

# The Complex Formation between $\text{Pb}^{2+}$ and the Maleate and Hydrogen Maleate Ions

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From emf measurements of  $[\text{Pb}^{2+}]$  and  $[\text{H}^+]$  at 25 °C the stability constants of the complexes between lead(II) and the maleate and hydrogen maleate ions have been determined in 1 M  $\text{NaClO}_4$ . The species  $\text{PbA}$ ,  $\text{PbA}_2$ ,  $\text{PbA}_3$ ,  $\text{PbHA}$ , and  $\text{Pb}(\text{HA})_2$  are formed. No mixed complexes could be detected.

There have been comparatively few studies made on the complex formation between  $\text{Pb}^{2+}$  and dicarboxylic acids,  $\text{H}_2\text{A}$ . This is probably due to the limited solubility of most lead(II) dicarboxylate salts. Measurements of  $\log [\text{H}^+]$  in buffers, the method generally employed, will then be less accurate. Central ion measurements do not suffer to the same extent from a low solubility and polarographic methods have been used in a number of cases. The more accurate potentiometric technique using a lead amalgam electrode does not seem to have been used to study such systems.

The prime purpose of the present investigation has been to determine which species are formed between  $\text{Pb}^{2+}$  and a dicarboxylic acid. Maleic acid (*cis*-butenedioic acid) was chosen since its dissociation constants are well separated, which will facilitate the interpretation of the data. Moreover, lead maleate is sufficiently soluble to permit potentiometric measurements with an amalgam electrode. The lead-maleate system has previously been studied by Yasuda, Yamasaki, and Ohtaki<sup>1</sup> using a glass electrode. These authors were interested in the trend in the value of the formation constant of the 1:1 complex for a series of divalent metal ions. The experimental conditions were hence chosen so that this complex could be expected to predominate. No effort was made

to find out if other complexes were also formed in the system. Nozaki, Mise, and Higaki<sup>2</sup> using polarographic measurements have reported stability constants for  $\text{PbA}$ ,  $\text{PbA}_2$ , and  $\text{PbA}_3$  in 0.2 M  $\text{NaClO}_4$ . The formation of the last complex is not firmly established since its presence was inferred from data in solutions, where a substantial amount of the perchlorate ions had been exchanged for the ligand. No evidence for protonated species has been presented.

## METHOD OF INVESTIGATION

The experiments have been carried out as potentiometric titrations in a 1 M  $\text{Na}(\text{ClO}_4)$  medium containing various total (analytical) concentrations of  $\text{H}^+$ ,  $H$ ; lead(II),  $B$ ; and maleate,  $A$ . Generally  $B$  and the ratio  $H/A$  were kept constant in an experiment.  $A$  was varied by the addition of a maleate buffer. The hydrogen ion concentration,  $h$ , and the concentration of  $\text{Pb}^{2+}$ ,  $b$ , were measured at 25 °C with the cells

$$- \text{glass} \mid \text{equilibrium solution S} \mid \text{ref} + \quad (\text{I})$$

$$E_g = E_g^\circ - 59.16(\text{mV}) \log(h/M) - E_j \quad (1)$$

$$- \text{Pb-Hg} \mid \text{equilibrium solution S} \mid \text{ref} + \quad (\text{II})$$

$$E_{\text{Pb}} = E_{\text{Pb}}^\circ - 29.58(\text{mV}) \log(b/M) - E_j \quad (2)$$

Solution S had the general composition  $B\text{Pb}(\text{II})$ ,  $HH^+$ ,  $1\text{MNa}^+$ ,  $AA^{2-}$ ,  $(1M + 2B + H - 2A)\text{ClO}_4^-$ . The determination of the liquid junction potential,  $E_j$ , is described in a later section. The cell parameters,  $E_g^\circ$  and  $E_{\text{Pb}}^\circ$ , were determined in solutions with known  $h$  and  $b$  values.  $E_{\text{Pb}}^\circ$  could in most titrations

be determined from the first point in a titration, where  $A=0$  and sufficient acid was present to suppress the hydrolysis of  $\text{Pb}^{2+}$ . It was not found convenient to add so much acid to the starting solution that  $E_g^\circ$  could also be determined. Instead  $E_g^\circ$  was determined in a separate solution before, and usually also after, a titration. This technique was also used to determine  $E_{\text{Pb}}^\circ$  for reverse titrations. The transfer of the glass electrode from the solution used for calibration to S and *vice versa* did not affect the accuracy of the measurements since  $E_g^\circ$  proved to be constant within 0.2 mV for several weeks.

