\circ$	14.9	13.6	18.3	2.5	19.2	24.0	32.4	27.9
$-\Delta H_2^\circ$	6.0	8.7	16.8	-3.1	29.7	32.9	40.4	31.4
$-\Delta H_3^\circ$	10.4	14.4	16.2	-0.1	20.1	27.7	28.1	9.8
$-\Delta H_4^\circ$	6.8	7.5	4.3		16.5	21.5	23.0	17.5
ΔS_1°	153	160	163	121	106	111	111	50
ΔS_2°	141	138	132	102	36	44	51	2
ΔS_3°	53	42	38	60	9	5	20	24
ΔS_4°	28	12	22		-18	-27	-30	-16
$-\Delta G_{\beta 4}^\circ$	149.7	149.0	161.5		124.9	145.9	169.2	104.2
$-\Delta H_{\beta 4}^\circ$	38.0	44.2	55.4		85.6	106.0	123.8	86.5
$\Delta S_{\beta 4}^\circ$	375	352	355		133	133	152	60

DISCUSSION

The complex formation functions of the mercury(II) halide, and thiocyanate, systems in pyridine, DMSO and water, are presented in Fig. 3. As already pointed out, the strong decrease of stability in the order $I^- > Br^- > Cl^-$ characteristic of water becomes much less marked in the aprotic solvents. This applies even more to pyridine than to DMSO. In pyridine a reversal even takes place at the fourth step, Table 3. The value of K_4 is indeed considerably higher for Cl^- than for Br^- and I^- (while the values for the two latter ligands are much the same).

The large difference between the complex formation functions of the halide systems in water, on one hand, and in the two aprotic solvents, on the other, is reflected in very different trends in the thermodynamic functions ΔH_j° and ΔS_j° , Fig. 4.

In water, the formation of halide complexes becomes much more exothermic in the sequence $Cl^- < Br^- < I^-$. In DMSO and, especially, in pyridine, these increases are much smaller; in the latter solvent the trend is even reversed in some cases, Table 3. This mainly reflects the decrease of $-\Delta H_{sv}^\circ(Cl^-)$ relative to $-\Delta H_{sv}^\circ(Br^-)$ and $-\Delta H_{sv}^\circ(I^-)$ between water and the aprotic solvents. In water the difference $\Delta H_{sv}^\circ(Cl^-) - \Delta H_{sv}^\circ(I^-) = -72\ kJ\ mol^{-1}$ while in DMSO and pyridine it has shrunk to -40 and $-36\ kJ\ mol^{-1}$, respectively,¹ *i.e.* changes of

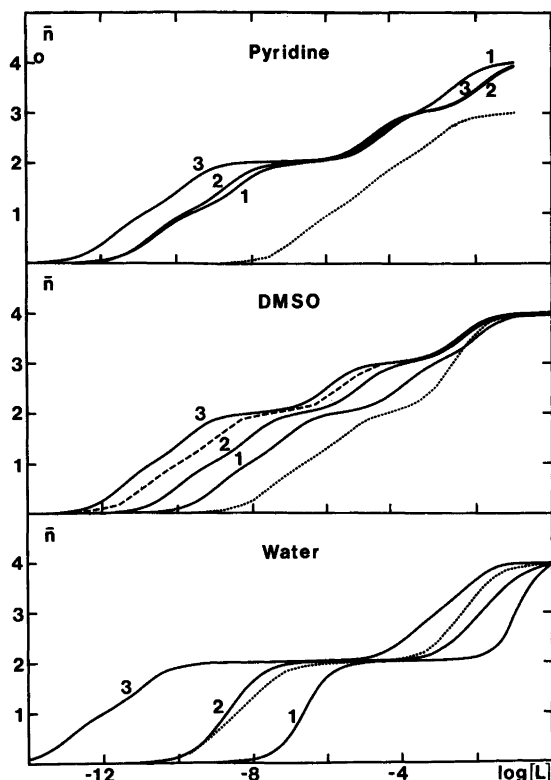


Fig. 3. The complex formation curves of the mercury(II) halide and thiocyanate systems in pyridine, DMSO and water. Full-drawn curves: chloride (1), bromide (2) and iodide (3). Media: pyridine, 0.1 M Et_4NClO_4 ; DMSO, 1 M NH_4ClO_4 ; water, 0.5 M NaClO_4 . Dotted curves: thiocyanate, same media as for the halides in pyridine and DMSO; 1 M NaClO_4 in water. Dashed curve: DMSO, bromide in 0.1 M NH_4ClO_4 .

