

Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution. X. Equilibrium and Enthalpy Measurements on Halide Systems of Zinc(II), Cadmium(II) and Mercury(II) in 0.1 M Ammonium Perchlorate

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The thermodynamics of the formation of zinc(II) bromide, cadmium(II) chloride, bromide and iodide, and mercury(II) bromide complexes in dimethyl sulfoxide (DMSO) have been studied in a 0.1 M ammonium perchlorate medium at 25 °C. The stability constants have been determined potentiometrically and, except for the mercury(II) bromide, also calorimetrically, and the enthalpy changes calorimetrically. The complexes are more stable in the present medium than in the 1 M ammonium perchlorate employed previously. The overall enthalpy changes are less favourable than in 1 M ammonium perchlorate, but the overall entropy gains are considerably more favourable. The coordination changes take place at the same steps as in 1 M medium, except for the zinc(II) bromide. In this system, the switch from octahedral to tetrahedral coordination moves from the first to the second step as the concentration of NH_4^+ is decreased from 1 to 0.1 M.

The thermodynamics of zinc(II), cadmium(II) and mercury(II) halide and thiocyanate complex formation in the aprotic solvent dimethylsulfoxide (DMSO) have previously been investigated for the ionic medium 1 M ammonium perchlorate.¹⁻⁵ It is of interest to investigate some of these systems at a lower concentration of ammonium perchlorate, in order to study the effects of a considerable quantitative change of the medium. The cadmium(II) halides have been chosen in order to examine how complexes formed by ligands of gradually changing bonding characteristics are influenced. By investigat-

ing also the zinc(II) and mercury(II) bromide systems, the effect on complexes of metal ions coordinating *via* bonds of different types can also be studied. The stability constants of the zinc(II) and cadmium(II) complexes have been determined both potentiometrically, by means of amalgam electrodes, and calorimetrically. Simultaneous determinations of the stabilities, *i.e.* the free energy changes, and the heats of reaction by calorimetric measurements are possible only under certain conditions⁶ which are, however, met for these systems.^{2,4} For mercury (II) bromide they are not, however, so constants of this system have only been determined potentiometrically, by means of the mercury electrode.

EXPERIMENTAL

Chemicals. The solid solvates $[\text{Zn}(\text{DMSO})_6](\text{ClO}_4)_2$, $[\text{Cd}(\text{DMSO})_6](\text{ClO}_4)_2$ and $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$, the ligand solutions and the amalgams used were prepared and analyzed as described previously.^{1,7-9}

Potentiometric measurements. The procedures used in the potentiometric measurements have been described elsewhere.^{1,3,5} As reference electrode, the very stable and reproducible cadmium amalgam electrode has been used. The zinc and cadmium amalgam electrodes and the mercury electrode all follow Nernst's law. Their standard potentials for the medium used have been determined previously.¹⁰ Three different values of the initial metal ion concentration were used in the potentiometric titrations, and each titration was repeated at least twice. The reproducibility was in

general better than 0.3 mV for the mercury(II) bromide and better than 0.4 mV for the zinc(II) and cadmium(II) halides. The emf's stayed constant within 0.5 mV for at least 15 h.

The stability constants β_j were calculated from the potentiometric measurements by the computer program EMK,¹¹ or for the reversed titrations used for the mercury(II) bromide system, by a modified version of this program. The formulas used in these programs have been long established.^{12,13}

In the zinc and cadmium systems, no experimental values were discarded in the final calculation of β_j . In the mercury bromide system, certain points had to be omitted, as will be further discussed below.

Calorimetric measurements. The calorimeter and the technique used have been described previously.^{2,4,5,14,15} The calibration constant ϵ , was the

same as before.⁵ The heats of dilution were determined by titrations where either the ligand or the central ion solution had been exchanged for pure ionic medium.^{2,4,5} In the mercury(II) bromide system it has, moreover, been possible to determine the heats of dilution of the intermediate complexes HgBr^+ , HgBr_2 and HgBr_3^- . These are around 60, 45 and 30 %, respectively, of the heat of dilution of Hg^{2+} . Enthalpy changes and stability constants have been calculated from the calorimetric measurements by the program KALORI.¹¹ For the final calculation of the enthalpy changes, the weighted means of the stability constants determined potentiometrically and calorimetrically were used as fixed parameters. Complete experimental data are available from the authors.

