Equilibrium and Enthalpy Measurements on the Zinc(II) Chloride, Bromide and Iodide Systems in Acetonitrile and Pyridine, and on the Mercury(II) Chloride, Bromide and Iodide Systems in Acetonitrile

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The thermodynamics of the formation of chloride, bromide and iodide complexes of zinc(II) in acetonitrile and pyridine, and of mercury(II) in acetonitrile, have been determined at 25 °C by means of potentiometric and calorimetric measurements. Pyridinium trifluoromethylsulfonate has been used as supporting electrolyte to an ionic strength of 0.1 M. The complex formation in the zinc(II) and mercury(II) halide systems is very strong in acetonitrile, and four complexes are formed for all halides of both metal ions. All zinc(II) halide complexes except the first bromide and iodide complexes are formed in exothermic reactions. All mercury(II) halide complexes are formed in strongly exothermic reactions. The stability constants observed in acetonitrile solution are large because acetonitrile solvates divalent ions poorly. The complex formation of the zinc(II) halides is considerably weaker in pyridine because of stronger solvation of the zinc(II) ion. Only two chloride and bromide and one iodide complex of zinc(II) are formed in pyridine.

The solvation of the species involved plays a very important role for all complex formation reactions in solution. If the metal ion and/or the ligand are strongly solvated their ability to form complexes is hampered. For a soft electron acceptor such as mercury(II) the solvation depends very much upon the electron donating properties of the solvent, i.e. on the ability of the solvent molecules to donate a shared electron pair into an empty orbital of an acceptor to give a strong covalent interaction. The donor properties of the two nitrogen donating solvents used in this study, acetonitrile and pyridine, are very different. Previous studies on the solvation of the neutral mercury(II) halide complexes showed that pyridine is a good electron donor, while acetonitrile has poor electron donor properties.[1,2] This is somewhat surprising, since acetonitrile solvates the soft univalent coinage metal ions well.[3] For the fairly hard electron acceptor zinc(II), the solvation depends more on the dipole properties of the solvent, and for the halide ions it depends on the hydrogen-bonding and electrostatic properties of the solvent. The zinc(II) ion is more weakly solvated in acetonitrile than in water,[4] while it is equally well solvated in pyridine as in aqueous solution.[5]

The stability constants of the mercury(II) halides have been determined potentiometrically by means of a mercury pool electrode. To evaluate these measurements it is necessary to determine the standard electrode potential of the couple $Hg(l)/Hg^{2+}$, $E°_{Hg(l)/Hg^{2+}}$, in acetonitrile versus a reference electrode; the silver electrode has been used as reference electrode in this study. $E°_{Hg(l)/Hg^{2+}}$ is calculated from experimental standard electrode potentials of the couples $Hg(l)/Hg_2^{2+}$ and Hg_2^{2+}/Hg^{2+} in acetonitrile. Mercury(II) is less stabilized compared to mercury(I) in acetonitrile than in any other solvent studied so far.[6] In order to keep mercury(II) in presence of metallic mercury, mercury(II) must be highly stabilized through complexation; mercury(II) forms much stronger halide complexes than mercury(I) does. The reproportionation of metallic mercury and mercury(II) to mercury(I) in solution is suppressed with a large excess of halide ions as the concentration of free mercury(II) becomes very low. This also means that the mercury(I) concentration is very small in spite of a fairly large reproportionation constant. The stability of the higher mercury(II) halide complexes can be determined without interference from mercury(I) in mercury(II) halide solutions with $\bar{n} > 3.2$, 2.9 and 2.3 for chloride, bromide and iodide, respectively.

The stabilities of the zinc(II) halide complexes have been determined potentiometrically by means of the zinc amal-

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gam electrode as described elsewhere.[7] The choice of ionic medium is very important for these measurements. Zinc, and also cadmium, amalgam surfaces become tarnished in deaerated pure solvents such as dimethylsulfoxide, acetonitrile and pyridine, but if the cation in the supporting electrolyte has acidic properties this effect is prevented. However, the metal ion concentration does not increase in the solutions in contact with a tarnished amalgam surface. This makes us believe that it is not an oxidation as reported previously.[7] The use of an ionic medium where the cation is a weak acid such as the ammonium and pyridinium ions, or the presence of traces of water, keeps the amalgam surface lustrous and fresh, and stable and reproducable potentials are obtained. Pyridinium trifluoromethylsulfonate was used as supporting electrolyte in this study, as an absolutely dry solvent was necessary. A trifluoromethylsulfonate salt was chosen because these are not explosive, and anhydrous compounds with high solubility in a large number of solvents can be prepared easily. The trifluoromethylsulfonate ion has the same complexating properties as the perchlorate ion, i.e. it forms no or very weak complexes with metal ions in solution.

The heats of complex formation have been determined calorimetrically. By combining these with the free energy changes calculated from the stability constants, the entropy changes are obtained. All measurements have been carried out at 25 °C.

Experimental

Chemicals. Anhydrous zinc(II) trifluoromethylsulfonate, $Zn(CF_3SO_3)_2$, was prepared and analyzed as described elsewhere.[4] Analysis: C: Found 6.59, Calc. 6.61 %.

Anhydrous mercury(II) trifluoromethylsulfonate, $Hg(CF_3SO_3)_2$, was prepared by adding trifluoromethylsulfonic acid (Fluka) to an aqueous slurry of yellow mercury(II) oxide (BDH, Reagent grade). After unreacted mercury(II) oxide had been filtered off, water was boiled off, and the compound was finally dried over P_2O_5 at 120 °C. Analysis: C: Found 4.81, Calc. 4.82 %.

Pyridinium trifluoromethylsulfonate, $C_5H_6NCF_3SO_3$, pyridinium chloride, C_5H_6NCl, and pyridinium bromide, C_5H_6NBr, were prepared by mixing pyridine, in excess, and aqueous solutions of trifluoromethylsulfonic acid, hydrochloric acid and hydrobromic acid, respectively, followed by the dehydration procedure described for mercury(II) trifluoromethylsulfonate. The melting points are 142–144, 215–217 and 222–223 °C for chloride, bromide and trifluorosulfonate, respectively.

Tetraethylammonium iodide, $(C_2H_5)_4NI$ (Fluka), was dried at 100 °C under vacuum and over P_2O_5. The iodide content was checked titrimetrically with a standard 0.100 M silver nitrate solution.

