

Solvation and Halogeno Complexation of the Cadmium(II) Ion in Hexamethylphosphoric Triamide

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The complexation of the cadmium(II) ion with bromide and iodide ions has been studied by calorimetry in hexamethylphosphoric triamide (HMPA) containing 0.1 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ as a constant ionic medium at 25°C . The formation of $[\text{CdX}_n]^{(2-n)+}$ ($n = 1, 2, 3, 4$ for $\text{X} = \text{Br}$; $n = 1, 2, 3$ for $\text{X} = \text{I}$) is revealed, and their formation constants, reaction enthalpies and entropies were determined. The ternary $\text{Cd}^{\text{II}}\text{--Br--I}$ system has also been examined and the formation of the $[\text{CdBr}_2\text{I}]^-$ and $[\text{CdBrI}]^0$ complexes is elucidated. The $\text{Cd}^{\text{II}}\text{--X}$ systems exhibit unusual thermodynamic behaviour that is not observed in the $\text{M}^{\text{II}}\text{--X}$ ($\text{M} = \text{Co}, \text{Zn}$) systems. The reaction enthalpies vary in the order, $\Delta H_1^\circ > \Delta H_2^\circ \approx \Delta H_4^\circ > \Delta H_3^\circ$ in the $\text{Cd}^{\text{II}}\text{--Br}$ system, while $\Delta H_1^\circ < \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ$ in the $\text{Zn}^{\text{II}}\text{--Cl}$ system. The ΔS° values, 179 and $187 \text{ J K}^{-1} \text{ mol}^{-1}$ for the formation of $[\text{CdBr}]^+$ and $[\text{CdI}]^+$, respectively, are significantly larger than the corresponding values in the Co^{II} and Zn^{II} systems. These facts strongly suggest that the cadmium(II) ion has a larger solvation number in HMPA. EXAFS spectroscopy provided evidence that the cadmium(II) ion is coordinated to five HMPA molecules, whereas cobalt(II) and zinc(II) ions are coordinated to four HMPA molecules.

Hexamethylphosphoric triamide (HMPA) is an aprotic donor solvent with a strong electron-pair donating ability (e.g. Gutmann's donor number, $D_N = 38.8$) and a medium relative permittivity ($\epsilon_r = 30$).^{1,2} The electron-pair donating ability of HMPA is even stronger than that of dimethylformamide (DMF, $D_N = 26.6$, $\epsilon_r = 36.71$) or dimethyl sulfoxide (DMSO, $D_N = 29.8$, $\epsilon_r = 46.68$). This implies that more energy is required to break a metal–solvent bond upon complexation in HMPA. However, the formation of $[\text{CoCl}]^+$ is exothermic in HMPA, although it is endothermic in DMF and DMSO. Furthermore, the complexation of cobalt(II), as well as zinc(II), with halide ions is significantly enhanced in HMPA over DMF and DMSO.^{3,4} The cobalt(II) ion is coordinated to six solvent molecules in DMF and DMSO, but only four in HMPA.^{3,5} An octahedral to tetrahedral geometry change around the metal ions thus occurs upon complexation with halide ions in DMF and DMSO;^{6,7} this does not happen in HMPA. A remarkable difference between the complexation behaviour of metal ions in HMPA and that in DMF or DMSO is therefore ascribed to the difference in their solvation structure in these solvents.

In HMPA, similar thermodynamic behaviour has been observed in the $\text{Co}^{\text{II}}\text{--X}$ and $\text{Zn}^{\text{II}}\text{--X}$ systems. This is not surprising because the crystal ionic radii of four-coordinate cobalt(II) and zinc(II) ions, 72 and 74 pm, respectively,⁸ are not appreciably different. They are neither hard nor soft ions. In contrast, the cadmium(II) ion has a large ionic radius when it is four-coordinate, 92 pm, and behaves as a soft ion. Thus, the cadmium(II) ion was expected to show different complexation behaviour in HMPA from that of the cobalt(II) and zinc(II) ions. Here, we describe the halogeno complexation and coordination structure of the cadmium(II) ion in HMPA studied by titration calorimetry and EXAFS spectroscopy.

Experimental

Materials

All chemicals used were of reagent grade. The HMPA solvate of cadmium(II) perchlorate $\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{HMPA}$ was prepared

according to the literature method.⁹ Tetra-*n*-butylammonium perchlorate, tetra-*n*-butylammonium bromide and tetra-*n*-butylammonium iodide were recrystallized once from a methanol–ether mixture and dried *in vacuo* over P_2O_5 at room temperature. HMPA was purified as described in ref. 10.