Table 1. The overall stability constants (β_j/M^{-j}) of the zinc(II) bromide complexes in DMSO, ionic medium 0.1 M ammonium perchlorate, at 25 °C. The constants have been determined potentiometrically and calorimetrically; the errors stated refer to three standard deviations. NP=number of points.

	Pot.	Cal.	Mean
β_1	74 ± 26	71 ± 57	73 ± 27
β_2	$(1.47 \pm 0.10) \times 10^5$	$(1.57 \pm 0.23) \times 10^5$	$(1.48 \pm 0.11) \times 10^5$
β_3	$(1.47 \pm 0.06) \times 10^7$	$(1.19 \pm 0.48) \times 10^7$	$(1.44 \pm 0.12) \times 10^7$
NP	185	181	

Table 2. The stability constants (β_j/M^{-j}) of cadmium(II) chloride, bromide and iodide complexes in DMSO, ionic medium 0.1 M ammonium perchlorate, at 25 °C. The constants have been determined potentiometrically and calorimetrically; the errors refer to three standard deviations.

	Pot	Cal.	Mean
Chloride			
β_1	$(2.36 \pm 0.37) \times 10^4$	$(2.22 \pm 0.35) \times 10^4$	$(2.29 \pm 0.25) \times 10^4$
β_2	$(2.49 \pm 1.54) \times 10^7$	$(1.71 \pm 0.54) \times 10^7$	$(1.91 \pm 0.82) \times 10^7$
β_3	$(5.79 \pm 1.05) \times 10^{10}$	$(5.04 \pm 1.45) \times 10^{10}$	$(5.48 \pm 0.80) \times 10^{10}$
β_3	$(1.54 \pm 0.32) \times 10^{13}$	$(0.88 \pm 0.31) \times 10^{13}$	$(1.21 \pm 0.22) \times 10^{13}$
NP	105	198	
Bromide			
β_1	4960 ± 250	4480 ± 800	4850 ± 420
β_2	$(1.72 \pm 0.38) \times 10^6$	$(1.15 \pm 0.72) \times 10^6$	$(1.52 \pm 0.41) \times 10^6$
β_3	$(2.90 \pm 0.15) \times 10^9$	$(2.70 \pm 0.94) \times 10^9$	$(2.87 \pm 0.47) \times 10^9$
β_4	$(1.97 \pm 0.12) \times 10^{11}$	$(1.67 \pm 1.26) \times 10^{11}$	$(1.94 \pm 0.64) \times 10^{11}$
NP	146	174	
Iodide			
β_1	386 ± 31	330 ± 75	370 ± 41
β_2	$(1.87 \pm 1.12) \times 10^4$	$(3.24 \pm 2.30) \times 10^4$	$(2.32 \pm 1.28) \times 10^4$
β_3	$(1.53 \pm 0.21) \times 10^7$	$(1.72 \pm 0.41) \times 10^7$	$(1.58 \pm 0.21) \times 10^7$
β_4	$(1.87 \pm 0.31) \times 10^8$	$(6.07 \pm 4.04) \times 10^8$	$(2.15 \pm 2.02) \times 10^8$
NP	122	174	

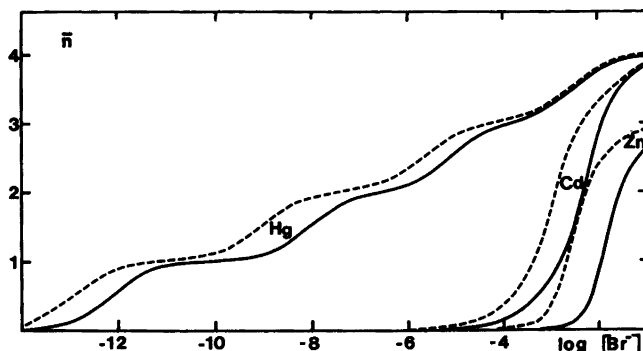


Fig. 1. The complex formation functions of the zinc(II), cadmium(II) and mercury(II) bromide systems in DMSO, ionic media 0.1 M and 1 M ammonium perchlorate (dashed and solid curves, respectively).

