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Potentiometric Investigation of Complexes Between Lead(II) and Ethylenedithiodiacetic Acid

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Complex formation between lead(II) and ethylenedithio diacetic acid (H_2L) has been studied at 25 °C in aqueous $0.5\,M$ sodium perchlorate medium. Measurements have been carried out with a glass electrode and with a lead amalgam electrode. In acidic medium and in the investigated concentration range experimental data can be explained by assuming the following equilibria:

$$Pb^{2+} + L^{2-} \rightleftharpoons PbL \qquad \log \beta_{101} = 3.62 \pm 0.03$$
$$Pb^{2+} + H^{+} + L^{2-} \rightleftharpoons PbHL^{-} \qquad \log \beta_{111} = 6.30 \pm 0.07$$

[Keywords: Complexes, lead(II); Ethylenedithiodiacetic acid]

Potentiometrische Untersuchungen an Komplexen von Blei(II) mit Ethylendithioessigsäure

Es wurde die Komplexbildung zwischen Pb(II) und Ethylendithioessigsäure (H_2L) bei 25 °C in wäßriger $0{,}5M$-Perchloratlösung untersucht. Die Messungen wurden mittels Glaselektrode und Bleiamalgamelektrode durchgeführt. In saurem Medium können im untersuchten Konzentrationsbereich die experimentellen Daten mit folgenden Gleichgewichten erklärt werden:

$$Pb^{2+} + L^{2-} \rightleftharpoons PbL \qquad \log \beta_{101} = 3{,}62 \pm 0{,}03$$
$$Pb^{2+} + H^{+} + L^{2-} \rightleftharpoons PbHL^{+} \qquad \log \beta_{111} = 6{,}30 \pm 0{,}07$$

Introduction

In a previous paper[1] the behaviour of lead(II) ions with thiodiacetic acid was examined and two different complex species were evidenced in solution in an acidic medium, PbL and PbHL^+ (L^{2-} is the anion of the acid). The corresponding stability constants were calculated at 25 °C in $0.5\,M$ $NaClO_4$.

In the frame of a systematic investigation of the complex species with containing sulphur ligands, the behaviour of ethylenedithiodiacetic acid(ethanedithiodiacetic acid, $HOOCCH_2$—S—CH_2CH_2—S—CH_2COOH) with lead(II) was now considered. The literature reports

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the value of the stability constant of the PbL species[2], determined at 25 °C in $0.1\,M$ $\mathrm{NaClO_4}$, but no mention is made on mixed complexes with hydrogen ion, that could be formed in solution owing to the polydentate nature of the ligand.

The present investigation was performed by measuring potentiometrically both metal and hydrogen ion concentrations with a lead amalgam and a glass electrode respectively. Thus, the interpretation of the experimental data is improved with respect to the measurement of the hydrogen ion concentration alone.

Experimental

Ethylenedithiodiacetic acid ("K & K") was used without further purification. The alkalimetric equivalent of the dried product was considered satisfactory.

Lead(II) perchlorate was prepared from PbO ("Merck"), dissolved in diluted perchloric acid. The analytical excess of hydrogen ion was determined by the *Gran* method[3] while the metal concentration was determined by complexometry.

Sodium perchlorate ("Merck") was utilised to obtain the working ionic strength. The salt concentration in the stock solution was determined by drying a known volume of solution at 125 °C.

All other chemicals were of analytical purity.

The potentiometric measurements were carried out with a Radiometer pHM4 potentiometer using the following cells:

(A) Pb (Hg) | test solution | reference electrode
(B) reference electrode | test solution | glass electrode

The reference electrode was similar to that described by *Forsling* et al.[4]:

$$\mathrm{Ag,\ AgCl}\ \left|\ \begin{array}{c} 0.49\,M\ \mathrm{NaClO_4} \\ 0.01\,M\ \mathrm{NaCl} \end{array}\ \right|\ \mathrm{NaClO_4}\ 0.50\,M$$

The Ag, AgCl electrode was prepared according to *Brown*[5]. The glass electrode ("Thalamid"-Jenaglass) was calibrated in concentration units, so, in this paper, the symbol $-\log[\mathrm{H}^+]$ is used instead of *pH*.