Mercury(II) chloride, bromide and iodide (red) were recrystallized from hot water, ethanol and acetone, respectively.

Metallic mercury (Ventron) was used without further purification.

Zinc amalgam was prepared and stored as described by Persson.[8] The amalgam contained ca. 3 % zinc. The exact concentration of zinc in the amalgam is not critical, since a two-phase amalgam is formed between 2.18 and 45 % Zn at 25 °C,[9] and the liquid amalgam phase with a well defined composition was used in the potentiometric measurements.

Potentiometric measurements. The apparatus and the procedure were the same as used before.[7] The reproducibilities of the measured EMF values were generally better than ±0.2 mV in both acetonitrile and pyridine. The final EMF values were reached within 20–30 min. The validity of Nernst's law for the zinc amalgam electrode was checked in the range $1 \le C_M \le 20$ mM in both solvents.

In order to assure that the solutions did not contain mercury(I), the mercury(II) solutions in the mercury electrode compartment initially contained a concentration of ligand, C_L, high enough to ensure that the predominant species was HgL_4^{2-}. These solutions were then titrated with a mercury(II) trifluoromethylsulfonate solution with the same C_{Hg} value as the HgL_4^{2-} solution. The titrations were continued until precipitation of mercury(I) halide was observed on the mercury pool surface. An $Ag(s)/Ag^+$ electrode with a silver(I) concentration of 10 mM was used a reference. The EMFs reached stable values within about 20 min and then stayed constant for several hours. They were, as a rule, reproducable within ±2 mV. The EMFs are given by $E = E_{02} + (RT/2F)\ln[Hg^{2+}]$ where E_{02} is the standard electrode potential of the couple $Hg(l)/Hg^{2+}$ relative to the silver reference electrode used. To relate the values of E measured to the free concentration of Hg^{2+} it is necessary to know E_{02}, which can not be determined directly owing to the reproportionation, but can be found from measurements of the $Hg(l)/Hg^{2+}$ and Hg^{2+}/Hg^{2+} couples. The E_{02}° standard electrode potential is given by the expression $E_{02}^\circ = (E_{01}^\circ + E_{12}^\circ)/2$, and the reproportionation constant, K_R, for the reaction $Hg(l) + Hg^{2+} \rightleftharpoons Hg_2^{2+}$ is given by $\log K_R = (E_{12}^\circ - E_{01}^\circ)/RTn^{-1}F^{-1}\ln10$. The values of the E_{01}° and E_{12}° standard electrode potentials have been determined as 451.4 and 609.6 mV, versus the standard $Ag(s)/Ag^+$ electrode, respectively, which means that $E_{02}^\circ = 530.5$ mV and $K_R = 472 \pm 15$.

The numerical calculations of the stability constants have been performed by the program EMK.[10] A modified version of this program allowing calculations on titration from high to low $\bar{n}$ was used for the mercury systems.[11]

Calorimetric measurements. The calorimeter and the procedure used were the same as described elsewhere.[12] The heats of dilution were determined for the metal and halide ions. All these heats were small. The enthalpy changes $\Delta H_{\beta j}^\circ$ of the complex formation reactions were calculated by the program KALORI,[10] which minimizes the least squares sum $U = \Sigma(Q_{exptl} - Q_{calcd})^2$. The stability constants obtained in the potentiometric measurements were used as fixed

parameters in the calculations of the enthalpy changes. It was possible to estimate the first stability constant, as the ratio K_1/K_2 could be estimated accurately from the calorimetric measurements, and the values of β_2, known from the potentiometric measurements. This gives values of K_1 of 1.3×10^{15}, 1.6×10^{16} and 2.6×10^{17} M^{-1} in the mercury(II) chloride, bromide and iodide systems respectively in acetonitrile. The errors in these constants are estimated to be less than 20 %.

Results

The overall stability constants for the zinc(II) halide complexes in acetonitrile and pyridine, and for the mercury(II) halide complexes in acetonitrile, are given in Table 1, and the stepwise stability constants are given in Tables 3 and 4. The complex formation functions for these systems are given in Figs. 1 and 2, and the complex distribution functions are shown in Figs. 3–5. Four mononuclear zinc(II) halide complexes are formed in acetonitrile, and the stepwise stabilities follow the order $Cl^- > Br^- > I^-$ in all four steps. The complex formation is much weaker in pyridine than in acetonitrile, and only two zinc(II) chloride and bromide complexes and one zinc(II) iodide complex are formed in pyridine. Four mononuclear complexes are formed in the mercury(II) halide systems in acetonitrile, and the stabilities increases in the expected order for a soft acceptor, $Cl^- < Br^- < I^-$.

The overall enthalpy changes at the formation of the zinc(II) halide complexes in acetonitrile and pyridine, and the corresponding values for the mercury(II) halide complexes in acetonitrile, are summarized in Table 2. In the zinc(II) halide systems all complexes are formed in exothermic reactions, except for the first bromide and iodide complexes in acetonitrile and pyridine, and the second

chloride complex in pyridine. All mercury(II) halide complexes in acetonitrile are formed in strongly exothermic reactions. The thermodynamic functions for the stepwise formation of zinc(II) and mercury(II) halide complexes in acetonitrile and pyridine are given in Tables 3 and 4.

Discussion

The complex formation thermodynamics for the zinc(II) and mercury(II) halide systems in acetonitrile, pyridine, dimethylsulfoxide and aqueous solution are given in Tables 3 and 4, and are illustrated in block diagrams in Figs. 6 and 7. The determined stability constants nicely reflect the solvation of the metal and halide ions in the studied solvents. The free energies and heats of hydration and of transfer from water to acetonitrile, dimethylsulfoxide and pyridine for the zinc(II), mercury(II), chloride, bromide and iodide ions are given in Table 5. The weakest solvation of the metal and halide ions is found in acetonitrile, and consequently the strongest complex formation is found in this solvent. The mercury(II) and zinc(II) ions are markedly more strongly solvated in dimethylsulfoxide than in water. The mercury(II) ion, a soft electron acceptor, is as expected, strongly solvated in the soft donor solvent pyridine, while the hard zinc(II) ion is equally well solvated in pyridine and water. The halide ions are considerably more strongly solvated in water than in the aprotic solvents owing to their ability to form hydrogen bonds in water. The strength of the hydrogen bond decreases in the order $Cl^- > Br^- > I^-$. This leads to the result that the chloride complexes will be relatively stronger compared to the iodide complexes in aprotic solvents than in water.

