

On the Formation of Cationic Cadmium(II) Halide Complexes in Molten Nitrate Media and Aqueous Solution

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Bengtsson, L. and Holmberg, B., 1990. On the Formation of Cationic Cadmium(II) Halide Complexes in Molten Nitrate Media and Aqueous Solution. – *Acta Chem. Scand.* 44: 447–454.

The complex formation between cadmium(II) and halide ions has been studied in molten equimolar (K,Na)NO₃ at 280°C and in aqueous solution at 25°C. Potentiometric measurements with fluoride ion-selective and Ag/AgX electrodes show the formation of only CdX⁺ (X = F, Cl, Br, I) in (K,Na)NO₃ melts with cadmium(II) nitrate in excess over halide. Corrections for the silver(I) halide solution chemistry were made in the data treatment for the systems studied with Ag/AgX electrodes. Structural investigations with Raman spectroscopy and liquid X-ray scattering were performed for the chloride and bromide systems in molten (K,Na)NO₃ and for the corresponding iodide system in concentrated aqueous solution. The formation of halide complexes in the melts is indicated in the Raman spectra showing direct Cd–X vibrations and a restoration of the nitrate D_{3h} symmetry due to the exchange of NO₃[–] for X[–] in the coordination sphere of Cd(II). Liquid X-ray scattering data further confirm that only CdX⁺ is formed in the melts. One Cd–X distance per halide is observed; Cd–Cl at 2.55 Å and Cd–Br at 2.63 Å. By analogy, only the formation of CdI⁺ in aqueous solution could be established by means of liquid X-ray scattering. One Cd–I distance per iodide at 2.77 Å and no Cd–Cd correlation could be observed.

The structure of the ions Ag₄I³⁺, Hg₂I³⁺, Pb₂X³⁺ (X = F, Cl, Br), Tl₂Br⁺ and Pb₂(OH)₂²⁺ in molten (K,Na)NO₃ and concentrated aqueous solution have been reported in preceding papers.^{1–6} The complexes of the d¹⁰s² metal ions Pb(II) and Tl(I) are all bent, with cation–anion–cation angles of about 90°. In Pb₂Cl³⁺, Pb₂Br³⁺ and Pb₂(OH)₂²⁺ remarkably short Pb–Pb separations are found, and it is believed that a substantial direct metal–metal interaction contributes significantly to the stability of these species in the melts. For the d¹⁰ ion Hg²⁺ in Hg₂I³⁺ a similar structure is found, but the structure of Ag₄I³⁺ is puzzling.^{1,2} Four distinct Ag–I interactions are observed, but no Ag–Ag correlations. The study of the complex formation between the d¹⁰ ion Cd²⁺ and halide ions in (K,Na)NO₃(l) under conditions favourable for the formation of Cd_nX species may thus throw further light on the bonding situation in complexes with anions as coordination centres and d¹⁰ or d¹⁰s² metal ions as ligands.

The solubility of Cd(l) in molten CdX₂ and MAICl₄ is rather high (X = F, Cl, Br, I; M = monovalent cation). The nature of the species formed have rendered much attention. The earlier work was reviewed in the middle of the sixties.^{7–9} Different types of results indicated the formation of Cd₂²⁺ or Cd₂X₂, or even larger polycadmium clusters. From this date a vast number of experiments have been performed. Some of the latest papers are given in Refs. 10–14. Almost all results suggest the formation of some

kind of Cd₂²⁺ entity “solvated” by halides. However, a simple model can not accurately explain all experimental evidence.

The complex formation between cadmium(II) and halide ions in molecular solvents has been thoroughly studied. The ions CdX_n^{2–n} (n = 1–6 for X = Cl, I; n = 1–4 for X = F, Br) are claimed to be formed. Only two reports on polycadmium species, viz. Cd₂F³⁺ and Cd₂I³⁺, appear to exist.^{15,16}

Similar investigations have been undertaken in aqueous and dimethyl sulfoxide (DMSO) nitrate melts. The content of molecular solvent in these melts have been varied, in order that effects of incomplete molecular solvation be studied. The formation of CdX_n^{2–n} (n = 1–3 for X = Cl, Br) is described. The polymetal complexes Cd₂Cl³⁺ and Cd₂Br³⁺ have also been claimed to exist.^{17,18}

The structure of the CdCl_n^{2–n} ions (n = 1–unknown) and CdI_n^{2–n} ions (n = 1, 3–4) in aqueous and/or DMSO solution have been determined by means of X-ray scattering. The Cd–Cl and Cd–I distances found are 2.55–2.60 Å^{19,20} and 2.75–2.80 Å,^{21–24} respectively.

Thermodynamic investigations of cadmium(II) halide association in molten anhydrous nitrates are also numerous. Many different techniques have been used, but only Bombi *et al.* seem to include the formation of Cd₂Cl³⁺ in molten (K,Li)NO₃ in their complexation model.²⁵ The formation of this type of Cd₂X³⁺ ions in anhydrous nitrate melts has been considered unlikely for electrostatic reasons,²⁶ but it is now firmly established that such arguments based on elec-

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trostatic repulsion theories are definitely not valid for Pb_2X^{3+} ions.^{4,27,28}

In the present study the complex formation in equimolar molten $(\text{K},\text{Na})\text{NO}_3$ at 280 °C and concentrated aqueous solution at 25 °C between cadmium(II) and halide ions is characterized both thermodynamically and structurally, in order to gain further knowledge on complexes with anions as coordination centres.