32 and 36 kJ mol^{-1} . For the formation of the first complex in water,⁴ the difference $\Delta H_1^\circ(\text{Cl}^-) - \Delta H_1^\circ(\text{I}^-) = 50.6 \text{ kJ mol}^{-1}$ while in DMSO and pyridine it has shrunk to 13.2 and 3.4 kJ mol^{-1} , respectively (Table 3), *i.e.* changes of 37 and 47 kJ mol^{-1} . Evidently much the larger part of these changes can be accounted for by the changes in $\Delta H_{\text{sv}}^\circ(\text{Cl}^-) - \Delta H_{\text{sv}}^\circ(\text{I}^-)$.

The remaining part is presumably in the main due to the different dielectric properties of the solvents used. The dielectric constants ϵ are 78.5, 46.4 and 12.3 for water, DMSO²⁰ and pyridine²¹, respectively. The electrostatic ion-ion interactions should thus be stronger in DMSO, and much stronger in pyridine, than they are in water. This should favour formation of chloride relative to iodide complexes, implying an additional decrease of the difference $\Delta H_1^\circ(\text{Cl}^-) - \Delta H_1^\circ(\text{I}^-)$ in the aprotic solvents, beyond that caused by the changes of $\Delta H_{\text{sv}}^\circ$. This effect should moreover be larger in pyridine than in DMSO, which fits with the excess changes actually found (5 kJ mol^{-1} for DMSO; 11 kJ mol^{-1} for pyridine). These excess heats are nevertheless not very large. Even large differences in the dielectric properties thus do not change very much the relative affinities of the halide ions for Hg^{2+} .

In water none of the complexes is much entropy stabilized; the values of $T\Delta S_j^\circ$ are generally small, often <0 . In DMSO, on the other hand, the entropy term contributes