The dielectric constant of acetonitrile, 36.0, is smaller than those of water, 78.5, and dimethylsulfoxide, 46.4, but larger than that of pyridine, 12.3. This means that the

Table 1. Overall stability constants, β_j/M^{-j}, for the formation of the zinc(II) and mercury(II) halide complexes in acetonitrile, and zinc(II) halide complexes in pyridine. Medium 0.1 M $C_5H_6N(CF_3SO_3)$; temperature 25 °C. The limits of error refer to three standard deviations; NP denotes the number of EMF measurements made for each system.

| Ligand	Cl^-	Br^-	I^-
Zinc(II); acetonitrile			
β_1	$(1.16 \pm 0.14) \times 10^8$	$(4.6 \pm 2.1) \times 10^5$	$(3 \pm 8) \times 10^4$
β_2	$(1.78 \pm 0.27) \times 10^{15}$	$(2.31 \pm 0.20) \times 10^{12}$	$(1.54 \pm 0.23) \times 10^{11}$
β_3	$(1.31 \pm 0.28) \times 10^{20}$	$(8.22 \pm 0.77) \times 10^{16}$	$(2.32 \pm 0.34) \times 10^{15}$
β_4	$(1.01 \pm 0.36) \times 10^{23}$	$(6.47 \pm 0.84) \times 10^{19}$	$(1.13 \pm 0.27) \times 10^{18}$
NP	165	201	142
Zinc(II); pyridine			
β_1	530 ± 35	$(6.67 \pm 0.44) \times 10^3$	279 ± 20
β_2	$(6.68 \pm 0.66) \times 10^4$	$(4.56 \pm 0.52) \times 10^5$	
NP	158	98	77
Mercury(II); acetonitrile			
β_2	$(4.07 \pm 0.60) \times 10^{29}$	$(2.93 \pm 0.56) \times 10^{31}$	$(1.93 \pm 0.40) \times 10^{34}$
β_3	$(2.60 \pm 0.44) \times 10^{32}$	$(1.61 \pm 0.35) \times 10^{37}$	$(4.95 \pm 1.50) \times 10^{41}$
β_4	$(2.05 \pm 0.47) \times 10^{35}$	$(2.92 \pm 0.88) \times 10^{40}$	$(5.1 \pm 2.2) \times 10^{44}$
NP	40	53	42
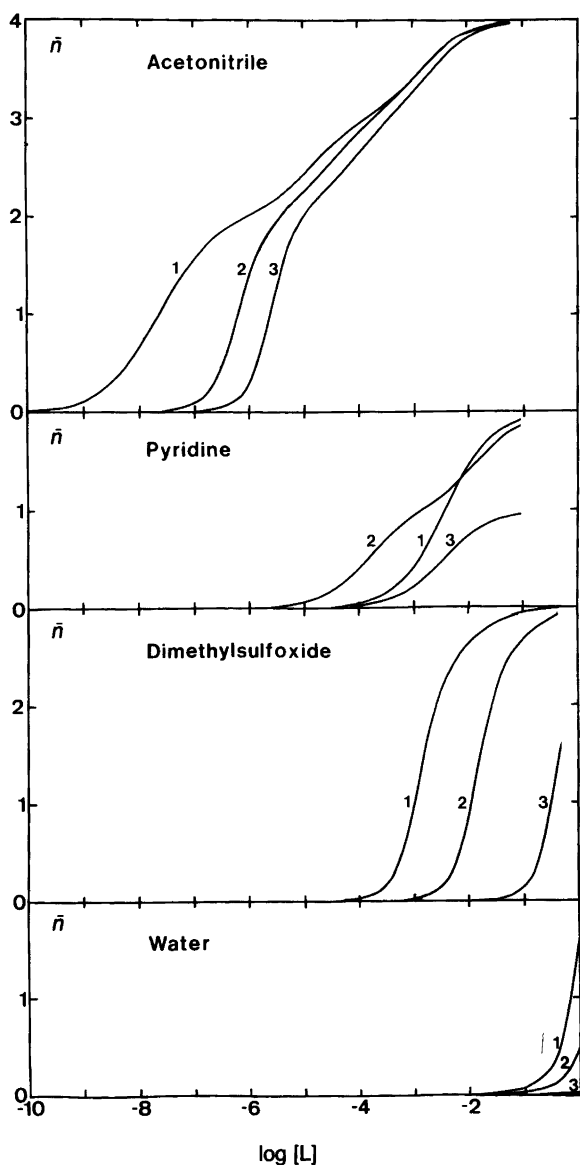
Fig. 1. The complex formation functions of the zinc(II) halide systems in acetonitrile, pyridine, dimethylsulfoxide and water, chloride (1), bromide (2) and iodide (3). Media: acetonitrile, 0.1 M $C_5H_6NCF_3SO_3$; pyridine, 0.1 M $(C_2H_5)_4NClO_4$; dimethylsulfoxide, 0.1 M NH_4ClO_4; water, 1.0 M $NaClO_4$.

electrostatic ion–ion interactions should be stronger in acetonitrile than in water and DMSO, but weaker than in pyridine. This will favour the formation of chloride complexes relative to iodide ones in acetonitrile compared to DMSO and vice versa compared to pyridine. This is indeed also found for all mercury(II) halide steps except the third one, and for all zinc(II) halide steps except the first one (Tables 3 and 4). The reason for the exceptions may lie in structural changes at the formation of these complexes. Water can not be included in this comparison, as the halide ions are hydrogen bonded in water, which counteracts this effect.