Experimental

Chemicals. KNO_3 , NaNO_3 , KF , KCl , NaCl , KBr , KI , NaI (all Merck, p.A.) and NaBr (J.T. Baker, Analyzed Reagent) were dehydrated at 130 °C before use. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck, p.A.) was dehydrated in vacuum at increasing temperature up to 130 °C. Standard Karl Fischer titrations showed the water content to be equal or lower than the detection limit of the analysis method, i.e. $\leq 1.0 \times 10^{-2}$ wt%. No deterioration of the nitrate to yield CdO was observed. Dried KF and $\text{Cd}(\text{NO}_3)_2$ were handled in a glovebox with a dry $\text{N}_2(\text{g})$ atmosphere. The AgCl (Riedel-de Haën, 99.6%), AgBr (Merck, 99%) and AgI (Ventron, 99.9%) were dehydrated over anhydrous $\text{Mg}(\text{ClO}_4)_2$.

Apparatus. The equipment has been described previously both for the EMF, Raman spectroscopy and liquid X-ray scattering experiments.^{4,27-31}

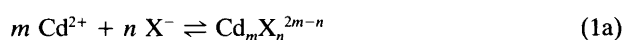
EMF measurements. The fluoride activities were measured in molten $(\text{K},\text{Na})\text{NO}_3$ at 280 °C using an LaF_3 -membrane electrode, and the activities of the other halides using Ag/AgX electrodes. The cells and measurement procedures were analogous to those described for the lead(II) halide systems,^{27,28} with the difference that a one-electron slope was assumed for all the halide electrodes and that the melt was kept under an atmosphere of dry $\text{O}_2(\text{g})$ to avoid any absorption of water. Oxidation of metallic silver and iodide ions in melts with high concentrations of uncomplexed divalent metal ion could be observed for the cadmium(II) systems as well.²⁸ The data were treated as described previously.^{27,28} The total concentrations used were $1.21 \times 10^{-4} \leq C_X \leq 1.07 \times 10^{-2}$ mol kg^{-1} and $6.58 \times 10^{-4} \leq C_{\text{Cd}} \leq 6.52 \times 10^{-1}$ mol kg^{-1} , $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$. The large majority of experimental data refer to the range $C_{\text{Cd}} \leq 0.10$ mol kg^{-1} .

The oxidation problems turned out to be more difficult to control for the cadmium(II) halide systems than for the corresponding lead(II) systems. For this reason the present study was confined to one temperature only, 280 °C.

Raman spectroscopy and liquid X-ray scattering. The present structural study was also analogous with the previous lead(II) halide investigation,⁴ except that the melts were kept under a dry oxygen atmosphere during the experiments. The melt compositions and physical properties are shown in Table 1. Only the chloride and bromide systems were studied in molten equimolar $(\text{K},\text{Na})\text{NO}_3$ at 280 °C. The fluoride system was disqualified by the low solubility of $\text{CdF}_2(\text{s})$ and the iodide system by the slow oxidation of iodide to iodine in melts with high concentrations of uncomplexed $\text{Cd}(\text{II})$. The corresponding aqueous cadmium(II) iodide system was studied at 25 °C. Correction for multiple scattering was performed for the aqueous solutions due to their low absorption (Table 1).

Results

Potentiometric measurements. The addition of $\text{Cd}(\text{NO}_3)_2$ to a melt containing halide ions causes changes in the measured EMF. The observed effects are assumed to arise from complex formation reactions that decrease the halide ion activity according to reaction (1).



$$\beta_{mn} = \frac{[\text{Cd}_m\text{X}_n^{2m-n}]}{[\text{Cd}^{2+}]^m[\text{X}^-]^n} \quad (1b)$$

Changes in fluoride ion activity are directly measured. The Ag/AgX electrodes, however, are not strictly inert under the conditions of measurements. Corrections for the silver halide solubility and complex formation have to be performed. These corrections are more important for the cadmium(II) halide systems than for the corresponding lead(II) systems, since the complex formation is stronger in the former. The corrections have been thoroughly described in an earlier paper.²⁸ In either case the evaluation of

$$C_X^{\text{Cd}} = \sum_{m,n} n[\text{Cd}_m\text{X}_n^{2m-n}] = \sum_{m,n} n\beta_{mn}[\text{Cd}^{2+}]^m[\text{X}^-]^n \quad (2)$$

Table 1. The composition, stoichiometric unit volume per cadmium atom, mass density and linear absorption coefficient of the melts and aqueous solutions investigated by liquid X-ray scattering.

System	C_K^a	C_{Na}^a	C_{Cd}^a	$C_{\text{NO}_3}^a$	C_X^a	$C_{\text{H}_2\text{O}}^a$	$V/\text{Å}^3$	$\rho/\text{g cm}^{-3}$	μ/cm^{-1}
$\text{Cd}(\text{NO}_3)_2-(\text{K},\text{Na})\text{NO}_3$	7.47	7.47	3.45	21.84	—	—	481.7	2.21 ^b	18
$\text{CdCl}_2-\text{Cd}(\text{NO}_3)_2-(\text{K},\text{Na})\text{NO}_3$	7.56	7.56	3.54	21.07	1.12	—	469.8	2.21 ^b	18
$\text{CdBr}_2-\text{Cd}(\text{NO}_3)_2-(\text{K},\text{Na})\text{NO}_3$	7.27	7.27	3.35	20.17	1.09	—	494.5	2.17 ^b	24
$\text{Cd}(\text{NO}_3)_2-\text{H}_2\text{O}$	—	—	3.02	6.05	—	46.53	549.2	1.55 ^c	11
$\text{CdI}_2-\text{Cd}(\text{NO}_3)_2-\text{H}_2\text{O}$	—	—	3.03	5.66	0.40	46.45	547.5	1.58 ^c	13

^aAll concentrations given in mol dm^{-3} . ^bThe density was determined at 280 °C. ^cThe density was determined at 25 °C.