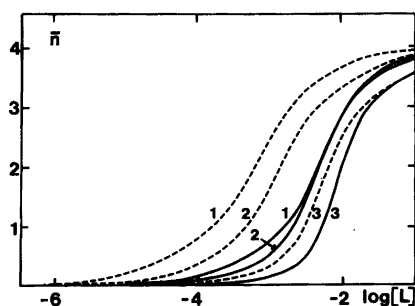


Fig. 2. The complex formation functions of the cadmium(II) halide systems in DMSO, ionic media 0.1 M and 1 M ammonium perchlorate (dashed and solid curves, respectively). Ligands: chloride(1), bromide(2), iodide(3).

MEASUREMENTS AND RESULTS

Zinc(II) bromide. In the range of central ion and ligand concentrations used in the potentiometric measurements, viz. $2.5 \text{ mM} \leq C_M \leq 19.0 \text{ Mm}$, and $0 \leq C_L \leq 75.1 \text{ mM}$, respectively, the complex formation is well described by three mononuclear complexes. Four complexes give about the same sum of least squares, but the error of the fourth stepwise constant K_4 is so large that the last complex remains hypothetical. No polynuclear complexes are formed in the ranges of C_M and C_L investigated. The results are in Table 1.

In the calorimetric measurements, the ranges of C_M and C_L used were $2.6 \text{ mM} \leq C_M \leq 16.2 \text{ mM}$ and $0 \leq C_L \leq 67.3 \text{ mM}$. Also these measurements indicate the formation of three mononuclear complexes.

The values of β_j are listed in Table 1 as are the weighted means of the values found by the two methods employed. The complex formation function calculated from the mean constants is plotted in Fig. 1. The means were also used in the final calculation of the values of $\Delta H_{\beta_j}^\circ$ listed in Table 4. In Fig. 3, the total molar enthalpy change Δh_v is plotted as a function of the ligand number \bar{n} . The stepwise stability constants K_j , their ratios K_j/K_{j+1} , and the thermodynamic functions ΔG_j° , ΔH_j° and ΔS_j° of the consecutive steps, calculated from the values of β_j and $\Delta H_{\beta_j}^\circ$ finally adopted, are collected in Table 6.

Cadmium(II) chloride, bromide and iodide. In the potentiometric measurements, the concentration ranges used for the chloride system were $3.3 \text{ mM} \leq C_M \leq 19.6 \text{ mM}$ and $0 \leq C_L \leq 54.6 \text{ mM}$, for the bromide system $2.3 \text{ mM} \leq C_M \leq 19.6 \text{ Mm}$ and $0 \leq C_L \leq 66.7 \text{ mM}$, and for the iodide system $1.3 \text{ mM} \leq C_M \leq 19.6 \text{ mM}$ and $0 \leq C_L \leq 75.0 \text{ mM}$. Within these ranges, four mononuclear complexes are formed in all the systems. No polynuclear complexes exist, which is not surprising as such complexes are seemingly not formed even in very concentrated solutions.¹⁶ The values of β_j are in Table 2.

In the calorimetric measurements, the range of concentration of cadmium(II) was $3.2 \text{ mM} \leq C_M \leq 19.7 \text{ mM}$, of chloride and bromide $0 \leq C_L \leq 59.1 \text{ mM}$, and of iodide $0 \leq C_L \leq 67.3 \text{ mM}$. Also by this method, four mononuclear complexes were found, and the values of β_j agree quite well with those found potentiometrically (Table 2). From the weighted means of β_j , see Table 2, the complex formation curves plotted in Fig. 2 have been calculated, and also the final values of $\Delta H_{\beta_j}^\circ$, see

Table 4. In Fig. 4, Δh_v is given as a function of \bar{n} . The curves of the bromide system have also been entered in Figs. 1 and 3. The constants and thermodynamic functions referring to the consecutive steps are collected in Table 5, and, for the bromide system, also in Table 6.

