

A Potentiometric Titration Study of the Complex Formation between Pb^{2+} and 1,2,3-Propanetricarboxylic Acid

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The stability constants for the complexes formed between Pb^{2+} and 1,2,3-propanetricarboxylic acid, H_3A , in an ionic medium of 1 M NaClO_4 and at 25.0 °C have been determined by potentiometric titrations with a lead amalgam electrode. Constants are reported for PbA , PbA_2 , Pb(HA) , Pb(HA)A , Pb(HA)_2 , $\text{Pb(H}_2\text{A)}$ (HA) and $\text{Pb(H}_2\text{A)}$. The formation of dinuclear species is indicated, but only estimates of the constants for Pb_2A_2 and HPb_2A_2 could be obtained due to the poor solubility of the lead salts.

In continuation of our study of the complex formation between some heavy metals (Pb^{2+} and Cd^{2+}) and polycarboxylic acids, we report here a study of the Pb^{2+} -1,2,3-propanetricarboxylate ion system, henceforth described as the $\text{Pb}^{2+}-\text{A}^{3-}$ system. Previous studies covered complex formation between Pb^{2+} and aliphatic¹⁻³ and aromatic⁴ dicarboxylates. Cd^{2+} was also included in the aromatic series. There is no report in the literature of any study of the $\text{Pb}^{2+}-\text{A}^{3-}$ system, although some studies of a number of divalent metal ions have been reported.^{5,6} Additional to the MA, MHA and MH_2A complexes identified for all the divalent metal ions studied, Campi *et al.*⁶ using spectrophotometry, obtained evidence for the formation of dinuclear species, $\text{H}_p\text{Cu}_2\text{A}$, in the copper system at rather high total metal ion concentrations (up to 20 mM). The formation of dinuclear species was not observed for any of Ni^{2+} , Co^{2+} , Mg^{2+} , Ca^{2+} and Ba^{2+} also studied by these authors.

In our study of the $\text{Pb}^{2+}-\text{A}^{3-}$ system, potentiometric titrations with the lead amalgam electrode

were carried out in the pH range 3 to 7 and at total Pb^{2+} concentrations in the range $B=0.3$ to 1.0 mM. The upper limit was set by precipitation problems at the beginning of those titrations in which total $\text{Pb}^{2+} > 0.5$ mM. Such wide variation in experimental conditions was used to facilitate the identification of polynuclear and protonated species.

EXPERIMENTAL

All measurements were made at 25.0 °C and in an ionic medium of 1 M NaClO_4 .

The protonation constants of the acid, H_3A , were determined from potentiometric titration data at six different total acid concentrations (8–25 mM). Each titration covered the n_{H} range from 0.13 to 2.9.

The method used in the investigation of the metal complexes followed closely that described in Refs. 1 and 3. Free hydrogen ion, h , and free Pb^{2+} , b , concentrations were measured with glass and lead amalgam electrodes as described there. The liquid junction potential, E_j , which was measured as described in Ref. 1, is given by

$$E_j = kh + l[\text{H}_3\text{A}] + m[\text{H}_2\text{A}] + n[\text{HA}] + o[\text{A}] \quad (1)$$

The values -53.6 , -0.5 , -8.1 , -18.8 and -33.1 mVM⁻¹ obtained for the constants k , l , m , n and o are much as expected from the Henderson equation. As the limiting equivalent conductivities, $\lambda_{0,i}$ of the 1,2,3-propanetricarboxylate ions are not available, the constants have been estimated from $\lambda_{0,i}$ values of related ions. Using the following $\lambda_{0,i}$ values taken from Refs. 7 and 8 (ion, $\lambda_{0,i}/\text{cm}^2 \text{ ohm}^{-1} \text{ equiv}^{-1}$): H^+ , 350; Na^+ , 50; ClO_4^- , 68; H_2A^- , 29.7 (hydrogen-glutarate ion); $1/2 \text{ HA}^{2-}$, 56.9 (glutarate ion); $1/3 \text{ A}^{3-}$, 70.2 (citrate ion) one finds $E_j/\text{mV} = -62h - 8.6[\text{H}_2\text{A}] - 17.4[\text{HA}] - 29.1[\text{A}]$. Hence the experimental coefficients may be assumed to

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contain only contributions from "true" liquid junction potential and small variations in activity coefficients.⁹ E_j calculated from eqn. (1) was used as a correction term to the measured emf. both with the lead amalgam and the glass electrodes.

All potentials were measured to ± 0.01 mV. Chemicals and solutions used were prepared as described in Ref. 1. 1,2,3-Propanetricarboxylic acid (Fluka, purum) was purified by treatment with decolourising charcoal. The formula weight of the purified acid was 176.4 (calc. 176.1).

CALCULATIONS AND RESULTS

The experimental data on the formation of the metal complexes were collected in a series of potentiometric titrations with buffers chosen to cover the entire $H_3A - H_2A^- - HA^{2-} - A^{3-}$ spectrum, assuming that H_2A^- , HA^{2-} and A^{3-} are the potential ligands in the system.