Table 2. Overall stability constants for CdX^+ in equimolar $(K,Na)NO_3(l)$ at 280 °C. The error limits define a 95 % confidence interval.

Halide	$\beta_{11}/kg\ mol^{-1}$	No. ^a
F	23.9 ± 0.3	38
Cl	28 ± 2	47
Br	123 ± 3	55
I	$(6.9 \pm 1.5) \times 10^2$	27

^aNumber of degrees of freedom.

C_X^{Cd} , i.e. the total concentration of halide which is uncomplexed by $Ag(I)$, is of fundamental importance. C_X^{Cd} may be expressed as the sum shown in eqn. (2).

Measurements at different C_{Cd} and C_X values give the information needed. An initial complexation model was determined by graphical data analysis, and thereafter the sum $\Sigma(E_{\text{exptl}} - E_{\text{calcd}})^2$ was minimized for the proper complexation model by the least-squares program EMFALL. The results are shown in Table 2.

The short Cd–Cd distances observed in some solid compounds,^{32–36} and the formation of Cd clusters in halide melts with dissolved Cd(I), may suggest that cadmium is a suitable ligand for the formation of polymetal complexes of the type Cd_mX^{2m-1} , $m > 1$. As seen in Table 2 no such species are detected by the potentiometric measurements. The formation of CdX^+ is fully sufficient to explain all potentiometric data obtained for all the halides once the proper corrections for the $Ag(I)$ chemistry have been performed. One should bear in mind, however, that only iodide systems with $C_{Cd} \leq C_I$ could be investigated, owing to the slow oxidation of iodide to iodine.

Raman spectroscopy and liquid X-ray scattering; systems $Cd(NO_3)_2-(K,Na)NO_3$. The structure of the pure solvent

$(K,Na)NO_3$ has been reported previously.⁴ Several infrared and Raman spectroscopy results have been published. Addition of $Cd(NO_3)_2$ to $(K,Na)NO_3$ causes changes in the internal nitrate bands similar to those observed for $Pb(NO_3)_2$. The effects indicate a distortion of the initial nitrate D_{3h} symmetry to C_s or C_{2v} .^{4,37–40} This distortion is stronger for melts containing Cd(II) than for the corresponding Pb(II) systems. Intense, direct cadmium–nitrate bands at about 200 and 260 cm^{-1} have also been reported. The distortions of the nitrate symmetry are best explained by an asymmetrical bonding by the cadmium(II) ion to two oxygens in the nitrate, out of the nitrate plane.^{4,37–40}

The results of the liquid X-ray scattering experiments on the $Cd(NO_3)_2-(K,Na)NO_3$ melt are shown in Table 3 and Fig. 1. A least-squares refinement of the data was performed, and the best-fitting coordination model is analogous to that reported for $Pb(NO_3)_2-(K,Na)NO_3$ melts.⁴ This model includes the coordination of four nitrates by each cadmium(II) ion via an asymmetrical bonding of two nitrate oxygens in each of the nitrates, placing the cadmium(II) ion out of the nitrate plane.

Raman spectroscopy and liquid X-ray scattering; systems $CdX_2-Cd(NO_3)_2-(K,Na)NO_3$. Halide ions introduced into the $Cd(NO_3)_2-(K,Na)NO_3$ melts are reported to restore the vibrational nitrate band spectrum towards that of pure $(K,Na)NO_3(l)$, which indicates the exchange of nitrates for halides in the first coordination sphere of cadmium(II), i.e. that cadmium(II) halide complexes are formed.^{38,40} Clarke and co-workers report direct Cd–Cl and Cd–Br vibrations at 264 and 164 cm^{-1} in molten $(K,Na)NO_3$.⁴¹ These signals are claimed to be caused by the $CdCl_3^-$ and $CdBr_4^{2-}$ ions, respectively. All spectra in that study were collected from melts with halide in large excess over cadmium(II). The cadmium(II) ion thus seems to be rather firmly solvated by nitrate ions, which are exchanged for halides upon complex

Table 3. Parameters used for calculation of the theoretical curves in Fig. 1; d = interatomic distance, b = temperature coefficient and n = number of interactions. The data given for $(K,Na)NO_3(l)$ served as a basis in the refinements of the parameters of the $Cd(NO_3)_2-(K,Na)NO_3$ melt. Refined parameters are given with one mean error in brackets.