Measurements

Calorimetry

Calorimetric measurements were carried out by using a fully automatic titration calorimetry system in a room thermostatted at $25 \pm 0.2^\circ\text{C}$. All cadmium(II) perchlorate solutions contained 0.1 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ as an ionic medium. In the binary system, cadmium(II) perchlorate solutions were titrated with 0.1 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NX}$ ($\text{X} = \text{Br}, \text{I}$) solution. A solution (40 cm^3) containing cadmium(II) perchlorate was placed in a stainless-steel vessel, the inside wall of which was coated with Teflon. The vessel, filled with dry argon gas and isolated from moisture with a P_2O_5 drying tube, was inserted in an aluminium block thermostatted at $25 \pm 0.0001^\circ\text{C}$ in an air bath. Portions of $(n\text{-C}_4\text{H}_9)_4\text{NX}$ titrant solution were introduced into the vessel from an autoburette (APB-118, Kyoto Electronics). Reaction heats measured at each titration point were in the range 0.1–2 J with an error of $\pm 0.02 \text{ J}$. Reaction heats thus obtained were corrected for heat of dilution of the titrant, which was found to be small in separate experiments. In the ternary $\text{Cd}^{\text{II}}\text{--Br--I}$ system, an initial solution containing both cadmium(II) and bromide ions was titrated with 0.1 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NI}$ solution. Alternatively, a solution containing both cadmium(II) and iodide ions was titrated with 0.1 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NBr}$.

EXAFS

Four solutions were prepared by dissolving the $\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{HMPA}$ solvate crystals in nitromethane (NM, solution A), in an NM–HMPA mixture of 0.62 mole fraction

HMPA (solution B) and in pure HMPA (solution C), and by dissolving $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in water (solution D). Total cadmium(II) concentrations in solutions A–D are 0.2, 0.2, 0.05 and 0.4 mol dm^{-3} , respectively. EXAFS spectra were measured around the Cd K-edge in transmission mode using the BL6B station at the Photon Factory of the National Laboratory for High Energy Physics.¹¹ White X-rays were monochromatized using an Si(311) double crystal. The apparent absorbance μx is obtained as $\ln(I_0/I)$, where I and I_0 denote intensities with and without sample solution, respectively, and were measured simultaneously by using ionization chambers filled with argon gas. Sample solutions were held in 5 or 10 mm thick Teflon cells with Mylar windows.

Data Analysis

Calorimetry

If the formation of only mononuclear complexes of a metal ion M^{2+} and ligands X^- and Y^- is assumed, the overall formation of the $[\text{MX}_p\text{Y}_q]^{(2-p-q)+}$ complex can be defined as follows:



$$\beta_{1pq} = [\text{MX}_p\text{Y}_q]^{(2-p-q)+} / [\text{M}^{2+}][\text{X}^-]^p[\text{Y}^-]^q \quad (2)$$

The heat q_i measured at the i th titration point is expressed by using the formation constant β_{1pq} and overall enthalpy $\Delta H_{\beta_{1pq}}^\circ$:

$$q_i = -(V_i \sum \beta_{1pq} \Delta H_{\beta_{1pq}}^\circ [\text{M}^{2+}]_i [\text{X}^-]^p [\text{Y}^-]^q - V_{i-1} \sum \beta_{1pq} \Delta H_{\beta_{1pq}}^\circ [\text{M}^{2+}]_{i-1} [\text{X}^-]^p [\text{Y}^-]^q) \quad (3)$$

where V_i denotes the volume of the test solution. The concentrations of free M^{2+} , X^- and Y^- ions are related to their respective total concentrations, $C_{\text{M},i}$, $C_{\text{X},i}$ and $C_{\text{Y},i}$, accord-

ing to the mass-balance equations:

$$C_{\text{M},i} = [\text{M}^{2+}]_i + \sum \beta_{1pq} [\text{M}^{2+}]_i [\text{X}^-]^p [\text{Y}^-]^q \quad (4)$$

$$C_{\text{X},i} = [\text{X}^-]_i + \sum p \beta_{1pq} [\text{M}^{2+}]_i [\text{X}^-]^p [\text{Y}^-]^q \quad (5)$$

$$C_{\text{Y},i} = [\text{Y}^-]_i + \sum q \beta_{1pq} [\text{M}^{2+}]_i [\text{X}^-]^p [\text{Y}^-]^q \quad (6)$$

Formation constants and enthalpies were determined by a non-linear least-squares calculation for data.¹²

EXAFS

Details of the data reduction of raw EXAFS spectra have been described elsewhere.^{13,14} A curve-fitting procedure in k -space for the refinements of structure parameters was applied to the Fourier-filtered $k^3 \cdot \chi(k)_{\text{obsd}}$ values to minimize $\sum k^6 [\chi(k)_{\text{obsd}} - \chi(k)_{\text{calcd}}]^2$. The model function $\chi(k)_{\text{calcd}}$ is given by

$$\chi(k)_{\text{calcd}} = \sum \left[\frac{n_j}{(k \cdot r_j^2)} \right] \exp \left(-2\sigma_j^2 k^2 - \frac{2r_j}{\lambda} \right) F_j(\pi, k) \times \sin[2kr_j + \alpha_j(k)] \quad (7)$$

based on the single-electron and single-scattering theory.^{15–18} The values of the back-scattering amplitude $F(\pi, k)$ were from ref. 19. The total scattering phase shift $\alpha(k)$ was approximated by the function $a_0 + a_1 k + a_2 k^2 + a_3/k^3$,²⁰ where the coefficients a_i ($i = 0, 1, 2, 3$) were evaluated by fitting the function to the theoretical phase shift values by Teo and Lee.¹⁹ a_0 , a_1 and λ (the mean free path of a photoelectron) were evaluated in advance from a standard sample of known structure, and were kept constant in the course of the structural analysis of unknown samples.