Following the procedure described in Ref. 3 and assuming that only mononuclear species are formed, the stability constants for the reaction



is written as

$$\alpha_{stu} = [B(H_2A)_s(HA)_t(A)_u] b^{-1} [H_2A]^{-s} [HA]^{-t} [A]^{-u} \quad (3)$$

The total analytical concentration of B is given by

$$B = b + \sum_s \sum_t \sum_u \alpha_{stu} b [H_2A]^s [HA]^t [A]^u \quad (4)$$

For buffers in which $\phi = [HA]/[A] \leq 3.5$, it may be assumed that complexes involving HA^{2-} and A^{3-} predominate and that $(t+u) \leq 3$. Eqn. (4) can then be rearranged to give

$$y_1 = \left(\frac{B}{b} - 1\right) a^{-1} = (\alpha_{001} + \alpha_{010}\phi) + (\alpha_{002} + \alpha_{011}\phi + \alpha_{020}\phi^2)a + (\alpha_{003} + \alpha_{012}\phi + \alpha_{021}\phi^2 + \alpha_{030}\phi^3)a^2 \quad (5)$$

Plots of y_1 as a function of $a = [A]$ at various constant ϕ (0.2 to 3.5) gave straight lines, indicating that $(t+u)$ is not greater than 2 (maximum total $A = 75$ mM).

For buffers in which $\phi > 3.5$, it was reasonable to assume that HA^{2-} and H_2A^- were the dominating ligating species. If $(s+t+u)$ is not greater than 2 then eqn. (4) can be rearranged to give

$$y_2 = \left(\frac{B}{b} - 1 - \alpha_{001}a - \alpha_{002}a^2 - \alpha_{011}[HA]a\right)[HA]^{-1} = (\alpha_{010} + \alpha_{100}\psi) + (\alpha_{020} + \alpha_{110}\psi + \alpha_{200}\psi^2)[HA] \quad (6)$$

$\psi = [H_2A]/[HA]$. Plots of y_2 as a function of $[HA]$ at approximately constant values of ψ (0.25 to 3.0) gave straight lines. Thus $(s+t+u) = 2$ (maximum total $A = 50$ mM).

Analysis of the intercepts and slopes from the $y_1(a)_\phi$ and $y_2([HA])_\psi$ plots suggested the formation of PbA , PbA_2 , $Pb(HA)A$, $Pb(HA)$, $Pb(HA)_2$, $Pb(H_2A)$ (HA) and $Pb(H_2A)$. Preliminary constants obtained were refined by the least-squares program Letagrop Vrid, version Etitr.¹⁰

Dinuclear species. The complexes identified as described above were found inadequate in fully explaining the titration data. In the pH range 6–7, the trend in $E_{calc.} - E_{exp.}$, which reached 1.0 mV at the beginning of the titration at $B = 0.7$ mM, was found to be independent of pH and was not removed by introducing $Pb^{2+} - OH^-$ complexes. It increased with an increase in total B , thus indicating the formation of polynuclear species. Because of the limited solubility of $Pb^{2+} - A^{3-}$ compounds it was not possible to investigate a broad range in B . Pb_2A_2 was found satisfactory in explaining the limited data. A small trend was also observed in the pH range 4 to 5.5, suggesting the formation of $H_pPb_2A_r$ complexes. Again, because of limited data, only an estimate of the constant for HPb_2A_2 could be obtained.

The results are presented in Table 1 as the equilibrium constants for the reaction



given by

$$\beta_{pqr} = [H_pB_qA_r] h^{-p} b^{-q} a^{-r} \quad (8)$$

DISCUSSION

The values of the stepwise protonation constants of 1,2,3-propanetricarboxylic acid obtained in this work ($\log k_n = 5.50, 4.39$ and 3.46) agree well with those (5.53, 4.36 and 3.41) found by Vanni and Gennaro¹¹ in 1 M KNO_3 .

Table 2 contains the stability constants with H_2A^- , HA^{2-} and A^{3-} as ligands according to eqn. (2). The proposed set of complexes comprises all conceivable mononuclear species with one or

Table 1. Stability constants for the lead (II)–1,2,3-propanetricarboxylate complexes. The quoted errors are equal to three standard deviations. For β_{122} only an estimate is given.

β_{011}	$(1.49 \pm 0.02) \times 10^3 \text{ M}^{-1}$
β_{012}	$(5.04 \pm 0.03) \times 10^4 \text{ M}^{-2}$
β_{022}	$(4.8 \pm 0.5) \times 10^8 \text{ M}^{-3}$
β_{111}	$(8.1 \pm 0.2) \times 10^7 \text{ M}^{-2}$
β_{212}	$(5.0 \pm 0.5) \times 10^{14} \text{ M}^{-4}$
β_{211}	$(3.9 \pm 0.2) \times 10^{11} \text{ M}^{-3}$
β_{112}	$(9.1 \pm 0.4) \times 10^9 \text{ M}^{-3}$
β_{312}	$(6.4 \pm 1.1) \times 10^{18} \text{ M}^{-5}$
(β_{122})	$(2.9 \pm 0.6) \times 10^{13} \text{ M}^{-4}$

two ligands save $\text{Pb}(\text{H}_2\text{A})_2$. From the data in the table the constant for the reaction $\text{Pb}(\text{H}_2\text{A})^+ + \text{H}_2\text{A}^- \rightleftharpoons \text{Pb}(\text{H}_2\text{A})_2$ can be estimated to be 5 M^{-1} , which is too small a value for a definite identification.

