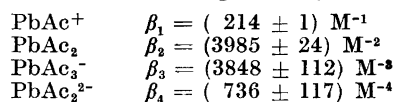


## The Complex Formation between Lead(II) Ions and Acetate Ions

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The complex formation between lead(II) ions and acetate ions has been studied by emf methods at 25.0°C in the ionic medium 3.0 M (Na<sup>+</sup>)ClO<sub>4</sub><sup>-</sup> by measuring the lead ion concentration with a lead amalgam electrode. The [Pb(II)] ranged from  $2 \times 10^{-3}$  to  $5 \times 10^{-2}$  M, and the acetate concentration was varied from 0 to 1.3 M. A suitable amount of HClO<sub>4</sub> was present in order to avoid the hydrolysis of lead<sup>1</sup>. The experimental values could be explained by assuming the complexes



The final complex constants were obtained by a generalized least square method using a Ferranti-Mercury computer and the "Letagrop Vrid" program.<sup>2-4</sup>

The acetate complexes of Pb<sup>2+</sup> have previously been the subject of a great number of investigations,<sup>5-15</sup> in which potentiometric, polarographic, conductometric and solubility methods have been applied. The earliest investigations were of a qualitative nature. Studies of the specific conductivity of lead acetate solutions at various dilutions made Noyes and Whitcomb<sup>5</sup> conclude the formation of undissociated lead acetate. Sanved<sup>7</sup> suggested, referring to solubility measurements made by Blomberg,<sup>6</sup> and summing up all the evidence known till then, that the ion probably formed was PbAc<sup>+</sup>. In addition, Blomberg considered the formation of PbAc<sub>3</sub><sup>-</sup> and PbAc<sub>5</sub><sup>3-</sup> likely.

A comparison of reported complexity constants of the lead-acetate system<sup>8-15</sup> is shown in Table 1, from which the disagreement with respect both to the species formed and to the values of the complex constants  $\beta_n$  is apparent. In this investigation the complex formation has been studied by the potentiometric titration method recommended by Leden.<sup>16</sup> With this technique the total concentration of the metal ion is kept constant during a titration, while the ligand concentration is changed gradually by additions from a burette. A large number of equilibrium solutions can thus be measured in a single experiment.

Table 1. Comparison of reported complexity of the lead-acetate system.

Investigator	Method	Ionic strength	Temp. °C.	$\beta_1 M^{-1}$	$\beta_2 M^{-2}$	$\beta_3 M^{-3}$	$\beta_4 M^{-4}$
Jacques <sup>8</sup>	emf.	0.00	25	480	14 400	—	—
Edmond and Birnbaum <sup>9</sup>	sol.	1.00	25	104	—	—	—
Purkayashita and Sen-Sarma <sup>10</sup>	cond.	vary	30	25	—	—	—
Toropova and Batyrshina <sup>11</sup>	pol.	2.00	20	167	—	250	125
Aditya and Prasad and Das <sup>12,13</sup>	emf	0.00	30	270	9 000	—	—
Suzuki <sup>14</sup>	emf			—	44 000	—	—
Burns and Hume <sup>15</sup>	pol.	1.98	25	150	840	3000	—
	emf	1.98	25	155	820	3350	—
	sol.	1.98	25	130	770	2450	—
This work	emf	3.00	25	214 ± 1	3985 ± 24	3848 ± 112	736 ± 117

## LIST OF SYMBOLS

The symbols used in the text are defined below for reference.

$c_{Pb}$  analytical concentration of lead(II) ion  
 $c_{Ac}$  » » » acetate ion  
 $c_{Na}$  » » » sodium ion  
 $c_H$  » » » hydrogen ion  
 $[Pb^{2+}]$  actual concentration of lead(II) ion  
 $[Ac^-]$  » » » acetate ion  
 $h$  » » » hydrogen ion

