A Potentiometric Study on the Complex Formation of the Lead(II)-Glycine System

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The complex formation between lead(II) and glycine was studied in 3 M $NaClO_4$ at 25 °C by emf. titrations, using amalgam and glass electrodes. The hydrogen, hydroxide and lead(II) ions were generated by constant-current coulometry. The experimental data were explained by the following complexes and formation constants:

$$\beta_{pqr}=[Pb_p(HA)_qH_r^{2p+rq}]/[Pb^{2+}]^p[HA]^q[H^+]^r.$$

PbA^+	$\log\beta_{11-1}=$	-5.04 ± 0.01
PbA_2	$\log\beta_{12-2}=$	-12.10 ± 0.01
$PbHA^{2+}$	$\log\beta_{110}=$	1.23 ± 0.01
$Pb(HA)_2^{2+}$	$\log\beta_{120}=$	1.75 ± 0.02
$Pb(HA)_3^{2+}$	$\log\beta_{130}=$	2.07 ± 0.02

By varying the lead(II) ion concentration, the glycine concentration and the pH, it was possible to cover ranges with high and varying mole fractions of each of these complexes.

The present work is part of a study of the complex formation of lead(II) and tin(II) ions with some amino acids.

Several potentiometric studies on the lead – glycine system, based on glass electrode measurements, have been reported.[1,2] The results have been surveyed by Maeda et al.,[3] who extended the investigations to a wider pH range and measured not only the hydrogen ion but also the lead ion concentration. At about the same time three other potentiometric studies[4,5,6] were published. The complexes reported and their formation constants are presented in Table 1 together with the result from a ^{207}Pb NMR study.[7] The constants are given here with Pb^{2+}, H^+ and glycine (= HA)

as components.* The titrations reported in Refs. 3–6 were all performed by titrating lead – glycine solutions with NaOH or $HClO_4$ in about the same pH range, i.e. 2.5–9, and at approximately the same c_{HA}/c_{Pb} ratio. The studies were made at 25 °C, and the ionic medium and electrodes used are listed in Table 1. An ASV (anodic stripping voltammetry) study[8] at very low lead ion concentrations did not reveal any complex formation. As the compilation of data does not give an unambiguous description of the system, the present reinvestigation was undertaken. We have covered a broader range of the quotient between

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*In Ref. 3, one of the values $\log\varkappa(PbA_2)$, $\log\beta(PbA_2)$ must be misprinted since otherwise $\log\varkappa(PbA_2)\neq\log\beta$ $(PbA_2)-2\log K_1$

Table 1. Reported values of the formation constants for $p\text{Pb}^{2+} + q\text{HA} + r\text{H}^+ \rightleftharpoons \text{Pb}_p(\text{HA})_q\text{H}_r^{2p+r}$ in the Pb(II) – HA system.

Formula	p,q,r	$\log \beta_{pqr}$[a] [3 M NaClO$_4$, Pb(Hg), GE]	$\log \beta_{pqr}$[b] (3 M NaClO$_4$, GE)	$\log \beta_{pqr}$[c] [1 M NaClO$_4$, Pb(Hg), GE]	$\log \beta_{pqr}$[d] (1 M NaClO$_4$, GE)	$\log \beta_{pqr}$[e] [3 M NaClO$_4$, Pb(Hg), GE]	$\log \beta_{pqr}$[f] [NaNO$_3$ (1.4–1.8) M, ^{207}Pb NMR]
H$_2$A$^+$	011	2.80±0.01	2.682±0.012	2.49±0.04	2.47	2.79±0.01	2.38±0.00
A$^-$	01–1	−10.21±0.01	−10.070±0.007	−9.73±0.04	−9.76		
PbHA^{2+}	110	1.20±0.04	1.810±0.108	1.02	2.84	1.23±0.01	1.48±0.08
Pb(HA)$_2^{2+}$	120			1.69		1.75±0.02	2.08±0.10
Pb(HA)$_3^{2+}$	130					2.07±0.02	
PbA$^+$	11–1	−4.93±0.02	−4.318±0.045	−4.95	−4.30	−5.04±0.01	
PbA$_2$	12–2	−11.92±0.04		−11.80	−10.20	−12.10±0.01	
Pb(OH)A	11–2		−11.956±0.050		−12.53		
Pb(HA)A$^+$	12–1			−4.76			

[a]Ref. 3. [b]Ref. 4. [c]Ref. 5. [d]Ref. 6. [e]This work. [f]Ref. 7.

glycine and lead(II) by titrating slightly alkaline glycine solutions with lead ions and acidic lead solutions with glycine. A comparison of the various results is given.