The reversibility of the equilibria was shown by titrations carried out in the reverse direction.

The large difference between the dissociation constants,  $\text{p}K_1 \approx 1.6$  and  $\text{p}K_2 \approx 5.6$ , made it convenient to divide the investigation in the following parts: (i) the proton-maleate system, (ii) the lead-hydrogen maleate system, (iii) the lead-maleate system, (iv) the lead-hydrogen maleate-maleate system (mixed complexes). The upper limit for the ligand concentration was set in the vicinity of 0.1 M, since Sandell<sup>3</sup> has shown that if more than about 10% of the perchlorate ions are exchanged variations in the activity factors become appreciable. The glass electrode measurements have been used only to calculate the  $\text{HA}^-$  and  $\text{A}^{2-}$  concentrations in the equilibrium solutions. No attempt was made to determine the ligand number,  $\bar{n}$ , since this quantity can only be obtained with low accuracy. In system (iv) this is caused by the high acidity and the small extent of the complex formation and in system (iii) by the limited solubility of lead maleate, which makes measurements at values of  $B$  larger than about 0.001 M impossible. The equilibrium analysis has therefore been founded on functions based on the amalgam measurements in conjunction with preliminary values of  $[\text{HA}^-]$  and  $[\text{A}^{2-}]$  from the glass electrode potentials.

The liquid junction potential in cells (I) and (II) can be expected to be caused mainly by the presence of  $\text{H}^+$ ,  $\text{HA}^-$ , and  $\text{A}^{2-}$  ions in S. The potential  $E_j$  defined by eqns. (1) and (2) includes an activity factor, which is generally assumed to be constant.  $E_j$  is then identified with the liquid junction potential. It can easily be shown from Henderson's expression for this potential that within the concentration

ranges used,  $E_j$  can be approximately written as

$$E_j = l[\text{H}^+] + m[\text{HA}^-] + n[\text{A}^{2-}] = E_{j,h} + E_{j,ha} + E_{j,a} \quad (3)$$

where  $l$ ,  $m$ , and  $n$  are constants.  $E_{j,h}$  was determined from cell (I) with  $A$  and  $B = 0$  and found to be  $-(58 \pm 2)h$  mV for  $h < 0.05$  M, which is close to the value calculated from the limiting molar conductivities and to the value reported by Ahrlund and Kullberg.<sup>4</sup> From their paper  $l$  is found to be  $-65$  mV  $\text{M}^{-1}$  at constant  $[\text{ClO}_4^-] = 1$  M. From this value  $l = -61$  mV  $\text{M}^{-1}$  can be estimated from the limiting molar conductivities for constant  $[\text{Na}^+] = 1$  M.  $E_{j,ha}$  and  $E_{j,a}$  were found from measurements with the glass electrode in a number of  $\text{HA}^- - \text{A}^{2-}$  buffers, which yielded  $m = -13.5$  mV  $\text{M}^{-1}$  and  $n = -9.2$  mV  $\text{M}^{-1}$ . Similar measurements in  $\text{H}_2\text{A} - \text{HA}^-$  buffers yielded  $m = -10$  mV  $\text{M}^{-1}$  for  $l = -58$  mV  $\text{M}^{-1}$ . This is not significantly different from the result obtained in the less acid buffers.

As pointed out by Biedermann and Ohtaki<sup>5</sup> the fact that  $E_j$  can be linearized is no proof of constant activity factors. These authors measured the changes in the emf of a probe for hydrogen ions in a 3 M perchlorate medium in which the cationic composition was varied and concluded that the observed changes were mainly due to a variation in the activity factor for  $\text{H}^+$ . It is likely that similar changes occur in our systems also, but it should be noted that the theoretically estimated values of  $l$ ,  $m$ , and  $n$  are of the same magnitude as the experimental values.

## EXPERIMENTAL

*Chemicals and analysis.* Unless otherwise stated all chemicals were of *p.a.* quality. The agreement was 0.1% or better between different methods of analysis or between replicate determinations when only one method was used.