$\beta_n$  equilibrium constant of the reaction  $Pb^{2+} + nAc^- \rightleftharpoons PbAc_n^{(n-2)-}$

$$\beta_n = \frac{[PbAc_n^{(n-2)-}]}{[Pb^{2+}][Ac^-]^n}$$

$$\alpha_0 = [Pb^{2+}]/c_{Pb}$$

$$\alpha_n = \frac{[PbAc_n^{(n-2)-}]}{c_{Pb}} = \frac{\beta_n [Ac^-]^n}{1 + \sum_1^N \beta_n [Ac^-]^n}$$

$$\bar{n} = \frac{c_{Ac-} [Ac^-]}{c_{Pb}}$$

## EXPERIMENTAL

*Method.* The experiments have been carried out as potentiometric titrations in which a starting solution of the composition



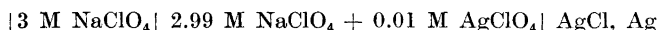
was titrated with acetate buffers containing equal concentrations of NaAc and HAc

and  $(3 - c_{Ac})$  M NaClO<sub>4</sub>. From another burette was added a solution of Pb(ClO<sub>4</sub>)<sub>2</sub> and NaClO<sub>4</sub> so that the total concentration of Pb(II) in each series was kept constant and  $2c_{Pb} + c_H + c_{Na} = 3$  M.

HClO<sub>4</sub> was added to the Pb(ClO<sub>4</sub>)<sub>2</sub> solutions so that pH ≤ 3 in the starting solutions. In this region the hydrolysis of the Pb<sup>2+</sup> could be neglected, according to the investigations of the hydrolysis of Pb<sup>2+</sup> made by Olin.<sup>1</sup> Solutions with  $c_{Pb} = 2, 25$  and 50 mM were titrated with three acetate buffers of different strength to cover the range  $c_{Ac} = 0 - 1.3$  M.

The [Pb<sup>2+</sup>] was measured with a lead amalgam electrode in the cell  
 (-)Pb-Hg |S| ref (+) (1)

The "Wilhelm" reference bridge of the type



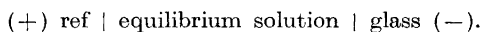
described by Forsling, Hietanen and Sillén<sup>17</sup> was used.

The emf of cell (1) may be written

$$E = E^\circ - 29.577 \log [\text{Pb}^{2+}] + E_j \quad (2)$$

where  $E^\circ$  is a constant, [Pb<sup>2+</sup>] the lead ion concentration at equilibrium in the solution S, and  $E_j$  the liquid junction potential at the junction S | 3 M NaClO<sub>4</sub>. Eqn. (2) has been written with the assumption that the activity coefficient factors remain constant and so may be included as constants in  $E^\circ$ . When a considerable proportion of the perchlorate ions have been exchanged by acetate ions the constancy of the activity factors is doubtful. As no correction has been made neither for this systematic error nor for the change of the liquid junction potential, the values of the highest complexes are not free from objection. Each titration series was repeated three times with different stock solutions and lead amalgam. The amalgam electrode, which consisted of a pool on the bottom of the titration vessel, gave constant and reproducible potentials. For identical points in each titration series, the difference between the emf values very seldom exceeded 0.05 mV. Except for the first point where the amalgam electrode took at least one hour to obtain a constant value, the equilibrium seemed to be obtained almost immediately. The potential remained constant for several hours except for the last measuring points in each series where a drifting towards higher emf values occurred.

In order to calculate  $c_{Ac}$  in the equilibrium solutions, the analytical hydrogen concentration of the stock solutions Pb(ClO<sub>4</sub>)<sub>2</sub> and NaClO<sub>4</sub> was determined potentiometrically by titrating the salt solutions with HClO<sub>4</sub> in 3 M (Na)ClO<sub>4</sub> and using a Gran extrapolation<sup>18</sup> to obtain the equivalence point. Before titrating the NaAc-solution in the same way, the acetate ions were converted to acetic acid by adding an equivalent amount of HClO<sub>4</sub>. All the solutions contained 3 M (Na)ClO<sub>4</sub> as the ionic medium. The emf was measured with a calibrated glass-electrode and the same reference bridge as before



