Thermodynamics of Lead(II) Halide Complex Formation in Calcium Nitrate Tetrahydrate - Acetamide Melts

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Z. Naturforsch. **56 a,** 832–836 (2001); received August 20, 2001

Presented at the NATO Advanced Study Institute, Kas, Turkey, May 4 - 14, 2001.

The complex formation between lead(II) ions and chloride and bromide ions in melts of $Ca(NO_3)_2 \cdot 4\,H_2O \cdot a CH_3CONH_2$ has been studied at different temperatures between 30 and 70 °C. The formation constants of the complexes PbX^+ and PbX_2 (X = Cl, Br) were determined from emf measurements by means of Ag/AgX electrodes. The dependence of the formation constants for $PbCl^+$ on the solvent melt composition has been analysed. The thermodynamic parameters ΔH^0_{11} and ΔS^0_{11} for PbX^+ complex formation have been estimated. The parameters are compared with the literature data for the same process in dilute aqueous solutions and in some hydrated and anhydrous salt melts.

Key words: Lead(II) Halide Complexes; Acetamide; Calcium Nitrate Tetrahydrate.

1. Introduction

In earlier studies on the ionic association in highly concentrated electrolyte solutions, mainly concentrated aqueous solutions of inorganic salts or molten inorganic salt hydrates (the so-called hydrous melts) have been used as reaction media. More recently, attention has been paid to low-temperature salt melts with an organic solvent, dimethyl sulphoxide for example [1], instead of water, and to eutectics of inorganic salts with organic compounds, such as acetamide. Some eutectics of acetamide with inorganic salt hydrates melt well below room temperature. The low freezing point allows the use of the apparatus and technique commonly used for aqueous solutions. A comprehensive review of the chemistry of molten acetamide and acetamide complexes was given by Kerridge in 1988 [2].

Although formation of metal halide complexes in molten acetamide was known [2], only a few papers on the formation constants of the complexes have been published. So far, the formation constants for cobalt(II) chloride complexes in molten acetamide [3] and in the mixture of acetamide with calcium nitrate tetrahydrate [4] and for cadmium(II) chloride and bromide in the mixture of acetamide and calcium nitrate tetrahydrate [5] have been determined. The complex formation equilibria in molten hydrated salts and highly concentrated aqueous solutions have attracted much more attention. Lead(II) halide complex formation has been investigated in aqueous melts of $Ca(NO_3)_2$ [6, 7], NH_4NO_3 [8] and in mixed solvents $Ca(NO_3)_2 - NH_4NO_3 - H_2O$ [9].

In previous work [5] the complex formation constants of cadmium(II) chloride and bromide complexes in the melt of $0.8\,CH_3CONH_2 - 0.2\,Ca(NO_3)_2 \cdot 4\,H_2O$ (here the numbers 0.8 and 0.2 are mole fractions) have been determined and the standard thermodynamic functions for the stepwise complex formation have been estimated. The present paper extends our research to lead(II) chloride and bromide complex formation in the same solvent and to melts with a wider range of the salt-to-acetamide mole ratio in $Ca(NO_3)_2 \cdot 4\,H_2O \cdot a CH_3CONH_2$ for two reasons: to provide additional data on metal complex formation in mixed solvents consisting of an organic compound and an inorganic salt hydrate, and to analyse the dependence of the complex formation constants on the composition of the solvent. Moreover, it might be interesting to compare the previous data for lead(II) halide complexes in hydrated salt melts and in dilute aqueous solutions with the present data on a mixed solvent.

2. Experimental

The solvent was prepared by melting together appropriate amounts of reagent grade calcium nitrate tetrahydrate (Merck) and acetamide (Merck) at about 70 °C in stoppered glass vessels. Once melted, the solvent remained liquid at room temperature. Stock solutions of calcium chloride, calcium bromide (Merck) and lead(II) nitrate in the solvent melt were prepared from reagent grade $CaCl_2 \cdot 6\,H_2O$ (Kemika, Zagreb), $CaBr_2 \cdot xH_2O$ (Merck), and $Pb(NO_3)_2$ (Merck), respectively.