Results

The calorimetric titration curves obtained are shown in Fig. 1 and 2. The $-q/(\delta v C_{\text{X},\text{tit}})$ values are plotted against the ratio

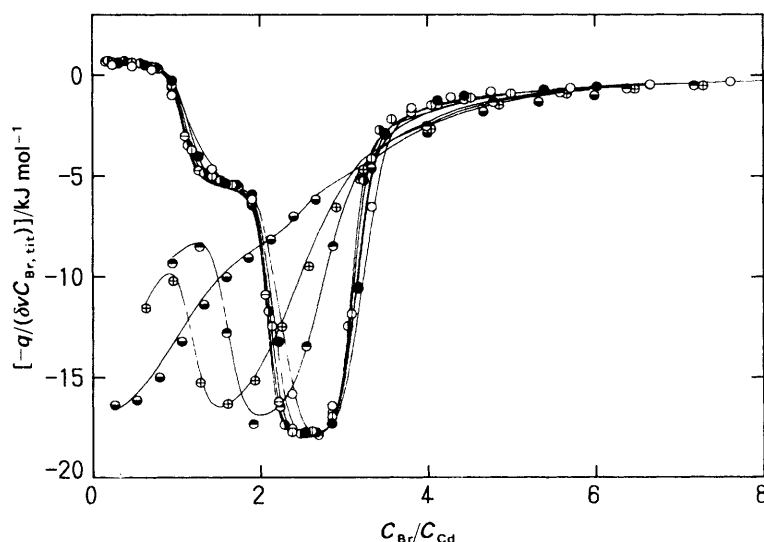


Fig. 1 Calorimetric titration curves of the $\text{Cd}^{\text{II}}\text{-Br}$ and $\text{Cd}^{\text{II}}\text{-I}$ systems. The initial concentrations of cadmium(II) and I^- are given in the table. The solid lines are calculated using constants in Tables 1 and 2.

	$[\text{Cd}]_{\text{init}}/\text{mol dm}^{-3}$	$[\text{I}]_{\text{init}}/\text{mol dm}^{-3}$
○	0.008413	0.0
●	0.01263	0.0
⊖	0.01683	0.0
⊙	0.02103	0.0
⊕	0.02525	0.0
⊗	0.009435	0.00519
⊕	0.009872	0.00960
⊗	0.01201	0.0243

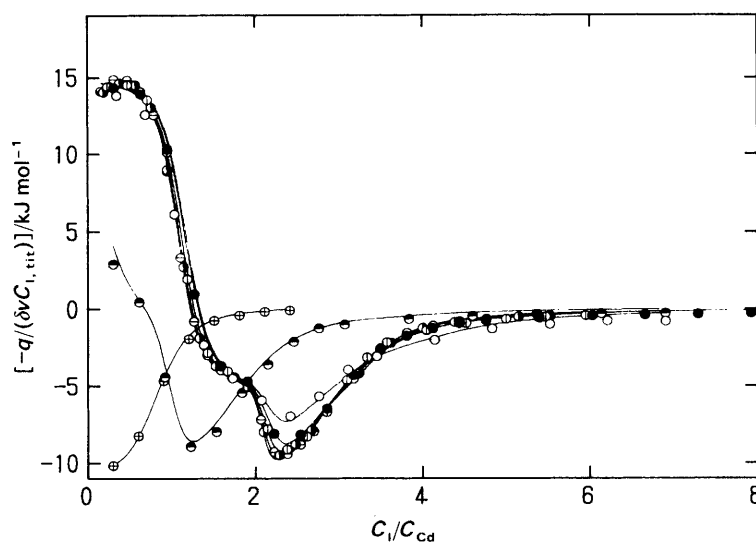


Fig. 2 Calorimetric titration curves of the Cd^{II} -I and Cd^{II} -Br-I systems. The initial concentrations of cadmium(II) and Br^- are given in the table. The solid lines are calculated using constants in Tables 1 and 2.