Mercury(II) bromide. In the reversed titrations performed for this system, the mercury(II) and bromide concentrations were varied in the ranges $2.5 \text{ mM} \leq C_M \leq 13.7 \text{ mM}$ and $8.0 \leq C_L \leq 58.3 \text{ mM}$. The actual concentration of mercury(II) reacting with bromide was calculated from the equivalence points observed in the titrations and found to be 0.1 mM less than the formal concentration. This agrees with the results obtained earlier in 1 M ammonium perchlorate medium and confirms the conclusion drawn that the discrepancy is due to an impurity in the DMSO, with a very strong affinity for mercury(II).⁵ Experimental points of $\bar{n} < 1.66$ could not be made to fit, evidently on account of an incipient formation of mercury(I). These points were discarded. Four mononuclear complexes are found, with constants listed in Table 3. No polynuclear complexes are indicated; no such complexes are, in fact, formed even in much more concentrated solutions of this system.^{17,18} The complex formation function is given in Fig. 1.

Table 3. The stability constants (β_i/M^{-i}) of the mercury(II) bromide complexes in DMSO, ionic medium = 0.1 M ammonium perchlorate, at 25°C. The constants have been determined potentiometrically; the errors refer to three standard deviations.

β_1	$(8.29 \pm 0.69) \times 10^{12}$
β_2	$(9.17 \pm 0.78) \times 10^{21}$
β_3	$(4.20 \pm 0.46) \times 10^{27}$
β_4	$(1.67 \pm 0.22) \times 10^{30}$
NP	361

Table 4. Overall enthalpy changes ($\Delta H_{\beta_j}/\text{kJ mol}^{-1}$) for the formation of the zinc(II) bromide, cadmium(II) chloride, bromide, iodide and mercury(II) bromide systems in DMSO, ionic medium 0.1 M ammonium perchlorate, at 25°C. The errors stated refer to three standard deviations.

System	$\text{Zn}^{2+} - \text{Br}^-$	$\text{Cd}^{2+} - \text{Cl}^-$	$\text{Cd}^{2+} - \text{Br}^-$	$\text{Cd}^{2+} - \text{I}^-$	$\text{Hg}^{2+} - \text{Br}^-$
$-\Delta H_{\beta_1}^\circ$	$-(22.3 \pm 1.7)$	4.9 ± 0.2	0.9 ± 0.3	$-(5.2 \pm 0.3)$	20.0 ± 0.6
$-\Delta H_{\beta_2}^\circ$	$-(42.2 \pm 0.5)$	$-(7.5 \pm 0.8)$	-14.9 ± 1.4	$-(26.8 \pm 2.6)$	44.1 ± 0.9
$-\Delta H_{\beta_3}^\circ$	$-(36.3 \pm 0.5)$	$-(14.0 \pm 0.3)$	$-(22.0 \pm 0.4)$	$-(33.3 \pm 0.5)$	68.5 ± 1.1
$-\Delta H_{\beta_4}^\circ$		1.5 ± 0.3	$-(10.6 \pm 0.6)$	$-(28.7 \pm 1.4)$	85.8 ± 1.4
NP	181	198	177	174	219

The calorimetric measurements have been performed in the ranges $3.2 \leq C_M \leq 15.7 \text{ mM}$ and $0 \leq C_L \leq 56.6 \text{ mM}$. As the function Δh_v does not display any marked points of equivalence (Fig. 3), any correction of C_M was neither indicated, nor needed. The smooth course of Δh_v is due to the fact that the values of ΔH_j° do not differ very much between the consecutive steps (Table 6). The values of $\Delta H_{\beta_j}^\circ$ are in Table 4, and the quantities calculated for the consecutive steps in Table 6.

