Cationic Lead(II) Halide Complexes in Molten Alkali-metal Nitrate

Part 2.—A Thermodynamic Investigation of the Chloride, Bromide and Iodide Systems

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The complex formation between lead(II) ions and chloride, bromide and iodide ions in molten equimolar (K,Na)NO₃ has been studied. The systems were investigated at four temperatures between 240 and 300 °C. The iodide system was only studied at one temperature, since I⁻ is oxidized to I₂ in melts rich in Pb(NO₃)₂. Halide-ion activities were measured in the systems (K⁺, Na⁺, Pb²⁺)-(NO₃⁻, X⁻), X⁻ = Cl⁻, Br⁻ and I⁻, by means of Ag/AgX electrodes. The formation of PbX₂, PbX⁺ and Pb₂X³⁺ was observed. Special interest was focused on the formation of cationic complexes with anions as coordination centres. The thermodynamic parameters ΔH°_{mn} and ΔS°_{mn} have been evaluated for the chloride and bromide systems. The results are: $\Delta H^{\circ}_{11} = -7.9$ kJ mol⁻¹, $\Delta S^{\circ}_{11} = 26.3$ J K⁻¹ mol⁻¹ for Pb²⁺ + Cl⁻ \rightarrow PbCl⁺; $\Delta H^{\circ}_{21} = 1.5$ kJ mol⁻¹, $\Delta S^{\circ}_{21} = 16.1$ J K⁻¹ mol⁻¹ for Pb²⁺ + Br⁻ \rightarrow PbBr⁺; $\Delta H^{\circ}_{21} = -7.1$ kJ mol⁻¹, $\Delta S^{\circ}_{21} = 1.9$ J K⁻¹ mol⁻¹ for PbBr⁺ + Pb² \rightarrow Pb₂Cl³⁺; $\Delta H^{\circ}_{21} = -7.1$ kJ mol⁻¹, $\Delta S^{\circ}_{21} = 1.9$ J K⁻¹ mol⁻¹ for PbBr⁺ + Pb²⁺ \rightarrow Pb₂Br³⁺. The parameters are compared with previous literature data and recent results obtained from the lead(II) fluoride system in (K,Na)NO₃(I).

The formation of Pb_2F^{3+} in alkali-metal nitrate based melts has been reported in the previous paper.¹ The thermodynamic results indicate that Pb_2F^{3+} might be stabilized by Pb–Pb interactions. An investigation of the influence of increasing covalent character of the lead(II) halide bond, from fluoride to iodide, may contribute to the understanding of this interesting class of complexes with anions as coordination centres.²

Lead(II) oxide and hydroxide systems as well as $PbO \cdot PbX_2$ mixtures exhibit a variety of discrete and extended cationic complexes in the solid state. Most of these mixtures are described as layers or chains of cationic $[PbOH^+]_{\infty}$ or $[PbO]_{\infty}$ entities surrounded by halide ions, but the coordination of halide ions by cations, *i.e.* lead(II), is certainly also an important structural feature of several compounds.³⁻¹⁵ A number of mixed lead(II) halide sulphide and selenide compounds with similar structures have also been reported.¹⁶

Many investigations on the structure of $PbCl_2$ have been performed.¹⁷⁻²⁴ The stable low-temperature modification is orthorhombic and the coordination of chloride ions may be described in terms of Pb_4Cl tetrahedra and Pb_3Cl pyramids. In $PbBr_2$ two crystallographically different bromide ions are surrounded by four and five lead(II) ions, respectively.²⁵ The $PbBr_2$ structure is geometrically similar to the layered structure of PbI_2 . The PbI_2 structure is complicated by structural polytypism, first described by Mitchell²⁶ and recently reviewed by Palosz and co-workers.²⁷

The coordination of chloride in molten $PbCl_2$ has been interpreted in terms of distorted Pb_4Cl tetrahedra, explaining the observation of different Pb–Pb distances in the radial distribution function, obtained from liquid X-ray scattering measurements.²⁸