Sodium perchlorate was prepared by neutralizing  $\text{Na}_2\text{CO}_3$  (Merck) with  $\text{HClO}_4$  (Merck) following the directions given by Biedermann.<sup>6</sup> The stock solution of the recrystallized product was analysed by evaporating weighed samples to constant weight. Tests for  $\text{Fe}^{3+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  were negative.

Lead perchlorate was prepared from  $\text{PbO}$  (Merck) and  $\text{HClO}_4$  as described by Olin.<sup>7</sup> The lead content of the stock solution was deter-

mined as  $\text{PbSO}_4$  after evaporation with  $\text{H}_2\text{SO}_4$ , and as  $\text{Pb}(\text{IO}_3)_2$  after precipitation with  $\text{HIO}_3$ .<sup>9</sup> The analytical hydrogen ion concentration was found from potentiometric titrations with dilute standard  $\text{HClO}_4$ . A Gran extrapolation was used for the equivalence point determination.

Silver perchlorate. A stock solution was prepared from  $\text{AgNO}_3$  (Merck) and  $\text{HClO}_4$  via  $\text{Ag}_2\text{O}$ . The silver ion concentration was found by a potentiometric titration with standard  $\text{NaCl}$ .

Perchloric acid solutions were prepared from  $\text{HClO}_4$  (Merck) by dilution. They were standardized against tris(hydroxymethyl)aminomethane and  $\text{KHCO}_3$ .

Sodium hydroxide solutions were prepared from a 50%  $\text{NaOH}$  (EKA Bohus) solution by dilution and standardized against  $\text{HClO}_4$ .

Maleic acid (Merck "zur Synthese") was used as received. A test by thin layer chromatography according to Stahl<sup>9</sup> for the presence of fumaric acid was negative. Separate tests indicated that this method is capable of detecting 0.2% fumaric acid in a sample of maleic acid. Stock solutions of the acid were standardized by potentiometric titrations with  $\text{NaOH}$  using the second equivalence point determined by a Gran extrapolation. The formula weight found was 116.1 (calc. 116.1). The various buffers containing  $\text{H}_2\text{A}$ ,  $\text{HA}^-$ , and  $\text{A}^{2-}$  were prepared by mixing stock solutions of maleic acid and sodium hydroxide. Lead amalgam was prepared by dissolving lead metal (Merck silberfrei) in mercury (Kebo redist.). The amalgam was stored under 0.02 M  $\text{HClO}_4$  in a  $\text{N}_2$  atmosphere and the lead concentration was 0.1% (weight). An amalgam prepared from mercury purified according to Whitnack and Sasseli<sup>10</sup> gave the same results.

*Apparatus.* The measurements were performed in an oil thermostat at  $25 \pm 0.1^\circ\text{C}$  using the salt bridge described by Forsling, Hietanen and Sillén.<sup>11</sup> The reference half-cell was 1 M  $\text{NaClO}_4$  | 1 M  $\text{ClO}_4^-$ , 0.99 M  $\text{Na}^+$ , 0.01 M  $\text{Ag}^+$  |  $\text{AgCl}$ ,  $\text{Ag}$ . The glass electrode, Beckman type 40498, was checked against the quinhydrone electrode in the acidity range covered by the titrations.

The  $\text{Ag}$ ,  $\text{AgCl}$  electrode was prepared according to Brown.<sup>12</sup> The emf's of cell (I) were measured to  $\pm 0.1$  mV with a Metrohm Herisau compensator E388. The emf's of the amalgam electrode were measured to  $\pm 0.01$  mV with a digital voltmeter, Data Precision 2520.

Nitrogen or argon was used for stirring and removal of oxygen from the solutions. The gas was purified by passing it through activated copper, 10%  $\text{NaOH}$ , 10%  $\text{H}_2\text{SO}_4$  and finally 1 M  $\text{NaClO}_4$ .

The glass electrode showed a constant potential within a few minutes after an addition. The potential of the amalgam electrode took about 20 min to reach a constant value. It was then stable within  $\pm 0.03$  mV for at least 12 h. Tests

showed that this electrode followed eqn. (2) within 0.2 mV in the  $B$  range studied,  $0.0003 \text{ M} < B < 0.01 \text{ M}$ .