Interaction	$(K,Na)NO_3^a$			$Cd(NO_3)_2-(K,Na)NO_3$		
	$d/\text{Å}$	$b/\text{Å}^2$	n	$d/\text{Å}$	$b/\text{Å}^2$	n
Cd–O _I				2.33(1)	0.0032(5)	4.3(1) ^c
Cd–O _{II}				3.00(1)	0.020(2)	4.4(2) ^c
Cd–O _{III}				3.25(1)	0.032(3)	4.6(2) ^c
Cd–N				2.69(1)	0.0034(8)	3.3(2) ^c
K–O	3.13(2)	0.035(3)	2.9(2) ^b			
Na–O	2.71(1)	0.017(2)	3.4(2) ^b			
K–K	4.75(2)	0.020(2)	0.55(3) ^b			0.44(4) ^b
K–Na	4.29(1)	0.041(2)	2.06(7) ^b			1.03(8) ^b
Na–Na	4.06(4)	0.038(9)	0.6(1) ^b			0.6(1) ^b
O–O	5.23(2)	0.051(4)	7.9(4) ^b			7.6(5) ^b
Cd–Cd				4.14(4)	0.031(8)	0.032(5) ^b
Cd–K				4.48(2)	0.039(4)	0.27(2) ^b
Cd–Na				3.99(1)	0.016(2)	0.34(2) ^b

^aFrom Ref. 4. ^bPer nitrate. ^cPer cadmium(II) atom.

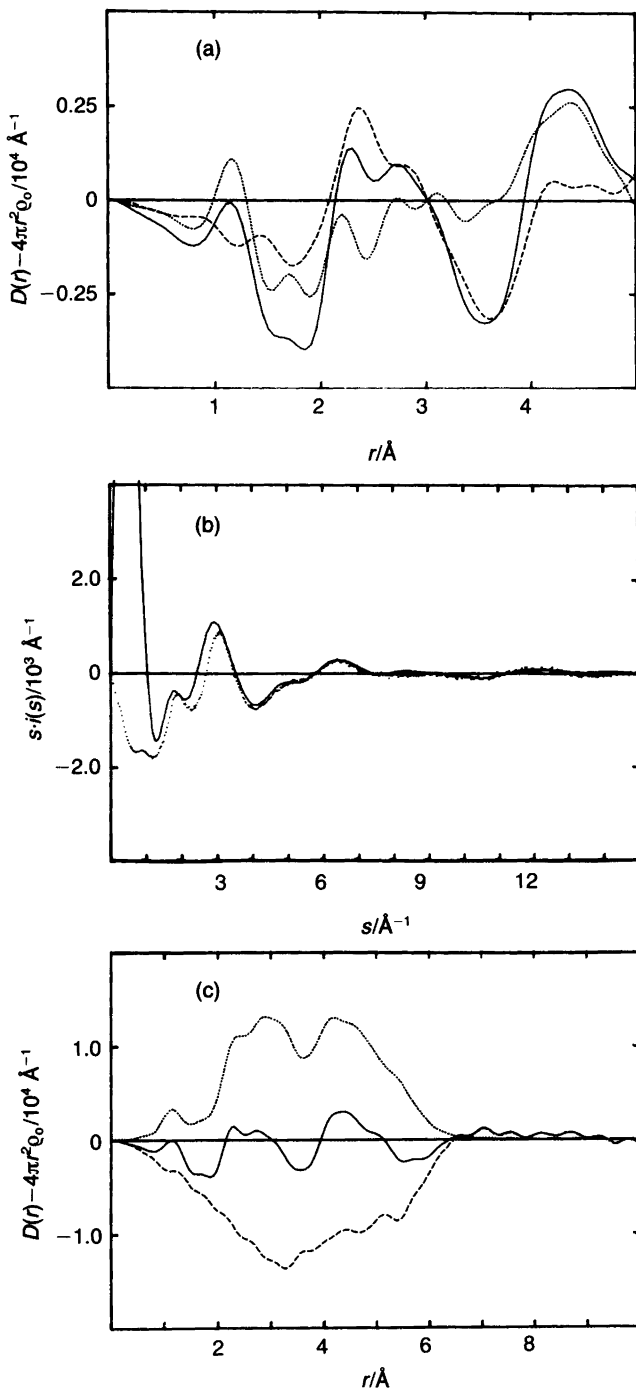


Fig. 1. The experimental results and the theoretical model for the $\text{Cd}(\text{NO}_3)_2$ - $(\text{K,Na})\text{NO}_3$ melt; (a) the differential RDF (----) between the $\text{Cd}(\text{NO}_3)_2$ - $(\text{K,Na})\text{NO}_3$ (—) and $(\text{K,Na})\text{NO}_3$ (····) melts, (b) the reduced intensity function of the theoretical model and experimental points, (c) the experimental reduced RDF (—) and the theoretical peak shapes according to the atomic parameters in Table 2 (····), and their difference (----).

