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Chloride and Bromide Complexes of Lead(II) in Aqueous Melts of Calcium Dinitrate — Ammonium Nitrate

*I. J. Zsigrai, M. R. Mićović, and I. J. Gal**

*Institute of Chemistry, Faculty of Sciences, University of Novi Sad, and *Department of Chemistry, Faculty of Sciences, University of Belgrade*

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The formation constants of $PbCl^+$, $PbCl_2$, $PbBr^+$ and $PbBr_2$ in melts of $Ca(NO_3)_2 \cdot a\,NH_4NO_3 \cdot x\,H_2O$ ($a = 1.5$, 2.33; $x = 3 - 9$) at 323 and 338 K have been determined from E_{MF} measurements in suitable concentration cells. The results are discussed in terms of Braunstein's ionic association model based on quasi-lattice statistical mechanics.

From our previous investigations we have reported thermodynamic data on the formation of halide complexes of Ag(I), Cd(II), Zn(II), Pb(II) and Hg(II) in aqueous ammonium nitrate melts[1-3], of Ag(I) and Cd(II) in mixtures of $Ca(NO_3)_2 - KNO_3 - H_2O$[4,5], and of Cd(II) in $Ca(NO_3)_2 - NH_4NO_3 - H_2O$.[6,7] The present paper extends our research to Pb(II) halide complexes in $Ca(NO_3)_2 \cdot a\,NH_4NO_3 \cdot x\,H_2O$, for two reasons: to provide additional data on metal complexes in very concentrated, charge-asymmetric, aqueous electrolytes, and to test whether any simple ionic association model based on quasi-lattice statistics, could interprete the experimental data. Moreover, it might be interesting to compare our previous data for lead chloride complexes in the charge-symmetric $NH_4NO_3 - H_2O$ system[2] with the present data in the charge-asymmetric $Ca(NO_3)_2 - NH_4NO_3 - H_2O$ system, and to verify whether changes in association constants follow the prediction of the reciprocal Coulomb-effect.

EXPERIMENTAL

The electromotive force (E_{MF}) of the following concentration cell was measured:

Ag, AgX	$Ca(NO_3)_2 \cdot a\,NH_4NO_3 \cdot x\,H_2O$ NH_4X (n_x) $Pb(NO_3)_2$ (n_{Pb})	$Ca(NO_3)_2 \cdot a\,NH_4NO_3 \cdot x\,H_2O$ NH_4X (n_x)	AgX, Ag

(Ag, AgX) is the silver-silver(I) halide electrode ($X = Cl^-$, Br^-), a and x are the numbers of moles of NH_4NO_3 and H_2O, respectively, per mole of $Ca(NO_3)_2$. The total concentration of the halide ligand is n_x (which is the same in both half-cells), and the total lead concentration n_{Pb}. Both concentrations are expressed in Temkin's ionic fractions.[8] As our E_{MF} data are too extensive to be tabulated in this paper, they are deposited at CCA*. Only measurements in the system Pb^{2+} — Br^- — $Ca(NO_3)_2 \cdot 2.33\ NH_4NO_3 \cdot 4.67\ H_2O$ at 338 K are presented in Table I as an example of the experimental data collected. The experimental facility, instruments, melt preparation and measurements have been described in our previous papers.[2,3,6] The E_{MF} values are accurate within ± 0.01 mV, and the temperature was kept constant within ± 0.05 °C. The concentration of lead in the melts was always kept below the limit determined by the PbX_2 solubility product.

TABLE I

E_{MF} *Data for the System* Pb^{2+} — Br^- — $Ca(NO_3)_2 \cdot 2.33\ NH_4NO_3 \cdot 4.67\ H_2O$ *at 338 K*

$n_{Br} = 0.84 \times 10^{-4}$		$n_{Br} = 2.53 \times 10^{-4}$		$n_{Br} = 4.23 \times 10^{-4}$	
$10^4\, n_{Pb}$	ΔE/mV	$10^4\, n_{Pb}$	ΔE/mV	$10^4\, n_{Pb}$	ΔE/mV
1.32	1.00	1.29	0.98	1.24	1.30
2.64	1.92	2.58	1.93	2.47	1.93
3.96	2.84	3.86	2.84	3.71	2.95
5.27	3.72	5.15	3.71	4.95	3.80
6.59	4.67	6.44	4.67	6.18	4.80
7.91	5.22	7.73	5.25	7.42	5.33