## RESULTS AND CALCULATIONS

The general composition of a complex will be written  $\text{H}_p\text{B}_q\text{A}_r$ . The stability constant of the complex is defined by

$$\beta_{p,q,r} = [\text{H}_p\text{B}_q\text{A}_r] h^{-p} b^{-q} a^{-r} \quad (4)$$

Preliminary values of the constants were obtained by standard graphical procedures. These values were then refined by the least squares program Letagrop Vrid, version Etitr.<sup>13</sup>  $U = \sum (E_{\text{calc}} - E_{\text{exp}})^2$  was minimized. Anticipating the results we shall in the following for the sake of simplicity set  $q = 1$ , i.e. only mononuclear complexes are formed.

*i. The  $\text{H}^+ - \text{A}^{2-}$  system.* Since this system has been thoroughly studied by Dellien and Malmsten<sup>14</sup> only a few titrations were performed.  $A$  was 0.010 or 0.025 M and  $\bar{n}$  was varied between 0.04 and 1.65. The values of the equilibrium constants obtained, viz.  $\beta_{1,0,1} = 10^{5.63} \text{ M}^{-1}$  and  $\beta_{2,0,1} = 10^{7.88} \text{ M}^{-2}$  are in good agreement with those reported by Dellien and Malmsten.

*ii. The  $\text{Pb}^{2+} - \text{HA}^-$  system.* It will be convenient to write the complexes  $\text{H}_p\text{BA}_r$ , with  $p = r$  as  $\text{B}(\text{HA})_n$  and the stability constants as  $\beta_n^{\text{HA}} = \beta_{n,1,n}(\beta_{1,0,1})^{-n}$ . Titrations were performed at  $B = 0.001$ , 0.005, and 0.010 M. Provisional values of  $[\text{HA}^-]$  were calculated from the expression  $(A - B + b)h\beta_{1,0,1}/(1 + \beta_{1,0,1}h + \beta_{2,0,1}h^2)$ , which is based on the assumption that  $\text{PbHA}$  and  $\text{PbA}$  are formed. The graphical treatment indicated that  $\text{Pb}(\text{HA})_2$  was also present. The numerical calculations, in which allowance for small amounts of  $\text{PbA}_n$  complexes were made, gave for 165 experimental points in  $\text{H}_2\text{A} - \text{HA}^-$  buffers the following values of the equilibrium constants with their estimated standard deviations<sup>15</sup> within parentheses:  $\beta_1^{\text{HA}} = 3.78(0.02) \text{ M}^{-1}$ ,  $\beta_2^{\text{HA}} = 5.3(0.3) \text{ M}^{-2}$ , and  $\sigma(E_{\text{Pb}}) = 0.03$  mV.  $E_j$  (mV) was calculated from eqn. (3) with  $l = -58 \text{ mV M}^{-1}$  and  $m = -10 \text{ mV M}^{-1}$ . Due to their small values the constants are very sensitive to the choice of  $l$  and  $m$ . A change of  $m$  from  $-10 \text{ mV M}^{-1}$  to  $-13.5 \text{ mV M}^{-1}$ , which value was obtained in  $\text{HA}^- - \text{A}^{2-}$  buffers, altered  $\beta_1^{\text{HA}}$  to  $3.49(0.02) \text{ M}^{-1}$  and

$\beta_2^{\text{HA}}$  to 4.7(0.3)  $\text{M}^{-2}$ , respectively.  $\sigma(E_{\text{Pb}})$  remained unchanged.

It may be shown that the change in  $\beta_1^{\text{HA}}$ ,  $\Delta\beta_1^{\text{HA}}$ , is approximately given by  $\Delta\beta_1^{\text{HA}} = \Delta m \ln 10/29.58$ , where  $\Delta m$  is the change in the coefficient of  $[\text{HA}^-]$ .