The constants will now be compared with those obtained in mono- and dicarboxylate systems. In Ref. 3 a linear relationship was found between $\log k_2$ of simple dicarboxylic acids and the $\log \alpha_{10}$ for the corresponding lead complexes. The value for the first lead acetate complex will also fall on this line if statistically corrected constants for the acids are used. The microscopic stability constants of 1,2,3-propanetricarboxylic acid are not known. If they are assumed to be equal in the first dissociation step, (compare the substituent effects found by Pearce and Creamer¹² for citric acid), the statistically corrected $\log k_3$ will be 4.0. The estimated value of α_{100} from the graph in Ref. 3 is then 50 M^{-1} , which is surprisingly close to the observed value (51 M^{-1}) considering the underlying assumptions. HA^{2-} exists in two forms and the statistical value of the quotient between the symmetric and unsymmetric form is 1/2. The two forms correspond to the glutarate and succinate ion, respectively. Since the protonation constant is smaller for the monohydrogenricarboxylate ion than for the di-

Table 2. Stability constants, α_{stuv} for the protonated complexes written as $\text{Pb}(\text{H}_2\text{A})_s(\text{HA})_t(\text{A})_u$.

α_{010}	258 M^{-1}
α_{020}	$5.0 \times 10^3 \text{ M}^{-2}$
α_{011}	$2.9 \times 10^4 \text{ M}^{-2}$
α_{100}	51 M^{-1}
α_{110}	$2.6 \times 10^3 \text{ M}^{-2}$

carboxylate ions, α_{010} is, as expected, smaller than for the corresponding dicarboxylate complexes. Proceeding as before *via* the microscopic protonation constants for HA^{2-} , α_{010} is estimated to be about 180 M^{-1} , again close to the observed value. The comparatively large value of $\beta_{011} = \alpha_{001}$ is probably caused by the combined effects of the addition of a more strongly ligating group and an increased number of geometric possibilities for coordination.

It has been necessary to include small amounts of polynuclear complexes in the model. Due to solubility limitations only the *B*-range 0.3–1.0 mM could be investigated. Hence it is difficult to identify these species. Dinuclear complexes appear, however, to adequately account for the polynuclearity. They have been reported to exist in the closely related Cd^{2+} –citrate system.¹³ Evidence for Pb_2A – the equivalent complex has been claimed⁶ to exist for Cu^{2+} – has not been found. This may be due to the fact that the compositions favouring its formation cannot be measured because of precipitation reactions. The structure of Pb_2A_2 may be reminiscent of the $\text{Sb}_2(\text{C}_4\text{H}_2\text{O}_6)_2^{2-}$ anion.¹⁴

Fig. 1 shows the distribution of Pb(II) on the various species for $B=0.7 \text{ mM}$ as a function of $-\log h$ at $A_{\text{tot}}=0.025 \text{ M}$. This value corresponds approximately to the total ligand concentration at mid-titration in this investigation.

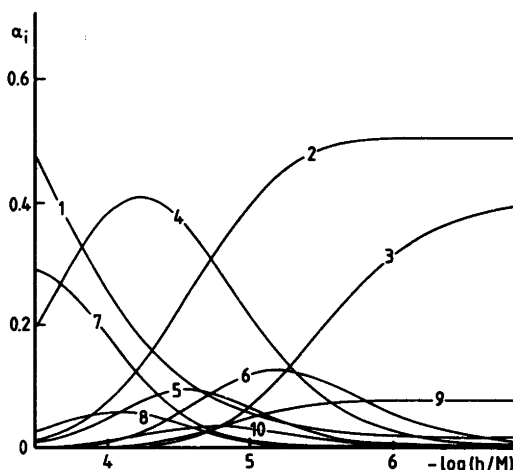


Fig. 1. Distribution of Pb^{2+} over the various species identified in the $\log h$ range studied. $B_{\text{tot}}=0.7 \text{ mM}$. $A_{\text{tot}}=0.025 \text{ M}$. (1) PbA , (2) PbA_2 , (3) PbA_2 , (4) $\text{Pb}(\text{HA})$, (5) $\text{Pb}(\text{HA})_2$, (6) $\text{Pb}(\text{HA})\text{A}$, (7) $\text{Pb}(\text{H}_2\text{A})$, (8) $\text{Pb}(\text{H}_2\text{A})(\text{HA})$, (9) Pb_2A_2 , (10) HPb_2A_2 .

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