$n_{Br} = 6.88 \times 10^{-4}$		$n_{Br} = 8.41 \times 10^{-4}$		$n_{Br} = 10.70 \times 10^{-4}$	
$10^4\, n_{Pb}$	ΔE/mV	$10^4\, n_{Pb}$	ΔE/mV	$10^4\, n_{Pb}$	ΔE/mV
1.30	1.20	1.28	0.91	1.27	1.00
2.60	1.95	2.56	1.87	2.54	1.94
3.91	2.85	3.85	2.79	3.80	2.85
5.21	3.55	5.13	3.65	5.07	3.55
6.51	4.42	6.41	4.63	6.34	4.55
7.81	5.20	7.69	5.22	7.60	5.30

RESULTS

The first two consecutive association constants were determined from the

$$K_1 = [PbX^+]/([Pb^{2+}]\,[X^-])$$

$$K_2 = [PbX_2]/([PbX^+]\,[X^-])$$

E_{MF} data according to the method of Braunstein et al.[9], modified for assymmetrical charge distribution in the melt.[10] The basic equation for the present case is:

$$\exp\left(-\frac{F\,\Delta E}{RT}\right) - 1 = \frac{1+a}{2+a} K_1 n_{Pb} - \frac{1+a}{2+a} (K_1^2 - 2\,K_1\,K_2)\, n_{Pb} n_X + \dots \quad (1)$$

where F is the Faraday constant, R the gas constant and ΔE the E_{MF} of the concentration cell. Eq. (1) is linear with respect to n_{Pb}, but may have terms of a higher order in n_X if PbX_3^- and PbX_4^{2-} are present. However, in the limiting case when n_X and n_{Pb} tend toward zero, we get

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$$\lim_{\substack{n_{\mathrm{Pb}} \to 0 \\ n_{\mathrm{X}} \to 0}} \frac{\partial}{\partial n_{\mathrm{Pb}}} \left(\exp\left(-\frac{F\,\Delta E}{RT}\right) - 1\right) = \frac{1+a}{2+a} K_1$$

$$\lim_{\substack{n_{\mathrm{Pb}} \to 0 \\ n_{\mathrm{X}} \to 0}} \frac{\partial^2}{\partial n_{\mathrm{Pb}}\, \partial n_{\mathrm{X}}} \left(\exp\left(-\frac{F\,\Delta E}{RT}\right) - 1\right) = \frac{1+a}{2+a} (2\,K_1 K_2 - K_1^2)$$

By plotting $\exp\left(-\frac{F\,\Delta E}{RT}\right) - 1$ against n_{Pb}, at constant a, T and halide concentration n_{X}, a practically straight line is obtained. Its slope at $n_{\mathrm{Pb}} = 0$ is determined. The slopes of such lines for different halide concentrations are then plotted against n_{X}, giving again a straight line whose intercept equals $\frac{1+a}{2+a} K_1$, and whose slope equals $\frac{1+a}{2+a} (2\,K_1 K_2 - K_1^2)$, so that the first two association constants are obtained. Figure 1 illustrates this procedure for $PbBr_2$ in the solvent $Ca(NO_3)_2 \cdot 2.33\ NH_4NO_3 \cdot 4.67\ H_2O$ at 338 K. This graphical method is simple and ensures that K_1 and K_2 are the true thermodynamic constants since they refer to the infinite dilution of Pb^{2+} and X^-. The association constants obtained are listed in Table II. The estimated error in K_1 is about ± 6%, and in K_2 ± 25—30%.

