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Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution. XI. Calorimetric measurements on the Zinc(II) and Cadmium(II) Bromide Systems in Various Ionic Media

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The thermodynamics of the formation of cadmium (II) and zinc(II) bromide complexes in various DMSO perchlorate media has been investigated calorimetrically. The complexes are more stable in Et_4N^+, Li^+ and Na^+ media than in the NH_4^+ media previously used. This is probably due to an ion pair formation between NH_4^+ and Br^-. This interaction also causes exceptionally large differences between the stabilities in 0.1 and 1 M NH_4^+ medium, much larger than those found between 0.1 and 1 M Li^+. The latter ones are of the magnitude expected from the difference in ionic strength. Thermodynamically, the stability decreases from the non-interacting medium ions to NH_4^+, and from 0.1 to 1 M media, are due to less favourable entropy terms. Those changes are partly compensated by more favourable enthalpy terms. They can be rationalized by considering the ion pair formation, and the solvation of the medium cations.

In most DMSO media, a switch from octahedral to tetrahedral coordination takes place for cadmium(II) halides at the formation of the second complex. Rather remarkably, this switch is delayed to the third step in 0.1 M and 1 M lithium perchlorate.

The thermodynamics of zinc(II), cadmium(II) and mercury(II) halide complex formation in dimethylsulfoxide (DMSO) has previously been investigated in 1 M and, partly, also in 0.1 M ammonium perchlorate media.[1-5] It is of interest to investigate some of these systems in media containing cations other than NH_4^+, especially as strong indications now exist that in aprotic solvents such as DMSO, NH_4^+ is prone to form complexes with hydrogen bonding ligands.[5] Consequently, the stability of chloride, and, to some extent, also of bromide complexes would be lower in ammonium media than in media containing other cations. Apart from this special effect, the general influence of large qualitative changes of the ionic medium on the complex formation is well worth investigating. Such data are largely missing for aprotic solvents which of course introduces an element of uncertainty into comparisons of results obtained in protic and aprotic solvents. In the case of water and DMSO, large differences are generally found between the thermodynamic parameters of a certain system of complexes.[2-4] One might ask to what extent these differences are in fact due to the solvent, and to what extent they can be accounted for by the different ionic media.

The ammonium perchlorate medium was introduced in the present investigations because it does not attack the amalgam electrodes used for the determination of the stabilities of the zinc(II) and cadmium(II) complexes.[1,3] The amalgams are, on the other hand, rapidly oxidized by solutions of anhydrous lithium, sodium or tetraethylammonium perchlorate. Especially in the case of zinc, the reactions are very fast. Also the pure mercury electrode is slowly attacked in these anhydrous perchlorate solutions.[5] If hydrated perchlorates are used, however, the oxidation is practically inhibited,[3] for $LiClO_4 \cdot 3H_2O$, or very slow, for $NaClO_4 \cdot H_2O$.

In most anhydrous perchlorate media, therefore, the stabilities of the complexes discussed cannot be measured potentiometrically by means of amalgam electrodes. In view of this, the results of some earlier investigations are questionable.[6-11] A comparison between different media necessitates another method of measurement.

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If the stability constants are not too large (or too small) and moreover the enthalpy changes vary considerably between the consecutive steps, these parameters can be determined simultaneously with reasonable precision from calorimetric measurements.[12] Among the present systems, the zinc(II) and cadmium(II) bromides comply well with these conditions[2,3] and have therefore been selected.

Cadmium(II) bromide has been most extensively studied, *viz.* in 0.1 M and 1 M lithium, 1 M sodium and 0.1 M tetrethylammonium perchlorate. Zinc(II) bromide has been studied only in 1 M sodium perchlorate. The temperature has been 25 °C.