According to *Biedermann* and *Sillén*[6], in a constant ionic medium the activity coefficients remain constant and the activities can be substituted by concentrations. Therefore, the *emf* of the cells (A) and (B) can be expressed, in mV units, as follows:

$$E_A = E_A^0 - 29.58 \log[\mathrm{Pb}^{2+}] - E_J$$

$$E_B = E_B^0 + 59.16 \log[\mathrm{H}^+] + E_J$$

where E_J is the junction potential between test solution and the liquid bridge of 0.50 sodium perchlorate ($-100[\mathrm{H}^+]$ mV under our experimental conditions) and E_A^0 and E_B^0 are constants. Knowing E_A^0 and E_B^0 determined before each set of measurements in the absence of the ligand, $[\mathrm{Pb}^{2+}]$ and $[\mathrm{H}^+]$ can be deduced from the above equations.

Lead amalgam was prepared by dissolving freshly cut metal ("Merck" silberfrei) in twice distilled mercury (1% *w*/*w*) and was stored under 20 *mM* $HClO_4$. Care was taken to avoid the oxidation of the amalgam. It was prepared fresh each week and during the measurements a strong of purified nitrogen was passed through the test solution.

Measurements were carried out at 25.0 ± 0.1 °C in 0.50 *M* sodium perchlorate as inert medium.

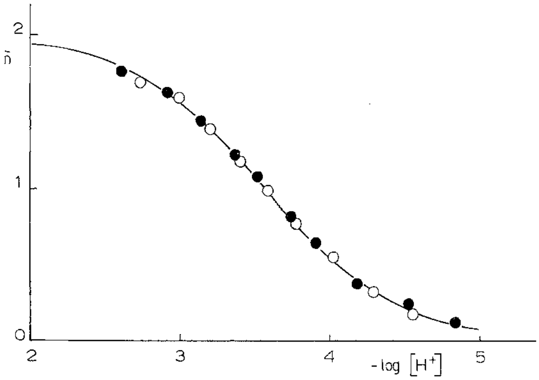

Fig. 1. Formation function of ethylenedithiodiacetic acid. Full curve calculated from the constants obtained in this work. C_L: ● 19.86 *mM*; ○ 9.93 *mM*

Results and Discussion

Several determinations of free ion concentrations were carried out by the amalgam electrode in solutions in which $C_L > C_M$ (the analytical concentrations of the ligand and of the metal ion respectively) at different values of $-\log[H^+]$, in order to determine the composition and the stabilities of the prevailing complex species. The metal concentration was varied from 2.30 to 6.90 *mM* and the ligand concentration from 7.50 to 20.0 *mM*. The value of $-\log[H^+]$ was maintained sufficiently low that hydrolytic products of the lead ion were always negligible[7].

Only 1:1 complexes were evidenced in the concentration range examined. This was proved by working at different metal and ligand concentrations. The calculated values of the constants are only function of the hydrogen ion concentration, meaning that mixed complexes with H^+, like PbH_qL^{q+}, are certainly present in solution. The conditional formation constant, β_1', was calculated for each value of $[H^+]$ by the following equations:

$$[\mathrm{Pb}L'] = C_M - [\mathrm{Pb}^{2+}]$$

$$[L^{2-}] = (C_L - [\mathrm{Pb}L'])/\alpha_L$$

$$\beta_1' = \frac{[\mathrm{Pb}L']}{[\mathrm{Pb}^{2+}]\,[L^{2-}]}$$

where

$$[\mathrm{Pb}L'] = [\mathrm{Pb}L] + [\mathrm{PbH}L^{+}] + [\mathrm{PbH}_2L^{2+}]$$

$$\alpha_L = 1 + \beta_{011}\,[\mathrm{H}^+] + \beta_{021}\,[\mathrm{H}^+]^2\,{}^*$$