For this cell

$$E = E^\circ - 59.15 \log h - E_j \text{ or}$$

$$E' = E + E_j = E^\circ - 59.15 \log h$$

$$E_j = -16.7 \times 10^{-6} h \text{ according to Biedermann and Sillén.}^{19}$$

A known starting volume,  $v_0$  ml, of the metal salt solution with the unknown hydrogen concentration,  $H_0$  M, was titrated with  $v$  ml  $H$  M HClO<sub>4</sub>. If  $v_e$  denotes the volume at the equivalence point we get

$$h = 10^{(E^\circ - E')/59.15} = \frac{v_0 H_0 + vH}{v_0 + v} = H \frac{v + v_e}{v_0 + v} \text{ or}$$

$$(v_0 + v) 10^{-E'/59.15} = 10^{-E^\circ/59.15} H(v + v_e)$$

Plotting  $(v_0 + v) 10^{-E'/59.15}$  against  $v$  we get a straight line which, when extrapolated to  $(v_0 + v) 10^{-E'/59.15} = 0$  gives  $v = -v_e$ . After that  $H_0$  is calculated from  $H_0 = v_e H / v_0$ .

From measurements of the HAc-Ac-system in 3 M (Na)ClO<sub>4</sub> the dissociation constant of HAc was calculated. As a mean value  $1.0 \times 10^{-5}$  M was obtained.

*Apparatus.* The measurements were performed in a paraffin oil thermostat at  $25.0^\circ \pm 0.1^\circ\text{C}$  using the electrode vessels and salt bridge designed by Forsling, Hietanen and Sillén.<sup>17</sup> The amalgam emf was measured to  $\pm 0.01$  mV by a Leeds and Northrup potentiometer type K-3, used in combination with the Leeds and Northrup galvanometer type 2430 and a saturated Weston cell as the standard cell.

The glass electrode emf was read on a Radiometer valve potentiometer PHM 4, reading accuracy  $\pm 0.2$  mV. A Beckman glass electrode (nr 1190-80) calibrated as described by Olin<sup>20</sup> was used. The nitrogen passed through the solutions in the titration vessel during the emf measurements was taken from a steel flask, and was led at room temperature through a tube<sup>21</sup> containing activated copper, a product of BASF called BTS-catalysator, in order to remove oxygen. The gas was further purified by passing through wash-bottles containing 10 %  $\text{H}_2\text{SO}_4$  and 10 % NaOH and was finally bubbled through 3 M  $\text{NaClO}_4$  to obtain the correct water vapor pressure.

*Chemicals.* Sodium perchlorate was prepared by neutralizing  $\text{Na}_2\text{CO}_3$  (Merck p.a.) with  $\text{HClO}_4$  (Merck p.a.) following the directions given in Ref.<sup>22</sup> The stock solution was analysed by evaporating a known weight of solution and weighing the residue as  $\text{NaClO}_4$ .

Perchloric acid solutions were prepared from  $\text{HClO}_4$  p.a. (ca. 70 %) and standardized against standard NaOH.

Lead(II) perchlorate solutions were prepared by dissolving PbO (Baker p.a.) in  $\text{HClO}_4$  (Merck p.a.) in the way described by Olin.<sup>23</sup> The lead was determined as lead sulfate by precipitating with  $\text{H}_2\text{SO}_4$ <sup>24</sup> or by evaporating known quantities with 20 %  $\text{H}_2\text{SO}_4$ .

Lead amalgam was prepared by dissolving bright lead metal (Merck silberfrei) in mercury. The concentration of lead in the amalgam was 4 % (weight). The amalgam was stored under ca. 20 mM  $\text{HClO}_4$ .

Sodium acetate,  $\text{NaCH}_3\text{COO} \cdot 3\text{H}_2\text{O}$  (Merck p.a.). Measuring series made with solutions of sodium acetate recrystallised from water gave the same result as solutions of nonrecrystallised sodium acetate. The sodium was determined as NaCl by evaporating a known amount with HCl.