DISCUSSION

In Tables 5 and 6, the equilibrium constants and thermodynamic functions of the consecutive steps, derived from the present measurements in 0.1 M ammonium perchlorate, are compared with those found previously in 1 M ammonium perchlorate.¹⁻⁵

The comparison between the cadmium(II) halide systems in the two media shows (Table 5) that the decrease of the ammonium perchlorate concentration causes a large increase of K_j (roughly ten times) for the chloride complexes and a considerably smaller one for the bromide complexes. For the iodide complexes, a small increase is found for K_1 and K_2 , while K_3 and K_4 even show a slight decrease between the 1 M and the 0.1 M medium. In DMSO, the pattern is thus distinctly different for different halides. In a protic solvent like water, on the other hand, much the same pattern is found for chloride and iodide, at least in sodium perchlorate media,¹⁹ and this pattern is moreover very similar to that found presently for iodide in DMSO. In these cases, the changes are of the magnitude to be expected as a consequence of the change of the activity conditions accompanying a decrease of the ionic strength, I , from ≈ 1 to ≈ 0.1 M. Especially for the chloride, but also for the bromide, the changes in DMSO between the two media are larger than expected, however. Most likely, this indicates a

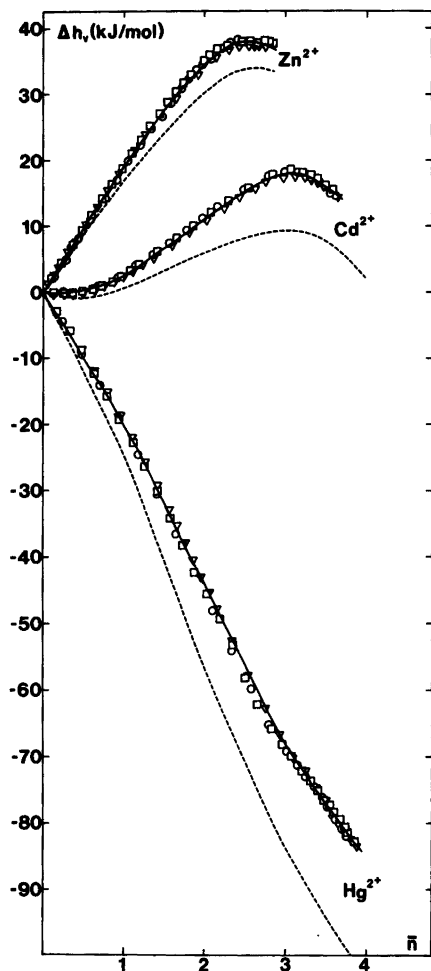


Fig. 3. The total molar enthalpy change Δh_v , as a function of the ligand number \bar{n} for the zinc(II), cadmium(II) and mercury(II) bromide systems in DMSO at 25°C. The symbols refer to the present titrations in 0.1 M ammonium perchlorate at the initial concentrations $C'_M = 4(\text{O})$, 8 (\square) and 16 mM (∇). The curves have been calculated from the values of β_j and ΔH_{β_j} obtained in 0.1 M and 1 M ammonium perchlorate (solid and dashed, respectively).

formation in DMSO of complexes between NH_4^+ and Cl^- and, to a lesser extent, between NH_4^+ and Br^- . Thus, NH_4Cl is not at all completely dissociated in DMSO at concentrations of NH_4^+ as high as 1 M, nor is NH_4Br .²⁰ On the other hand, NH_4I probably is, as are also all the sodium halides in water.