Rao and co-workers investigated the coordination in mixed PbO-PbCl₂ glasses using X-ray scattering, XANES and EXAFS.²⁹⁻³¹ Structure elements such as Pb₄O tetrahedra and various Pb_mCl entities were used to describe the results. Fused PbCl₂-MCl systems have been examined both thermodynamically and structurally. In liquid PbCl₂-LiCl mixtures Pb-Pb interactions at distances comparable to those in pure molten PbCl₂³² have been observed, indicating related structure elements in the melts.²⁸ The PbBr₂-MBr and PbI₂-MI systems have also been subject to interest, but only a few brief reports on polynuclear species have appeared in the literature.³³⁻³⁶ Phase diagrams of mixed lead(1) halides reveal a few mixed solid halides. For some of these the crystal structures have been solved.³⁷⁻³⁹ Electron diffraction and Raman spectroscopy studies on gas-phase and matrix-isolated PbX₂ and mixed PbX₂-PbY₂ halides show bent structure elements with X-Pb-X or X-Pb-Y angles of *ca.* 94°.⁴⁰⁻⁴²

The complexation of lead(II) with halide ions in molecular solvents, has been summarized recently.⁴³ A few reports on the formation of 'polynuclear' complexes $Pb_m X_n^{2m-n}$ have appeared.^{44,45} Yatsimirskii *et al.* and Fedorov *et al.* claim that $M_2 X^{3+}$ ions (M = Pb, Cd; X = Cl, Br, I or SCN) are formed in aqueous solutions,^{46,47} the cadmium(II) complexes being stronger than the corresponding lead(II) complexes. An increasing stability with increasing size of the halide ion is also observed. Magnetic measurements on mixed lead(II) halides have indicated the presence of Pb_2I^{3+} complexes in the $PbI_2 \cdot 3PbCI_2$, $PbI_2 \cdot 3PbBr_2$, $2PbI_2 \cdot 3PbCI_2$ and $2PbI_2 \cdot 3PbBr_2$ phases.⁴⁸

The lead(II) halide systems have been extensively investigated in molten nitrate media. Most experiments have been performed with an excess of halide over lead(II), though. The experimental data from such studies only reveal PbX⁺, PbX₂ and anionic species. Many experimental methods have been used involving e.m.f. measurements with Ag/ AgX electrodes,49-59 Pd/PdO/PbO electrodes58,59 and Pb electrodes,60 solubility of AgX(s)⁶¹ and of PbCrO₄(s),⁶²⁻⁶⁴ freezing-point depression^{65,66} and polarography.⁶⁷⁻⁷⁰ The results are summarized in table 1. The use of metallic lead as a lead(II) indicator electrode^{55,60} is bound to cause erroneous results owing to severe oxidation of the metal in nitrate melts, especially in the presence of such a good oxide-ion acceptor as lead(II).⁷¹ Gaur and co-workers reported the use of a Pd/PdO/PbO electrode for measuring the lead(II) activities in molten KNO3 · Ba(NO3)2 mixtures, 58, 59 by analogy with the Cd^{II} electrode used by Inman.⁷² The electrode function was apparently puzzling because the experimental Nernst slope was considerably larger than the expected theoretical one. The calculated theoretical slope was based on the assumption that PbO is the solid phase containing lead(II) in equilibrium with the nitrate melt. The formation of the solid $SPbO \cdot Pb(NO_3)_2$ is, however, of great importance in molten alkali-metal nitrate systems containing PbO and $Pb(NO_3)_2$.^{73, 74} The assumption that the solid containing lead(II) is $5PbO \cdot Pb(NO_3)_2$ would give theoretical values which are 6/5 larger than those considered by the authors. The corrected theoretical slopes coincide almost perfectly with the experimental ones. The electrode thus seems to work well in molten nitrate media, but it obviously suffers from the drawback that it cannot be used at high lead(II) concentrations owing to the extensive solubility of PbO and/or $5PbO \cdot Pb(NO_3)_2$ in such melts.⁷¹

The present study is devoted to the complexation of lead(II) with chloride, bromide and iodide in molten equimolar (K,Na)NO₃. The emphasis has been placed on the formation of cationic complexes with the halides as coordination centres for lead(II) ions. Hence, we have chosen to measure the changes in halide activity as a function of lead(II) concentration using Ag/AgX electrodes and applying the proper corrections for the changes in silver halide solubility and complexation. The measurements are extended over a temperature interval 240–300 °C in order that ΔH_{mn}° and ΔS_{mn}° for the association processes be estimated. These thermodynamic parameters are of great value for the understanding of the fundamental coordination chemistry of this class of complexes with anions as coordination centres.

