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Metal Halide and Pseudohalide Complexes in Dimethyl Sulfoxide Solution. III. Equilibrium Measurements on the Cadmium(II) Chloride, Bromide, Iodide, and Thiocyanate Systems

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The formation of chloride, bromide, iodide, and thiocyanate complexes of cadmium(II) in dimethyl sulfoxide has been studied at 25 °C by central ion measurements. An approximately constant ionic medium of an ionic strength = 1 M has been provided by the addition of ammonium perchlorate. In the case of chloride, measurements have also been performed in a lithium perchlorate trihydrate medium of the same ionic strength. All the complexes formed are more stable in DMSO than in water, but the difference is smaller the less prone the ligand is to form hydrogen bonds.

As stated in the first paper of this series,[1] the aim of the present investigations is to compare the strength of the halide and pseudohalide complexes formed in protic and aprotic solvents by acceptors of different bonding characteristics. As the protic solvent of reference water is the obvious choice, while dimethyl sulfoxide (DMSO) has been selected as the aprotic solvent. In the present paper, the formation of chloride, bromide, iodide, and thiocyanate complexes of cadmium(II) in the two solvents is compared. The aqueous systems have been very extensively, and carefully, investigated before. In DMSO, on the other hand, it seems that only the cadmium chloride system has been studied,[2] and moreover in a most exploratory manner.

In the present study, the stabilities of the cadmium(II) systems in DMSO have been determined potentiometrically by means of a cadmium amalgam electrode. A salt medium of an ionic strength $I = 1$ M has been employed. The corresponding measurements in aqueous solution refer to sodium perchlorate media which would therefore *per se* have been the best choice also for the DMSO measurements. Though sodium perchlorate is certainly soluble enough in DMSO,[3] this is nevertheless impossible on account of the low solubility of sodium chloride [3] (0.09 M) which would allow only fairly low concentration of free chloride ion in a 1 M sodium ion solution. For the ammonium [4] and the lithium ions,[3] on the other hand, not only the perchlorates but also the halides (except the fluorides) and the thiocyanates are sufficiently soluble. The present measurements have therefore been performed in ammonium and lithium perchlorate media. The temperature has been 25 °C.

The cadmium amalgam electrodes work very well in DMSO solutions of anhydrous ammonium perchlorate, yielding very stable and reproducible potentials; see below. In solutions of anhydrous lithium perchlorate, on the other hand, the amalgam is rapidly oxidized. No oxidation occurs, however, in 1 M solutions of the hydrate $LiClO_4.3H_2O$ in DMSO. As it is of primary interest to study the conditions in a completely anhydrous medium, all the systems have been measured in ammonium perchlorate solutions. In order to find out, however, how the stability of the complexes is influenced by a change of medium, the chloride system has also been measured in a solution of the lithium perchlorate hydrate.

Calculations of stability constants from potentiometric measurements of the free central ion con-

centration. The formulas used have been derived previously [5,6] and only a summary will therefore be given here. The overall stability constant β_{ji} for the complex M_iL_j is defined as

$$\beta_{ji} = [M_iL_j]/[M]^i[L]^j \tag{1}$$

The stepwise stability constant for the jth mononuclear complex is defined as

$$K_j = [ML_j]/[ML_{j-1}][[L] \tag{2}$$

If polynuclear complexes are formed as well, the following formulas are valid for the simplest case, that of dinuclear complexes:

$$C_M = [M]X + 2[M]^2Y \tag{3}$$

$$C_L = [L] + [M][L]\frac{dX}{d[L]} + [M]^2[L]\frac{dY}{d[L]} \tag{4}$$

$$\text{where } X = 1 + \sum_{j=1}^{N} \beta_j[L]^j \text{ and } Y = \sum_{j=1}^{P} \beta_{j2}[L]^j \tag{5,6}$$

If only mononuclear complexes are formed, $Y = 0$.