	$[\text{Cd}]_{\text{init}}/\text{mol dm}^{-3}$	$[\text{Br}]_{\text{init}}/\text{mol dm}^{-3}$
○	0.00580	0.0
●	0.01263	0.0
⊖	0.01683	0.0
⊙	0.02103	0.0
⊕	0.02523	0.0
⊗	0.01045	0.01224
⊕	0.01062	0.02371

of the total concentrations of ligand to metal ions, C_X/C_M , where q , δv and $C_{X,\text{tit}}$ denote the measured heat of reaction, the volume of an aliquot of the added titrant and the concentration of X^- ion in the titrant solution, respectively. Calorimetric data were analysed by assuming the formation of a set of complexes, and various sets were examined and compared. In the binary Cd^{II} -Br and Cd^{II} -I systems, set (1, 2, 3, 4), assuming the formation of $[\text{CdBr}]^+$, $[\text{CdBr}_2]^0$, $[\text{CdBr}_3]^-$ and $[\text{CdBr}_4]^{2-}$, and set (1, 2, 3), assuming the formation of $[\text{CdI}]^+$, $[\text{CdI}_2]^0$, and $[\text{CdI}_3]^-$ are the most plausible. However, the parameter values of mono- and di-halogeno complexes involved large uncertainties due to their strong complexation. In order to obtain these values, we examined the ternary Cd^{II} -Br-I system, and binary and ternary data were analysed simultaneously by taking into account the formation of ternary complexes. The whole titration curves can be explained in terms of the formation of ternary $[\text{CdBrI}]^0$ and $[\text{CdBr}_2\text{I}]^-$, in addition to the binary $[\text{CdBr}_n]^{(2-n)+}$ ($n = 1, 2, 3, 4$) and $[\text{CdI}_n]^{(2-n)+}$ ($n = 1, 2, 3$) complexes. The formation of other ternary complexes such as $[\text{CdBrI}_2]^-$ is almost negligible under the experimental conditions. The stepwise formation constants, reaction enthalpies and entropies of the binary complexes determined by using data for the binary systems are shown in Table 1, along with those obtained by taking into account the formation of ternary complexes. The values obtained in the ternary system are not significantly different from those from the binary systems, while the standard deviations of the parameter values, especially those of the iodo complexes, became small. The thermodynamic parameters of formation of ternary $[\text{CdBrI}]^0$ and $[\text{CdBr}_2\text{I}]^-$ are shown in Table 2. The solid lines in Fig. 1 and 2, calculated by using the formation constants and enthalpies shown in Tables 1 and 2, reproduce the experimental points well. The distribution of species is shown in Fig. 3.

The extracted EXAFS spectra weighted by k^3 of the sample solutions are shown in Fig. 4. The phase of oscillations is appreciably different for the various solutions, indicating different Cd-O interactions. The radial structure functions $|F(r)|$, uncorrected for phase shift, are shown in Fig. 5. The first intense peaks appearing around 170 pm are due to the Cd-O bonds in the first coordination sphere, the position of which shifts to a longer r value in the order A (167 pm) < B (171 pm) \approx C (172 pm) < D (178 pm). The medium

Table 1 Thermodynamic parameters, $\log(K_n/\text{mol}^{-1} \text{ dm}^3)$, $\Delta H_n^\circ/\text{kJ mol}^{-1}$ and $\Delta S_n^\circ/\text{J K}^{-1} \text{ mol}^{-1}$, for the stepwise formation reaction, $[\text{CdX}_{n-1}]^{(3-n)+} + X^- = [\text{CdX}_n]^{(2-n)+}$ ($X = \text{Br}, \text{I}$), in 0.1 mol dm^{-3} ($n\text{-C}_4\text{H}_9\text{NClO}_4$ HMPA solution at 25°C^a)

	binary		ternary	
	Cd ^{II} -Br	Cd ^{II} -I	Cd ^{II} -Br	Cd ^{II} -I
$\log K_1$	9.2 (0.4)	7.3 (0.8)	9.3 (0.4)	7.2 (0.4)
$\log K_2$	6.9 (0.4)	5.5 (0.8)	7.0 (0.4)	5.4 (0.4)
$\log K_3$	4.5 (0.2)	2.65 (0.07)	4.5 (0.2)	2.26 (0.08)
$\log K_4$	1.9 (0.3)	—	1.9 (0.2)	—
ΔH_1°	0.6 (0.2)	14.7 (0.3)	0.6 (0.3)	14.7 (0.3)
ΔH_2°	-5.4 (0.3)	-4.9 (0.4)	-5.6 (0.3)	-4.9 (0.4)
ΔH_3°	-18.4 (0.4)	-12.1 (0.5)	-18.4 (0.4)	-12.2 (0.5)
ΔH_4°	-5.7 (1)	—	-6.4 (1)	—
ΔS_1°	177 (9)	189 (16)	179 (9)	187 (8)
ΔS_2°	114 (7)	88 (15)	116 (8)	86 (8)
ΔS_3°	24 (6)	10 (3)	25 (6)	10 (3)
ΔS_4°	17 (10)	—	15 (8)	—
R^b	0.0324	0.0373	0.0406	
N^c	108	85	244	

^a Values in parentheses refer to three standard deviations. ^b The Hamilton R -factor. ^c The number of calorimetric data points.