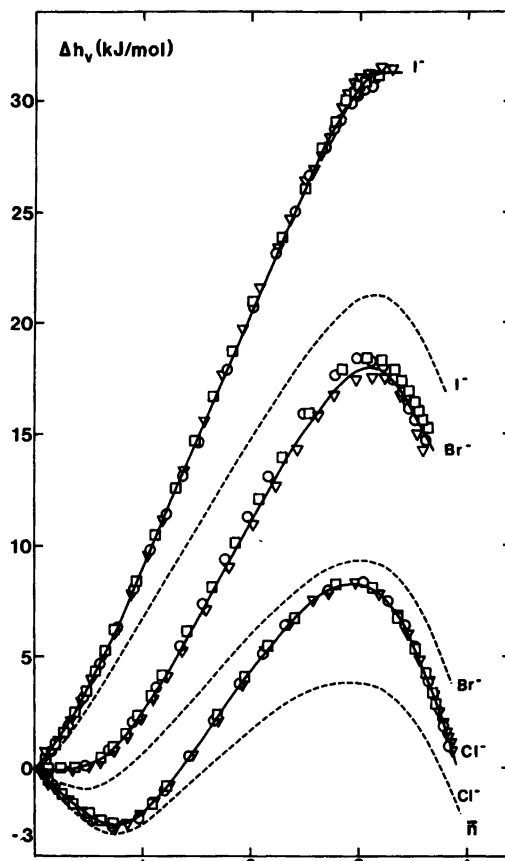


Fig. 4. The total molar enthalpy change Δh_v , as a function of the ligand number \bar{n} for the cadmium(II) chloride, bromide and iodide systems in DMSO, at 25°C. The symbols refer to the present titrations in 0.1 M ammonium perchlorate, at values of C'_M stated in Fig. 3. The curves have been calculated for 0.1 M and 1 M ammonium perchlorate (solid and dashed, respectively), as described in Fig. 3.

An attempt to determine calorimetrically, by adding lithium halide solutions to ammonium perchlorate, the stability of the ammonium halide complexes did not give coherent results. The reason might well be that NH_4^+ and Li^+ act rather differently as medium cations, as will be shown in the next paper of this series.²¹

The complex formation postulated follows the order of increasing electrostatic interaction but already on account of the low charge density of NH_4^+ a simple electrostatic interpretation seems hardly

Table 5. Equilibrium constants (K_i/M^{-1}) and thermodynamic functions (ΔG_i° , $\Delta H_i^\circ/kJ\ mol^{-1}$; $\Delta S_i^\circ/JK^{-1}\ mol^{-1}$) for the stepwise formation of cadmium(II) chloride, bromide and iodide complexes in DMSO at 25°C.

	0.1 M NH_4ClO_4			1 M $NH_4ClO_4^a$		
	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-
$\log K_1$	4.36	3.69	2.57	3.23	2.92	2.18
$\log K_2$	2.92	2.50	1.80	1.97	1.91	1.37
$\log K_3$	3.46	3.28	2.83	2.58	2.75	2.93
$\log K_4$	2.34	1.83	1.13	1.75	1.68	1.18
K_1/K_2	27	16	5.9	18	10	6.4
K_2/K_3	0.29	0.17	0.09	0.24	0.15	0.03
K_3/K_4	13	28	58	6.7	12	58
$-\Delta G_1^\circ$	24.9	21.0	14.7	18.4	16.7	12.5
$-\Delta G_2^\circ$	16.7	14.7	10.3	11.2	10.9	7.8
$-\Delta G_3^\circ$	19.7	18.7	16.2	14.7	15.7	16.8
$-\Delta G_4^\circ$	13.4	10.4	6.1	10.0	9.5	6.7
$-\Delta H_1^\circ$	4.9	0.9	-5.2	6.3	3.9	-2.4
$-\Delta H_2^\circ$	-12.5	-15.8	-21.5	-15	-17	-27
$-\Delta H_3^\circ$	-6.7	-7.2	-6.6	-1	-2	5
$-\Delta H_4^\circ$	15.5	11.4	4.8	12.2	13	9.5
ΔS_1°	67	68	67	41	43	50
ΔS_2°	98	101	106	88	94	117
ΔS_3°	88	87	76	53	59	40
ΔS_4°	-7	-3	4	-7	-12	-10
$-\Delta H_{\beta 4}^\circ$	1.2	-10.7	-38.1	2	-2.1	-15
$\Delta S_{\beta 4}^\circ$	246	253	253	175	184	197

^aRef. 2.

sufficient. That such an interpretation is, in fact, wholly inadequate is shown by the behaviour of the cadmium(II) bromide system in lithium perchlorate media.²¹ Certainly, the complex formation in DMSO between NH_4^+ and halide ions is mainly due to the hydrogen bonding properties of the ligands. In an aprotic solvent where no better partners are available, NH_4^+ will participate in those hydrogen bonds which in a protic solvent such as water would be formed between Cl^- , or Br^- , and the solvent molecules.