The emf of the following cell

$$\begin{array}{l|l|l|l|l}
-\mathrm{Cd(Hg)} & C_M \text{ M Cd-} & 1.00 \text{ M} & C_M' \text{M Cd-} & \\
 & (ClO_4)_2 & & (ClO_4)_2 & \\
 & C_L \text{ M} & NH_4ClO_4 & NH_4ClO_4 & \text{Cd-} \\
 & NH_4L & & \text{to} & \text{(Hg)+} \\
 & NH_4ClO_4 & & I = & \\
 & \text{to} & & 1.00 \text{ M} & \\
 & I = & & & \\
 & 1.00 \text{ M} & & &
\end{array}$$

can be expressed as

$$E = E_k - (RT/2F) \ln [M] \tag{7}$$

where E_k includes the potential of the reference electrode and the liquid junction potentials. For the initial solutions where $C_L = 0$ and $[M] = C_M$, $E = E'$. Hence

$$E_M = E - E' = (RT/2F) \ln (C_M/[M]) = (RT/2F) \ln (X + 2[M]Y)$$

If only mononuclear complexes are formed E_M is evidently a function of [L] only. The functions $C_L(C_M)_{E_M}$ are then straight lines with intercepts $C_L = [L]$ for $C_M = 0$ and slopes equal to the ligand number $\bar{n} = (C_L - [L])/C_M$. Corresponding values of [L] and X can thus be obtained, and hence the stability constants β_j (and K_j), provided that the complexes are not so strong that the extrapolated values of [L] are $\simeq 0$.

If polynuclear complexes are also formed E_M is a function of [M] as well, and the curves $C_L(C_M)_{E_M}$ will no more be straight lines with a slope $= \bar{n}$. Extrapolated to $C_M = 0$ they will nevertheless yield [L], and from X(L]) the mononuclear constants β_j can still be calculated. For $C_M = 0$, the slopes of the $C_L(C_M)_{E_M}$-curves will be

$$k(E_M) = \left(\frac{\delta C_L}{\delta C_M}\right)_{C_M = 0} = \bar{n}_I - \frac{2Y}{XX'} \tag{9}$$

where $\bar{n}_I$ is the ligand number referring to the mononuclear complexes. At least in principle, the function Y and hence the stability constants of the dinuclear complexes present can be calculated from eqn. (6) once the constants of the mononuclear complexes are known.[7] In practice, however, it is fairly difficult to determine the slopes $k(E_M)$ with the necessary precision.

If only mononuclear complexes are formed, or generally after extrapolation to $C_M = 0$, the Bodländer equation is valid

$$\bar{n}_I = \frac{d \log X}{d \log [L]} \simeq \frac{\Delta \log X}{\Delta \log [L]} \simeq \frac{2F}{RT \ln 10} \frac{\Delta E_M}{\Delta \log [L]} \tag{10}$$

implying that $\bar{n}_I$ can be calculated from the slope of the function $E_M([L])$.

When the complex formation is so strong that no reliable values of [L] are obtained by the extrapolarion described above, [L] can be found from the integrated Bodländer equation.

$$\log ([L]_0/[L]_j) = \int_{X([L]_j)}^{X([L]_0)} \frac{1}{\bar{n}_I} d \log X \tag{11}$$

provided that the complexes are mononuclear so that $\bar{n}_I$ can be found from the slopes of the $C_L(C_M)_{E_M}$-lines.

It must further be practicable to extend the measurements to an upper limit $[L]_0$ possible to determine independently, *e.g.* by extrapolation. For very strong complexes, a value of $[L]_0 > NC_M$ has then to be chosen.

From the functions $X([L])$ and $Y([L])$ thus found, preliminary evaluations of the constants β_j have been performed both graphically and by means of the computer program NPA ("Numerical Polynomial Approximation").

The final values of the constants have been determined numerically from eqn. (8) by means of the computer program EMK developed at this Center. Similar programs [9] have been used before for the treatment of emf and calorimetric data [10,11] but these have been confined to systems of mononuclear complexes.