## CALCULATIONS AND RESULTS

Using the method of Fronæus<sup>25</sup> it was found as a preliminary result that polynuclear complexes did not seem to be present. Neglecting the liquid junction potential eqn. (2) may be written

$$E = E^\circ - 29.577 \log [\text{Pb}^{2+}] \quad (3)$$

and we write

$$E_0 = E^\circ - 29.577 \log c_{\text{Pb}} \quad (4)$$

when S (1) is the starting solution. Thus

$$E' = E - E_0 = 29.577 \log \frac{c_{\text{Pb}}}{[\text{Pb}^{2+}]} \quad (5)$$

The values of  $c_{\text{Ac}}$  were plotted against  $E'$  with  $c_{\text{Pb}}$  as parameter, after which it was possible to plot  $c_{\text{Ac}}$  as a function of  $c_{\text{Pb}}$  with  $E'$  as parameter. Straight lines of the form

$$c_{\text{Ac}} = [\text{Ac}^-] + \bar{n} c_{\text{Pb}} \quad (6)$$

were obtained for every value of  $E'$ .

Thus assuming only mononuclear species to be present in the solutions investigated, the complex formation can be written



The system is then defined by the complexity constants

$$\beta_n = \frac{[\text{PbAc}_n^{(n-2)-}]}{[\text{Pb}^{2+}][\text{Ac}^-]^n}, \quad 1 \leq n \leq N \quad (8)$$

The total lead content  $c_{\text{Pb}}$  is

$$c_{\text{Pb}} = [\text{Pb}^{2+}] \left( 1 + \sum_1^N \beta_n [\text{Ac}^-]^n \right) \quad (9)$$

Introducing, according to Leden's method<sup>16</sup>

$$F_0(\text{Ac}^-) = c_{\text{Pb}}/[\text{Pb}^{2+}] \quad (10)$$

and inserting (9) we get

$$F_0(\text{Ac}^-) = 1 + \sum_1^N \beta_n [\text{Ac}^-]^n \quad (11)$$

$F_0(\text{Ac}^-)$  was calculated from (5)

$$F_0(\text{Ac}^-) = 10^{E'/29.577}$$

The coefficients  $\beta_n$  were then obtained graphically by forming

$$F_1(\text{Ac}^-) = \frac{F_0(\text{Ac}^-) - 1}{[\text{Ac}^-]} = \sum_1^N \beta_n [\text{Ac}^-]^{n-1}$$

from which  $\beta_1$  was obtained as the intercept on the ordinate axis by extrapolating  $F_1(\text{Ac}^-)$  to  $[\text{Ac}^-] = 0$ , and  $\beta_2$  as the slope. This procedure was repeated, and for  $F_3(\text{Ac}^-) = (F_2(\text{Ac}^-) - \beta_2)/[\text{Ac}^-]$  a straight line  $F_3(\text{Ac}^-) = \beta_3 + \beta_4[\text{Ac}^-]$  was obtained, indicating that the four mononuclear complexes  $\text{PbAc}^+$ ,  $\text{PbAc}_2$ ,  $\text{PbAc}_3^-$ ,  $\text{PbAc}_4^{2-}$  were present. As  $[\text{Ac}^-]$  was not known from the measurements, this way of calculation could be applied directly only to the titration series where  $c_{\text{Pb}}$  was small and thus  $[\text{Ac}^-] \approx c_{\text{Ac}}$ . The estimated values of the complex constants obtained in this way were then refined by a generalized least square method using a Ferranti-Mercury computer and the "Letagrop Vrid"<sup>4</sup> program, a development of the "Letagrop" program.<sup>2,3</sup> In the head program, HP, chapter 1-5 could directly be used, chapter 0 was divided into one part containing operations applicable under rather general conditions, and a special program, SP, devised for this actual problem (Table 2). The data needed for the calculations are punched in two strips. The first includes the number of titration series; the number of measuring points in each series;  $E_0$  ( $E_5$ );  $c_{\text{Pb}}$  ( $B_1$ );  $c_{\text{Ac}}$  ( $U_k$ );  $E$  ( $Z_k$ ). The letters bracketed are the symbols in the computer language. Table 3 gives  $c_{\text{Ac}}$  and  $E$  for the five titration series. On the second data strip the guessed values of the constants, the number of the constants we want to vary, the steps ( $h_i$ ) these are to be varied in, and a number of  $s_{ik}$ -terms are punched. If  $N$  constants are to be varied  $N(N-1)/2$  number of  $s_{ik}$ -terms must be inserted. For the explanation of the  $h_i$  and  $s_{ik}$ -terms see below.