EXPERIMENTAL

Chemicals. The solvates $[Zn(DMSO)_6](ClO_4)_2$ and $[Cd(DMSO)_6](ClO_4)_2$ were prepared and analyzed as described previously.[13] The *lithium solvate* was prepared as follows: $LiClO_4 \cdot 3H_2O$ (1.0 mol) was dissolved in 400 ml (3.3 mol) 2,2-dimethoxypropane. After 2 h 250 ml (3.5 mol) DMSO was added and the resulting mixture was shaken for 1/2 h. The acetone and methanol formed, and the excess of 2,2-dimethoxypropane and DMSO were then evaporated at 100 °C which took ≃2 h. Analysis: Found: S: 25.9 %, C: 21.2 %, H: 5.73 %; calculated for 2 DMSO: S: 24.4 %, C: 18.3 %, H: 4.61 %. The compound thus contains somewhat more than 2 DMSO per lithium, corresponding to a formula $LiClO_4 \cdot 2.3DMSO$. It is extremely hygroscopic and must be handled in dry atmosphere. *$NaClO_4 \cdot 2DMSO$* was prepared as follows: $NaClO_4 \cdot H_2O$ (2.0 mol) was shaken with a mixture of 250 ml 2,2-dimethoxypropane (2.0 mol) and 300 ml DMSO (4.2 mol). A phase transformation took place which was complete in 1/2 h. On cooling to 5 °C, more crystals precipitated. The compound was collected on a Büchner funnel and than dried in vacuum under continous pumping for 40 h at room temperature. Analysis: Found: S: 22.4 %; Calc: S: 23.0 %. *Lithium, sodium* and *tetraethylammonium bromide* and *tetraethylammonium perchlorate* were dried in vacuum at 100 °C. The bromide content was determined titrimetrically. The *dimethylsulfoxide* was purified as described elsewhere.[13]

Apparatus. The titration calorimeter used has been described previously.[14,15]

Procedure. The technique and procedure have been described elsewhere.[3] The initial metal concentrations were $C'_M = 5$, 10 and 20 mM and the ligand solution added contained the appropriate bromide of $C_L = 100$ or 500 mM. To all solutions, perchlorate had been added so that the concentration of medium cations was 0.1 or 1 M. For the cadmium bromide system, a total of six titrations were performed in each medium studied, for the zinc bromide system twelve titrations. The number of points measured for each medium, NP, is stated in Table 1. All titrations were carried out at least twice.

The calculations of the overall stability constants β_j and entropy changes $\Delta H^\circ_{\beta j}$ have been performed by the computer program KALORI.[16]

The analyses were performed at the Department of Analytical Chemistry of this Chemical Center.

MEASUREMENTS AND RESULTS

Cadmium(II) bromide. In 0.1 M tetraethylammonium and 1 M sodium perchlorate, the ranges of cadmium(II) and bromide concentrations were 4.0 mM $\leq C_M \leq$ 20.0 mM and $0 \leq C_L \leq$ 48.9 mM. Four mononuclear complexes are indicated, with the values of β_j and $\Delta H^\circ_{\beta j}$ listed in Table 1. For reasons given below, the errors stated refer to a confidence limit of 95 %, corresponding to 1.96σ. The precision achieved corresponds to a reproducibility in the individual points measured of $\lesssim$0.025 J. Under these conditions, fairly precise values are obtained even for the fairly unstable $CdBr_2$ which never reaches 20 % of C_M, Fig. 5.

In 0.1 and 1 M lithium perchlorate, much the same ranges were used, *viz.* 4.0 mM $\leq C_M \leq$ 20.0 mM and $0 \leq C_L \leq$ 46.8 mM. Also here four mononuclear complexes are indicated, but the random errors of β_j and $\Delta H^\circ_{\beta j}$ are considerably larger than in the previous media, Table 1. This reflects a markedly poorer reproducibility of the individual points, *viz.* $\lesssim$0.045 J. Especially the errors in β_j become uncomfortably large, but within a confidence limit of 95 % all values of β_j are nevertheless significant. Most of them are not, however, within the confidence limit 99.7 %, corresponding to 3σ which has been applied in earlier measurements.[1-5]

The total molar enthalpy change Δh_v is given as a function of the ligand number $\bar{n}$ in Fig. 1. The complex formation curve $\bar{n}$ (log $[Br^-]$) is given in Fig. 3, and the distribution of the complexes α (log $[Br^-]$) in Fig. 5.