The complex formation constants of PbX^+ and PbX_2 have been determined from electromotive force (emf) measurements of the concentration cell (1) where Ag/AgX is the silver-silver(I) halide electrode and X is chloride or bromide. The emf was measured after successive addition of a $Pb(NO_3)_2$ stock solution to the test melt containing a known concentration of calcium chloride or calcium bromide, equal in both half-cells:

$$\mathrm{Ag/AgX}\left|\begin{array}{l}\mathrm{Ca(NO_3)_2 \cdot 4H_2O\cdot}\\ a\mathrm{CH_3CONH_2}\\ \mathrm{CaX_2,\ Pb(NO_3)_2}\end{array}\right|\left|\begin{array}{l}\mathrm{Ca(NO_3)_2 \cdot 4H_2O\cdot}\\ a\mathrm{CH_3CONH_2}\\ \mathrm{CaX_2}\end{array}\right|\mathrm{AgX/Ag} \tag{1}$$

The temperature was adjusted to ±0.1 °C, and stable emf values (±0.05 mV) were obtained within 15 minutes. In preliminary experiments the validity of the Nernst equation for chloride and bromide concentration cells was tested. The theoretical Nernst slope was obtained within ±1%. This indicates that the halide salts in the solvent melt behave ideally in the concentration range tested and justify the neglect of the liquid junction potential. The total concentrations were $1 \cdot 10^{-3} \le c_X$ / mol kg$^{-1} \le 8 \cdot 10^{-3}$ and $0.7 \cdot 10^{-4} \le c_{Pb}$ / mol kg$^{-1} \le 4 \cdot 10^{-3}$.

3. Results and Discussion

The complex formation between Pb^{2+} and the halide ion,

$$m\,\mathrm{Pb}^{2+} + n\,\mathrm{X}^- \rightleftharpoons \mathrm{Pb}_m\mathrm{X}_n^{2m-n}, \tag{2}$$

may be characterized by a set of overall formation constants:

$$\beta_{mn} = \frac{[\mathrm{Pb}_m\mathrm{X}_n^{2m-n}]}{[\mathrm{Pb}^{2+}]^m[\mathrm{X}^-]^n}. \tag{3}$$

Since junction potentials are negligible in dilute solutions, the change in emf of the cell upon addition of $Pb(NO_3)_2$ can be given by the equation

$$\exp\left(\frac{F\Delta E}{RT}\right) = 1 + \sum_{m=1}^{M}\sum_{n=1}^{N} n\beta_{mn}[\mathrm{Pb}^{2+}]^m[\mathrm{X}^-]^n, \tag{4}$$

where ΔE is the emf of the concentration cell, F the Faraday constant, and m and n are the stoichiometric coefficients of (2). A preliminary test of (4) showed that $\exp(F\Delta E/RT)$ was a linear function of $[\mathrm{Pb}^{2+}]$ and $[\mathrm{X}^-]$. Hence, $M = 1$ and $N = 2$, indicating that only the complexes PbX^+ and PbX_2 were formed in measurable amounts in the investigated range of concentration. The formation constants have been calculated by the use of two different methods. The first one was the method of Braunstein et al. [10]. The basic equation for the present case is

$$[\exp(-F\Delta E/RT) - 1]/c(\mathrm{Pb}) \tag{5}$$

$$= \beta_{11} + (2\beta_{12} - \beta_{11}^2)[\mathrm{X}^-] + \dots .$$

Briefly, this method is based on the extrapolation of the function $\exp(-F\Delta E/RT) - 1$ to zero metal ion and ligand concentration according to the equations

$$\lim_{c(\mathrm{X}),c(\mathrm{Pb})\to 0} [\partial \exp(-F\Delta E/RT) - 1]/\partial c(\mathrm{Pb}) = \beta_{11}, \tag{6}$$

$$\lim_{c(\mathrm{X}),c(\mathrm{Pb})\to 0} [\partial^2 \exp(-F\Delta E/RT) - 1]/\partial c(\mathrm{Pb})\partial c(\mathrm{X})$$

$$= 2(\beta_{12} - \beta_{11}^2). \tag{7}$$

In the above equations c(Pb) and c(X) are the stoichiometric lead(II) and halide ion concentrations, respectively. This method is simple and ensures that β_{11} and β_{12} are true thermodynamic constants since they refer to infinite dilution of Pb^{2+} and X^-. The second method of calculation was a simple curve fitting. The experimental data were fitted according to (5), employing a least-squares program yielding the best fitting parameters β_{11} and β_{12}.

Table 1. Overall formation constants in melts $Ca(NO_3)_2 \cdot 4 H_2O \cdot aCH_3CONH_2$.