The program EMK requires information about the formulas of the complexes formed. The best values of the various β_{ji} involved are found by minimizing the error square sum

$$U(\beta_j)=\sum_{i=1}^{N} w_i(E_{\mathrm{M},i,\mathrm{calc}}-E_{\mathrm{M},i})^2 \quad (12)$$

where w_i is a weighting term, here always $=1$. For this calculation values of [L] and [M] are computed by simultaneous solvation of eqns. (3) and (4). This procedure is started by the introduction of suitable initial values of β_{ji}, obtained by the preliminary evaluations described above. Good initial values of β_{ji} very much facilitate the attainment of the final values satisfying eqn. (12). Especially when several complexes, among them also polynuclear ones, exist simultaneously the progress to the final values of β_{ji} is otherwise fairly slow.

EXPERIMENTAL

Chemicals. The hexasolvate $Cd(DMSO)_6(ClO_4)_2$ has been prepared and analyzed as described previously.[1]

The *lithium* and *ammonium chlorides* (BDH), the *ammonium bromide* (B & A) and the *ammonium iodide* (Baker Analyzed) were dried at 120 °C and their halide content checked titrimetrically. The *ammonium thiocyanate* (Merck) was dried at 110 °C, and the thiocyanate content determined titrimetrically. The *ammonium perchlorate* (Baker Analyzed) was dried at 110 °C. The *lithium perchlorate* (G. F. Smith) contained 2.97 mol water per mol perchlorate, as determined by heating to 150 °C.

Dimethyl sulfoxide was purified as described before.[1] The stock solutions of the various ligands contained <0.2 % water by volume while the ammonium perchlorate solution contained <0.07 %. These determinations of traces of water were performed by a modified Karl Fischer method.[12]

Cadmium amalgam containing 7 % cadmium was prepared and stored as described by Persson,[13] except that the dissolution took place at 80 °C. Small variations in the cadmium content are of no importance as at 25 °C a two phase amalgam is formed [14] between 6 and 14 % Cd.

Apparatus. To keep the hygroscopic DMSO as dry as possible all measurements were performed in a glove-box, containing the Linde molecular sieve 4A XW. Further, predried nitrogen gas, presaturated with DMSO, was led through the box in order to prevent any moisture from entering. The relative humidity in fact never exceeded 4 %.

The nitrogen gas which had also been freed from oxygen was led through the electrode solutions in order to protect the amalgam electrodes from oxidation and to ensure a good mixing. Cadmium amalgam was used also for the reference electrodes as the otherwise very useful silver halide electrodes are easily dissolved in excess halide, on account of the ready formation in DMSO of higher soluble silver halide complexes.[19]

Commercial Ingold vessels were used for the electrode solutions, which were kept at 25.0 ± 0.1 °C by means of water circulating in an outer jacket around the vessels. The ligand solutions were added from a Metrohm piston burette. All parts of the apparatus in contact with DMSO were made from either glass or teflon. The measurements were performed with a Leeds & Northrup 7555 type K-5 potentiometer combined with a 9828 D.C. null detector, allowing a precision of ±0.01 mV.

Procedure. Ligand solution T of the concentration C_L' (v ml) was added to a cadmium solution S of the initial concentration C_M'($V_0=$ 10.00 ml) in the left half-cell. In the resulting solution, the total concentration of cadmium(II), C_M, decreases to $C_\mathrm{M}=C_\mathrm{M}'V_0/(V_0+v)$. The emf E actually measured is therefore due not only to the complex formation but also to the dilution. In order to find the E_M of eqn. (8), the following correction has to be introduced

$$E_\mathrm{M}=E-E'-(RT/2F)\ \ln\ [(V_0+v)/V_0] \quad (13)$$

Series were performed with at least three different values of C_M' and two different values of C_L'. Each series was repeated at least twice. The reproducibility was in general better than ±0.04 mV for low values of C_L and better than ±0.4 mV for high ones. Complete potentiometric data are obtainable from the authors.

To check that the cadmium amalgam electrode behaved according to Nernst's law in the DMSO solution, the emf's of cells containing no ligand were measured as a function of the metal ion concentration. These measurements were arranged as titrations where the metal ion solution was titrated into the initial 1.00 M NH_4ClO_4 solution. The value of E_k calculated varied within ±0.4 mV for 2 mM$\leq C_\mathrm{M}\leq$ 40 mM.