Zinc(II) bromide. In the 1 M sodium perchlorate medium used, measurements were performed in the ranges 4.0 mM $\leq C_M \leq$ 19.8 mM and $0 \leq C_L \leq$ 180 mM. An excellent fit was obtained with three mononuclear complexes. Introduction of a fourth complex did not improve the fit. The values of β_j and $\Delta H^\circ_{\beta j}$ obtained are listed in Table 1. The precision achieved corresponds to a reproducibility

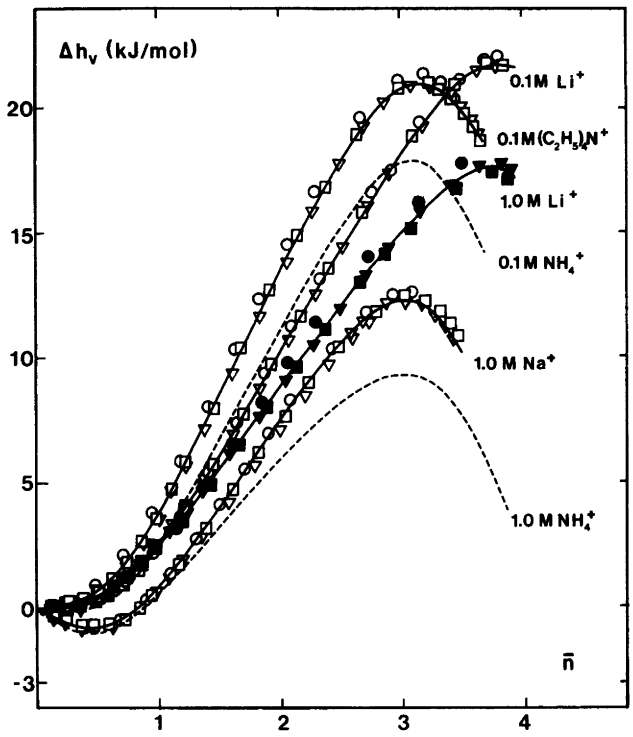

Fig. 1. The total molar enthalpy change Δh_v as a function of $\bar{n}$ for the cadmium bromide system in various perchlorate media. The symbols refer to the initial concentrations $C'_M = 5$(○), 10 (□) and 16 mM (▽), in the present measurements. The solid curves have been calculated from the values of β_j and $\Delta H^\circ_{\beta j}$ found. Dashed curves refer to previous measurements in 0.1 M and 1 M NH_4^+ media.

Table 1. Overall stability constants (β_j/M^{-j}) and overall enthalpy changes ($\Delta H_{\beta j}$/kJmol^{-1}) for the formation of cadmium(II) bromide complexes in various DMSO media, at 25 °C. The errors refer to a 95 % confidence limit. NP denotes number of observations (aliquotes added) for each system.