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solvent melt	halide	physical method	T/°C	β_{11}	β_{12}	eta_{13}	β_{14}	ref.
(K _{0.5} , Na _{0.5})NO ₃	Br	Ag/AgX electrode	255 303 306 319	198 153 121	1.02 × 10 ⁴			49
(K _{0.5} , Na _{0.5})NO ₃	Cl	Ag/AgX electrode	325	75				50
(K _{0.5} , Na _{0.5})NO ₃	Cl	Ag/AgX electrode	250 275 300	175 173 143				51
(K _{0.25} , Na _{0.75})NO ₃ (K _{0.5} , Na _{0.5})NO ₃	Br	Ag/AgX electrode	280 300 240 280 300 280	180 160 250 190 170	1.40×10^{4} 1.12×10^{4} 3.12×10^{4} 1.62×10^{4} 1.19×10^{4}			52
$(K_{0.75}, Na_{0.25})NO_3$ $(K_{0.5}, Li_{0.5})NO_3$	Cl Br	Ag/AgX electrode	280 300 160 180 200 160 200	200 175 250 230 205 990 730	1.64×10^{-1} 1.17×10^{4} 2.75×10^{4} 2.14×10^{4} 1.84×10^{4} 3.96×10^{5} 2.19×10^{5}			53
(K _{0.5} , Na _{0.5})NO ₃	Br	Ag/AgX electrode	275 300	215 204				54
(K _{0.5} , Na _{0.5})NO ₃	Cl	Ag/AgX electrode	230 250	500 400	$\begin{array}{c} 7.46 \times 10^{4} \\ 4.82 \times 10^{4} \end{array}$	3.24 × 10 ⁶ 1.46 × 10 ⁶	7.21×10^{7} 2.09×10^{7}	55
(K _{0.5} , Na _{0.5})NO ₃	Br	Ag/AgX electrode	230 250	526 426	8.49×10^4 5.13×10^4			56
$NH_4NO_3 \cdot 2H_2O$ $NH_4NO_3 \cdot 1.5H_2O$ $NH_4NO_3 \cdot 3H_2O$ $NH_4NO_3 \cdot 2H_2O$ $NH_4NO_3 \cdot 2H_2O$	Cl Br	Ag/AgX electrode	40 55 70 70 70 40 55 70	72 72 71 89 54 123 110 101	$\begin{array}{c} 3.10 \times 10^{3} \\ 2.74 \times 10^{3} \\ 2.41 \times 10^{3} \\ 2.94 \times 10^{3} \\ 2.11 \times 10^{3} \\ 3.94 \times 10^{3} \\ 5.06 \times 10^{3} \\ 4.85 \times 10^{3} \\ 1.00 \times 10^{4} \\ 1.00 \times $			57
$NH_4NO_3 \cdot 3H_2O$ $NH_4NO_3 \cdot 3H_2O$			70 70	77	1.00×10^{-3} 4.47×10^{-3}		_	
(K _{0.876} , Ba _{0.062})NO ₃	Cl Br I	Pd/PdO/ PbO electrode Ag/AgX electrode	315 335 335 295 315 335 295 315 335	79 73 69 169 152 137 3687 2900 2383	$\begin{array}{c} 2.61 \times 10^{3} \\ 1.90 \times 10^{3} \\ 1.45 \times 10^{3} \\ 1.42 \times 10^{4} \\ 1.16 \times 10^{4} \\ 0.95 \times 10^{4} \\ 5.42 \times 10^{6} \\ 2.84 \times 10^{6} \\ 1.93 \times 10^{6} \end{array}$		5	8, 59
(K _{0.5} , Na _{0.5})NO ₃	Cl	Pb electrode	280	226	1.46 × 10 ⁴			60