T/K	a	β^{m}_{11}	β^{M}_{11}	$\beta^{\mathrm{x}}_{11}/10^2$	$\beta^{\mathrm{m}}_{12}/10^2$	$\beta^{\mathrm{M}}_{12}/10^2$	$\beta^{\mathrm{x}}_{12}/10^2$
Chloride complexes:							
303	4.00	23.6±1.3	18.1±1.0	5.0±0.3	2.7±1.0	1.6±0.6	1.2±0.4
323	4.00	25.0±1.1	19.4±0.9	5.3±0.2	5.1±1.4	3.1±0.8	2.3±0.6
333	4.00	25.7±1.2	20.1±0.9	5.4±0.2	4.8±1.4	2.9±0.9	2.1±0.6
	3.00	23.4±1.5	17.6±1.1	4.5±0.3	3.5±2.0	2.0±1.1	1.3±0.7
	2.00	21.9±1.8	15.9±1.3	3.7±0.3	3.3±2.2	1.7±1.1	1.0±0.6
343	4.00	26.4±1.8	20.7±1.4	5.6±0.4	4.4±0.9	2.7±0.6	2.0±0.4
Bromide complexes:							
303	4.00	37.4±0.6	28.6±0.5	7.9±0.1	5.2±1.1	3.1±0.6	2.3±0.5
313	4.00	37.3±1.2	28.7±0.9	7.9±0.2	6.1±1.7	3.6±1.0	2.7±0.8
323	4.00	41.6±1.9	32.3±1.5	8.8±0.4	6.4±3.4	3.8±2.0	2.9±1.5
333	4.00	42.5±1.0	33.1±0.8	9.0±0.2	6.6±2.6	5.1±2.1	3.0±1.1
343	4.00	44.3±1.5	35.1±1.2	9.4±0.3	10.0±2.5	6.1±1.5	4.4±1.1

a: mole of CH_3CONH_2 per mole of $Ca(NO_3)_2 \cdot 4 H_2O$; β^{m}_{mn}: molal scale $(\mathrm{kg\ mol^{-1}})^n$; β^{M}_{mn}: molarity scale $(\mathrm{dm^3\ mol^{-1}})^n$; β^{x}_{mn}: ion fraction scale. The error limits define a 95% confidence interval.

The results obtained with the two methods agreed very well, the difference being well within the experimental uncertainty. The mean values of the constants are given in Table 1. The equilibrium constants presented in Table 1 were calculated using 1 mol kg^{-1} as a standard state, but they are expressed also in molarities (mol dm^{-3}) and in ion fraction. The relation between the activity models in dilute solutions comes out to be $\beta^{\mathrm{M}}_{mn} = \beta^{\mathrm{m}}_{mn}/d^{m+n-1}$ and $\beta^{\mathrm{x}}_{mn} = \beta^{\mathrm{m}}_{mn}/(M_0/(2+a))^n$, where β^{M}_{mn}, β^{m}_{mn} and β^{x}_{mn} are the formation constants expressed in molarity, molality and ion fraction, respectively, d is the density of the melt and M_0 is the molar mass of the melt $Ca(NO_3)_2 \cdot 4 H_2O \cdot aCH_3CONH_2$. The densities of the melt were determined picnometrically at different temperatures, the variation of the density with the solute concentration being negligible. The dependence of the melt density on temperature and melt composition in the temperature range 30 - 70 °C and the composition range 0.5 - 0.9 mole fraction of acetamide can be rationalised according to the equation

$$d/\mathrm{g\ cm^{-3}} = 2.020 - 1.06 \cdot 10^{-3} \cdot t + (3.00 \cdot 10^{-4} \cdot t - 0.882) \cdot x, \qquad (8)$$

where t is the temperature in °C and x mole fraction of acetamide. The molar and ion fraction scale are employed in order to compare the formation constants and the thermodynamic parameters of association with the literature data for the association in pure water as solvent and in anhydrous melts.