	$Cd^{2+} - Br^-$				$Zn^{2+} - Br^-$
	0.1 M Et_4N^+	1 M Na^+	1 M Li^+	0.1 M Li^+	1 M Na^+
β_1	$(8.3 \pm 0.8) \times 10^3$	$(3.0 \pm 0.3) \times 10^3$	$(3.6 \pm 1.1) \times 10^3$	$(6.1 \pm 2.2) \times 10^3$	36 ± 10
β_2	$(6.4 \pm 1.6) \times 10^6$	$(6.9 \pm 2.0) \times 10^5$	$(3.0 \pm 2.1) \times 10^6$	$(7.2 \pm 4.6) \times 10^6$	$(4.6 \pm 0.2) \times 10^4$
β_3	$(1.6 \pm 0.4) \times 10^{10}$	$(1.0 \pm 0.2) \times 10^9$	$(2.7 \pm 1.9) \times 10^9$	$(8.0 \pm 6.6) \times 10^9$	$(5.2 \pm 0.4) \times 10^6$
β_4	$(2.6 \pm 1.1) \times 10^{12}$	$(7.4 \pm 0.3) \times 10^{10}$	$(6.0 \pm 5.6) \times 10^{12}$	$(1.0 \pm 1.0) \times 10^{13}$	
$-\Delta H_{\beta 1}$	0.0 ± 0.2	2.8 ± 0.2	0.3 ± 0.3	$-(0.3 \pm 0.3)$	$-(23.7 \pm 2.7)$
$-\Delta H_{\beta 2}$	$-(17.9 \pm 1.2)$	$-(10.8 \pm 1.8)$	$-(2.8 \pm 2.7)$	$-(4.2 \pm 2.0)$	$-(43.1 \pm 0.6)$
$-\Delta H_{\beta 3}$	$-(25.3 \pm 0.5)$	$-(17.4 \pm 0.8)$	$-(26.7 \pm 9.3)$	$-(31.7 \pm 5.0)$	$-(36.3 \pm 0.2)$
$-\Delta H_{\beta 4}$	$-(15.7 \pm 0.5)$	$-(4.0 \pm 1.3)$	$-(16.2 \pm 0.5)$	$-(20.8 \pm 0.5)$	
NP	120	120	102	112	188

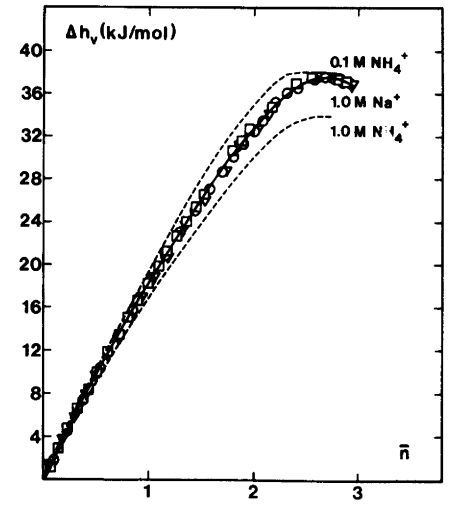

Fig. 2. The total molar enthalpy change Δh_v as a function of $\bar{n}$ for the zinc(II) bromide system in various perchlorate media. The symbols refer to the initial concentrations $C'_M = 5$(○), 10(□) and 20 mM(▽) in 1 M Na^+ medium. The solid curve has been calculated from the values of β_j and $\Delta H^\circ_{\beta j}$. Dashed curves refer to previous measurements in 0.1 M and 1 M NH_4^+ media.

in the individual points of $\lesssim 0.035$ J. Under these conditions, even the values of β_j and $\Delta H_{\beta 1}$ are well determined, however, in spite of the fact that the unstable $ZnBr^+$ at most reaches only $\simeq 7\,\%$, Fig. 6. The functions $\Delta h_v(\bar{n})$, $\bar{n}$ (log $[Br^-]$) and α (log $[Br^-]$) are plotted in Figs. 2, 4 and 6, respectively.

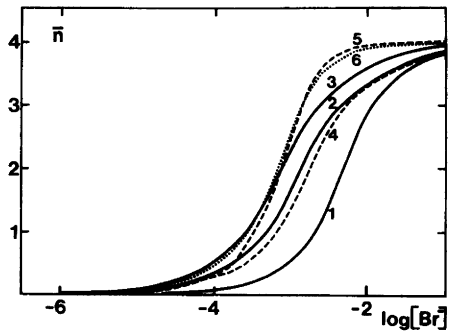

Fig. 3. The complex formation functions of the cadmium(II) bromide system in the perchlorate media 1 M NH_4^+ (1), 0.1 M NH_4^+ (2), 0.1 M Et_4N^+ (3), 1 M Na^+ (4), 1 M Li^+ (5) 0.1 M Li^+ (6).