Calculations were also performed on the assumption that only PbHA was formed.  $\beta_1^{\text{HA}}$  then became 4.09  $\text{M}^{-1}$ . Beside increased standard deviations,  $E_{\text{calc}} - E_{\text{exp}}$  showed systematic deviations. Although small, these deviations cannot be removed by simply changing the coefficients in the expression for  $E_j$ . Only by the addition of a second degree term in  $[\text{HA}^-]$  would they disappear. In order to eliminate a  $\beta_1^{\text{HA}}$  value of 5  $\text{M}^{-1}$  from the equilibrium model the coefficient of such a  $[\text{HA}^-]^2$  term would need to be about 60  $\text{mV M}^{-2}$ . If present, this term ought to have been detected in the  $E_j$  determination. In summary we propose the following equilibrium constants  $\beta_1^{\text{HA}} = 3.8 \pm 0.3 \text{ M}^{-1}$  or  $\beta_{1,1,1} = (1.6 \pm 0.3) \times 10^6 \text{ M}^{-2}$

$\beta_2^{\text{HA}} = 5 \text{ M}^{-2}$  or  $\beta_{2,1,2} = 9 \times 10^{11} \text{ M}^{-4}$

The value for  $\beta_2^{\text{HA}}$  probably represents an upper limit and no estimate of the uncertainty can be given. A comparison between experimental and calculated values of  $\eta = \log(B_C/b)$  where  $B_C = B - \sum_1^3 \beta_{0,1,i} b a^i$  is made in Fig. 1.

*iii. The  $\text{Pb}^{2+} - \text{A}^{2-}$  system.* The measurements were carried out in buffers with  $[\text{A}^{2-}]/[\text{HA}^-] = 0.75$  and 2.  $B$  was 0.001 M or less on account of the low solubility of lead maleate.  $a$  was calculated from  $a = (H - h)/(2\beta_{2,0,1}h + \beta_{1,0,1} + \beta_{1,1,1}b)h$  and  $E_j$  as  $-13.5[\text{HA}^-] - 9.2[\text{A}^{2-}]$ . The graphical treatment indicated the formation

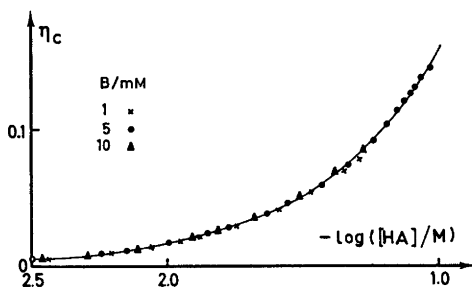


Fig. 1.  $\eta_c$  as a function of  $\log[\text{HA}^-]$ .  $\eta_c$  is calculated from  $B_C$ , which is  $B$  reduced by the terms for PbA, PbA<sub>2</sub> and PbA<sub>3</sub>. Drawn curve is calculated from the stability constants determined in this investigation.

of PbA, PbA<sub>2</sub>, and PbA<sub>3</sub>. There are significant deviations from a model with only PbA and PbA<sub>2</sub> when  $[\text{A}^{2-}] > 0.07 \text{ M}$ , *i.e.* close to its upper limit in the experiments. The presence of PbA<sub>3</sub> might therefore be a bit uncertain. The numerical treatment of 139 experimental points yielded the following values of  $\beta(\sigma(\beta))$ :  $\beta_{0,1,1} = 5.54(0.02) \times 10^2 \text{ M}^{-1}$ ,  $\beta_{0,1,2} = 1.06(0.01) \times 10^4 \text{ M}^{-2}$ , and  $\beta_{0,1,3} = 2.4(0.1) \times 10^4 \text{ M}^{-3}$ .  $\sigma(E_{\text{Pb}})$  was 0.09 mV. An inspection of  $E_{\text{calc}} - E_{\text{exp}}$  suggests that a main contribution to  $\sigma(E_{\text{Pb}})$  is errors in  $E_{\text{Pb}}^0$ , which was determined from only one point in each titration. A calculation in which  $E_{\text{Pb}}^0$  was varied individually for each titration gave  $\beta_{0,1,1} = 5.60(0.03) \times 10^2 \text{ M}^{-1}$ ,  $\beta_{0,1,2} = 1.10(0.01) \times 10^4 \text{ M}^{-2}$ ,  $\beta_{0,1,3} = 2.2(0.1) \times 10^4 \text{ M}^{-3}$ , and  $\sigma(E_{\text{Pb}}) = 0.04 \text{ mV}$ . The average shift in  $E_{\text{Pb}}^0$  was 0.2 mV. In summary we propose the following equilibrium constants

$$\beta_{0,1,1} = (5.57 \pm 0.09) \times 10^2 \text{ M}^{-1}$$

$$\beta_{0,1,2} = (1.08 \pm 0.03) \times 10^4 \text{ M}^{-2}$$

$$\beta_{0,1,3} = (2.3 \pm 0.3) \times 10^4 \text{ M}^{-3}$$

A comparison between experimental and calculated values of  $\eta_c = \log(B_C/b)$  where  $B_C = B - \sum_1^3 \beta_{0,1,i} b a^i$  is made in Fig. 2.