In one of the series, a direct analytical determination of C_M was carried out at the end of the titration by means of atomic absorption.

No significant deviation was found from the calculated value, implying that neither had any amalgam been dissolved, nor had any evaporation of solvent taken place.

MEASUREMENTS AND RESULTS

Cadmium chloride in 1 M ammonium perchlorate. Both the graphical and the NPA evaluation of the data formally indicate no less than six complexes though the last two only at quite high chloride concentrations. If these exist at all, they are in any case much weaker than the previous ones. Within the limits of error, the same set of constants is obtained by both methods. A difference is apparent between $k(E_M)$ and $\bar{n}_I$ which might mean that polynuclear complexes exist. The corresponding values of Y and [L] can in fact be fitted with a complex M_2L_9. The constants obtained have then been employed as initial values in the EMK program. The final values resulting from this calculation do not differ very much from the initial ones except that $\beta_5 = 0$. This is not unexpected, since already the provisional value of β_5 had an error $\simeq 100$ %. If the dinuclear complex is excluded, the value of β_5 becomes significant but that of β_6 insignificant. However, as the error square sum (eqn. 12) was $\simeq 85$ % higher for this last set of complexes, the first set tried is preferred so far. The first four mononuclear constants are found to be the same in both cases.

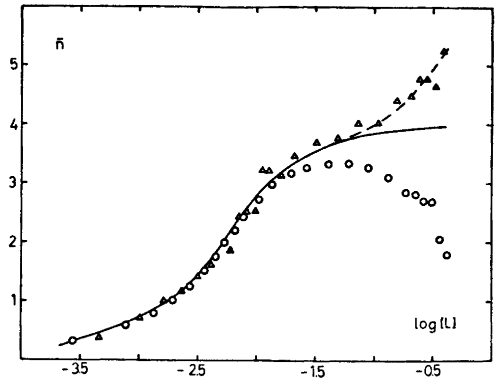

Fig. 1. The complex formation function of the cadmium(II) chloride system in 1 M NH_4ClO_4. The fulldrawn curve calculated from the constants β_1 to β_4. If the constants β_6 and β_{92} are included, the deviation indicated by the dashed curve results (for the average $C_M' = 10$ mm). Values of $k(E_M)$ denoted by circles, values of $\bar{n}_I$ from eqn. (10) by triangles. [L] in M.

The complex formation function computed from the preferred set of constants (Table 1) is plotted in Fig. 1. The values of $\bar{n}_I$ calculated from the Bodländer equation (eqn. 10) agree well with this function, and so do the slopes from the $C_L(C_M)E_M$ for low values of [L]. The deviation due to the hypothetical complex M_2L_9 becomes perceptible for $[L] \gtrsim 30$ mM. For the highest value of C_M used, its maximum concentration would reach $\simeq 26$ %, at $[L] \simeq 163$ mM.

Cadmium bromide. Graphical and NPA evaluation of the measurements indicate five mononuclear complexes. For high values of [L], a difference exists between $k(E_M)$ and $\bar{n}_I$, though not at all as marked as in the chloride system.

The difference could be fitted with either of the complexes M_2L_8 and M_2L_9. The EMK program gives the best fit with the same set of

Table 1. The overall stability constants, β_j, for the cadmium(II) systems. The limits of error given correspond to three standard deviations, as obtained by the computer, or as estimated.

Medium →	NH_4ClO_4, 1 M				$LiClO_4.3H_2O$, 1 M
Ligand →	Cl^-	Br^-	I^-	SCN^-	Cl^-
β_1/M^{-1}	1600 ± 100	850 ± 80	156 ± 10	64 ± 1	4150 ± 150
β_2/M^{-2}	$(1.2 \pm 0.7)10^5$	$(5 \pm 3)10^4$	$(4 \pm 2)10^3$	520 ± 30	$(1.5 \pm 0.3)10^6$
β_3/M^{-3}	$(5.2 \pm 0.8)10^7$	$(3.6 \pm 0.5)10^7$	$(3.2 \pm 0.2)10^6$	850 ± 90	$(2.0 \pm 0.2)10^9$
β_4/M^{-4}	$(2.7 \pm 0.5)10^9$	$(1.6 \pm 0.2)10^9$	$(4.9 \pm 0.2)10^7$	–	$(4.5 \pm 0.7)10^{11}$
β_6/M^{-6}	$(2.8 \pm 0.8)10^{10}$	$(3.7 \pm 1.8)10^9$	–	–	$(6 \pm 3)10^{12}$
β_{92}/M^{-10}	$(6 \pm 2)10^{21}$	$(3.7 \pm 1.5)10^{20}$	–	–	$\simeq 10^{26}$