A comparison of the values of $\Delta H_{\beta 4}^\circ$ and $\Delta S_{\beta 4}^\circ$ shows that the overall stability increase between the two NH_4^+ media is very much an entropy effect, see Table 5. A general increase of the entropy gain as I decreases is certainly to be expected from the circumstance that a lower concentration of NH_4^+ means less order in the bulk solvent. The desolvation

accompanying the formation of cadmium(II) halide complexes will then result in a larger total loss of order, and hence in a more favourable entropy.

Such an increase of the entropy gain is generally accompanied by a less favourable enthalpy change, as part of the energy gained by solvation of medium ions is lost when I decreases. As to the present systems, this partial compensation is prominent in the case of the iodide. To some extent it also occurs for the bromide, while for the chloride the value of $\Delta H_{\beta 4}^\circ$ is much the same in both media. This may be rationalized by postulating that in 1 M NH_4^+ medium extensive reactions involving Cl^- , and Br^- , take place which make the values of $\Delta H_{\beta 4}^\circ$ less favourable than they would otherwise be. Most likely, these reactions are the dissociations of NH_4Cl , and NH_4Br , which accompany the formation of the cadmium complexes. As NH_4Cl and NH_4Br are

formed much more extensively in 1 M than in 0.1 M NH_4^+ , the dissociation will be a more prominent reaction in the former medium.

On the whole, the values of ΔH_j° and ΔS_j° of the individual steps follow the same pattern though the picture is somewhat modified by changes in the relative magnitudes. In both media, the values of ΔS_2° are the most favourable of all ΔS_j° and those of ΔH_2° the most unfavourable of all ΔH_j° . The values of ΔS_3° and ΔH_3° are much larger in 0.1 M than in 1 M medium, however.

Already at a time when the octahedral structure of the solvated Cd^{2+} , and the tetrahedral structure of the finally formed CdX_4^{2-} were only reasonable postulates, the very high values of ΔH_2° and ΔS_2° in DMSO were interpreted as indicating a switch from octahedral to tetrahedral coordination at the formation of CdX_2 . Later on, the structures postulated for the initial solvate and the final tetrahalide

complex have been fully confirmed by direct determination of their structures by X-ray diffraction.^{8,16} That the switch mainly takes place at the second step in DMSO has also been recently confirmed, and moreover both by nuclear magnetic resonance measurements²² and by studies of the Cd(II)/Cd(Hg) electrode kinetics²³ in halide solutions. In the NMR spectra, large increases of the ^{113}Cd chemical shifts are found between the first and the second complex for all the halide systems, clearly indicating that the second step involves an abrupt change of coordination. As to the electrode kinetics, iodide and bromide, but not chloride complexes, participate in the charge transfer reaction. The different behaviour is presumably due to the circumstance that the larger halide ions are able to form bridges between the electrode and the divalent cadmium in solution. For those systems where the halide complexes do participate in the reaction, the rate of the charge

Table 6. Equilibrium constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j° , $\Delta H_j^\circ/\text{kJ mol}^{-1}$; $\Delta S_j^\circ/\text{JK}^{-1}\text{mol}^{-1}$) for the stepwise formation of zinc(II), cadmium(II) and mercury(II) bromide complexes in DMSO at 25 °C.

	0.1 M NH_4ClO_4			1 M $\text{NH}_4\text{ClO}_4^a$		
	Zn^{2+}	Cd^{2+}	Hg^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
$\log K_1$	1.86	3.69	12.92	0.85	2.92	12.14
$\log K_2$	3.31	2.50	9.05	2.89	1.91	8.06
$\log K_3$	1.98	3.28	5.66	1.35	2.75	5.14
$\log K_4$		1.83	2.60		1.68	2.54
K_1/K_2	0.04	16	7.5×10^3	0.09	10	1.2×10^4
K_2/K_3	21	0.17	2.4×10^3	35	0.15	8.3×10^2
K_3/K_4		28	1.2×10^3		12	4.0×10^2
$-\Delta G_2^\circ$	10.6	21.0	73.7	4.8	16.7	69.3
$-\Delta G_3^\circ$	18.9	14.2	51.6	16.5	10.9	46.0
$-\Delta G_4^\circ$	11.3	18.7	32.3	7.7	15.7	29.3
$-\Delta G_5^\circ$		10.4	14.8		9.5	14.5
$-\Delta H_1^\circ$	-22.3	0.9	20.0	-27.8	3.9	24.7
$-\Delta H_2^\circ$	-19.9	-15.8	24.1	-9.1	-17	31.9
$-\Delta H_3^\circ$	5.9	-7.2	24.4	4.2	-2	27.8
$-\Delta H_4^\circ$		11.4	17.3		13	19.1
ΔS_1°	110	68	180	110	43	149
ΔS_2°	130	101	92	85	94	47
ΔS_3°	18	87	26	12	54	5
ΔS_4°		-3	-8		-12	-16
$-\Delta H_{\beta 3}^\circ$	-36.3	-22.1	68.5	-32.7	-15	84.4
$\Delta S_{\beta 3}^\circ$	258	256	298	207	196	201