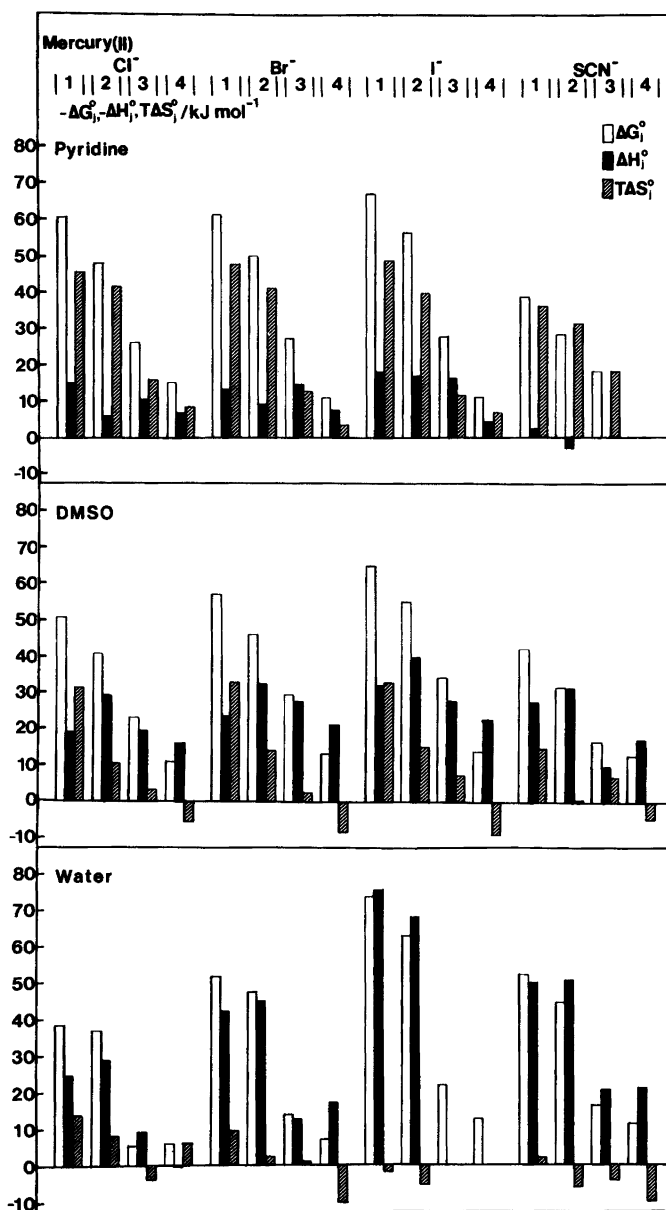


Fig. 4. Changes of free energy (white), enthalpy (black) and entropy (hatched) for the consecutive steps of the mercury(II) halide and thiocyanate systems in pyridine (0.1 M Et_4NClO_4), DMSO (1 M NH_4ClO_4) and water (0.5 M NaClO_4 for the halides; 1 M NaClO_4 for thiocyanate), at 25 °C.

heavily to the stability of the first complex in all the halide systems; it is also quite important in the second step. In pyridine, this tendency is further strengthened. The entropy terms are completely predominating for the stabilities of the first two steps in the halide systems, and of large importance also for the following ones. These trends reflect that the aprotic solvents are much less ordered than water, and that pyridine is considerably less ordered than DMSO. In the latter solvent structural evidence clearly indicates a certain amount of order.²² Also, the very exothermic heats of transfer of Hg^{2+} between water and the aprotic solvents (-76 and -160 kJ mol^{-1} for DMSO and pyridine, respectively¹) certainly indicate stronger solvate bonds and hence more well-ordered solvates in the aprotic solvents which on desolvation should result in larger entropy gains. For each solvent the total entropy gain $\Delta S_{\beta 4}^{\circ}$ for all four steps is much the same for all the halides, Table 3. The difference between pyridine and DMSO is large, however, well over 200 $\text{J K}^{-1} \text{mol}^{-1}$.

As to the thiocyanate system, the reactions are still quite exothermic in DMSO, Fig. 4, but in pyridine the values of ΔH_j° are all ≈ 0 . In this respect, the difference between DMSO and pyridine is larger for thiocyanate than for any of the halides. The values of ΔS_j° are throughout smaller for thiocyanate, as is to be expected for a ligand of lower symmetry than the halide ions, Table 3. The difference is much the same in both solvents, *viz.* ≈ 80 $\text{J K}^{-1} \text{mol}^{-1}$. A remarkable feature is the relatively high value of ΔS_3° for the thiocyanate system both in DMSO and pyridine, higher than for any of the halide systems in the same solvent. Most plausibly, this may be interpreted as indicating an especially strong solvation of the second thiocyanate complex.

To sum up, the changes of the thermodynamic functions between water, DMSO and pyridine for the complex formation reactions studied can be very coherently interpreted in the light of the known differences between these solvents.

Firstly, the increasing strength of the solvation of Hg^{2+} as the bond to the solvent donor atom becomes more covalent means a large increase in the heat of desolvation. Consequently, less exothermic values of ΔH_j° are generally found in the aprotic solvents than in water; this applies especially to pyridine, coordinating through the soft nitrogen atom. This trend is strongly counteracted, however, in such systems where the ligand is able to form hydrogen bonds and therefore is more strongly solvated in water than in the aprotic solvents (Cl^- , to a less extent Br^-). In fact, not very different values of ΔH_1° and ΔH_2° are found for the chloride system in water and DMSO, and the following steps are in fact less exothermic in water than in DMSO.

Secondly, the much less ordered structure of the aprotic solvents implies that the entropy gains on desolvation becomes much larger than in water. Again, this applies especially to pyridine. The desolvation entropies are further increased on account of the stricter order of the stronger solvates formed in the aprotic solvents. The final result will be large overall gains of entropy, especially in pyridine.

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