Table 1. Overall stability constants of PbX_n^{2-n} in molten nitrate media

solvent melt	halide	physical method	T/°C	β ₁₁	β_{12}	β_{13}	β_{14}	ref.
KNO ₃	Cl Br	AgX solubility	480 450	25 66	$4.95 imes 10^2$ $4.95 imes 10^2$			61
(K _{0.5} , Na _{0.5})NO ₃	Cl Br	PbCrO₄ solubility	250 275 300 250 275 300	193 86 64 193 140 118	$\begin{array}{c} 4.16\times10^{3}\\ 2.77\times10^{3}\\ 2.08\times10^{3}\\ 1.04\times10^{4}\\ 0.30\times10^{4}\\ 0.25\times10^{4} \end{array}$	$\begin{array}{c} 8.94 \times 10^{4} \\ 2.98 \times 10^{4} \\ 2.23 \times 10^{4} \\ 1.12 \times 10^{5} \\ 0.32 \times 10^{5} \\ 0.55 \times 10^{5} \end{array}$		62
LiClO ₄	Cl	PbCrO ₄ solubility	275 300	282 470	2.39×10^{4} 4.42×10^{4}	1.12×10^{6} 1.87×10^{6}		63
(K _{0.5} , Na _{0.5})NO ₃	Cl Br	PbCrO ₄ solubility	275 275	118 140	$\begin{array}{c} 5.08\times10^{3}\\ 9.01\times10^{3} \end{array}$	2.73×10^{5} 3.87×10^{5}		64
NaNO ₃	Cl	cryoscopy	306		$4.20 imes 10^3$			65
NaNO ₃	Cl	cryoscopy	306	706				66
(K _{0.614} , Li _{0.386})NO ₃	Cl	polaro- graphy	180	494	1.74 × 10 ⁴			67
(K _{0.5} , Na _{0.5})NO ₃	Cl	polaro- graphy	280	226	$7.28 imes 10^3$			68
(K _{0.53} , Na _{0.17} , Li _{0.30})NO	3 Cl Br	polaro- graphy	145 145	247 870	$\begin{array}{c} 3.20 \times 10^{4} \\ 2.46 \times 10^{5} \end{array}$			69
(K _{0.53} , Na _{0.17} , Li _{0.30})NO	³ Cl	polaro- graphy	160 179 207	659 376 212				70

Table 1. (cont.)

All constants are expressed in mole-fraction units.

Chemicals

Experimental

 KNO_3 , NaNO₃, Pb(NO₃)₂, KCl, NaCl, KBr, KI, NaI (all Merck, pA) and NaBr (J. T. Baker, Analyzed Reagent) were dried at 130 °C during at least one week before use and were stored over drying agents. The drying procedure was checked by heating the chemicals in vacuum for 6 h, revealing no further loss of weight. The AgCl (Riedel de Haen, 99.6%), AgBr (Merck, 99%) and AgI (Venton, 99.9%) were dehydrated over anhydrous Mg(ClO₄)₂.

Apparatus

The furnaces, temperature control, cell construction and measurements have been described previously.⁷⁵⁻⁷⁷

E.M.F. Measurements

The use of silver electrodes⁷⁷ in combination with solid silver halide is a well established method for measuring the halide-ion activity in molten salts.^{78,79}. In the experiments a platinum rod with a fresh silver layer [electrolysed in an aqueous dicyanoargentate(1)]

solution and thoroughly dried] with a small amount of solid AgX present, was used as a halide-ion electrode. The cell may be described schematically as

	(K,Na)NO ₃ (l)	$(K,Na)NO_3(l)$	
Ag	AgX(s)	AgX(s)	Ag
	(K,Na)X	(K,Na)X	
		$ Pb(NO_{2})_{0} $	

where X stands for Cl, Br or I. The contact between test and reference melts was provided by a ceramic plug. Solid $Pb(NO_3)_2$ or solidified stock melts $(K,Na)NO_3^ Pb(NO_3)_2$ were added in small portions to a test melt containing a known amount of (K,Na)X. Stable e.m.f.s. $(\pm 0.1 \text{ mV})$ were obtained within 15 min. A typical experimental run comprised 10–15 melt compositions.

At high Pb^{2+}/X^{-} ratios the silver layer on the electrode became oxidized. The lead(II) ion is a strong oxide-ion acceptor,⁷¹ enhancing the oxidative properties of the nitrate melt and causing the oxidation even of such a noble metal as silver. Oxidation of the silver layer was avoided by using low Pb^{2+}/X^{-} ratios [to minimize the concentration of lead(II) uncomplexed by halide]. In order to trace any influence on the experimental data caused by dissolved silver by oxidation the $Pb(NO_3)_2$ titrations were performed using different timescales. The oxidation of the silver layer on the electrodes is a fairly slow process, that would have produced inconsistent results when analogous melt compositions were studied on different timescales. All dubious data that could be traced in this way were removed before the numerical data treatment.

The total concentrations used were $8.9 \times 10^{-3} \le C_x/\text{mol kg}^{-1} \le 98.9 \times 10^{-3}$ and $0.01 \le C_{\text{Pb}}/\text{mol kg}^{-1} \le 0.51$ for the chloride and bromide systems and $5.1 \times 10^{-4} \le C_1/\text{mol kg}^{-1} \le 12.4 \times 10^{-4}$ and $5.0 \times 10^{-4} \le C_{\text{Pb}}/\text{mol kg}^{-1} \le 20.0 \times 10^{-4}$ for the iodide system. All experimental data, but for a few points in the chloride and bromide melts, have $C_{\text{Pb}}/\text{mol kg}^{-1} \le 0.15$. The low concentrations used in the iodide system are due to the low solubility of PbI₂ (< 10^{-3} mol kg^{-1}). The solubilities of PbCl₂ and PbBr₂ at 280 °C are considerably higher, 1.26 mol kg^{-1} and 0.34 mol kg^{-1}, respectively. A further complication in the iodide system was oxidation of iodide ions to iodine, whenever the amount of lead(II) was comparable to or higher than the amount of iodide in the melt. A combination of this effect and the very high stability of the complex PbI₂, being the predominant lead(II) iodide species over a large composition range, made it impossible to obtain any accurate information on the cationic complex Pb₂I³⁺.