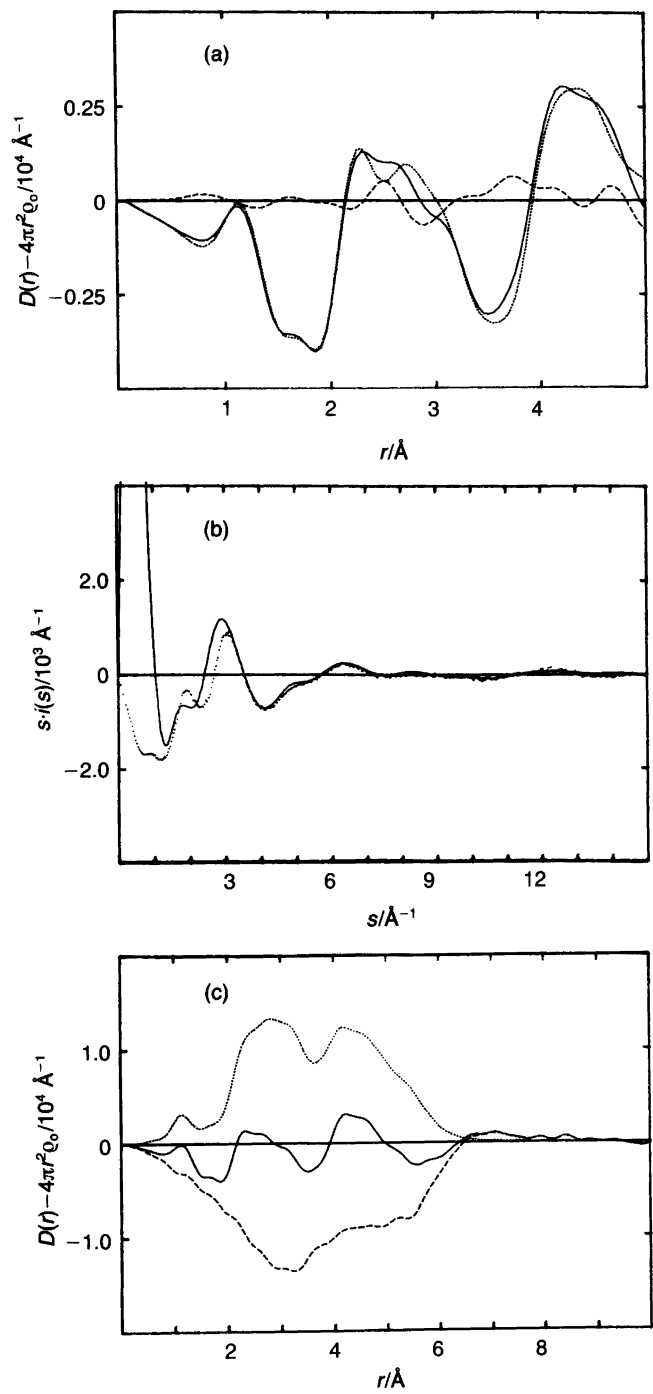


Fig. 2. The experimental results and the theoretical model for the CdCl_2 - $\text{Cd}(\text{NO}_3)_2$ - $(\text{K,Na})\text{NO}_3$ melt; (a) the differential RDF (----) between the CdCl_2 - $\text{Cd}(\text{NO}_3)_2$ - $(\text{K,Na})\text{NO}_3$ (—) and $\text{Cd}(\text{NO}_3)_2$ - $(\text{K,Na})\text{NO}_3$ (····) melts, (b) the reduced intensity function of the theoretical model and experimental points, (c) the experimental reduced RDF (—) and the theoretical peak shapes according to the atomic parameters in Tables 3 and 4 (····), and their difference (----).

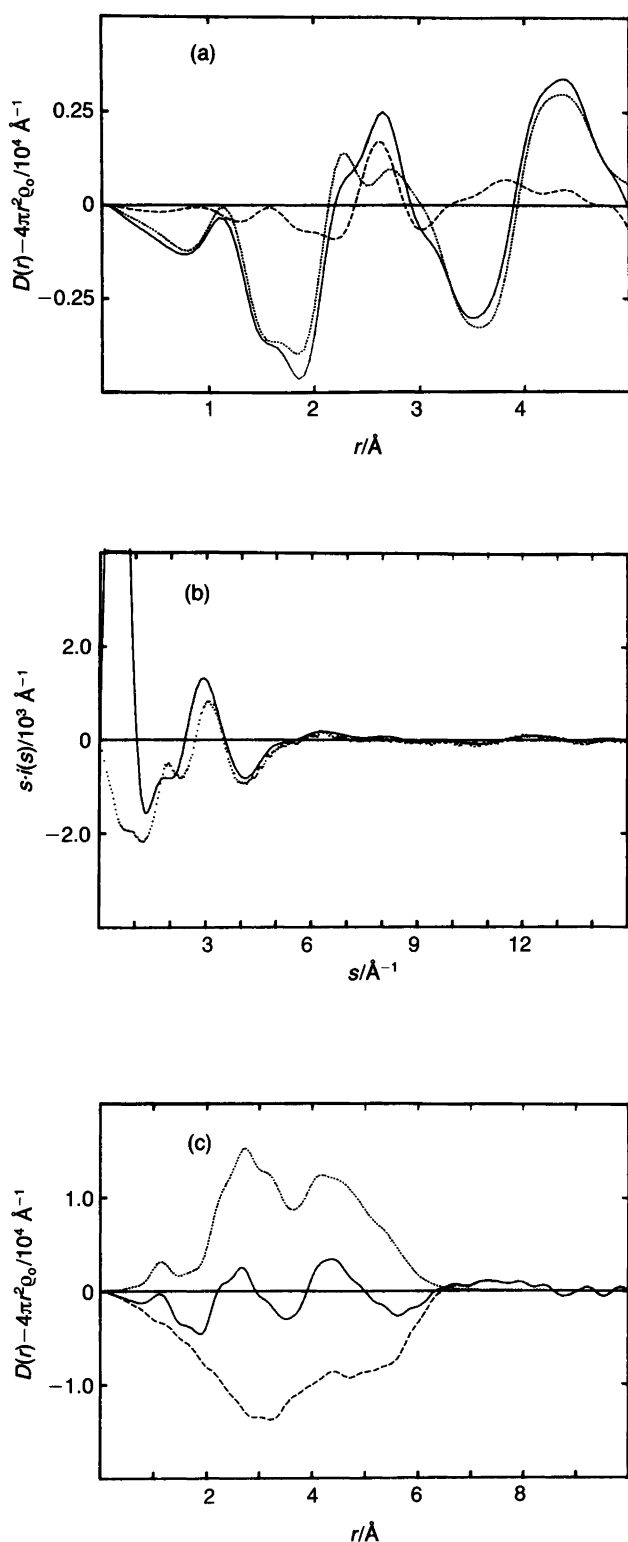


Fig. 3. The experimental results and the theoretical model for the $\text{CdBr}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ melt; (a) the differential RDF (----) between the $\text{CdBr}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ (—) and $\text{Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ (····) melts, (b) the reduced intensity function of the theoretical model and experimental points, (c) the experimental reduced RDF (—) and the theoretical peak shapes according to the atomic parameters in Tables 3 and 4 (····), and their difference (----).