^aRefs. 4 (Zn^{2+}), 2 (Cd^{2+}) and 5 (Hg^{2+}).

transfer increases tremendously between the first and the second step. The complexes CdBr_2 and CdI_2 thus give large contributions to the exchange current which can be correlated with the change of coordination taking place at their formation. The close connection between values of ΔH_1° and ΔS_1° , and the rate of the charge transfer, is further demonstrated by results found for the cadmium thiocyanate complexes. Contrary to what has been found for the halides, the values of ΔH_2° and ΔS_2° are both quite small, indicating that in the thiocyanate system no drastic change of coordination takes place at the second step.² In consistency with this, the rate of the charge transfer due to $\text{Cd}(\text{SCN})_2$ is quite low.²⁴

The circumstance that ΔS_3° and ΔH_3° are much larger relative to ΔS_2° and ΔH_2° in 0.1 M than in 1 M NH_4^+ medium (Table 5), means that the change of coordination is less clear-cut in the more dilute medium. In this case, the switch seemingly extends over two steps which would imply that the second step exists as both octahedral and tetrahedral coordination isomers.

For the zinc(II) and mercury(II) bromide complexes, similar increases of stability occur between 1 M and 0.1 M NH_4^+ medium as in the case of the cadmium(II) bromide (Table 6). This proves, of course, that they are due to the ligand and not to the metal ion involved, just as has been implied in the reasoning above.

As only three complexes are formed in the zinc system, $\Delta H_{\beta 3}^\circ$ and $\Delta S_{\beta 3}^\circ$ must be used for the comparison of the overall thermodynamics. As the switch to tetrahedral coordination has by then taken place not only for Hg(II) and Cd(II), but also for Zn(II), *cf.* below, the exclusion of the last step does not matter very much, however. The picture emerging is very similar for all the systems. A considerable increase of $\Delta S_{\beta 3}^\circ$ from 1 M to 0.1 M medium is partly compensated by more unfavourable values of $\Delta H_{\beta 3}^\circ$. It should be noted, however, that both effects are markedly larger for Hg(II) than for Cd(II) and, especially, Zn(II). In consideration of the huge differences in strength and nature of the complexes, these differences in behaviour seem indeed modest.

For the zinc(II) bromide system, the relative size of ΔS_1° and ΔS_2° changes between 1 M and 0.1 M medium (Table 6). The tendency found already for the cadmium(II) systems, that the switch to tetrahedral coordination occurs at a later stage as the concentration of medium ions decreases, is thus so marked for zinc(II) bromide that the step of the main

switch really changes. Considering that a higher concentration of medium ions ought to encourage the extra desolvation of the metal ion accompanying the change of coordination, it seems natural that the change should tend to occur at an earlier stage in the more concentrated medium, as is in fact the case. For the zinc(II) bromide system, the change from 1 M to 0.1 M medium means that its behaviour starts to resemble that found for the iodide and thiocyanate system already in 1 M medium.⁴

For the zinc(II) bromide system, the coordination change postulated from the thermodynamic data cannot be confirmed by studies of the kinetics of the Zn(II)/Zn(Hg) electrode, as the bromide complexes do not participate in the charge transfer.²⁵

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