With the assumption that the system could be explained by (7) for  $n = 1, 2, 3, 4$ , the computer calculated the  $[\text{Ac}^-]$  using the "Kuska loop"<sup>3</sup> that is found in chapter 0. The principle is as follows. From a starting guessed value of  $[\text{Ac}^-]$  the computer calculates  $c_{\text{Ac calc}}$  from

Table 2. LETAGROP VRID. Chapter 0.

- Chapter 0; Variables 1; Title; Satsvis 1;  $H = \Psi \log(10)$ ;  $i = 0$ ;  $F = 0$ ;  
 Jump 17,  $t = 8$ ; Jump 1;  
 2) Read ( $s$ ); Print ( $s$ ) 2, 0;  $A_{13} = s + 0.1$ ; Newline;  $q = 0$ ;  $i = 0$ ;  
 30)  $i = i + 1$ ;  $F_i = q + 1 + 0.1$ ; Print ( $F_i$ ) 2,0; Read ( $j$ );  $F(i + 20) = q + j + 0.1$ ;  
 Print ( $q + j$ ) 2,0; Print ( $j$ ) 2,0; Jump 31;  
 32)  $k = 1(1)j$ ;  $o = q + k$ ; Read ( $U_o$ ); Read ( $Z_o$ ); Repeat;  $q = q + j$ ; Jump 30,  $s > i$ ;  
 $D_{13} = q + 0.1$ ; Across 1/4;  
 3)  $X = 0$ ;  $F_0 = 0$ ;  $k = p$ ; Jump 16;  
 6)  $V = D$ ;  $G = 2$ ;  $E_0 = EB$ ; Jump 7;  
 8)  $D_0 = \Psi \text{mod}(B_0 - B)$ ; Jump 10,  $E_0 > D_0$ ; Jump 9,  $B > B_0$ ;  $G = 0.5$ ;  $D = GD$ ;  
 $V = V - D$ ; Jump 7;  
 9)  $D = GD$ ;  $\bar{V} = V + D$ ; Jump 7;  
 14)  $W = Z_0 - Z_k$ ; Jump 11,  $t = 0$ ;  
 12)  $X = X + G_0 WW$ ;  $F_0 = F_0 + G_0$ ;  $k = k + 1$ ; Jump 13,  $k > q$ ; Jump 5,  $F > 5$ ;  
 Jump 19,  $k > s$ ; Jump 5;  
 15) Across 1/1;  
 18) Jump 13,  $t = 3$ ; Jump 25,  $F > 5$ ;  $q = \Psi \text{intpt}(D_{13})$ ;  $o = 0$ ;  
 $o = o + 1$ ;  $s = \Psi \text{intpt}(F_{o+20})$ ;  $E_{(n+1)} = F_{(o+40)}$ ; Jump 25;  
 20) Jump 23,  $F > 5$ ;  $r = 1$ ;  $G_1 = n + 1$ ; Read ( $H_1$ );  $\Psi_7(361)H_1$ , 1;  $F = 10$ ;  $o = 0$ ;  
 21)  $o = o + 1$ ;  $s = \Psi \text{intpt}(A_{13})$ ; Jump 24,  $o > s$ ;  $p = \Psi \text{intpt}(F_o)$ ;  $q = \Psi \text{intpt}(F_{(o+20)})$ ;  
 $E_{(n+1)} = F_{(o+40)}$ ;  $\Psi_7(301)E_{(n+1)}$ , 1; Newline;  $t = 1$ ; Jump 3;  
 23)  $F_{(o+40)} = E_{(n+1)}$ ; Jump 21;  
 24)  $F = 0$ ; Across 2/4;  $\rightarrow$ ;  
 SP  
 1) Title; Blyacetat; Newline; Jump 2;  
 16) Print ( $E_1$ )0,3; Print ( $E_2$ )0,3; Print ( $E_3$ )0,3; Print ( $E_4$ )0,3; Jump 18,  $5 > F$ ;  
 Print ( $E_5$ )3,2; Jump 18;  
 25)  $B_1 = F_{(o+60)}$   
 5)  $B = U_k$ ;  $D = 0.001$ ; Jump 6;  
 7)  $C_1 = E_1 V$ ;  $C_2 = E_2 VV$ ;  $C_3 = E_3 VVV$ ;  $C_4 = E_4 VVVV$ ;  $W = 1 + C_1 + C_2 + C_3 + C_4$ ;  
 $Y = C_1 + 2C_2 + 3C_3 + 4C_4$ ;  
 $B_0 = \bar{V} + B_1 Y/W$ ; Jump 8;  
 10)  $Y = \Psi \log(W)$ ;  $Z_0 = E_5 + 29.577 Y/H$ ;  $G_0 = 1$ ; Jump 14;  
 11) Newline; Print ( $k$ ) 2,0; Print ( $U_k$ )0,3; Print ( $Z_k$ )0,3; Print (100W)2,1;  
 Jump 12;  
 13) Print ( $X$ ) 0,5; Newline; Jump 15,  $t = 1$ ;  
 17) Across 2/4;  
 31) Read ( $W$ ); Print ( $W$ ) 3,2;  $F_{(i+40)} = W$ ; Read ( $W$ ); Print ( $W$ ) 0,3;  
 $F_{(i+60)} = W$ ; Newline; Jump 32;  $\Psi_{\text{exp}}$ ; close;  $\rightarrow$ ;