The complexes ML_6 and M_2L_9 should be considered as hypothetical, *cf.* p. 256.

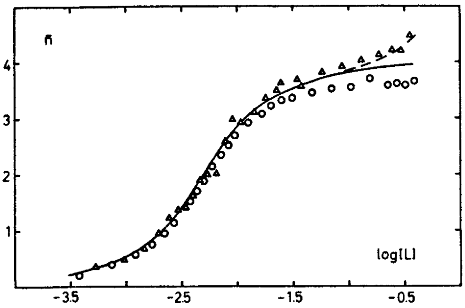

Fig. 2. The complex formation function of the cadmium(II) bromide system. Symbols, see Fig. 1.

complexes as was preferred for the chloride system.

The complex formation function calculated from the parameters given in Table 1 is drawn in Fig. 2. The $\bar{n}_I$ values from eqn. 10 agree well with the curve. The concentration of the hypothetical complex Cd_2Br_3 would never exceed ≃16 %.

Cadmium iodide. In the iodide system only the first four mononuclear complexes are indicated by the graphical evaluation as well as by the NPA. Much the same constants are found by both methods and these agree well with the final values calculated by the EMK program, Table 1. From the final constants, the complex formation function in Fig. 3 has been calculated. In this case, not only the values of $\bar{n}_I$ calculated from the Bodländer equation but also the values found from the slopes of the $C_M(C_L)_{E_M}$ lines fall on the curve for all values of [L].

On standing the originally almost colourless ammonium iodide solution developed an increasingly deeper colour as DMSO slowly oxidized iodide to iodine.[15] No significant differences in the emfs measured were found, however, if freshly prepared iodide solutions were used or if the solutions had been kept for two weeks. The change during such a period evidently does not matter.

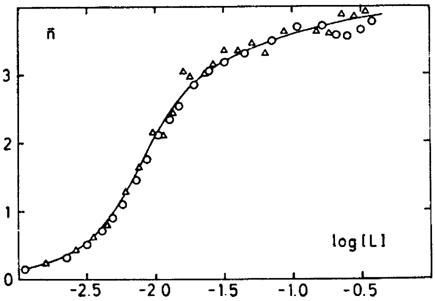

Fig. 3. The complex formation function of the cadmium(II) iodide system. Symbols, see Fig. 1.

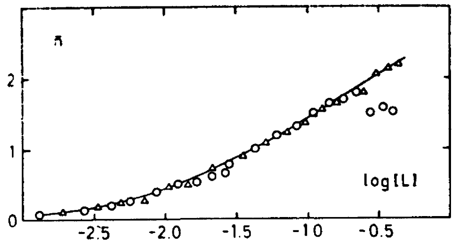

Fig. 4. The complex formation function of the cadmium(II) thiocyanate system. Symbols, see Fig. 1.

Cadmium thiocyanate. The graphical evaluation indicated only the first three mononuclear complexes. The constants found agreed well with the final ones calculated by the EMK program. These are given in Table 1 and the resulting complex formation function in Fig. 4. The values of $\bar{n}_I$ (eqn. 10) fit well to the curve and so do the $C_L(C_M)_{E_M}$ slopes except for a few points at the highest ligand concentrations.