Among the solvents studied so far, acetonitrile is the only solvent where four zinc(II) halide complexes have
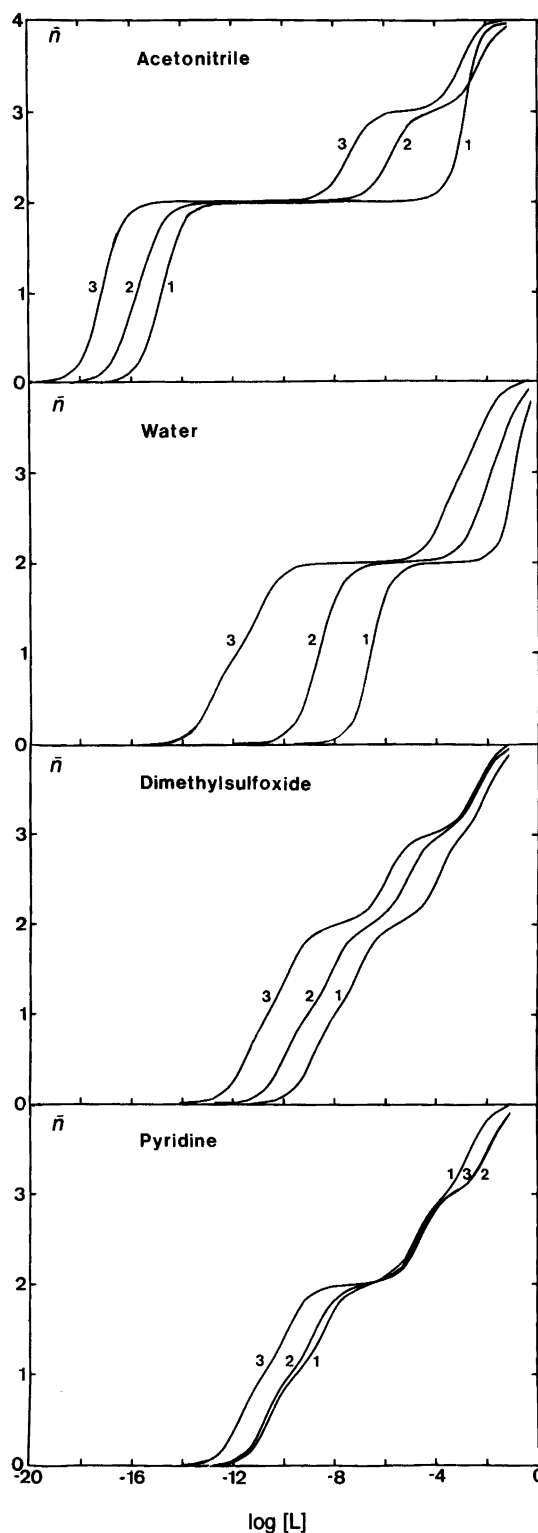

Fig. 2. The complex formation functions of the mercury(II) halide systems in acetonitrile, pyridine, dimethylsulfoxide and water, chloride (1), bromide (2) and iodide (3). Media: acetonitrile, 0.1 M $C_5H_6NCF_3SO_3$; pyridine, 0.1 M $(C_2H_5)_4NClO_4$; dimethylsulfoxide, 0.1 M NH_4ClO_4; water, 0.5 M $NaClO_4$.
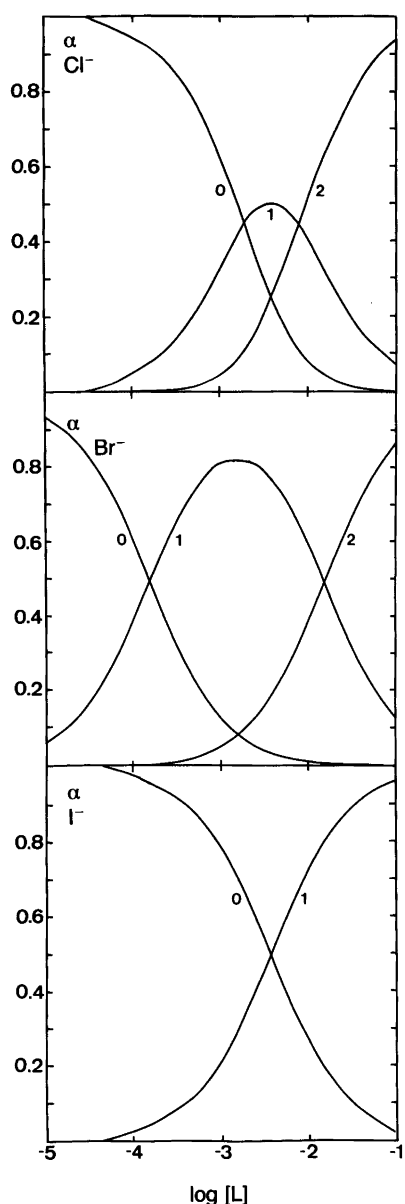
Fig. 3. Distribution of zinc(II) halide species in acetonitrile.

Fig. 4. Distribution of zinc(II) halide species in pyridine.

been thermodynamically characterized. The weak solvation of zinc(II) and halide ions is the reason why four complexes can be formed in acetonitrile. All the stepwise stability constants of the zinc(II) halides in acetonitrile decrease as expected in the order $Cl^- > Br^- > I^-$, as zinc(II) is a hard borderline acceptor with preference for hard donors. The thermodynamic pattern for the formation of the zinc(II) halide systems in acetonitrile shows many similarities to the same systems in DMSO. The complexes in acetonitrile are formed in much more exothermic reactions than in DMSO because less energy is consumed in the desolvation processes owing to the weaker solvation (Table 5). The first complex is surpressed in acetonitrile, as it is in water and DMSO, and it is shown by a small K_1/K_2 ratio, which decreases in the order $Cl^- > Br^- > I^-$, while the other complexes have regions of predominance
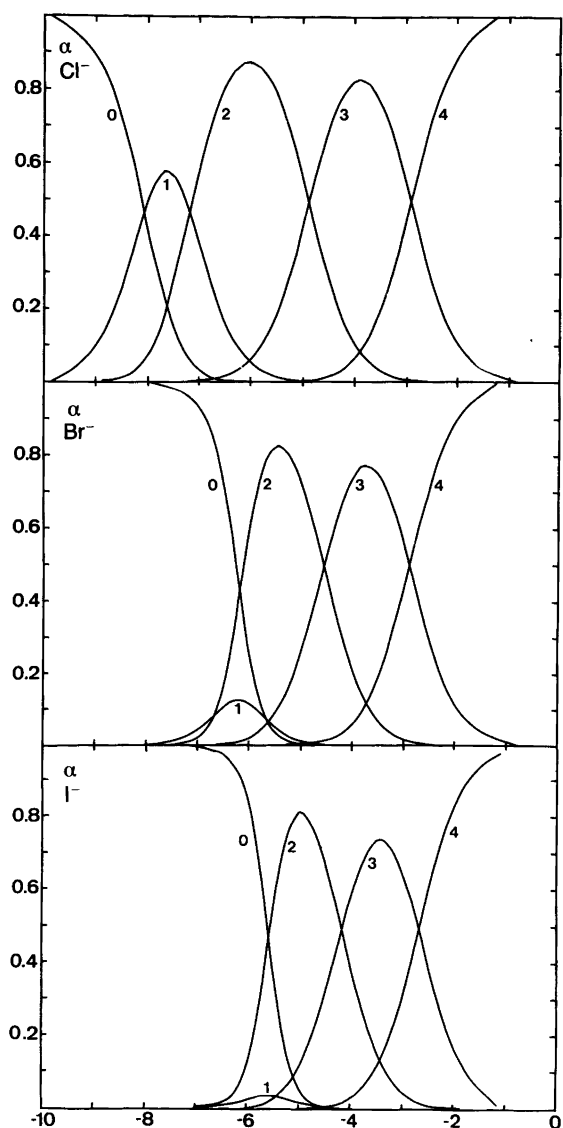
(Fig. 3). Because of the narrow range of existence of the first complex, especially for the iodide system, only the sums of the thermodynamic functions for the first two steps can be determined precisely, and consequently there are large errors in the stepwise parameters.