Table 2 Comparison of thermodynamic parameters, $\log(K/\text{mol}^{-1} \text{dm}^3)$, enthalpies, $\Delta H^\circ/\text{kJ mol}^{-1}$, and entropies, $\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$, for the stepwise formation of ternary halogeno complexes of cadmium(II) at 25 °C^a

reaction	log <i>K</i>	ΔH°	ΔS°
$[\text{CdBr}]^+ + \text{Br}^- \rightarrow [\text{CdBr}_2]^0$	7.0 (0.4)	−5.6 (0.3)	116 (8)
$[\text{CdI}]^+ + \text{Br}^- \rightarrow [\text{CdBrI}]^0$	7.2 (0.6)	−12.6 (1.2)	95 (12)
$[\text{CdBr}]^+ + \text{I}^- \rightarrow [\text{CdBrI}]^0$	5.1 (0.7)	1.5 (1.2)	103 (13)
$[\text{CdI}]^+ + \text{I}^- \rightarrow [\text{CdI}_2]^0$	5.3 (0.5)	−4.9 (0.4)	84 (9)
$[\text{CdBr}_2]^0 + \text{Br}^- \rightarrow [\text{CdBr}_3]^-$	4.5 (0.3)	−18.4 (0.4)	25 (6)
$[\text{CdBrI}]^0 + \text{Br}^- \rightarrow [\text{CdBr}_2\text{I}]^-$	4.9 (0.7)	−18.1 (0.9)	33 (14)
$[\text{CdBr}_2]^0 + \text{I}^- \rightarrow [\text{CdBr}_2\text{I}]^-$	3.4 (0.2)	−11.2 (0.8)	27 (6)
$[\text{CdI}_2]^0 + \text{I}^- \rightarrow [\text{CdI}_3]^-$	2.65 (0.08)	−12.2 (0.5)	10 (2)

^a Values in parentheses refer to three standard deviations.

intense peaks at 310–320 pm observed for solutions A, B and C may be due to the non-bonding Cd···P interaction.

The structure parameters which best reproduce the observed Fourier-filtered $k^3 \cdot \chi(k)$ function were then optimized by the non-linear least-squares method. The range of k space used for the optimization was $4.5 < k/10^{-2} \text{ pm}^{-1} < 12.0$. The range of filtering was $0.9 < r/10^2 \text{ pm} < 2.3$, which includes the main peak in the observed $|F(r)|$ function. The interatomic distance, the Debye–Waller factor and the number of interactions for the Cd—O bond of solutions A, B and C were determined on the basis of the parameters, λ , a_0 and a_1 , obtained by analysing EXAFS of solution D contain-

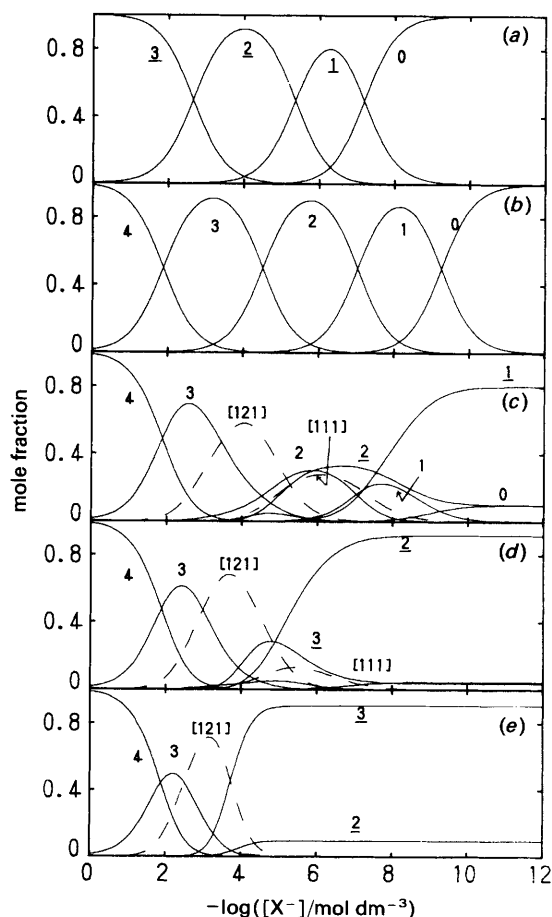


Fig. 3 Distribution of species in the binary Cd^{II}–Br and Cd^{II}–I and ternary Cd^{II}–Br–I systems in HMPA. R_c represents the concentration ratio of iodide to cadmium(II) ions in solution. n represents the complex $[\text{CdX}_n]^{(2-n)+}$. (a) X = I; (b) X = Br, $R_c = 0$; (c) X = Br, $R_c = 1$; (d) X = Br, $R_c = 2$; (e) X = Br, $R_c = 5$