Experimental

Method. The measurements were performed as potentiometric titrations at 25 °C, using the automatic titrator described elsewhere.[9,10] The variations of activity factors and liquid-junction potentials were kept at a minimum by using 3 M NaClO$_4$ as salt medium. The free concentrations of lead and hydrogen ions were measured with a lead amalgam electrode and a glass electrode, using the cells

– Pb(Hg) | Equilibrium solution S | Ref. +

– Glass | Equilibrium solution S | Ref. +

The reference electrode was

Ag,AgCl | 0.010 M Ag$^+$, 2.99 M Na$^+$, 3.00 M ClO$_4^-$

The emf's of the cells are related to the concentrations of Pb^{2+} and H$^+$, b and h, by the equations

$$E_B = E_B^0 + (59.16/2)\log(b/\text{M}) + E_j$$

$$E_H = E_H^0 + 59.16 \log (h/\text{M}) + E_j$$

E_j is the liquid-junction potential formed between the test solution S and the 3M NaClO$_4$ of the salt bridge. The value determined by Biedermann and Sillén,[11] $E_j = -17\ h/\text{M}$ mV was used.

The lead ions were generated in the test solution by constant-current electrolysis, using the circuit.[9,12]

Ag,AgCl||0.1 M NaCl, 2.9 M NaClO$_4$|3 M NaClO$_4$ |Solution S| Pb(Hg)

Hydrogen and hydroxide ions were generated coulometrically as described by Ciavatta.[13]

The lead amalgam electrodes attained equilibrium values within a few minutes and remained constant to within 0.01 mV. The glass electrode (Jena N 1180) also attained stable values, ±0.01 mV, within a few minutes.

After preliminary measurements, two types of titrations were performed.

a. To 50 ml of a starting solution of c_{HA} glycine in 3 M NaClO$_4$, c_{OH} hydroxide ions were added coulometrically, after which c_{Pb} lead ions, generated from lead amalgam, were added stepwise. Titration data were collected for c_{Pb} in the range 0.02–1 mM, c_{HA} 50–100 mM and c_{OH} 0.5–0.9 mM, the higher c_{OH} being used only in the most concentrated glycine solutions. The ratio c_{HA}/c_{Pb} thus varied between 50 and 5000. At still higher c_{OH} no equilibrium was attained by the amalgam electrode, at least not within a reasonable time. This was probably due to hydroxide precipitation

caused by a local excess of lead ions around the generating electrode during the electrolysis.

b. To 50 ml of a starting solution consisting of 3 M $NaClO_4$, first 1 mM hydrogen ions and then c_{Pb} lead ions were generated, after which 0–20 ml of c_{HA} glycine in 3.00 M $NaClO_4$ were added. c_{Pb} ranged from 0.5 to 1 mM and c_{HA} from 0.5 to 1.2 M. The ratio c_{HA}/c_{Pb} thus varied between zero and 2400.

A description of the titration assembly, practical details and the program system used to govern different types of titrations is given separately.[10] We have also described factors that caused drifting amalgam emf.-values, notably at low c_{Pb}, and how these problems were overcome.

Chemicals and analysis. Stock solutions of $NaClO_4$, $HClO_4$ and $AgClO_4$ were prepared and analysed as described in Ref. 14. Lead amalgam was prepared and stored as described earlier.[15] Measurements with glycine (Merck, *p.a.*) recrystallized from aqueous ethanol agreed with results obtained using non-recrystallized glycine. A check with an amino acid analyzer showed that the content of other amino acids in the glycine employed was negligible.
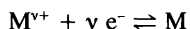
Calculations

For evaluation of experimental data the ETITR version of Letagrop[16] was first used. As our titration procedures differ from those used when Letagrop was developed, other possibilities for correcting for systematic errors were needed. For this reason a refinement program with a flexibility suited to our calculations was written. The refinement is based on least-squares cycles. The minimized function is

$$F = \Sigma w_i^* \Delta_i^2$$

where Δ_i is the difference between the calculated and the observed emf., $E_{calc} - E_{obs}$, and w_i is the weight factor, which is proportional to $1/(\Sigma \Delta_i^2)$. The calculated emf. is computed from

$$E_{calc} = E^o + G \cdot \log[M^{v+}] \qquad (1)$$

where $G = RT \ln 10/vF$ and M^{v+} is the cation in the electrode reaction

$$M^{v+} + v\, e^- \rightleftharpoons M$$

With this choice of Δ the sensitivity of each point is less dependent on the concentration of M^{v+} than if, for instance, $\Delta = [M^{v+}]_{calc} - [M^{v+}]_{obs}$. The total concentrations of the components are calculated as

$$c_{tot} = (Y_1 + Y_2 \cdot x)/(1 + Y_3 \cdot x)$$

where x is the independent variable (volume added in volumetric titrations and charge in coulometric titrations) and Y_1, Y_2 and Y_3 are parameters for each component. The program is dimensioned for five components which may be given in any order. For each experimental point, the free concentrations of the components are computed by the Newton-Raphson method.