DISCUSSION

Cadmium(II) bromide. The stability constants and thermodynamic functions derived for the consecutive steps from the values of β_j and $\Delta H^\circ_{\beta j}$ collected in Table 1 are listed in Table 2. In this table, the values determined previously in 0.1 M and 1 M ammonium perchlorate have also been entered.[3,5]

As has been pointed out before,[5] a stability increase larger than expected from the decrease of the ionic strength takes place between 1 M and 0.1 M ammonium perchlorate. This is most likely caused by a complex formation between NH_4^+ and Br^- which, of course, becomes much less extensive as the concentration of NH_4^+ is decreased. As this reaction is presumably due to a hydrogen bond formation $NH_4^+ - Br^-$, the cadmium(II) bromide complexes should be more stable in media where the medium cation cannot form such bonds. Moreover, the stability increase should be larger in 1 M than in 0.1 M media.

These effects are indeed all observed, Table 2. When 0.1 M NH_4^+ is exchanged for 0.1 M Et_4N^+, of no ability to form hydrogen bonds, a further stability increase takes place. A similar increase is found if 0.1 M NH_4^+ is exchanged for 0.1 M Li^+ though in this case special effects occur which will be further discussed below. When 1 M NH_4^+ is exchanged for 1 M Na^+, or 1 M Li^+, the increases are much larger. Moreover, the difference between 0.1 M and 1 M Li^+ is much smaller than between 0.1 M and 1 M NH_4^+. In the former case, the stabilities change about as much as is expected from the change in ionic strength.[17] This difference between the NH_4^+ and the Li^+ media stands out very clearly in the complex formation curves, Fig. 3.

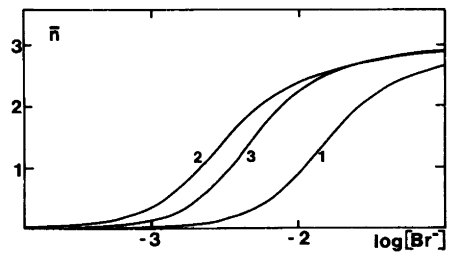

Fig. 4. The complex formation functions of the zinc (II) bromide system in the perchlorate media 1 M NH_4^+ (1), 0.1 M NH_4^+ (2), 1 M Na^+ (3).

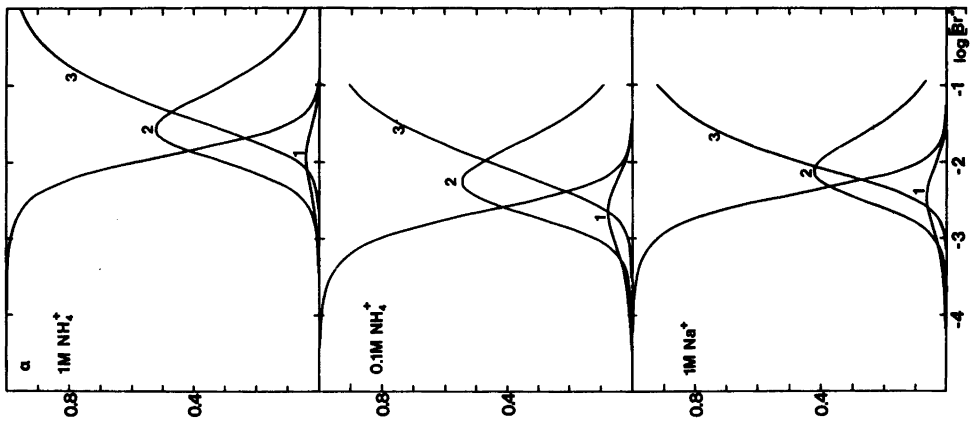

Fig. 6. The complex distribution functions of the zinc(II) bromide system in the ionic media investigated.