Cadmium chloride in 1 M lithium perchlorate trihydrate. In order to keep the water content constant during the titrations, also the 1 M lithium chloride solution used as a titrant had

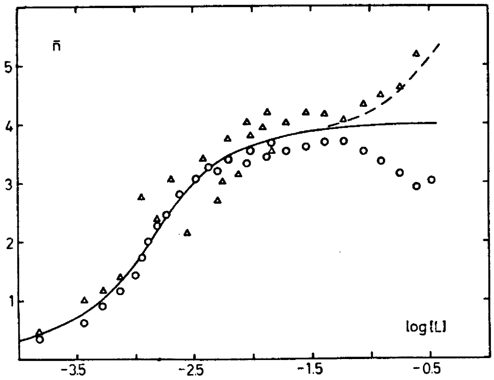

Fig. 5. The complex formation function of the cadmium(II) chloride system in 1 M $LiClO_4.3H_2O$. Symbols, see Fig. 1.

a concentration of water = 3.00 M. In the series employing 0.1 M lithium chloride, where the ligand solution already contained 2.70 M water from the supplementary lithium perchlorate no further water was added. In these cases the water content of the cell solution therefore varied between 2.70 and 3.00 M. It was checked separately that this variation did not bring about any significant change of the emf measured.

The value of [L] cannot be accurately determined from extrapolations of the $C_L(C_M)_{E_M}$ lines. A preliminary graphical evaluation using eqn. (11) gives $\beta_1 \approx 4000$ M^{-1}. Since the system might not be strictly mononuclear (*cf.* the $\tilde{n}_I$ (log [L]) plot in Fig. 5) the integrated Bodländer equation (11) should not be used in the evaluation of the constants. Nor is it possible to employ Hedström's method,[5] which presupposes constant values of C_M in each series in order to ensure a reasonably simple treatment. In the beginning of the titrations, however, the values of $\tilde{n}_I$ from eqn. (10) do not differ significantly from the $C_L(C_M)_{E_M}$ slopes. Consequently only mononuclear complexes exist in this region, and values of the constants β_1 to β_4 can be calculated with the EMK program. In the upper region where the values of $\tilde{n}_I$ and $k(E_M)$ do differ, the values of [L] can, on the other hand, be found by extrapolation. The function X_4 is then calculated[5,6] from the values of β_1 to β_3 already found, and hence the values of β_4 to β_6. The value of β_4 thus found agrees well with that found before by means of the EMK program.

The resulting set of β_j is introduced in eqn. 6 and the Y polynomial calculated. The corresponding values of Y and [L] can be fitted with a complex M_2L_9. Finally all the data are introduced in the EMK program, with the values of β_1 to β_4 fixed. The β_6 value does not change appreciably from that obtained earlier, while β_5 vanishes. The final result (Table 1) is thus concordant with those reported above for the chloride and bromide systems in 1 M ammonium perchlorate (*cf.* also Figs. 1, 5 and 6).

DISCUSSION

As stated previously,[1] complexes formed by ligands able to form strong hydrogen bonds should be much more stable in aprotic solvents than in water relative to complexes formed by ligands not able to form such bonds. Moreover, if the solvation of the metal ion is not much stronger in the aprotic solvent, the complexes formed by hydrogen bonding ligands must be not only relatively but also absolutely stronger in aprotic solvents. This tendency is further strengthened if the activity of the solvent is lower in the aprotic medium. Whether this is the case for DMSO relative to water is uncertain. The lower concentration of solvent molecules in DMSO (14.0 M, as against 55.3 M in water, at 25 °C) acts in this direction but the strong hydrogen bonding between the water molecules might well more than compensate this effect. On the other hand the lower dielectric constant of DMSO ($D = 46.4$, as against 78.4 for water, at 25 °C) will certainly tend to increase the stability of all complexes in DMSO relative to water.

As is obvious from the values of K_j collected in Table 2, a large increase of the stability relative to water occurs for the chloride complexes and a somewhat smaller for the bromide ones while the changes in stability for the iodide and thiocyanate complexes are modest. All the systems are stronger in DMSO than in water, however.