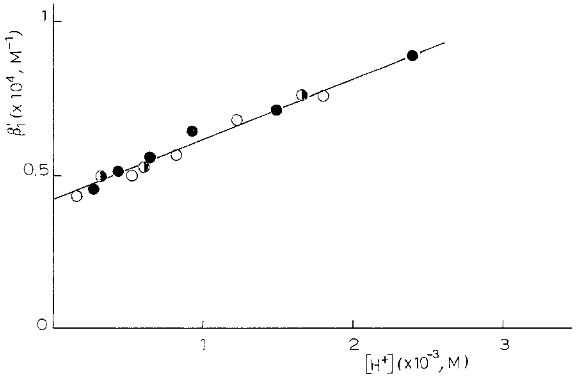

Fig. 2. Conditional formation constant of the lead(II)-ethylenedithiodiacetate complex, β_1' vs. $[\mathrm{H}^+]$. ○ $C_M = 2.30\,mM$, $C_L = 7.50\,mM$; ◑ $C_M = 4.60\,mM$, $C_L = 20.0\,mM$; ● $C_M = 6.90\,mM$, $C_L = 16.7\,mM$

The protonation constants of the ligand, utilized in the calculation, are referred to the used experimental conditions of temperature and ionic medium and were determined by potentiometric titrations of ethylenedithiodiacetic acid with sodium hydroxide. The formation function, $\bar{n}\,(-\log[\mathrm{H}^+])$, plotted in Fig. 1, was calculated by the expression:

$$\bar{n} = (C_{\mathrm{H}} - [\mathrm{H}^+])/C_L$$

where C_{H} is the total hydrogen ion concentration. A minimization computing program gives the following values for the cumulative protonation constants:

$$\log\beta_{011} = 3.90 \pm 0.02 \qquad\qquad \log\beta_{021} = 7.13 \pm 0.03$$

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* β_{pqr} generally represents the formation constant of the $\mathrm{Pb}_p\mathrm{H}_qL_r$ species.

Some of the experimental data for the lead(II)—ethylendithiodiacetate system are plotted in Fig. 2. An example of calculation is reported in Table 1. The plot of β_1' vs. $[H^+]$ gives a straight line with positive slope and intercept, meaning that two complex species are predominant in solution, PbL and PbHL^+, the formation constants of which are related to β_1' by the expression:

$$\beta_1' = \beta_{101} + \beta_{111}\,[H^+]$$

Table 1. *Calculation of the conditional stability constant of the lead(II) complex of ethylenedithiodiacetic acid at various* $-\log[H^+]$ *values* ($C_M = 6.90 \times 10^{-3} M$; $C_L = 1.67 \times 10^{-2} M$)

$-\log[H^+]$	$-\log[Pb^{2+}]$	$\log \alpha_L$	$\log \beta_1'$
2.62	2.50	1.99	3.95
2.83	2.64	1.63	3.85
3.04	2.84	1.29	3.81
3.20	2.96	1.06	3.75
3.39	3.14	0.81	3.72

Table 2. *Logarithms of the stability constants of the lead(II) complexes with thiodiacetic and ethylenedithiodiacetic acid*

	Thiodiacetic[1]	Ethylenedithiodiacetic acid
$\log \beta_{101}$	3.36	3.62 ± 0.03
$\log \beta_{111}$	5.74	6.30 ± 0.07

The values of the stability constants, deduced from the slope and intercept with a least-squares treatment, are listed in Table 2, together with the corresponding values of the lead—thiodiacetate complexes.

The value of the stability constant of the PbL species agrees with that obtained by *Suzuki* and *Yamasaki*[2] if the different experimental conditions are considered. The value is greater than of the corresponding complex with thiodiacetate. The basicity of the ligands being very similar, probably also the sulphur atoms take part in the coordination even if the affinity of lead ions towards ethereal sulphur is relatively low. This trend is analogous for some transition metals[8,9], but is opposite for zinc and cadmium[10].

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