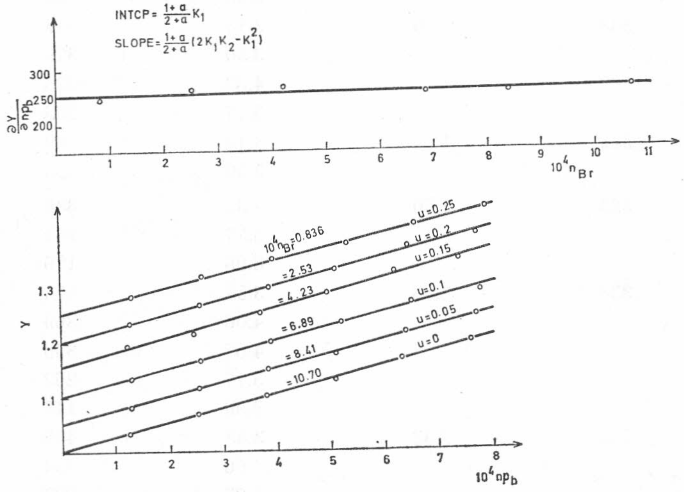

Figure 1. Graphical determination of K_1 and K_2 for bromide complexes in melt $Ca(NO_3)_2 \cdot 2.33\ NH_4NO_3 \cdot 4.67\ H_2O$ at 338 K. $Y = \exp(-F\,\Delta E/RT) - 1$. For the sake of clarity, the lines Y vs. n_{Cd} are shifted along the ordinate by an amount of u indicated on each line.

TABLE II

The Association Constants K_1 *(*PbX^+*) and* K_2 *(*PbX_2*) in* $Ca(NO_3)_2 \cdot a\,NH_4NO_3 \cdot x\,H_2O$ *(Ion Fraction Scale)*

X	T/K	a/mol	x/mol	K_1	K_2
Cl^-	338	1.50	3.04	186	116
			3.50	165	55
			4.33	153	66
			5.77	125	80
			6.34	112	56
			8.96	72	36
	338	2.33	3.53	173	52
			4.06	164	44
			4.67	143	81
			5.77	120	44
	323	2.33	3.53	221	64
			4.06	203	101
			4.67	186	40
			5.77	148	70
			8.96	79	108
Br^-	353	1.50	3.13	437	218
			3.50	392	196
	338	1.50	3.13	448	287
			3.50	379	179
			4.33	325	224
			5.77	252	86
	323	1.50	3.13	469	258
			3.50	413	115
	323	1.50	4.33	336	107
			5.77	267	177
			8.96	176	41
	338	2.33	3.53	423	176
			4.06	369	126
			4.67	330	165
			5.77	263	118
			8.96	143	72
	323	2.33	3.53	436	259
			4.06	394	258
			4.67	329	208
			5.77	276	138
			8.96	169	63

DISCUSSION

Table I shows that the association constants decrease with the temperature and water content of the melt, and that the bromide complexes are more stable than the corresponding chloride complexes as was expected. The quotient K_1/K_2 for a given temperature and melt composition lies always except in two cases, between 1.6 and 3.7. This is, indeed, close to the statistical value for non-directional ligand coordination in molten salts.[1,4] Namely, if we assume that the average quasi-lattice coordination number is $Z = 6$ for the nitrate melt[4,11], then the statistical ratio for non-directional ligand coordination[11] is $K_1/K_2 = 2\,Z/(Z - 1) = 2.4$. In dilute aqueous solutions this ratio is expected to be higher.

Ionic association models for aqueous melts have been developed, mostly along the statistical-mechanical model of Blander[12] for charge-symmetric anhydrous melts. Of course, there is no strict border line between aqueous melts and aqueous solutions, but there is a difference in concepts. Usually, for aqueous melts we adopt the concept of ionic quasi-lattice, as for anhydrous molten salts. At low water content of the melt we might assume, for example, that only cations are hydrated and thus neglect the hydration of anions (if cations have higher charges and/or smaller radii than anions). This assumption is, in terms of the ionic quasi-lattice concept, equal to placing the water molecules on the anion sublattice, i. e. on the anion sites. Thus we may postulate, simply for the purpose of practical statistical-mechanical calculation, that aqueous melts are molten salt systems whose water content is insufficient for H_2O molecules to occupy all coordination sites around the cations.

The first ionic association model for aqueous melts was developed by Braunstein[13]. His model is based on the ionic quasi-lattice concept and derived by statistical-mechanical calculations, but it is valid only for low concentration of water. The model predicts the dependence of the first association constant K_1 on temperature and water content of the melt:

$$\frac{Z}{K_1 + 1 + \frac{Z - 1}{1 + y}} = \exp\left(\frac{\Delta A}{RT}\right) + y \exp\left(\frac{\Delta A - \Delta h}{RT}\right) \qquad (2)$$

K_1 is the first consecutive association constant, Z is the average quasi-lattice coordination number (usually taken $Z = 6$), y is the mole ratio of water to the salt anions (in our case: H_2O/NO_3^-), ΔA is the energy increase of the metal-ligand bond (say, $Pb^{2+} - X^-$) relative to the metal-salt anion bond ($Pb^{2+} - NO_3^-$), whereas Δh refers to the increase of metal-water interaction. R and T have their usual meaning. According to the model, the energy parameters ΔA and Δh should be temperature independent (at least in a large temperature region). ΔA obviously depends on the type of associated ligand, but not Δh. The model is valid at constant salt composition of the melt and thus it cannot predict how the constant K_1 depends on the ratio of $Ca(NO_3)_2$/ /NH_4NO_3. Two other association models for aqueous melts bave been proposed[5,14]. They are valid for higher water content, but have more parameters and require additional data.