The differences between the halides in this respect are nevertheless so profound that a switch of the affinity sequence takes place between water and DMSO. In water, (*b*)-sequences $Cl^- < Br^- < I^-$ are found almost invariably for all the stepwise constants K_1 to K_2, Table 2 (though the trends are not very strongly marked; Cd^{2+} being a rather typical border line acceptor). In DMSO on the other hand the values of K_1, K_2 and though less marked, also K_4, follow (*a*)-sequences $Cl^- > Br^- > I^-$. Only in the case of K_3, a (*b*)-sequence still persists. Like in water, the complex formation curves get steeper from chloride to iodide, *cf.* Fig. 6. This certainly indicates that the bonds become increasingly covalent as the ligand becomes larger, and softer. The first complexes which are formed between oppositely charged ions are obviously more favoured relative to the

Table 2. Stability of cadmium halide and pseudohalide complexes in DMSO and water, at 25 °C.

Ligand	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-
	DMSO, 1 M NH_4ClO_4				DMSO, 1 M $LiClO_4.3H_2O$			
K_1	1600	850	156	64	4150			
K_2	75	59	26	8.1	360			
K_3	430	720	800	1.6	1300			
K_4	52	44	15		230			
K_1/K_2	21	14	6	8	12			
K_2/K_3	0.17	0.08	0.03	5	0.28			
K_3/K_4	8.3	16	53		5.7			
	Water, 1 M $NaClO_4$				Water, 3 M $NaClO_4$			
K_1	22.3	36.5	75	20.7	38.5	57	121	24.5
K_2	2.7	2.9	6	4.7	4.4	3.9	5	3.9
K_3	0.43	1.7	49	1.1	1.5	9.5	137	4.0
K_4		2.6	19	0.70		2.4	40	
K_1/K_2	8.3	12	13	4.4	8.7	15	24	6.3
K_2/K_3	6.3	1.7	0.12	4.3	2.9	0.41	0.04	0.98
K_3/K_4		0.7	2.6	1.6		4.0	3.4	
Ref.	20	21	22		8,16			

latter ones, the stronger the electrostatic attraction exerted by the ligand. Conversely, the latter complexes are more favoured relative to the first ones, the larger the covalent contribution to the bonding.

The increase of covalency in the sequence stated also manifests itself in the circumstance that, in aqueous solution, the formation reactions become increasingly exothermic.[16,17]

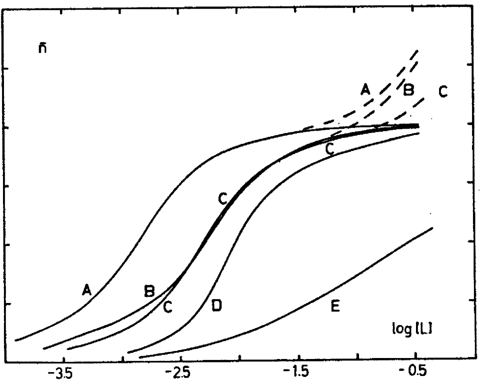

Fig. 6. The complex formation functions for: chloride (B), bromide (C), iodide (D) and thiocyanate (E), all in 1 M NH_4ClO_4, and for chloride in 1 M $LiClO_4.3H_2O$ (A). The fulldrawn curves calculated from β_1 to β_4 (E from β_1 to β_3). The dashed curves refer to the deviations found when the hypothetical β_5 and β_{92} are included.

The complex formation of the chloride system is considerably stronger in 1 M lithium perchlorate trihydrate than in 1 M ammonium perchlorate in spite of the fact that the presence of water in a concentration as high as 3 M would *per se* tend to lower the complexity. The most probable reason for the somewhat unexpected increase seems to be that the ammonium ions are associated to the chloride ions via hydrogen bonds which would make the ligand less available for complex formation. This is of course equivalent to a statement that at the present conditions ammonium chloride is far from completely dissociated in DMSO.

The water molecules added with the lithium perchlorate do not seem to interfere extensively with Cl^- in DMSO. Most plausibly they are taken care of by the cations present, presumably in the first hand by the hydrophilic Li^+. For this ion, DMSO may not compete so strongly as it certainly does for Cd^{2+}.