Table 4. Refined atomic parameters for the $\text{CdX}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ melts; d = interatomic distance, b = temperature coefficient and n = number of distances. The results obtained for the $\text{Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ melt served as refinement basis. The parameters are given with one mean error in brackets.

Melt		Cd-X
$\text{CdCl}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$	$d/\text{\AA}$	2.55(1)
	$b/\text{\AA}^2$	0.002(1)
	n	0.97(8) ^a
$\text{CdBr}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$	$d/\text{\AA}$	2.63(1)
	$b/\text{\AA}^2$	0.0020(9)
	n	1.06(5) ^a

^aPer halide.

formation in the melts. The Cd-X bands at about 260 and 160 cm^{-1} were verified for the $\text{CdX}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ melts in Table 1.

The difference between the experimental, reduced radial distribution functions (RDF) of the melts $\text{CdX}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ and $\text{Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$, reduced intensity functions and reduced radial distribution functions for the $\text{CdX}_2\text{-Cd}(\text{NO}_3)_2\text{-(K,Na)NO}_3$ melts in Table 1 are shown in Figs. 2 and 3. The difference curves of Figs. 2a and 3a do not exhibit any signs of dramatic cadmium(II) nitrate coordination changes, as observed for the lead(II) halides.⁴ The reason might be that no $\text{Cd}_m\text{X}_n^{2m-n}$ complexes, $m > 1$, are formed. There are weak but distinct Cd-X peaks at about 2.5 and 2.6 Å, however. The results of a least-squares refinement is shown in Table 4. The Cd-Cl distances are in excellent agreement with those of the $\text{CdCl}_n^{2-n}(\text{aq})$ ions (2.55–2.60 Å).^{19,20} The broad band at about 4.5 Å is somewhat shifted towards shorter distances for both systems, and may reflect the smaller radius of Cd^{2+} compared with the solvent cations K^+ and Na^+ . There is no sign of Cd-Cd or X-X contacts in any $\text{Cd}_m\text{X}_n^{2m-n}$ entity. The number of Cd-X interactions per halide is very close to one, which also confirms the absence of any complex species other than CdX^+ , $\text{X} = \text{Cl}$ and Br . The interpretations of the potentiometric measurements are thus confirmed by the liquid X-ray scattering data.

Liquid X-ray scattering: systems $\text{Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ and $\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$. Yatsimirskii and Shutov reported the formation of CdI^+ and Cd_2I^{3+} ions from solubility measurements of PbI_2 in aqueous solution.¹⁶ The Cd-I and Cd-Cd distances in Cd_2I^{3+} should be easy to detect by liquid X-ray scattering. The composition of the $\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ solution (Table 1) was chosen in such a way that 40 % of the iodide should be present as Cd_2I^{3+} according to the data of Ref. 16. The reduced RDFs of the $\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ solutions (Table 1) and their difference are shown in Fig. 4, as well as experimental results and final structural model for the $\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ system.

The exchange of nitrates for iodide ions causes complex formation between cadmium(II) and iodide, which is ob-