According to eq. 2, there is a linear relationship between $Z(K_1 + 1 + (Z - 1)/(1 + y))^{-1}$ and y, at constant temperature and salt composition of the melt. From the intercept of the straight line and from the slope $(\Delta A - \Delta h)$ ΔA can be calculated. The application of eq. 2 to our K_1 values (from Table II) are presented in Figure 2 and 3.

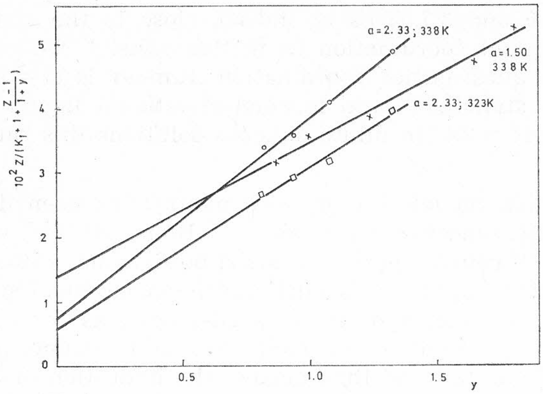

Figure 2. Eq. 2 applied to PbCl$^+$ formation. The value of *a* in Ca(NO$_3$) · *a* NH$_4$NO$_3$ and the temperature given for each line.

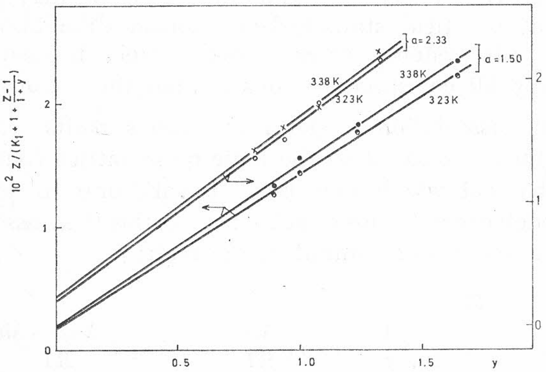

Figure 3. Eq. 2 applied to PbBr$^+$ formation. The value of *a* and temperature given for each line.

A fairly good linear relationship is obtained up to about $y = 1.8$. From the interceptsand slopes of the straight lines the energy parameters ΔA and Δh were calculated. They are listed in Table III, and their values are self-consistent in respect to the model. Namely, for the two temperatures (323 and 338 *K*) the energy parameters have similar values.

TABLE III

The Energy Parameters ΔA *and* Δh

Complex	*a*	*T*/*K*	—ΔA/kJ mol^{-1}	—Δh/kJ mol^{-1}
PbCl$^+$	1.50	338	12.0	1.1
	2.33	323	13.9	4.0
		338	13.7	4.0
PbBr$^+$	1.50	323	17.0	5.2
		338	17.4	5.2
	2.33	323	16.7	5.3
		338	16.9	5.1

The Δh values for Cl^- and Br^- ligands are close for $a = 2.33$, but the value of $\Delta h = -1.1$ kJ mol^{-1} for Cl^- at $a = 1.50$ is too low. (This is probably due to the uncertainty caused by the scattering of experimental points in the corresponding line of Figure 2).

It is interesting to compare the energy parameters ΔA for PbX^+ with the corresponding values of CdX^+, and even more so the ΔA values of PbX^+ in the symmetric melt NH_4NO_3 and the charge-asymmetric melt $Ca(NO_3)_2 \cdot 2.33$ NH_4NO_3. (ΔA is a brond-energy parameter which refers to the anhydrous melt (at $y = 0$), but no direct measurements in anhydrous NH_4NO_3 or $Ca(NO_3)_2 \cdot a$ NH_4NO_3 can be made owing to the decomposition of ammonium nitrate above 150 ^{0}C[6,7]). The relevant data are listed in Table IV.