Ahrland et al. have interpreted a marked endothermic step, accompanied by a large entropy gain as a coordination switch, from octahedral to tetrahedral configuration in the zinc(II) halide systems, at which a substantial desolvation takes place.[11] The first two steps of the zinc(II) halide systems in acetonitrile are strongly entropy stabilized, and the enthalpy terms are less favourable than for the third step. This indicates that a substantial desolvation takes place during the first two steps. However, one can not assign a coordination switch and a major desolvation to a certain step, as the thermodynamic functions are similar
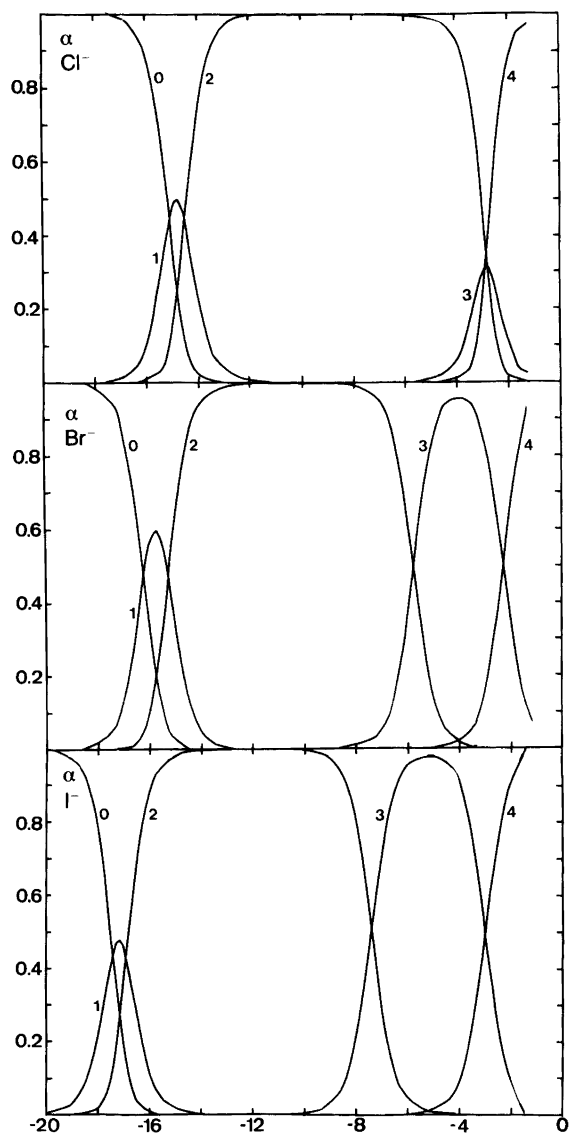
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Fig. 5. Distribution of mercury(II) halide species in acetonitrile.

Table 2. Overall enthalpy changes, $\Delta H^\circ_{\beta j}$/kJ mol^{-1}, for the formation of the zinc(II) and mercury(II) halide complexes in acetonitrile, and zinc(II) halide complexes in pyridine. Medium 0.1 M C$_5$H$_6$N(CF$_3$SO$_3$); temperature 25 °C. The limits of error refer to three standard deviations; NP denotes the number of aliquots added for each system.

Ligand	Cl$^-$	Br$^-$	I$^-$
Zinc(II); acetonitrile			
$\Delta H^\circ_{\beta 1}$	−5.8±0.8	0.9±2.3	12±6
$\Delta H^\circ_{\beta 2}$	−12.9±0.9	−8.4±0.7	6.8±0.6
$\Delta H^\circ_{\beta 3}$	−33.7±1.0	−29.2±0.9	−7.9±0.7
$\Delta H^\circ_{\beta 4}$	−45.0±1.5	−33.7±1.4	−7.9±0.9
NP	119	83	117
Zinc(II); pyridine			
$\Delta H^\circ_{\beta 1}$	−2.5±0.5	0.3±0.4	20.1±1.1
$\Delta H^\circ_{\beta 2}$	−4.2±1.0	−8.2±1.2	
NP	52	51	32
Mercury (II); acetonitrile			
$\Delta H^\circ_{\beta 1}$	−50.5±0.6	−58.9±0.3	−67.6±0.3
$\Delta H^\circ_{\beta 2}$	−92.0±0.9	−108.0±0.4	−127.2±0.4
$\Delta H^\circ_{\beta 3}$	−123.1±1.9	−139.1±0.5	−168.3±0.5
$\Delta H^\circ_{\beta 4}$	−142.5±1.3	−171.0±0.6	−210.7±0.8
NP	81	136	127

for the first two steps. In spite of a lack of structural evidence, one can, however, assume that the solvated zinc(II) ion is six-coordinated in an octahedral fashion, and the tetrahalozincate(II) complexes are regular tetrahedra in acetonitrile solution, as in aqueous[26,27] and dimethylsulfoxide[28,29] solutions.