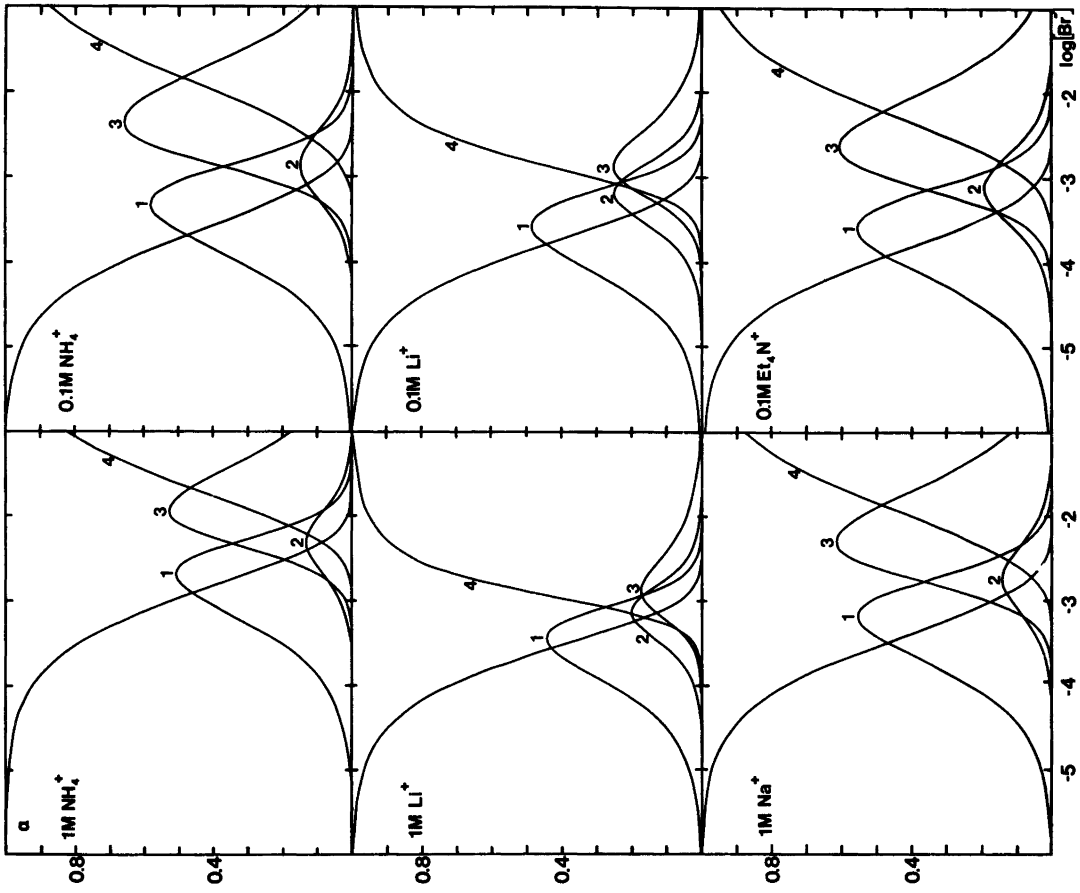

Fig. 5. The complex distribution functions of the cadmium(II) oromide system in the ionic media investigated.

Table 2. Stability constants (K_j/M^{-1}) and thermodynamic functions (ΔG_j°, ΔH_j°/kJ mol^{-1}; ΔS_j°/J K^{-1} mol^{-1}) for the stepwise formation of cadmium(II) bromide complexes in various DMSO perchlorate media, at 25 °C.