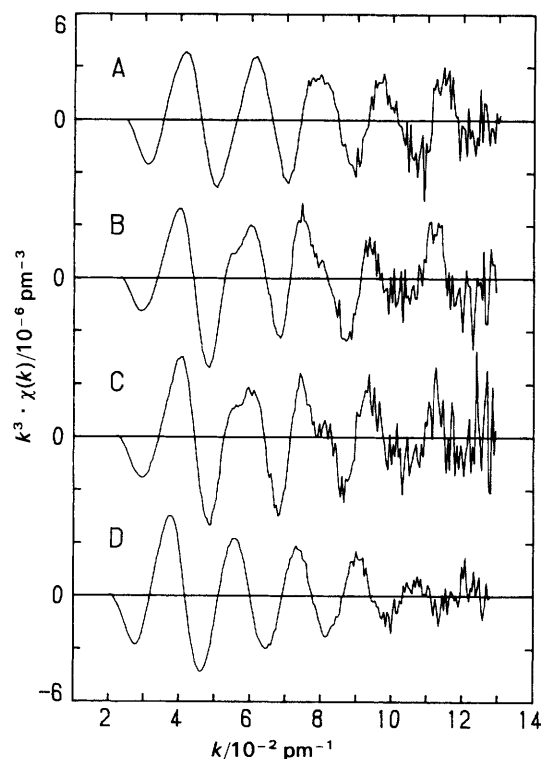


Fig. 4 Extracted EXAFS oscillations in the form of $k^3 \cdot \chi(k)$ for solutions A–D

ing $[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$ of known structure, i.e. Cd—O length and coordination number of 231 pm and 6.²¹ The results are summarized in Table 3. As seen in Fig. 6, the solid curves, calculated using the parameters in Table 3, reproduce the experimental curves well (dotted lines).

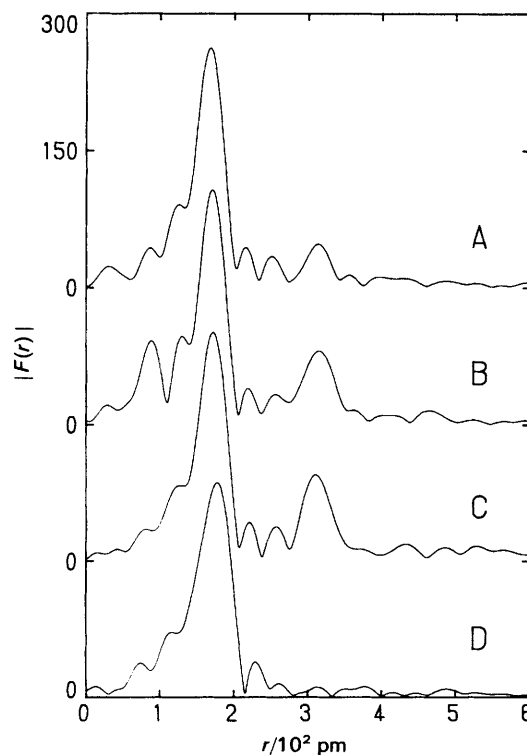
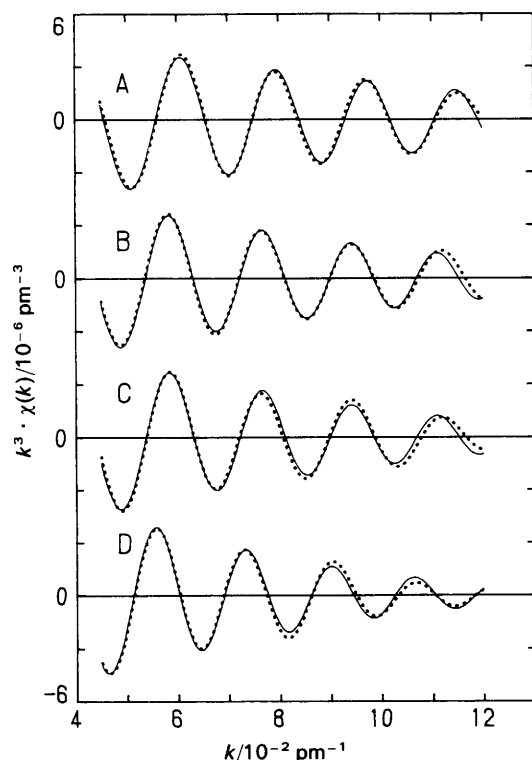


Fig. 5 Radial structure functions $F(r)$, uncorrected for phase shift, for solutions A–D