*iv. Mixed complexes.* The absence of mixed complexes is indicated by the measurements in section (iii), since  $\log(B/b) = f(a)$  is independent of the ratio  $[\text{A}^{2-}]/[\text{HA}^-]$  in the buffer. In order to test this point further we have tried to estimate the best experimental conditions for detecting such complexes.

Assume that the mixed complex Pb(HA)A is formed. Then

$$B \simeq b(1 + \beta_1^{\text{HA}}[\text{HA}^-] + \beta^* \beta_{0,1,1}[\text{HA}^-]a + \beta_{0,1,1}a + \beta_{0,1,2}a^2) = b\phi \quad (5)$$

where Pb(HA)<sub>2</sub> and PbA<sub>3</sub> have been neglected and  $\beta^*$  is the formation constant of the mixed complex from PbA and HA<sup>-</sup>. From (2) and (5) one obtains

$$\left( \frac{\partial E}{\partial [\text{HA}^-]} \right)_{a,B} = - \frac{RT}{2F} \left( \frac{\partial \ln \phi}{\partial [\text{HA}^-]} \right)_{a,B} - \left( \frac{\partial E_j}{\partial [\text{HA}^-]} \right)_{a,B} \quad (6)$$

and

$$\left( \frac{\partial \ln \phi}{\partial [\text{HA}^-]} \right)_{a,B} = \frac{\beta_1^{\text{HA}} + \beta^* \beta_{0,1,1} a}{\phi} \quad (7)$$

The greatest change in  $E$  due to the formation of Pb(HA)A on varying  $[\text{HA}^-]$  is found when

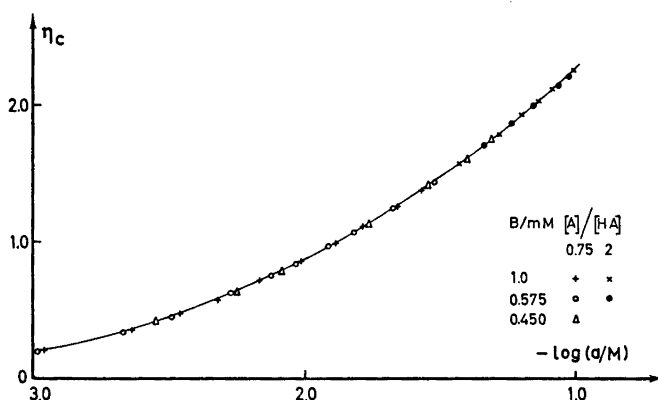


Fig. 2.  $\eta_c$  as a function of  $\log a$ . In the calculation of  $\eta_c$  terms for  $PbHA^+$  and  $Pb(HA)_2$  have been subtracted. Drawn curve is calculated from the stability constants determined in this investigation.