	1 M NH_4^+	0.1 M NH_4^+	0.1 M EtN_4^+	1 M Na^+	1 M Li^+	0.1 M Li^+
log K_1	2.92	3.69	3.92	3.48	3.56	3.79
log K_2	1.91	2.50	2.88	2.36	2.93	3.07
log K_3	2.75	3.28	3.40	3.17	2.94	3.05
log K_4	1.68	1.83	2.21	1.85	3.35	3.11
K_1/K_2	10	16	11	13	4.3	5.3
K_2/K_3	0.15	0.17	0.30	0.15	0.96	1.03
K_3/K_4	11.8	28	16	21	0.39	0.88
$-\Delta G_1^\circ$	16.7	21.0	22.4	19.9	20.3	21.6
$-\Delta G_2^\circ$	10.9	14.2	16.5	13.5	16.7	17.5
$-\Delta G_3^\circ$	15.7	18.7	19.4	16.8	16.8	17.4
$-\Delta G_4^\circ$	9.5	10.4	12.6	10.6	19.1	17.7
$-\Delta H_1^\circ$	3.9	0.9	0.0	2.8	0.3	−0.3
$-\Delta H_2^\circ$	−17	−15.8	−17.9	−13.6	−3.1	−4.0
$-\Delta H_3^\circ$	−2	−7.2	−7.3	−6.6	−23.9	−27.5
$-\Delta H_4^\circ$	13	11.4	9.5	13.4	10.5	10.9
ΔS_1°	43	68	75	57	67	73
ΔS_2°	94	101	115	91	66	72
ΔS_3°	59	87	90	83	137	151
ΔS_4°	−12	−3	10	−9	29	23
$-\Delta H_{\beta 4}^\circ$	−2	−10.6	−15.7	−4.0	−16.2	−20.8
$\Delta S_{\beta 4}^\circ$	184	252	290	221	299	319

In the NH_4^+ media, the very positive values of ΔS_2° and ΔH_2° indicate that the switch from the octahedral coordination represented by the solvate $Cd(DMSO)_6^{2+}$ present initially[18] to the certainly tetrahedral coordination[19] of the finally formed $CdBr_4^{2-}$ takes place at the formation of $CdBr_2$.[3,5] This inference is confirmed by measurements of the Cd(II)/Cd(Hg) electrode kinetics in bromide solutions containing 1 M NH_4^+ where a considerable increase of the exchange current is found as the second complex is formed.[20] Also studies of the nuclear magnetic resonance spectra of cadmium bromide solutions in NH_4^+ media lead to the same conclusion.[21] The ^{113}Cd chemical shift increases dramatically between the first and the second complex, clearly indicating a change of coordination at this step.

In 0.1 M Et_4N^+ and 1 M Na^+ medium the same pattern is found as in the NH_4^+ media, Table 2. In the Li^+ media, on the other hand, this switch occurs at the formation of $CdBr_3^-$, as indicated by the large values of ΔS_3° and ΔH_3°. This difference between Li^+ on one hand and NH_4^+, Et_4N^+ and Na^+ on the other is somewhat surprising. To judge from the solvation enthalpies,[22] Li^+ is the most strongly solvated among the medium cations concerned. One would therefore expect that Li^+ would tend to bring about the desolvation accompanying the switch of coordination more easily than the other ions, *i.e.* to cause the switch to take place at an earlier and not, as is in fact found, at a later step.

For the Li^+ media, the values of ΔH_3° are in fact so endothermic that the stability of $CdBr_3^-$ becomes fairly low, in spite of the very positive ΔS_3°. While in the other media $CdBr_2$ is the only complex that never reaches a very large share of C_M, both $CdBr_2$ and $CdBr_3^-$ are severely suppressed in the Li^+ media, Fig. 5. As a consequence, the complex formation curves are much steeper for the Li^+ media, Fig. 3.

The values of the overall enthalpy and entropy

changes $\Delta H^\circ_{\beta 4}$ and $\Delta S^\circ_{\beta 4}$ show that the decreases of stability generally taking place between 0.1 M and 1 M media are due to less favourable values of $\Delta S^\circ_{\beta 4}$ in the more concentrated media, Table 2. These entropy losses are partly compensated by more favourable, *i.e.* less endothermic, values of $\Delta H^\circ_{\beta 4}$. Evidently, the increase of solvent order brought about by an increased ionic strength always causes a decrease of the entropy to be gained by complex formation. The break-up of the cadmium(II) solvates means a smaller entropy gain, the more well-ordered the surrounding medium. On the other hand, the more extensive solvate formation in the more concentrated medium means an energy gain which is reflected in a more favourable overall enthalpy term.

In the NH_4^+ media, the formation of cadmium(II) complexes moreover implies a further increase of the concentration of free medium cations by the break-up of ion-pairs NH_4Br. This brings about a further decrease of $\Delta S^\circ_{\beta 4}$ which, of course, becomes more marked the higher the concentration of the ionic medium.