Only two zinc(II) chloride and bromide complexes, and one zinc(II) iodide complex are formed in pyridine solution. All these complexes except the second zinc(II) bromide complex are strongly entropy stabilized. The thermodynamic pattern in pyridine is different from that found in the other solvents studied. Zinc(II) is coordinated to six pyridines, most probably in an octahedral fashion, in pyridine solution.[30] The structures of the ZnX$_2$(C$_5$H$_5$N)$_2$ complexes in the solid state are slightly distorted tetrahedra.[31-33] The positive ΔG°_{tr} value found for the zinc(II) ion (Table 5), on the transfer from water to pyridine, reflects

mainly differences in the bulk properties between the solvents, and not the strength of the zinc–solvate bonds.[5] The aqueous bulk will only be marginally affected by the introduction of zinc(II) ions, as the freedom of water molecules coordinated to a zinc(II) ion and of water molecules in the bulk differ only slightly. The large negative value of ΔH°_{tr}(aq→py) shows that the Zn–N(py) bond is stronger and more covalent than the Zn–O(aq) one. The introduction of zinc(II) ions into pyridine will affect the pyridine bulk considerably. Since the dielectric constant of pyridine is low, the charge of the zinc(II) ion will order the pyridine bulk considerably, as the pyridine molecules will be oriented around the zinc(II) ion along their dipole. This effect is less pronounced in the other solvents studied, as their dielectric constants are higher. The strong zinc(II)–pyridine bonds ensure that the desolvation process will be markedly endothermic. The most endothermic steps, the second one in the chloride system and the first ones for the bromide and iodide systems, correspond to the most positive entropy changes. The desolvation will mainly occur at these steps. In the chloride system a gradual change in coordination number will also take place at the formation of the first complex, seen by a fairly large ΔS° value and a small ΔH°_1 value. No anionic complexes can be formed in pyridine, since sufficiently high free ligand concentrations necessary for the formation of such complexes can not be obtained in pyridine for solubility reasons.

The stabilities of the mercury(II) halide complexes increase in the order Cl$^-$ < Br$^-$ < I$^-$ in water, DMSO and pyridine. This sequence is also found for the first three steps in acetonitrile, but for the final fourth step the stabil-

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 zinc(II) halide complexes in acetonitrile, pyridine, DMSO and water at 25 °C.

	Acetonitrile[a] 0.1 M PyHCF₃SO₃			Pyridine[a] 0.1 M PyHCF₃SO₃			Dimethylsulfoxide[b] 1.0 M NH₄ClO₄			Water[c] 1.0 M NaClO₄		
	Cl⁻	Br⁻	I⁻	Cl⁻	Br⁻	I⁻	Cl⁻	Br⁻	I⁻	Cl⁻	Br⁻	I⁻
$\log K_1$	8.07	5.67	4.50	2.73	3.82	2.45	1.93	0.85	−0.70	−0.19	−0.57	−1.52
$\log K_2$	7.19	6.70	6.69	2.11	1.83		3.90	2.89	1.41	−0.42	−0.82	
$\log K_3$	4.87	4.55	4.18				2.23	1.34	0.15	0.75	0.52	
$\log K_4$	2.89	2.89	2.69				<1.0					
K_1/K_2	7.56	0.093	0.0065	4.10	97.6		0.011	0.009	0.008	2	2	
K_2/K_3	209	140	323				46	35	19	0.07	0.05	
K_3/K_4	95	45	3				>17					
$-\Delta G_1^\circ$	46.0	32.3	25.7	15.6	21.8	14.0	11.1	4.8	−4.0	1.1	−3.3	−8.7
$-\Delta G_2^\circ$	41.0	38.2	38.2	12.1	10.5		22.2	16.5	8.0	−2.4	−4.7	
$-\Delta G_3^\circ$	27.8	26.0	23.9				12.9	7.7	0.9	4.3	3	
$-\Delta G_4^\circ$	16.5	16.5	15.4									
$-\Delta H_1^\circ$	5.8	−0.9	−12	2.5	−0.3	−20.1	−22.3	−27.8	−19.0	−5	−1.5	
$-\Delta H_2^\circ$	7.1	9.3	5.2	−6.7	8.4		−0.8	−9.1	−29.4	−38	−42	
$-\Delta H_3^\circ$	20.9	20.8	14.7				10.2	4.2	−12.7	0	8	
$-\Delta H_4^\circ$	11.3	4.5	0.0									
$-\Delta S_1^\circ$	135	112	127	44	74	114	112	110	50	15	−6	
$-\Delta S_2^\circ$	114	97	110	63	7		77	85	127	120	125	
$-\Delta S_3^\circ$	23	17	31				9	12	45	14	−17	
$-\Delta S_4^\circ$	17	40	51									

[a]This work. [b]Refs. 7 and 13. [c]Refs. 14 and 15.

ities are fairly similar, with the bromide complex as the most stable one (Table 4). The thermodynamic pattern for the formation of the mercury(II) halide complexes in acetonitrile has similarities to what was found in aqueous solution.[17–22] These similarities probably depend on a similar bond character in the mercury(II)–solvate bonds in water and acetonitrile. The complexes in the mercury(II) halide systems are much more stable in acetonitrile than in water, DMSO and pyridine. This because the halide ions are more weakly solvated in acetonitrile than in the other solvents, while the mercury(II) ion is solvated equally well in acetonitrile and water (Table 5). All mercury(II) halide complexes are formed in exothermic reactions, which become more exothermic in the sequence Cl⁻ < Br⁻ < I⁻. This is due to the increasing softness of the halides and thereby an increasing strength and degree of covalency of the mercury(II)–halide bond formed. The first two complexes are very stable in all halide systems in acetonitrile. The ratio K_1/K_2 is in all cases small, less than 10, which means that the first complex will never predominate (Fig. 5). This pattern is also found for the chloride and bromide complexes in water, while the first complex has a fairly wide range of predominance in DMSO and pyridine (Figs. 1A and 1B in Ref. 13). The first two mercury(II) halide complexes in acetonitrile are mainly enthalpy stabilized, but there is also a fairly large entropy contribution (Fig. 6). In this respect there is a strong similarity to what is found for an aqueous solution. The stabilities of the third complexes

are very much weaker than the second ones (Table 5). This means that the neutral complexes have an extraordinarily wide range of existence (Fig. 5). The third and fourth complexes are also enthalpy stabilized, and the entropy terms are close to zero or negative (Table 4 and Fig. 7). The large free energy and enthalpy terms found in acetonitrile are due to the weak solvation, as the energy consumed at the desolvation at the complex formation is comparatively small (Table 5). The heats of formation of mercury(II) chloride complexes decrease by about 10 kJ mol⁻¹ for each complex formed. A similar pattern is seen for the bromide and iodide complexes, but here the heats of complex formation are the same for the third and fourth steps, and about 20 kJ mol⁻¹ less than ΔH_2°(Table 5). This difference between the chloride system on one hand, and the bromide and iodide complexes on the other, is also seen in the entropies.