Results and Discussion

The Ag/AgX electrode provides accurate and consistent information about changes in the halide-ion activity. Additions of $Pb(NO_3)_2$ to the $(K^+, Na^+)-(NO_3^-, X^-)$ melts cause changes in halide activities which may be ascribed to complex formation. The e.m.f., however, involves effects from changes in the silver halide solution chemistry as well. Corrections for the solubility of AgX(s) and complex formation between silver(1) and the halides have to be performed. The influence from mixed lead(11) silver halide complexes is assumed to be negligible.

Before describing the corrections made for the silver halide systems some definitions have to be made. The equilibria $A e^{\mathbf{Y}(a)} \rightarrow A e^{+} + \mathbf{Y}^{-}$ (1a)

$$\operatorname{AgX}(s) \rightleftharpoons \operatorname{Ag}^{*} + X$$
 (1*u*)

$$K_{\rm s}^{\rm Ag} = [\rm Ag^+][\rm X^-] \tag{1b}$$

$$mAg^{+} + nX^{-} \rightleftharpoons Ag_{m}X_{n}^{m-n}$$
(2*a*)

$$\beta_{mn}^{Ag} = \frac{[Ag_m X_n^{m-n}]}{[Ag^+]^m [X^-]^n}$$
(2b)

define the silver halide speciation. Complexation by lead(II) is expressed in the same way

$$mPb^{2+} + nX^{-} \rightleftharpoons Pb_m X_n^{2m-n} \tag{3a}$$

$$\beta_{mn} = \frac{[Pb_m X_n^{2m-n}]}{[Pb^{2+}]^m [X^-]^n}.$$
(3*b*)

When titrating the test melt with $Pb(NO_3)_2$ the solubility of AgX(s) and relative abundance of different $Ag_m X_n^{m-n}$ complexes are changed due to changes in the activity of free halide. The activity of free halide ions is, in turn, changed owing to complex formation between lead(II) and the halides. The e.m.f. measurements may then be split into two separate cases. The sums used below involve all complex ions, *i.e.* the starting value in the summations is 1 for both *m* and *n*.

(1) No added $Pb(NO_3)_2$:

$$C_{\rm X} = [{\rm X}^{-}] + \sum_{m,n} n [{\rm Ag}_m {\rm X}_n^{m-n}] = C_{\rm X}^{\circ} + S_{{\rm Ag}{\rm X}}$$
(4*a*)

where $C_{\rm X}^{\rm o}$ = concentration of halide calculated from added amount of (K,Na)X and

$$S_{Agx} = C_{Ag} = [Ag^{+}] + \sum_{m,n} m[Ag_{m}X_{n}^{m-n}].$$
(4b)

From a knowledge of the K_s^{Ag} and β^{Ag} values of the AgX systems^{51,75,76,80-86} the free halide ion concentration, $[X^-]_0$, when no Pb(NO₃)₂ has been added, can be evaluated. An e.m.f. $E(C_{Pb} = 0)$ is measured:

$$E(C_{\rm Pb} = 0) = E_0 - k \log([X^-]_0/\text{mol } kg^{-1}).$$
(5)

(2) Pb(NO₃)₂ is added:

$$C_{\rm X} = [{\rm X}^{-}] + \sum_{m,n} n[{\rm Ag}_m {\rm X}_n^{m-n}] + \sum_{m,n} n[{\rm Pb}_m {\rm X}_n^{2m-n}]$$

= $C_{\rm X}^{\rm o} + S_{\rm Ag X}.$ (6)