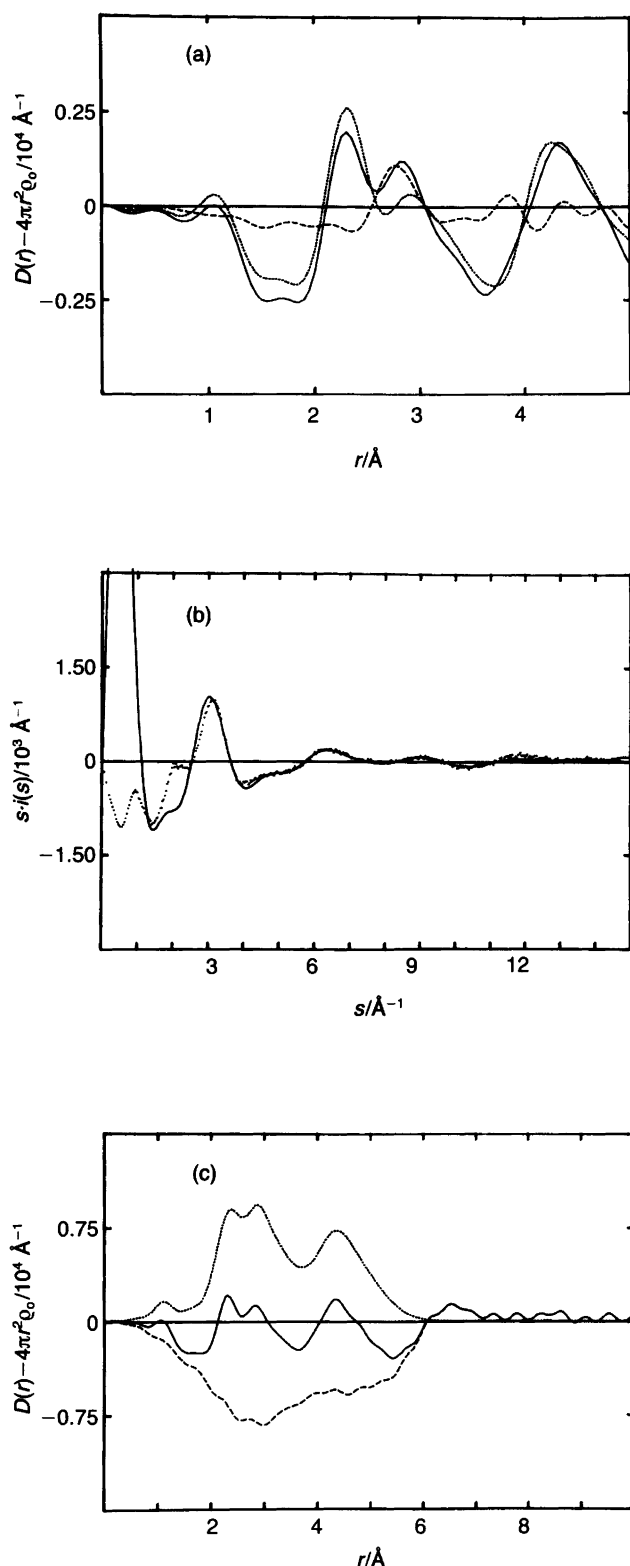


Fig. 4. The experimental results and the theoretical model for the $\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ solution; (a) the differential RDF (----) between the $\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ (—) and $\text{Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ (⋯), (b) the reduced intensity function of the theoretical model and experimental points, (c) the experimental reduced RDF (—) and the theoretical peak shapes according to the atomic parameters in Table 5 (⋯), and their difference (----).

served by the appearance of a new Cd-I peak at 2.77 \AA. The results of a least-squares refinement are shown in Table 5. The uncomplexed cadmium(II) ions are assumed to exist as $\text{Cd}(\text{NO}_3)(\text{H}_2\text{O})^+$.⁴² The Cd-O and Cd-I distances obtained are in good agreement with previously reported data.²¹⁻²⁴ No significant decrease in the number of Cd-O₁ distances per cadmium(II) is observed on complexation with iodide. This is not surprising, however, since the iodide concentrations used is low compared to the cadmium(II) concentration. The most remarkable feature is the total absence of any Cd-Cd distances, indicating that no Cd_2I^{3+} ions are present in the solution. The results thus match those of the corresponding chloride and bromide systems in molten $(\text{K},\text{Na})\text{NO}_3$, i.e. only CdX^+ can be detected.

Discussion

The solvated cadmium ion. The cadmium(II) ion exists as a nitrate solvate, which is best described as $\text{Cd}(\text{NO}_3)_4^{2-}$. The asymmetrical bidentate coordination mode is the same as in the tetranitrato solvates of silver(I), lead(II) and thallium(I) ions in molten equimolar $(\text{K},\text{Na})\text{NO}_3$.^{1,4,5}

The observed Cd-O₁ distance of 2.33 \AA is in good agreement with the Cd-O distances in the solvates, $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ and $\text{Cd}(\text{DMSO})_6^{2+}$, both in the solid state and in solution.⁴²⁻⁴⁹ The ion $\text{Cd}(\text{NO}_3)(\text{H}_2\text{O})_5^+$ has also been observed in aqueous solution.⁴² A monodentate coordination model was proposed, with a Cd-O-N angle of about 120°. Similar models have also been suggested for the corresponding sulphate and phosphate complexes, with Cd-O-S and Cd-O-P angles of 130-140°. ^{42,48,50} In water and DMSO cadmium(II) is assumed to remain coordinated to six oxygen atoms, and the Cd-O distances reported vary between 2.26 and 2.33 \AA. The single nitrate coordination proposed in aqueous solution is thus considerably more open than that found in a molten nitrate medium.

Cadmium halide complexes. The complete failure to detect any polycadmium complexes under conditions which have been optimized for such detection is a significant result of this study.

A number of authors have considered the formation of Cd_2X^{3+} ions in molecular solvents and nitrate melts.¹⁵⁻¹⁸ The existence and stability of Cd_2F^{3+} reported by Leden may be somewhat uncertain. As pointed out by the author himself, the very high cadmium(II) concentrations used may change the properties of the ionic medium considerably. Such effects on the measured activities are, of course, not separable from those arising from actual complex formation. The stability constants of $\text{Cd}_2\text{Cl}^{3+}$ and $\text{Cd}_2\text{Br}^{3+}$ in aqueous and DMSO nitrate melts suffer from large statistical uncertainties, which are of the same magnitude as the stability constants themselves. They may for this reason be seriously questioned.^{17,18} The use of Cd or Cd(Hg) electrodes in molten nitrates, especially in the presence of uncomplexed cadmium(II), is somewhat du-

Table 5. Parameters used for calculation of the theoretical curves in Fig. 4; d = interatomic distance, b = temperature coefficient and n = number of interactions. The data given for $\text{Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ served as a basis in the refinements of the parameters of the $\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$ solution. Refined parameters are given with one mean error in parentheses. The interactions including O_{II} represent correlations between the central atom and second coordination sphere oxygens.