Table 3 Bond lengths, r/pm , Debye–Waller factors, σ/pm , and coordination numbers, n , for the Cd–O interaction of solvated cadmium(II) ion^a

solution	solute	r/pm	σ/pm	n	solvent
A	$[\text{Cd}(\text{HMPA})_n]^{2+}$	217 (1)	5.6 (2)	3.9 (0.1)	NM
B	$[\text{Cd}(\text{HMPA})_n]^{2+}$	223 (1)	6.4 (2)	4.5 (0.1)	NM–HMPA ^d
C	$[\text{Cd}(\text{HMPA})_n]^{2+}$	223 (1)	7.2 (2)	4.8 (0.1)	HMPA
D	$[\text{Cd}(\text{H}_2\text{O})_6]^{2+}$	231 ^{b,c}	8.4 (2)	6 ^{b,c}	water

^a The values in parentheses refer to one standard deviation. ^b The values were kept constant. ^c Ref. 21. ^d The mixture of 0.62 mole fraction HMPA.

**Fig. 6** Comparison of the observed Fourier-filtered $k^3 \cdot \chi(k)$ curves of the main peak in Fig. 5 (.....) and the calculated curves (—) for solutions A–D

Discussion

Thermodynamics of Halogeno Complexation in HMPA

The $[\text{CdX}]^+$, $[\text{CdX}_2]^0$, $[\text{CdX}_3]^-$ and $[\text{CdX}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) complexes are extensively formed in water,^{22,23} DMF²⁴ and DMSO.²⁵ The cadmium(II) ion is octahedrally coordinated in these oxygen-donor solvents. As tetrahalogeno cadmium(II) complexes have a tetrahedral geometry without bound solvent molecules,²⁶ an octahedral to tetrahedral geometry change should occur at some point upon complexation with halide ions. Irregular variations of thermodynamic parameters are thus expected when the coordination geometry is changed, because an extensive liberation of solvent molecules from the coordination sphere usually leads to relatively large reaction enthalpies and entropies. In DMF the stepwise formation constants vary in the order $K_1 > K_3 > K_2 > K_4$, and the corresponding enthalpies and entropies vary in the order $\Delta H_2^\circ > \Delta H_3^\circ > \Delta H_1^\circ > \Delta H_4^\circ$ and $\Delta S_2^\circ > \Delta S_3^\circ > \Delta S_1^\circ > \Delta S_4^\circ$, suggesting that an octahedral to tetrahedral geometry change occurs at the second consecutive

step, i.e. $[\text{CdX}(\text{DMF})_5]^+ + \text{X}^- \rightarrow [\text{CdX}_2(\text{DMF})_2]^0 + 3\text{DMF}$. The same applies in DMSO. Interestingly, the change occurs at the third consecutive step in water, i.e. $[\text{CdX}_2(\text{H}_2\text{O})_4]^0 + \text{X}^- \rightarrow [\text{CdX}_3(\text{H}_2\text{O})]^- + 3\text{H}_2\text{O}$. If the cadmium(II) ion is six-coordinated also in HMPA, an octahedral to tetrahedral geometry change may take place as in water, DMF and DMSO.

As seen in Table 1, no irregular variation of K_n was found in HMPA, i.e. $K_1 > K_2 > K_3 > K_4$ in both the $\text{Cd}^{\text{II}}\text{--Br}$ and $\text{Cd}^{\text{II}}\text{--I}$ systems. The same has been found in the $\text{Co}^{\text{II}}\text{--X}$ and $\text{Zn}^{\text{II}}\text{--X}$ systems in HMPA. However, looking at the enthalpy and entropy values, a considerable difference is seen in the variation profile of ΔH_n° and ΔS_n° . The reaction enthalpy and entropy values vary in the order, $\Delta H_1^\circ < \Delta H_2^\circ < \Delta H_3^\circ < \Delta H_4^\circ < 0$ and $\Delta S_1^\circ > \Delta S_2^\circ > \Delta S_3^\circ > \Delta S_4^\circ > 0$, in the $\text{Zn}^{\text{II}}\text{--Cl}$ system. The same applies for the $\text{Zn}^{\text{II}}\text{--Br}$ and $\text{Zn}^{\text{II}}\text{--I}$ systems, though the tri- and tetra-halogeno complexes are not formed. In the $\text{Cd}^{\text{II}}\text{--X}$ systems, a different variation profile was found, i.e. $\Delta H_1^\circ \approx 0 > \Delta H_2^\circ \approx \Delta H_4^\circ > \Delta H_3^\circ$ for $\text{X} = \text{Br}$, and $\Delta H_1^\circ > 0 > \Delta H_2^\circ > \Delta H_3^\circ$ for $\text{X} = \text{I}$. Although the reaction entropies vary in a regular manner, as in the $\text{Zn}^{\text{II}}\text{--X}$ systems, $\Delta S_1^\circ > \Delta S_2^\circ > \Delta S_3^\circ > \Delta S_4^\circ$, the values are significantly different. Indeed, the ΔS_1° values of 179 and 187 $\text{J K}^{-1} \text{mol}^{-1}$ for the formation of $[\text{CdBr}]^+$ and $[\text{CdI}]^+$ are significantly larger than the respective values (101 and 102 $\text{J K}^{-1} \text{mol}^{-1}$) for the formation of $[\text{ZnBr}]^+$ and $[\text{ZnI}]^+$. These results cannot be explained in terms of a simple substitution of a coordinating HMPA molecule with an entering bromide or iodide ion, suggesting that more than one bound HMPA molecule is liberated upon formation of $[\text{CdBr}]^+$ and $[\text{CdI}]^+$. It is thus supposed that the cadmium(II) ion is coordinated with more than four HMPA molecules in HMPA. This is not unexpected because the cadmium(II) ion, which has a large ionic radius, may be able to accommodate five HMPA molecules in the primary coordination sphere.