Assuming a theoretical one-electron slope, case (1) provides E_0 . The e.m.f. $E(C_{Pb})$ at each melt composition now gives the free halide ion concentration [X⁻]. For the lead(II) halide complexation, the sum

$$C_{X}^{Pb} = [X^{-}] + \sum_{m,n} n [Pb_{m} X_{n}^{2m-n}]$$

= [X⁻] (1 + \sum n \beta_{mn} n \beta_{mn} [Pb^{2+}]^{m} [X^{-}]^{n-1}) = [X^{-}] Y (7)

is of fundamental interest. This sum may be evaluated taking the difference

$$\Delta E = E(C_{\rm Pb}) - E(C_{\rm Pb} = 0)$$
$$= E_{\rm corr} + k \log \left(C_{\rm X}^{\rm Pb} / [{\rm X}^{-}] \right) = E_{\rm corr} + k \log Y$$
(8)

where

 $E_{\rm corr} = k \log \left([X^-]_0 / C_{\rm X}^{\rm Pb} \right)$

$$= k \log \{ [X^{-}]_{0} / (C_{X}^{\circ} + S_{AgX} - \sum_{m n} n [Ag_{m}X_{n}^{m-n}]) \}.$$
(9)

halide	T/°C	$\beta_{11}/\mathrm{kg} \mathrm{\ mol}^{-1a}$	$\beta_{\scriptscriptstyle 12}/{ m kg^2}~{ m mol^{-2a}}$	$eta_{21}/\mathrm{kg^2} \; \mathrm{mol^{-2a}}$	no.º
Cl	240.0	14.13+0.40	71.0 ± 2.8	6.43 ± 0.80	35
	260.0	12.85 + 0.16	67.4 ± 3.2	5.79 ± 0.38	23
	280.0	12.49 ± 0.10	60.0 + 1.1	5.73 ± 0.34	49
	300.0	11.50 ± 0.11	50.1 ± 1.4	5.42 ± 0.49	27
Br	240.0	18.43 ± 0.35	197.6±6.5	11.46 ± 1.86	33
	260.0	18.36 ± 0.32	117.1 ± 5.3	10.50 ± 1.19	50
	280.0	17.31 ± 0.26	112.8 ± 3.4	9.47 ± 1.76	46
	300.0	16.61 ± 0.47	79.1 ± 5.8	8.63 ± 2.66	27
I	280.0	85.4±9.8	$(1.27 \pm 0.22) \times 10^{5}$	$(2.9 \pm 1.8) \times 10^{2b}$	44

Table 2. Overall stability constants for $Pb_m X_n^{2m-n}$ in (K,Na)NO₃(l) at different temperatures

^a The standard state is 1 mol kg⁻¹, but the formation constants may be expressed in mole-fraction units after multiplication with (10.747 mol kg⁻¹)^{m+n-1}. ^b The value is estimated from a few points at high lead(II) concentrations and merely represents the order of magnitude of the stability of Pb₂I³⁺. ^c Number of degrees of freedom. The error limits define a 95% confidence interval.

The lead(II) halide complexation may be described either by overall stability constants, eqn (3b), or by stepwise constants K_{mn} according to

$$K_{mn} = \frac{[\mathrm{Pb}_m X_n^{2m-n}]}{[\mathrm{Pb}^{2+}][\mathrm{Pb}_{m-1} X_n^{2m-2-n}]}$$
(10*a*)

$$K_{mn} = \frac{[\mathrm{Pb}_m X_n^{2m-n}]}{[\mathrm{F}^-][\mathrm{Pb}_m X_{n-1}^{2m-n+1}]}.$$
 (10*b*)

The correction term E_{corr} may be calculated for each melt composition from eqn (9), since $[X^-]$ and the equilibrium constants for the silver halide systems are known. Corrected experimental data were fitted to eqn (7) and (8) by use of a least-squares program EMFALL, as described previously.¹

The results obtained at four different temperatures are displayed in table 2. Only the complexes PbX₂, PbX⁺ and Pb₂X³⁺ were detected for all three halides, analogous to the lead(II) fluoride system. No higher anionic or cationic complexes, nor any polynuclear, *i.e.* polyhalide, species (apart from PbX₂) were found. The fraction α_{mn} of the different species is defined as

$$\alpha_{mn} = \frac{n[\mathrm{Pb}_m \mathbf{X}_n^{2m-n}]}{C_{\mathbf{X}}^{\mathrm{Pb}}} \tag{11}$$

and may be used to elucidate the distribution of halide ions on various complexes as a function of lead(II) concentration. Such curves are displayed in fig. 1, using typical total halide concentrations for each system. The experiments were designed to provide detailed information of the cationic metal complexes. This resulted in inaccurate values of the formation constants for PbX₂. These constants more or less served as correction factors in the computations of the other stability constants. Since lower concentrations of Pb(NO₃)₂ have been used in the chloride, bromide and especially in the iodide systems than in the fluoride case,¹ the values of the stability constants are expressed in molality units. The use of mole-fraction units hardly changed the results, apart from a proportional factor.

or



Fig. 1. The distribution α_{mn} of X⁻ in the complexes $Pb_m X_n^{2m-n}$ in molten (K,Na)NO₃ at 280 °C. (a) The chloride system, $C_{Cl} = 0.1 \text{ mol } \text{kg}^{-1}$; (b) The bromide system, $C_{Br} = 0.1 \text{ mol } \text{kg}^{-1}$; (c) The iodide system, $C_{I} = 1 \times 10^{-3} \text{ mol } \text{kg}^{-1}$.