The structure of the acetonitrile-solvated mercury(II) ion has not been studied so far. It is, however, reasonable to assume that it is six-coordinated in an octahedral fashion as the other solvated mercury(II) ions studied so far.[34,35] The thermodynamic properties in acetonitrile indicate that the desolvation takes place at the formation of the first two mercury(II) halide complexes. The HgX₂ complexes are weakly solvated in acetonitrile,[2] and one can assume that two acetonitrile molecules are coordinated to mercury(II) at long bond distances in a linearly distorted tetrahedron with an X–Hg–X angle close to 172°[1] in this complex. This

Table 4. Equilibrium constants, K_j/M^{-1}, and thermodynamic functions, $\Delta G_j°$, $\Delta H_j°$/kJ mol^{-1}; $\Delta S_j°$/J K^{-1} mol^{-1}, for the stepwise formation of mercury(II) halide complexes in acetonitrile, pyridine, DMSO and water at 25 °C.

	Acetonitrile[a] 0.1 M PyHCF$_3$SO$_3$[e]			Pyridine[b] 0.1 M PyHCF$_3$SO$_3$[e]			Dimethylsulfoxide[c] 1.0 M NH$_4$ClO$_4$			Water[d] 1.0 M NaClO$_4$		
	Cl$^-$	Br$^-$	I$^-$	Cl$^-$	Br$^-$	I$^-$	Cl$^-$	Br$^-$	I$^-$	Cl$^-$	Br$^-$	I$^-$
$\log K_1$	15.1	16.2	17.4	10.59	10.73	11.72	8.89	10.01	11.48	6.74	9.05	12.87
$\log K_2$	14.51	15.24	16.87	8.40	8.73	9.83	7.05	8.07	9.75	6.48	8.28	10.95
$\log K_3$	2.81	5.74	7.41	4.60	4.71	4.83	3.97	5.13	5.96	0.58	2.41	3.78
$\log K_4$	2.90	3.26	3.02	2.64	1.9	2.0	1.97	2.35	2.47	1.00	1.26	2.38
K_1/K_2	3.8	9.8	3.5	155	101	77	69	86	54	1.8	5.9	83
K_2/K_3	5×10^{11}	2.7×10^9	3.7×10^9	6300	10 300	1.0×10^5	1210	878	6230	4×10^5	7×10^5	1.5×10^7
K_3/K_4	0.81	305	2.5×10^4	90	640	700	101	603	3110	0.7	14	35
$-\Delta G_1°$	86.2	92.6	99.4	60.4	61.3	66.9	50.8	57.1	65.5	38.5	51.7	73.4
$-\Delta G_2°$	82.8	87.0	96.3	47.9	49.8	56.1	40.3	46.1	55.7	37.0	47.3	62.5
$-\Delta G_3°$	16.0	32.8	42.3	26.2	26.9	27.6	22.7	29.3	34.0	4.9	13.8	21.6
$-\Delta G_4°$	16.6	18.6	17.2	15.1	11	11	11.2	13.4	14.1	5.7	7.2	12.7
$-\Delta H_1°$	50.5	58.9	67.6	14.9	13.6	18.3	19.2	24.0	32.4	24.7	42.2	75.3
$-\Delta H_2°$	41.5	49.1	59.6	6.0	8.7	16.8	29.7	32.9	40.4	28.9	44.8	67.8
$-\Delta H_3°$	31.1	31.1	41.1	10.4	14.4	16.2	20.1	27.9	28.1	9.2	12.0	
$-\Delta H_4°$	19.7	31.9	42.4	6.8	7.5	4.3	16.5	21.5	23.0	0.4	17.2	
$\Delta S_1°$	120	113	107	153	160	163	106	111	111	46	32	-6
$\Delta S_2°$	139	127	123	141	138	132	36	44	51	27	8	-18
$\Delta S_3°$	-51	6	4	53	42	38	9	5	20	-14	6	
$\Delta S_4°$	-10	-44	-85	28	12	22	-18	-27	-30	20	-33	
$\Delta G_{\beta 4}°$	201.6	231.0	255.2	149.7	149.0	161.5	124.9	145.9	169.2	86.1	120.0	170.3
$\Delta H_{\beta 4}°$	142.8	171.0	210.7	38.0	44.2	55.4	85.6	106.0	123.8	62.4	116.2	185
$\Delta S_{\beta 4}°$	197	201	149	375	352	355	133	133	152	79	13	-49

This work. [b]Ref. 11. [c]Ref. 16. [d]Refs. 17–22. [e]Pyridinium trifluoromethylsulfonate.

Table 5. Gibbs free energies and heats of hydration, $\Delta G°_{hyd}$, $\Delta H°_{hyd}$/kJ mol^{-1}, and Gibbs free energies and heats of transfer,[5,23] $\Delta G_{tr}°$, $\Delta H_{tr}°$/kJ mol^{-1}, from water to acetonitrile(AN), dimethylsulfoxide(DMSO) and pyridine(Py) for the zinc(II), mercury(II), chloride, bromide and iodide ions.

Ion	$\Delta G°_{hyd}$[a]	$\Delta H°_{hyd}$	$\Delta G_{tr}°(AN)$	$\Delta H_{tr}°(AN)$	$\Delta G_{tr}°(DMSO)$	$\Delta H_{tr}°(DMSO)$	$\Delta G_{tr}°(Py)$	$\Delta H_{tr}°(Py)$
Zn^{2+}	-2027.6	-2063[b]	68.6	20.1	-46.9	-62.2	9.6	-86.4
Hg^{2+}	-1825.5	-1845[b]	3.1	-5.5	-67.9	-76	-79.1	-147.5
Cl$^-$	-317.1	-366[c]	41.7	20.5	39.4	18.1	34.2	27.9
Br$^-$	-303.3	-335[c]	31.4	8.0	26.3	3.8	20.5	10.6
I$^-$	-256.9	-294[c]	19.4	-6.8	9.1	-11.8	19.4	-8.0

[a]Ref. 24. [b]Ref. 25. [c]Ref. 20.