Interaction	$\text{Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$			$\text{CdI}_2\text{-Cd}(\text{NO}_3)_2\text{-H}_2\text{O}$		
	$d/\text{\AA}$	$b/\text{\AA}^2$	n	$d/\text{\AA}$	$b/\text{\AA}^2$	n
(1) "CdI ⁺ " ^e Cd-I				2.77(1)	0.0043(9)	1.0(1) ^a
(2) $\text{Cd}(\text{NO}_3)(\text{H}_2\text{O})_5^+$						
Cd-O _I	2.325(3)	0.012(1)	6.0(1) ^b	2.312(3)	0.013(1)	6.0(1) ^b
O _I -O _I	3.36(3)	0.045(8)	13(2) ^b	3.35(3)	0.042(7)	13(2) ^b
Cd-N	3.2(1)	0.04(1)	1.1(2) ^b	3.2(1)	0.04(1)	0.8(2) ^b
Cd-O _{II}	4.29(1)	0.039(2)	6.7(3) ^b	4.27(1)	0.040(3)	6.7(3) ^b
(3) NO_3^-						
N-O _{II}	3.5(1)	0.04(2)	3.2(8) ^c	3.5(1)	0.03(2)	2.7(9) ^c
(4) Bulk H_2O						
O _I -O _I	2.96(1)	0.013(1)	3.2(1) ^d	2.95(1)	0.014(2)	3.3(1) ^d
O _I -O _{II}	4.81(4)	0.07(2)	1.2(3) ^d	4.84(3)	0.060(9)	2.4(3) ^d

^aPer iodide. ^bPer cadmium(II) atom. ^cPer nitrate. ^dPer uncomplexed water molecule. ^eThe cadmium(II) atom remains solvated by an unknown number of water molecules and/or nitrates. ^fThe internal nitrate atomic parameters were taken from Refs. 1 and 2.

bious owing to oxidation of the cadmium metal. The apparent experimental evidence for $\text{Cd}_2\text{Cl}^{3+}$ in molten (K,Li) NO_3 might for that reason be of an artificial nature.²⁵ The PbI_2 solubility measurements by Yatsimirskii and Shutov show the formation of Cd_2I^{3+} in aqueous solution.¹⁶ On the other hand, our liquid X-ray scattering experiments in aqueous solution clearly exclude the formation of $\text{Cd}_2\text{I}^{3+}(\text{aq})$. An obvious explanation for this discrepancy is that the use of PbI_2 in the solubility measurements may cause results which are impaired by the formation of mixed cadmium(II)-lead(II) iodide species. Summing up, it seems that no conclusive evidence exists for species such as Cd_2X^{3+} , either in aqueous solution or in ionic melts.

The sequence of stability for the CdX^+ complexes in molten equimolar (K,Na) NO_3 at 280 °C is $\text{F} \approx \text{Cl} < \text{Br} < \text{I}$, which may be compared with the sequence $\text{F} < \text{Cl} < \text{Br} < \text{I}$ for the stability of cadmium(II) halide complexes in aqueous solution (1 mol dm^{-3} NaClO_4 ; 25 °C).¹⁵ The cadmium(II) fluoride complexes thus seem stronger relative to the other halide systems in the melt, as compared to aqueous solution. This effect may reflect the absence of hydrogen-bonded fluoride in the ionic liquid. The lead(II) halide systems, on the other hand, exhibit a stability sequence of $\text{Cl} \approx \text{Br} < \text{F} \approx \text{I}$ in both media.⁵¹ The lead(II) fluoride complexes are considerably stronger than in the corresponding cadmium(II) system, and effects caused by hydrogen bonding to fluoride in aqueous solution are thus less obvious.

A vast number of publications describe the complex formation between cadmium(II) and halide ions in molten anhydrous nitrate media. Only studies in equimolar (K,Na) NO_3 at temperatures of about 280 °C, where silver halides were used as indicating systems, can be directly compared with our data. Sinistri and Pezzati made AgX

solubility measurements ($\text{X} = \text{Cl}, \text{Br}$), and arrived at the same complexation model as we did, i.e. only CdX^+ is formed.^{52,53} Their stability constants at 280 °C (interpolated from the stability constants given for 275 and 300 °C), $\beta_{11}(\text{CdCl}^+) = 51 \text{ mol}^{-1} \text{ kg}$ and $\beta_{11}(\text{CdBr}^+) = 108 \text{ mol}^{-1} \text{ kg}$, differ only slightly from ours (Table 2). The reason for the difference may be that the inclusion of AgX alone in the calculations does not sufficiently account for the solubility and complexation of Ag(I). The results from potentiometric work utilizing Ag/AgX electrodes, without corrections for the Ag(I) chemistry, deviate considerably from ours.^{54,55}

The formation of CdX^+ ions in molten equimolar (K,Na) NO_3 is established by the EMF results and confirmed by the structural studies. These results are hardly stunning, but they add further support to the interpretation of thermodynamic data in terms of complex formation in molten alkali-metal nitrates. The strategy of first performing thermodynamic investigations to establish a proper speciation model, and then determine the structure of the predominating species, has so far without any exception given consistent and valuable information.^{1-6,27,28} Whenever the thermodynamic results have suggested the formation of polymetallic ions, the structural studies have confirmed the predicted number of central anion-metal ligand interactions and/or number of metal-metal interactions. The results obtained for the cadmium(II) halide systems show two very important features of this strategy: (1) $M_m\text{X}^{2m-1}$ complexes are not invariably found, (2) the thermodynamic and structural results are consistent also when no $M_m\text{X}^{2m-1}$ species are formed.

These implications regarding the general methods and strategy used are of fundamental importance.

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Received September 14, 1989.