The values of $\Delta S^\circ_{\beta 4}$ are largest for the Li^+ media which would indicate a lower degree of order than in any of the other media investigated. This is another circumstance difficult to reconcile with the fact that Li^+ is the most strongly solvated among the medium cations.[22] On the other hand, it is completely in line with the inability of Li^+ to bring about the switch to tetrahedral coordination at as early a step as the other medium ions do.

Though the complex formation of the cadmium(II) bromide system differ considerably between various DMSO media of the same concentration, these differences are nevertheless much smaller than those found between, say, 1 M media in DMSO and water. This is valid even in the case of NH_4^+ media which bring about especially low stabilities in DMSO.

Zinc(II) bromide. The stability constants and thermodynamic functions derived for the consecutive steps from the values of Table 1 are listed in Table 3, together with the values for 0.1 M and 1 M ammonium perchlorate.

The complexes are more stable in 1 M Na^+ than in 1 M NH_4^+ medium but the pattern of the complex formation is very similar in Na^+ and NH_4^+ media. This is made very clear by the complex formation curves, Fig. 4, and the distribution curves, Fig. 6. The overall increase of stability between 1 M NH_4^+ and 1 M Na^+ medium is also here due to a more favourable value of the entropy term, $\Delta S^\circ_{\beta 3}$, partly compensated by a less favourable enthalpy term, $\Delta H^\circ_{\beta 3}$. So far, the medium influence is very similar for zinc(II) and cadmium(II) bromide.

Table 3. Stability constants (K_j/M^{-1}) and thermodynamic functions (ΔG°_j, ΔH°_j/kJ mol^{-1}; ΔS°_j/J K^{-1} mol^{-1}) for the stepwise formation of zinc(II) bromide complexes in various DMSO perchlorate media, at 25 °C.

	1 M NH_4^+	0.1 M NH_4^+	1 M Na^+
$\log K_1$	0.85	1.86	1.56
$\log K_2$	2.89	3.31	3.11
$\log K_3$	1.35	1.98	2.05
K_1/K_2	0.009	0.036	0.028
K_2/K_3	35	21	11
$-\Delta G^\circ_1$	4.8	10.6	8.9
$-\Delta G^\circ_2$	16.5	18.9	17.7
$-\Delta G^\circ_3$	7.7	11.3	11.7
$-\Delta H^\circ_1$	−27.8	−22.3	−23.4
$-\Delta H^\circ_2$	−9.1	−19.9	−19.7
$-\Delta H^\circ_3$	4.2	5.9	6.8
ΔS°_1	110	110	108
ΔS°_2	85	130	126
ΔS°_3	12	18	16
$-\Delta H^\circ_{\beta 4}$	−32.7	−36.3	−36.3
$\Delta S^\circ_{\beta 4}$	207	259	250

The switch from octahedral to tetrahedral coordination takes place mainly at the formation of the second complex in 0.1 M NH_4^+, but already at the formation of the first one in 1 M NH_4^+. In this respect, 1 M Na^+ medium behaves as 0.1 M NH_4^+, Table 3. One would perhaps rather expect that Na^+, more strongly solvated than NH_4^+, would rather encourage an early desolvation, with accompanying switch of coordination.

Obviously, the factors governing these coordination switches are still not sufficiently well-known to warrant any safe predictions about the influence of various solvents and ionic media.

Previous comparisons between aqueous and DMSO media. In earlier papers in this series, stabilities of halide complexes measured in aqueous sodium perchlorate media and DMSO ammonium perchlorate media have been compared.[1-4] The present measurements show that the increases of stabilities between water and DMSO under these conditions

are smaller than would be found if both solutions contained Na^+ as medium cation. The same would be true for any other ion exerting no specific interaction in either solvent with the halide ions. For practical reasons, such a choice of medium cation has not been possible. It should be borne in mind, however, that the actual effects of the change of solvent are, in fact, even larger than shown by the comparisons performed in the previous papers.[1-4]

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