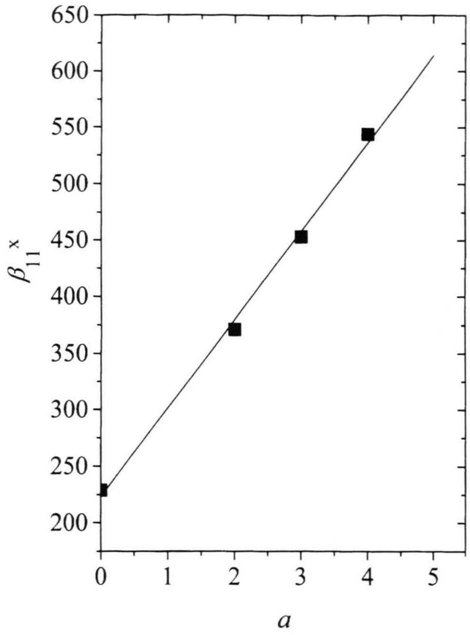

Fig. 1. The dependence of β^{x}_{11} on the composition of molten $Ca(NO_3)_2 \cdot 4 H_2O \cdot aCH_3CONH_2$ at 333 K. The value for pure $Ca(NO_3)_2 \cdot 4 H_2O$ (a = 0) is from [6].

The results in Table 1 show that the bromide complexes are more stable than the corresponding chloride complexes, as it was expected. The formation constants, except in one case for β_{12}, increase with temperature, as do some literature data for dilute aqueous solutions [11].

Little information on metal ion complex formation in molten acetamide and in mixtures of acetamide with inorganic salts has been reported. Thus, no data for lead(II) halide complex formation in the acetamide - calcium nitrate tetrahydrate system are available, but in dilute aqueous solutions and in aqueous salt melts numerous data on lead(II) halide complex formation have been reported.

The formation constants reported here are of the same order of magnitude as the corresponding constants in water [12]. For example, in aqueous solutions at 25 °C values of β^{M}_{11} for $PbCl^+$ formation between 13 dm^{3}mol^{-1} and 17 dm^{3}mol^{-1}, and for $PbBr^+$ between 18 dm^{3}mol^{-1} and 50 dm^{3}mol^{-1} have been reported, as compared to 18.1 dm^{3}mol^{-1} and 28.6 dm^{3}mol^{-1}, respectively, in $Ca(NO_3)_2 \cdot 4 CH_3CONH_2$ at 30 °C.

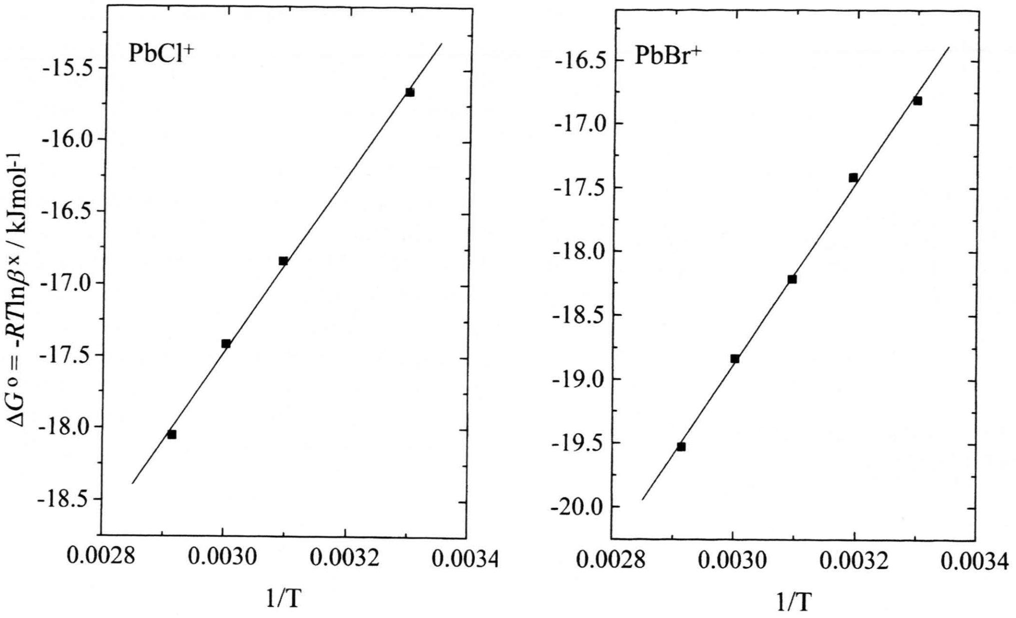

Fig. 2. Temperature variation of ΔG^0_{11} for the $PbCl^+$ and $PbBr^+$ complex formation. The standard state is unity ion fraction.