The optional parameters to be refined are the stability constants, the parameters of the total concentrations and E^o in eqn. (1). When refining an E^o value, each cycle starts with a sequence where this E^o value is adjusted to give $\Sigma \Delta_i = 0$ before the shifts are calculated. In this way large shifts are avoided. The program is dimensioned for three different emf. values per experimental point.

In another program, the distributions of complexes and free ions are calculated and displayed in a graph as a function of the independent variable (charge or volume of the titrator, or total or free concentration of some component). Apart from giving a graphical representation of final results the program is useful for designing titrations when some information on the complexation has been obtained. The programs are written in Basic and Fortran versions.

Results

The pK_a of the glycinium ion was determined by coulometric generation of hydrogen and hydroxide ions in 1.7, 2.2 and 11 mM glycine solutions in 3 M $NaClO_4$ for 2.3 < pH < 3.3. The result, pK_a = 2.79±0.01, agreed with that obtained by Maeda *et al.*,[3] determined by volumetric emf. titrations under the same conditions, but differed significantly from the value obtained by Corrie *et al.*[4] (Table 1).

As all titrations in this investigation were performed at pH<8, the complexity constants were evaluated with the dominant glycine molecule as
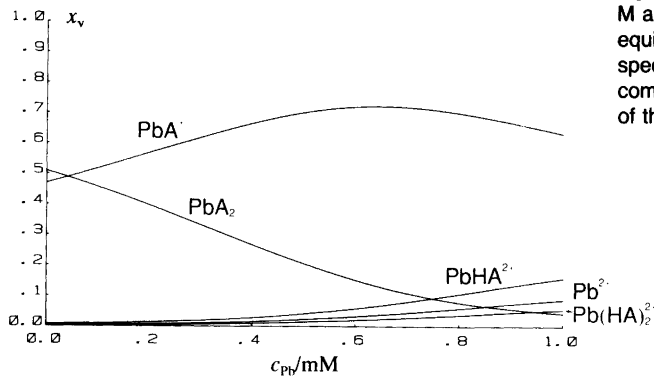
Fig. 1. Distribution of lead(II) for $c_{HA} = 0.1067$ M and $c_H = -0.74$ mM, calculated with the equilibrium constants given in the text. The species $Pb(HA)_3^{2+}$ and the hydroxo complexes have been left out since the sum of their fractions never exceeds 0.02.

Fig. 2. Distribution of lead(II) for $c_{Pb} = 1.135$ mM and $c_H = 0.98$ mM as function of c_{HA}.
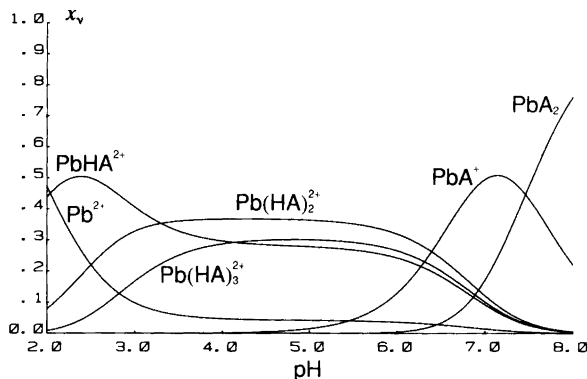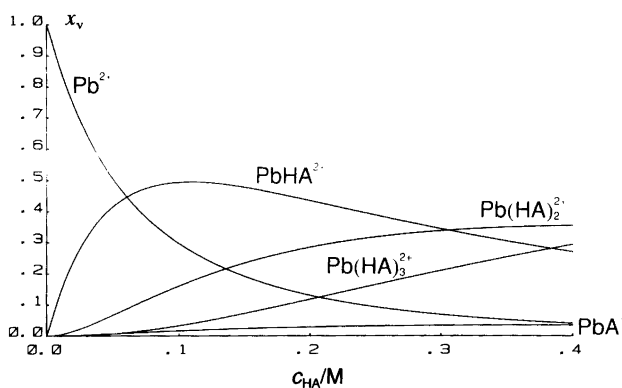

Fig. 3. Distribution of lead(II) for $c_{Pb} = 1$ mM, $c_{HA} = 0.4$ M as a function of pH.

component. Thus, an accurate determination of pK_a for glycine, which must be made well above pH 9, was not necessary. Such measurements would have had to be made with a hydrogen electrode, since the glass electrodes used started to deviate from ideal behaviour around pH 9. If the glycinate ion is used as a component the error

in the pK_a value is included in the complexity constant.