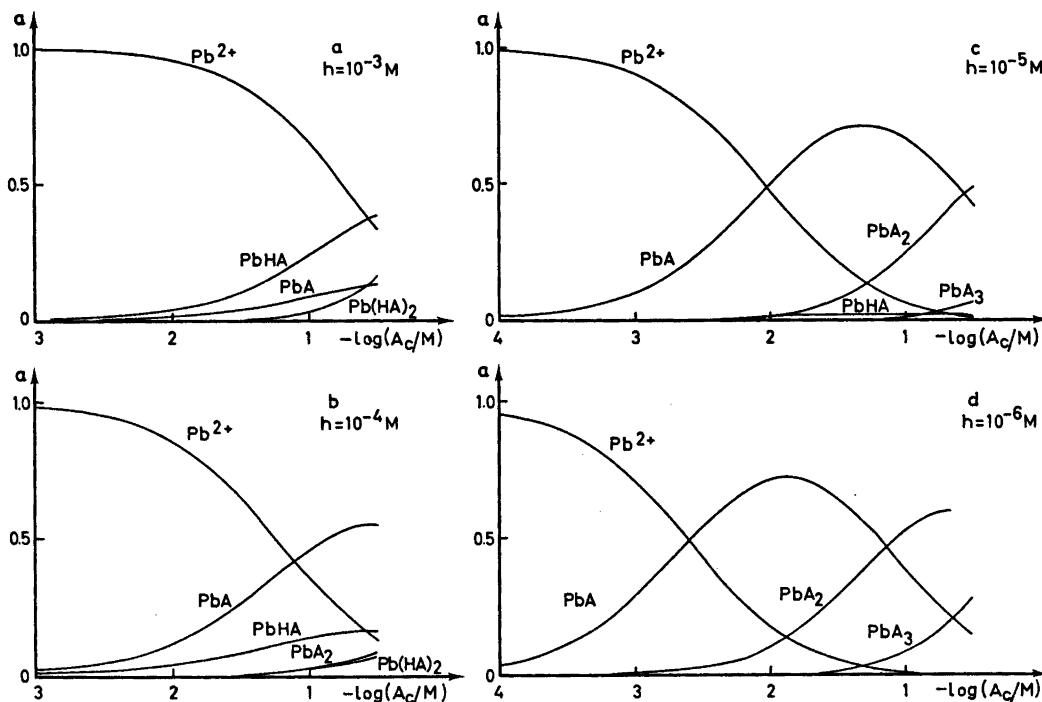


Fig. 3. The relative amounts ( $\alpha$ ) of the lead maleate complexes, at different values of  $h$ , as a function of  $\log A_c$ .  $A_c$  is the total maleate concentration not bound to  $Pb(II)$ .

$\beta^* \beta_{0,1,1} a / \phi$  is a maximum. This occurs at  $a \approx 0.01 M$  for small values of  $\beta^*$ . Data from a titration with  $HA^-$  at constant  $a = 0.01 M$  could, however, be fully explained by the previously proposed complexes. Mixed com-

plexes are thus not formed in detectable amounts.

The distribution of lead(II) on the proposed species as a function of  $\log A_c$  is shown in Fig. 3 at four selected values of  $h$ .  $A_c$  is the

total maleate concentration not bound to Pb(II).

The experimental data can be obtained from the authors on request.

## DISCUSSION

There is agreement between the present results and those of Nozaki *et al.*<sup>2</sup> on the formation of PbA, PbA<sub>2</sub>, and PbA<sub>3</sub>. The values of the step stability constants, 550, 20, and 2 M<sup>-1</sup>, respectively, show that the first complex has considerable strength whereas the stabilities of the higher complexes rapidly decline. A more extensive discussion of these values will be postponed until accurate data have been collected for the complex formation of Pb<sup>2+</sup> with other simple dicarboxylate ions.

As can be expected from the low basicity of the hydrogen maleate ion the stability constant for PbHA is small and the step stability constant for Pb(HA)<sub>2</sub> is only about 1 M<sup>-1</sup>. This value is so small that the presence of Pb(HA)<sub>2</sub> cannot be regarded as fully established. Evidence for the formation of Pb(HA)A<sup>-</sup> could not be found. An estimate based on eqn. (6) and the expected accuracy of the amalgam electrode suggests that the equilibrium constant of the reaction PbA + HA<sup>-</sup> = Pb(HA)A<sup>-</sup>, β\*, cannot be larger than about 1 M<sup>-1</sup>. A small value for β\* is reasonable. A comparison with the constant for the reaction Pb<sup>2+</sup> + HA<sup>-</sup> = PbHA<sup>+</sup> suggests that it should be less than β<sub>1</sub><sup>HA</sup>, *i.e.* < 4 M<sup>-1</sup>. From the extensive data on the lanthanoid-malonate systems<sup>16</sup> one finds that the value of β\* is about one half of the value of β<sub>1</sub><sup>HA</sup>. Protonated complexes are not formed in significant amounts in the rare earth-maleate systems,<sup>14</sup> which demonstrates the weakness of the hydrogen maleate ion as ligand.

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