TABLE IV

ΔA *Values for* CdX^+ *and* PbX^+ *in* NH_4NO_3 *and* $Ca(NO_3)_2 \cdot 2.33$ NH_4NO_3

melt	MX^+	$-\Delta A$/kJ mol^{-1}	reference
NH_4NO_3	$CdCl^+$	15.5	2
	$CdBr^+$	16.7	
	$PbCl^+$	10.5	
	$PbBr^+$	10.9	
$Ca(NO_3)_2 \cdot 2.33$ NH_4NO_3	$CdCl^+$	18.6	6
	$CdBr^+$	21.0	7
	$PbCl^+$	13.8	this work (mean values)
	$PbBr^+$	16.8	

Table IV shows that the energy parameters for CdX^+ are always more negative (relatively, stronger bond) than the corresponding values for PbX^+, which is in agreement with the fact that cadmium halide complexes are more stable than lead halide complexes in most electrolyte solutions. More interesting is the conmparison between the ΔA values in pure NH_4NO_5 and in the charge-asymmetric melt $Ca(NO_3)_2 \cdot 2.33$ NH_4NO_3. It can be seen thal ΔA values are more negative in the latter melt in all cases. This is quite surprising and in contradiction to the reciprocal Coulomb-effect. Namely, if we compare the formation of a MX^+ species in pure NH_4NO_3 and pure $Ca(NO_3)_2$, in terms of an exchange of anions between sites around M^{2+} and Ca^{2+} or NH_4^+, then the two reactions can be written as follows:

$$M^{2+}NO_3^- + NH_4^+Cl^- \rightarrow M^{2+}Cl^- + NH_4^+NO_3^-$$

$$M^{2+}NO_3^- + Ca^{2+}Cl^- \rightarrow M^{2+}Cl^- + Ca^{2+}NO_3^-$$

The above equations take into account only pairwise bond-energies and nearest-neighbour interactions. Since the effective radius of Cl^- is smaller than that of a NO_3^- ion, (which has, incidentally, a planar configuration), and since Ca^{2+} is a cation of higher charge and smaller radius than NH_4^+, the reciprocal Coulomb-effect predicts that the first reaction is energetically more favorable than the second, and we should expect a more negative ΔA value in NH_4NO_3 than in $Ca(NO_3)_2$. Consequently, one would expect a similar trend if ΔA values are compared between pure NH_4NO_3 and mixtures of NH_4NO_3—$Ca(NO_3)_2$. However, Table IV shows, that just the opposite trend is valid in all cases. Of course, one can argue that a Coulomb-type interaction between ions is not the sole effect which governs ionic association processes in molten salts, but it has been demonstrated in many systems that it is, indeed, a very important effect.[11] At first glance, a possible explanation of the anomalous behaviour could lay in the association of divalent cations with nitrate ions. In that case, larger species like $Ca(NO_3)^+$ and $Cd(NO_3)^+$ are, at least partly formed. However, this must be ruled out since in $Ca(NO_3)_2 \cdot KNO_3$ melts cadmium behaves normally, in agreement with the reciprocal Coulomb-effect.[5,6] It seems, thus, that the cause of anomaly is the ammonium nitrate component of the melt. It is quite possible that the melt contains traces of free ammonia, so that small amounts of $Cd(NH_3)^{2+}$ could be formed. Even calcium forms a weak complex of the type $Ca(NH_3)^{2+}$ [15], but not Pb^{2+}. In the presence of water, Pb^{2+} can form $Pb(OH)^+$, but such a hydrolysis seems less likely to occur in a melt containing small amounts of water and a large excess of Ca^{2+} over Pb^{2+}. At present, we can only conclude that the data in Table IV need further clarification.

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SAŽETAK

Kloridni i bromidni kompleksi olova(II) u vodenim talinama kalcij-dinitrata — amonij-nitrata

I. J. Zsigrai, M. R. Mićović i I. J. Gal

Određene su konstante nastajanja $PbCl^+$, $PbCl_2$, $PbBr^+$ i $PbBr_2$ u talinama $Ca(NO_3)_2 \cdot a\,NH_4NO_3 \cdot x\,H_2O$ ($a = 1{,}5$ i $2{,}33$; $x = 3 - 9$) kod 323 i 338 K mjerenjem elektromotorne sile koncentracijskog članka.

Dobiveni rezultati analizirani su primjenom Braunstein-ovog modela asocijacije iona u vodenim talinama.

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