The stability constants obtained for PbX⁺ and PbX₂ agree very well with the literature values for (K,Na)NO₃, melts in table 1. The formation constants in (K,Li)NO₃(l) are somewhat higher. In molten KNO₃-Ba(NO₃)₂ the complex formation is more pronounced than in (K,Na)NO₃(l) in spite of the higher temperatures used. The stronger complexation in these molten nitrates might be ascribed to the reciprocal Coulomb effect.^{87.88} The complexation in aqueous NH₄NO₃ melts is weak, most likely due to a strong solvation of lead(II) by water molecules.

The thermodynamic parameters ΔH_{mn}° and ΔS_{mn}° for the chloride and bromide complexation reactions have been estimated from the temperature variation of $\Delta G_{mn}^{\circ} = -RT \ln K_{mn}$. From fig. 2 and 3 it is seen that ΔG_{11}° and ΔG_{21}° are good linear functions of T for both systems. The standard enthalpy and entropy changes have been estimated by linear-regression analysis as temperature independent constants in the actual temperature range. The results are given in table 3. Selected values from table 1 have been used to evaluate the enthalpies and entropies for the formation of PbX⁺ in table 4. The parameters of table 4 and our results all show large differences. The results obtained by PbCrO₄ solubility seem somewhat strange, since both ΔS_{11}° and ΔH_{11}° have



Fig. 2. ΔG_{mn}° versus T for stepwise formation of PbCl⁺ and Pb₂Cl³⁺ in molten (K, Na)NO₃ in the temperature range 240–300 °C. The standard state is unity mole fraction.



Fig. 3. ΔG_{mn}° versus T for stepwise formation of PbBr⁺ and Pb₂Br³⁺ in molten (K, Na)NO₃ in the temperature range 240–300 °C. The standard state is unity mole fraction.

large negative values.⁶² The reason for this deviation might arise from the experimental difficulties of using a spectrophotometric method. The chloride system explored using Ag/AgX electrode e.m.f. measurements agree very well with our data,⁵¹ but the bromide system deviates markedly.⁵² The deviating parameters for the bromide system may be due to the neglection of corrections for the AgBr complexation and solubility or the use of a complexation model disregarding the formation of Pb₂Br³⁺. Both these effects are far more important in the bromide case than for the chloride.

The ΔS_{mn}° values found for the formation of PbF⁺ and PbF₂ were interpreted as a

Table 3. Standard enthalpy and entropy values of the stepwise formation of $Pb_m X_n^{2^{m-n}}$ in molten (K,Na)NO₃ between 240 and 300 °C

reaction	$\Delta H_{mn}^{\circ}/\mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta S^{\circ}_{mn}/J \text{ K}^{-1} \text{ mol}^{-1a}$
$Pb^{2+} + Cl^- \rightarrow PbCl^+$	-7.9 ± 1.0	26.3 + 1.9
$PbCl^+ + Pb^{2+} \rightarrow Pb_{a}Cl^{3+}$	1.5 ± 0.8	16.1 + 1.4
Pb ²⁺ + Br ⁻ → PbBr ⁺	-4.6 ± 1.0	35.2 ± 1.9
$PbBr^+ + Pb^{2+} \rightarrow Pb_2Br^{3+}$	-7.1 ± 0.6	1.9 ± 1.1

^a The standard state refers to unity mole fraction. The errors quoted are two mean errors obtained from linear regression.