In order to analyse the dependence of the complex formation constants on the melt composition in the $Ca(NO_3)_2 \cdot 4\,H_2O \cdot a CH_3CONH_2$ mixed solvent, we determined the formation constants for lead(II) chloride formation in the melts with a = 2, 3 and 4. As seen from Table 1, the formation constants decrease with decreasing a, i. e. with increasing calcium nitrate content in the melt. This behaviour is thought to be the result of the competition by calcium cations for halide anions, leading to calcium halide complex formation. Increase of calcium ion concentration decreases the number of available sites in the co-ordination sphere of the chloride ions which results in a decrease of the lead(II) chloride formation constants.

The values of β^x_{11} for $PbCl^+$ formation *vs.* a, together with the value for pure calcium nitrate tetrahydrate are plotted in Fig. 1, from which it can be seen that β^x_{11} is a good linear function of a in the range $0 < a < 4$. The dependence of β^x_{11} on a can be rationalised according to the equation

$$\beta^x_{11} = 223.4 + 78.14a. \qquad (9)$$

Using the constants in Table 1, the standard thermodynamic functions for the stepwise complex formation for the melt $Ca(NO_3)_2 \cdot 4\,H_2O \cdot 4\,CH_3CONH_2$ can be calculated. The standard enthalpy and entropy changes ΔH^0_{11} and ΔS^0_{11} have been estimated from the temperature variation of $\Delta G^0_{11} = -RT \ln \beta_{11}$. From Fig. 2 it is seen that ΔG^0_{11} is a good linear function of temperature. Thus, ΔH^0_{11} and ΔS^0_{11} have been estimated by linear regression analysis as temperature independent constants in the temperature range studied. The thermodynamic data for PbX_2 formation are omitted, because the corresponding ΔG^0 values are too uncertain for a meaningful evaluation. The results are summarised in Table 2. The thermodynamic parameters in Table 2 have been calculated from the stepwise formation constants on the ion fraction scale.

Table 2. Standard enthalpy and entropy values for the PbX^+ formation in $Ca(NO_3)_2{\cdot}4H_2O{\cdot}4CH_3CONH_2$ in the temperature range 303 - 353 K.

Process	ΔH^0_{11}/kJ mol^{-1}	ΔS^0_{11}/J mol^{-1} K^{-1}
$Pb^{2+} + Cl^- \rightleftharpoons PbCl^+$	2.5±0.2	59.9±0.6
$Pb^{2+} + Br^- \rightleftharpoons PbBr^+$	4.0±0.5	68.5±1.5

The errors quoted are standard deviations obtained from linear regression.

It is interesting to compare the standard enthalpies and entropies for the formation of PbX^+ in different solvents. In Table 3 selected values of ΔH^0 and ΔS^0 in dilute aqueous solution and in nitrate melts are com-

Table 3. Standard enthalpy and entropy values for the PbX^+ formation in different solvents[a].

Solvent	T/°C	Ligand	ΔH^0_{11}/kJ mol^{-1}	ΔS^0_{11}/J mol^{-1}K^{-1}	Ref.
H_2O, ionic strength = 0	25	Cl	18.3	116	[13]
		Br	12.0	92.6	
$Ca(NO_3)_2 \cdot 4\,H_2O \cdot 4\,CH_3CONH_2$	30 - 70	Cl	2.5	59.9	this work
		Br	4.0	68.5	
$Ca(NO_3)_2 \cdot 4\,H_2O$	60 - 80	Cl	–5.2	29.0	[6]
		Br	–5.8	36.0	
$KNO_3 \cdot NaNO_3$	240 - 300	Cl	–7.9	26.3	[14]
		Br	–4.6	35.2	

[a] The standard state refers to unity ion (or mole) fraction.

pared with our values in the mixed solvent $Ca(NO_3)_2 \cdot 4\,H_2O \cdot 4\,CH_3CONH_2$.

As seen, formation of PbX^+ in $Ca(NO_3)_2 \cdot 4\,H_2O \cdot 4\,CH_3CONH_2$ renders positive ΔH^0_{11} and ΔS^0_{11} values not too dissimilar to those in dilute aqueous solutions, while the ΔH^0_{11} values in anhydrous and aqueous nitrate melts are negative. This indicates that the thermodynamics of the complex formation process are similar to those in these aqueous solutions, but quite different from those in aqueous and anhydrous melts. The reason for that is thought to be the "water-like" nature of molten acetamide, i. e. strong solvation of lead(II) ions by acetamide. The solvate complexes have probably a lower stability towards increasing temperature than the alternative halide complexes, which can result in a positive enthalpy for lead halide(II) complex formation.

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