Coordination Number of the Cadmium(II) Ion

In Table 3, the number of Cd–O interactions n is different among solutions A, B and C. As HMPA contains a strongly electron-donating oxygen atom, whereas nitromethane does not, the observed Cd–O interaction is evidently due to the HMPA molecules coordinated to the metal ion. The n value of solution A, prepared by dissolving crystals of $\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{HMPA}$ into nitromethane, is close to 4, indicating that the main species in solution A is $[\text{Cd}(\text{HMPA})_4]^{2+}$. The n value of solution B, containing an excess of HMPA in nitromethane, is 4.5, which is appreciably larger than that of solution A. The value in pure HMPA is 4.8. The increasing n implies the presence of a five-coordinate cadmium(II) ion as the main species in pure HMPA. The Cd–O bond length is 217 pm in solution A, and is elongated to 223 pm in solution C (pure HMPA). The elongation, possibly due to a repulsion between coordinating HMPA molecules, is consistent with an increase in the number of HMPA molecules coordinated to the cadmium(II) ion.

In Fig. 5, the peak around 310 pm is ascribed to the Cd–P(HMPA) interaction. Interestingly, the peak height of solution C is significantly larger than that of solution A. This might show that the extent of thermal motion of the bound HMPA molecules is sterically hindered as a result of crowding in the primary coordination sphere of the cadmium(II) ion. Accordingly, the evidence from EXAFS spectroscopy leads to the conclusion that the cadmium(II) ion is coordinated with five solvent molecules in HMPA. This conclusion is consistent with that obtained thermodynamically.

Ternary Complexation

In Table 2, the thermodynamic parameters for the following reactions of X^- ($X = \text{Br}, \text{I}$) in HMPA are summarized:



With respect to a given X^- ion, ΔH° value for reaction (8) is appreciably larger than that for reaction (9), i.e. 7.0 and 6.4 kJ mol⁻¹ for $X = \text{Br}$ and I , respectively. Note that the corresponding values for the Zn^{II} ion are similar,⁴ which is expected because the zinc(II) ion is a hard ion, and thus the strength of metal-solvent bond within $[\text{ZnX}(\text{HMPA})_3]^+$ may not be appreciably changed depending on the kind of bound X^- ion. On the other hand, as the cadmium(II) ion behaves as a soft ion, the fractional charge on the central metal ion may decrease with increasing polarity of X^- , i.e. $\text{Cl}^- < \text{Br}^- < \text{I}^-$, which may lead to a weaker $\text{Cd}-\text{O}(\text{HMPA})$ bond in $[\text{CdI}(\text{HMPA})_3]^+$ than in $[\text{CdBr}(\text{HMPA})_3]^+$. The $\{\Delta H^\circ [\text{eqn. (8)}] - \Delta H^\circ [\text{eqn. (9)}]\}$ values for $X = \text{Br}$ and I are similar. The same applies for $\{\Delta S^\circ [\text{eqn. (8)}] - \Delta S^\circ [\text{eqn. (9)}]\}$, implying that no appreciable steric interaction is involved upon complexation.

No significant difference in the ΔH° and ΔS° values is seen for reactions, $[\text{CdBr}_2]^0 + \text{Br}^- \rightarrow [\text{CdBr}_3]^-$ and $[\text{CdBrI}]^0 + \text{Br}^- \rightarrow [\text{CdBr}_2\text{I}]^-$. The same is seen for reactions, $[\text{CdBr}_2]^0 + \text{I}^- \rightarrow [\text{CdBr}_2\text{I}]^-$ and $[\text{CdI}_2]^0 + \text{I}^- \rightarrow [\text{CdI}_3]^-$. This demonstrates that the strength of $\text{Cd}-\text{O}(\text{HMPA})$ bonds within $[\text{CdBr}_2(\text{HMPA})_2]^0$, $[\text{CdBrI}(\text{HMPA})_2]^0$ and $[\text{CdI}_2(\text{HMPA})_2]^0$ is not appreciably different. The ΔH° values are relatively large and negative. It is thus supposed that metal-HMPA bonds within the dihalogeno complexes are weakened, probably due to electron donation from ligands to the central metal ion.

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