 Table 4. Standard enthalpy and entropy values of the formation of PbX⁺ calculated for different molten nitrate solvents

solvent melt	halide	temperature range/°C	$\Delta H_{11}^{\circ}/kJ \text{ mol}^{-1}$	$\frac{\Delta S_{11}^{\circ}/J}{\text{mol}^{-1a}}$	ref.
(K,Na)NO ₃	Cl	250–300 250–300	-10.3 ± 5.4 -54.4 ± 13.7	23.6 ± 9.9 -60.9 ± 24.9	51 62
	Br	240–300 250–300	-15.9 ± 0.3 -24.5 ± 3.9	15.0 ± 0.6 - 3.2 ± 7.2	52 62
(K,Li)NO ₃	Cl Br	160–200 160–200	-8.5 ± 1.0 -13.0°	26.4 ± 2.2 27.4°	53 53
(K,Ba)NO ₃	Cl Br I	315–355 295–335 295–335	-10.4 ± 0.8 -15.1 ± 0.2 -31.3 ± 1.2	$18.7 \pm 1.3 \\ 16.1 \pm 0.4 \\ 13.1 \pm 2.0$	58, 59 58, 59 58, 59
$NH_4NO_3 \cdot 2H_2O$	Cl Br	40–70 40–70	-0.4 ± 0.3 -5.9 ± 0.3	34.2 ± 0.8 21.3 ± 0.9	57 57

^a The standard state is unity mole fraction for all nitrate solvents. ^b Only values at two temperatures are available. The errors quoted are two mean errors obtained from linear regression.

result of a significant entropy contribution from nitrate ions.¹ These contributions were attributed to differences in rotational and vibrational degrees of freedom between nitrate ions coordinated to lead(II) and to solvent cations. This interpretation is supported by the high ΔS_{11}° values which are also found for the formation of PbCl⁺ and PbBr⁺ in molten (K,Na)NO₃. The presence of lithium cations and to a lesser extent barium cations would be expected to cause a lower ΔS_{11}° , since both ions probably interact more strongly with nitrate ions than sodium and potassium ions. A smaller difference in degrees of freedom between bulk nitrates and nitrates coordinated to lead(II) would yield a smaller contribution to ΔS_{11}° . Lower values of ΔS_{11}° are indeed found in (K,Li)NO₃(I) and to a lesser extent in KNO₃-Ba(NO₃)₂(I). The ammonium ion, on the other hand, is often compared with the potassium ion regarding polarizability and size. High ΔS_{11}° values are thus expected and found.

The stabilities of the PbX⁺ complexes, X = F, Cl and Br, exhibit a minimum for X = Cl. The cause of this minimum is the $T\Delta S_{11}^{\circ}$ contribution, while the $-\Delta H_{11}^{\circ}$ values decrease in the order F > Cl > Br. This observation is not surprising though, bearing in

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mind the unique physical properties of the fluoride ion compared to the other halides, for which a more continuous change is observed.

The thermodynamic parameters for the process

$$PbX^{+} + Pb^{2+} \rightleftharpoons Pb_{2}X^{3+}$$
(12)

are sometimes uncertain owing to the rather high relative errors in the stability constants. It is obvious, though, that the coordination of a second lead(II) ion by bromide is energetically more favourable than by chloride, as indicated by the ΔH_{21}° values. A very low ΔS_{21}° value (of the same magnitude as ΔS_{21}° for Pb₂F³⁺) is found for Pb₂Br³⁺, indicating the coordination of the second lead(II) to be geometrically restricted. Since the bromide ion is far more polarizable than the fluoride ion, increased covalency of the Pb-X bonds might stabilize the Pb₂Br³⁺ ion.

The low ΔS_{21}° value of the fluoride system was interpreted in terms of Pb-Pb interactions between coordinated lead(II) ions stabilizing the Pb₂F³⁺ ion. Pb₂Cl³⁺, on the other hand, shows a larger ΔS_{21}° and a positive ΔH_{21}° . The positive thermodynamic parameters for Pb₂Cl³⁺ might be due to a maximum in electrostatic Pb²⁺-Pb²⁺ repulsion. In Pb₂F³⁺ the repulsion may be reduced without a large loss of stabilizing energy, merely by increasing the Pb-Pb distance, since the Pb-F bond is essentially electrostatic. In Pb₂Br³⁺ the repulsion may be offset by a larger donation of electron density to the coordinated lead(II) ions, since the Pb-Br bond is essentially covalent. The chloride system is intermediate to the fluoride and bromide system, and the thermodynamic parameters may reflect the inadequacy of either mechanism for reduction of the electrostatic Pb²⁺-Pb²⁺ repulsion.

These hypotheses about the origins of the thermodynamic patterns are of course at the present stage of rather a speculative nature. The ideas are at the moment tested in structural investigations on the lead(II) halide systems in molten $(K,Na)NO_3$ at 280 °C by means of liquid X-ray techniques and Raman spectroscopy.

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