is in agreement with the result that the desolvation of importance for the thermodynamics takes place at the formation of the two first steps. The $\Delta S_3°$ value is negative and the $\Delta S_4°$ value is close to zero in the chloride system, while in the bromide and iodide systems the $\Delta S_3°$ values are close to zero and the $\Delta S_4°$ values are negative. This may indicate that in acetonitrile the structure of $HgCl_3^-$ is different from the structures of $HgBr_3^-$ and HgI_3^-. The HgX_3^- complex is possibly a trigonal bipyramid, with two solvent molecules in the axial positions (which are most probably very loosely coordinated with acetonitrile) or a distorted tetrahedron with a solvent molecule loosely coordinated in the fourth vertex. Previous studies on HgX_3^- complexes in DMSO have shown that $HgCl_3^-$ is a trigonal bipyramid, and the $HgBr_3^-$ and HgI_3^- complexes are slightly distorted tetrahedra.[36,37] The tetrahalomercurate(II) complexes are most probably regular tetrahedra in acetonitrile solution, as they are in aqueous and dimethylsulfoxide solutions.[38–42]
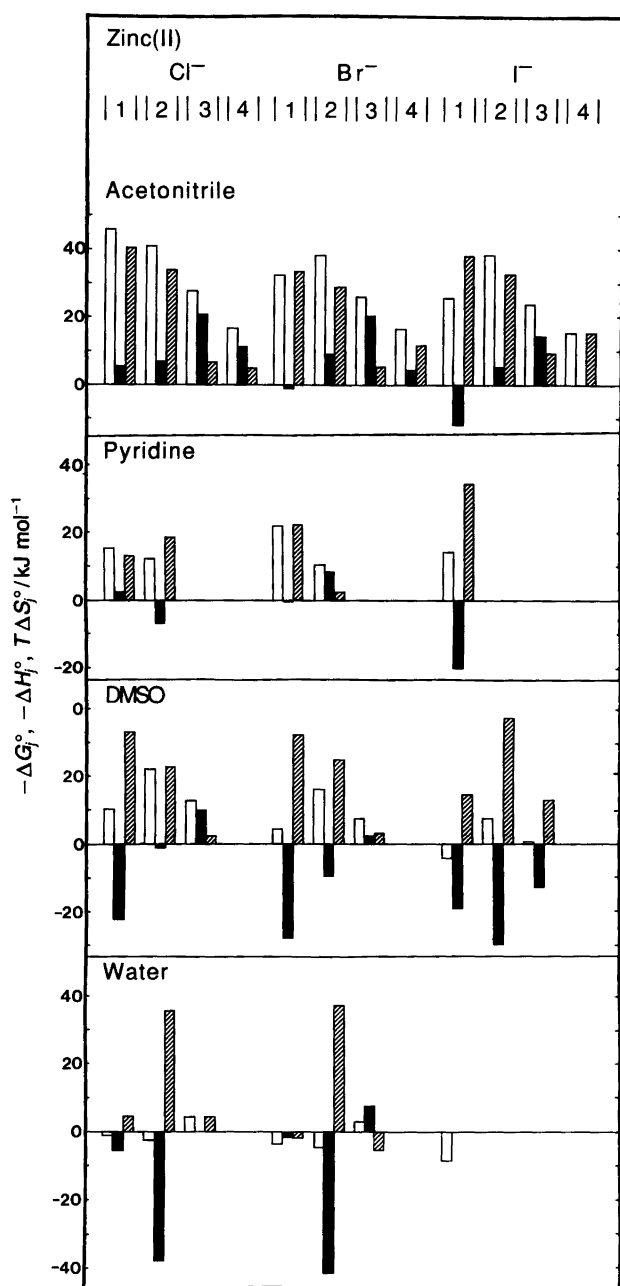
Fig. 6. Changes of free energy (white), enthalpy (black) and entropy (hatched) for the consecutive steps of the zinc(II) halide systems in acetonitrile (0.1 M $C_5H_6NCFN_3SO_3$), pyridine (0.1 M $(C_2H_5)_4NClO_4$), dimethylsulfoxide (0.1 M NH_4ClO_4) and water (1.0 M $NaClO_4$), at 25 °C.
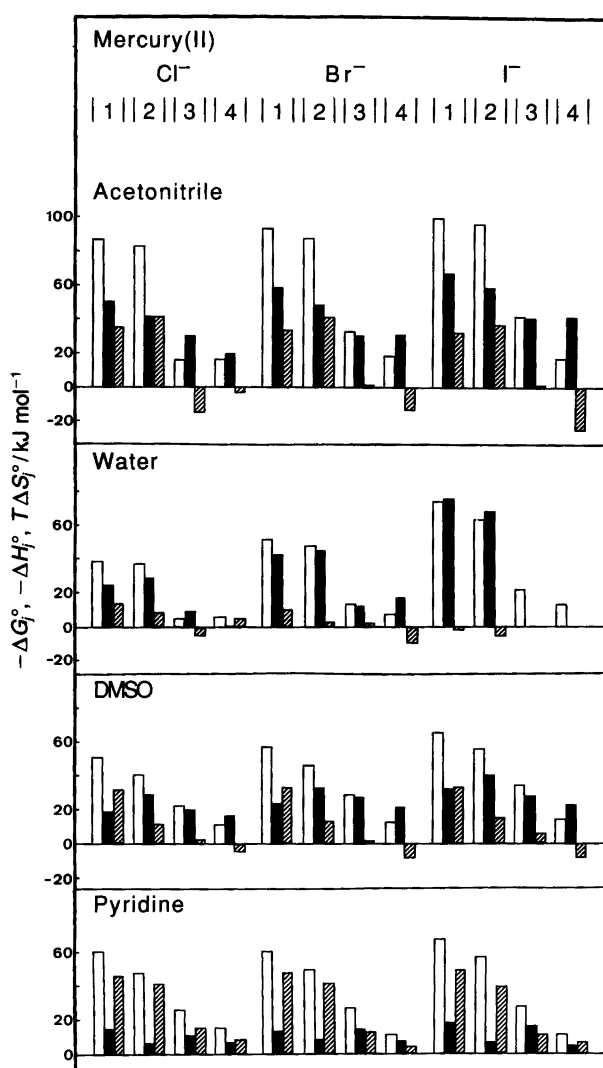

Fig. 7. Changes of free energy (white), enthalpy (black) and entropy (hatched) for the consecutive steps of the mercury(II) halide systems in acetonitrile (0.1 M $C_5H_6NCF_3SO_3$), pyridine (0.1 M $(C_2H_5)_4NClO_4$), dimethylsulfoxide (0.1 M NH_4ClO_4) and water (0.5 M $NaClO_4$), at 25 °C.

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