As seen from the low values of K_2/K_3, the second complex of the halide systems has a narrow range of existence in DMSO. This is also the case in aqueous solution though much less marked. From the thermodynamic functions of the aqueous systems it has been inferred that a change from octahedral to tetrahedral coordination takes place, and moreover mainly at the third step.[18] A similar change of coordination is the most likely cause of the peculiarities in the relative stabilities of the complexes observed in DMSO. However, a good understanding of the processes involved presupposes that all the thermodynamic functions for the formation of the complexes are known. The next logical step is therefore to determine the enthalpy changes ΔH°_j of the consecutive formation reactions and from these, and the stability constants already known, also the entropy changes ΔS°_j. Such a determination, foreseen already at the planning of the present investigations, has in fact already been performed and the results will be reported in the next paper of this series. It may be mentioned already now, however, that a switch from an octahedral to a tetrahedral coordination is very clearly indicated for all the halide systems also in DMSO. In view of the narrow range of existence of the second complex found for both DMSO and water, Table 2, it is somewhat surprising, however, that the main part of the coordination change takes place at different steps in the two solvents, *viz.* already at the second step in DMSO while, as stated earlier, at the third step for water. This result shows that for a meaningful discussion of structure and bonding in solution based on thermodynamic data, a complete knowledge of all pertinent functions is necessary.

The calorimetric measurements also shed new light on the question of the complexes beyond the fourth one indicated in the chloride and bromide systems. Those effects which have been interpreted as possibly due to the formation of such complexes seem after all rather to be due to changes in the activity conditions, as will be fully discussed in the next paper. For all the systems investigated, the complex finally formed is most probably the mononuclear tetrahedral ML_4^{2-}.

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REFERENCES

1. Ahrland, S. and Björk, N. O. *Acta Chem. Scand. A 28* (1974) 823.
2. Burrus, R. T. *Polarographic studies in dimethyl sulfoxide,* Diss., University of Tennessee, 1962.
3. Kenttämaa, J. *Suom. Kemistilehti 33 B* (1960) 179.
4. Maxey, B. W. and Popov, A. I. *J. Amer. Chem. Soc. 89* (1967) 2230; *91* (1969) 20.
5. Fronæus, S. In Jonassen, H. B. and Weissberger, A., Eds., *Technique of Inorg. Chem.* Interscience, New York, London 1963, Vol. 1, Chapter 1.
6. Ahrland, S., Chatt, I., Davies, N. R. and Williams, A. A. *J. Chem. Soc.* (1958) 264.
7. Fronæus, S. *Komplexsystem hos koppar,* Diss., University of Lund, 1948.
8. Leden, I. *Potentiometrisk undersökning av några kadmiumsalters komplexitet,* Diss., University of Lund, 1943.
9. Karlsson, R. and Kullberg, L. *Chem. Scr. 9* (1976) 54.
10. Ahrland, S., Avsar, E. and Kullberg, L. *Acta Chem. Scand. A 28* (1974) 855.
11. Kullberg, L. *Acta Chem. Scand. A 28* (1974) 829, 897.
12. Karlsson, R. and Karrman, K. J. *Talanta 18* (1971) 459.
13. Persson, H. *Acta Chem. Scand. 24* (1970) 3739.
14. Hansen, M. *Constitution of Binary Alloys,* 2nd Ed., 1958, p. 420 as quoted in *Gmelin* 8th Ed., Nr *34* [*A*] Quecksilber, 1962, p. 1100.
15. Reynolds, W. L. *Progr. Inorg. Chem. 12* (1970) 1 (p. 58).
16. Gerding, P. *Acta Chem. Scand. 20* (1966) 79.
17. Ahrland, S. *Helv. Chim. Acta 50* (1967) 306.
18. Ahrland, S. *Struct. Bonding 15* (1973) 167.
19. Le Demezet, M., Madec, C. and L'Her, M. *Bull. Soc. Chim. Fr.* (1970) 365.
20. Vanderzee, C. E. and Dawson, H. J. *J. Amer. Chem. Soc. 75* (1953) 5659.
21. Kivalo, P. and Ekari, P. *Suom. Kemistilehti B 30* (1957) 116.
22. Gerding, P. *Acta Chem. Scand. 22* (1968) 1283.

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