In the calculations, the hydroxo complexes of lead(II), reported by Olin,[17] have been included. In the slightly alkaline glycine solutions (type a titrations), the main complexes were PbA^+ and PbA_2. As a consequence of this, pH decreased

during the lead generation. Fig. 1 shows how the complex formation changed during the lead ion generation in one of these titrations.

In the acidified glycine solutions (type b titrations) the dominant complexes were found to be $Pb(HA)_n^{2+}$ ($n= 1,2,3$) and the increase in pH was due to the hydrolysis of glycine. The distribution of the complexes in one of these titrations, as a function of the glycine concentration added, is shown in Fig. 2.

To show the pH dependence of the complex formation, the distribution in Fig. 3 is calculated for $c_{Pb} = 1$ mM and $c_{HA} = 0.4$ M. At this high c_{HA}/c_{Pb} ratio the hydrolysis of the lead ions is totally suppressed, cf. Fig. 7a in Ref. 3.

Discussion

From Table 1 it is seen that the formation constants for $PbHA^{2+}$, PbA^+ and PbA_2 reported by Maeda et al.[3] agree well with ours. The species $Pb(HA)_2^{2+}$ and $Pb(HA)_3^{2+}$ found in our work were not detected within the concentration ranges of their study. A recalculation of the distribution diagram in Fig. 7a in their work, using our constants, gives 6.5% as the maximum fraction of $Pb(HA)_2^{2+}$ at pH 5.

The study of Corrie et al.[4], based on glass-electrode measurements, reports notably higher values of $\beta(PbHA^{2+})$ and $\beta(PbA^+)$. The difference in $pK_a(H_2A^+)$ should be noticed. Their additional $PbH_{-1}A$ species, also reported by Khayat et al.,[6] was not detected in our measurements. Precipitation occurred when we extended these to pH > 8, at varying glycine concentrations, in an attempt to distinguish between the complexes PbA_2 and $PbH_{-1}A$.

Bottari et al.[5] and Khayat et al.[6] have studied the system in 1 M $NaClO_4$. Their descriptions of the complex formation differ, however. Khayat's investigation is based on glass-electrode measurements, while Bottari et al. also used a lead amalgam electrode. Khayat used commercial $NaClO_4$ (Merck G.R.). Anodic stripping analysis[18] studies show that it is still necessary to purify the sodium perchlorate, as was originally recommended by Sillén et al.[14]

The lead ions used in the investigations were prepared in different ways. Khayat used $Pb(ClO_4)_2$ (Fluka purum), Maeda et al. and Bottari et al. recrystallized lead perchlorate prepared from lead(II) oxide and perchloric acid, and we

produced lead ions electrolytically from lead amalgam.[15]

The dominant complexes found in our study and that of Bottari et al. are the same. The percentage of our additional complex, $Pb(HA)_3$, has probably never exceeded 4% in their study. They suggest the formation of $PbHA_2^+$. It is hard to distinguish this complex from PbA^+ as their concentrations are practically proportional in the wide pH range where HA is the dominant glycine species.

The use of methods other than potentiometry is interesting. The existence of $Pb(HA)^{2+}$ and $Pb(HA)_2^{2+}$ has been confirmed by the ^{207}Pb NMR study of Nakashima et al.[7] in sodium nitrate medium.

An ASV study of lead-glycine solutions has been made at very low lead ion concentrations, ca. 10^{-8} M, by Brown et al.[8] at pH 4.68 and different glycine concentrations (5, 10, 50 and 100 mM). The ionic strength was fixed at 0.1 M with KNO_3. Though the report states that no complex formation takes place, according to our calculations ca. 37% of the lead ions should be complexed in the strongest glycine solution. There is a slight trend in the listed $E_{1/2}^*$ values (Table VII in Ref. 8), and it would be interesting to test the sensitivity of the method at higher lead ion concentrations.

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