$$c_{\text{Ac calc}} = [\text{Ac}^-] + c_{\text{Pb}} \bar{n} = [\text{Ac}^-] + c_{\text{Pb}} \frac{\sum_1^4 n \beta_n [\text{Ac}^-]_n}{1 + \sum_1^4 \beta_n [\text{Ac}^-]_n} \quad (12)$$

The graphically estimated values of  $\beta_n$  were inserted.  $[\text{Ac}^-]$  is then systematically varied till a value of  $c_{\text{Ac calc}}$  is found that fulfills the condition

$$|c_{\text{Ac exp}} - c_{\text{Ac calc}}| \leq 0.00001 c_{\text{Ac exp}} \quad (13)$$

Starting with  $[\text{Ac}^-]$  equal to a correction term, 0.001 M, double this term is added to  $[\text{Ac}^-]$  until (13) is fulfilled or else until  $c_{\text{Ac calc}} > c_{\text{Ac exp}}$ . In the latter case the correction term is halved at each turn and is subtracted or added to  $[\text{Ac}^-]$ , depending on whether  $c_{\text{Ac calc}}$  is larger or less than  $c_{\text{Ac exp}}$ . When the desired adjustment is arrived at,  $E_{\text{calc}}$  is obtained from (3), (4), (10), and (11)

Table 3. The corresponding values of  $c_{Ac\ exp}$  and  $E$  for the lead(II)acetate system.

$c_{Pb} = 2.000\text{ mM}$ $E_0 = 882.04\text{ mV}$		$c_{Pb} = 2.000\text{ mM}$ $E_0 = 883.27\text{ mV}$		$c_{Pb} = 2.000\text{ mM}$ $E_0 = 882.36\text{ mV}$		$c_{Pb} = 25.00\text{ mM}$ $E_0 = 849.83\text{ mV}$		$c_{Pb} = 50.0\text{ mM}$ $E_0 = 840.88\text{ mV}$	
$c_{Ac\ exp}$ mM	$E\text{ mV}$	$c_{Ac\ exp}$ mM	$E\text{ mV}$	$c_{Ac\ exp}$ mM	$E\text{ mV}$	$c_{Ac\ exp}$ mM	$E\text{ mV}$	$c_{Ac\ exp}$ mM	$E\text{ mV}$
1.513	884.99	7.23	894.56	31.9	912.89	1.205	850.36	2.308	841.30
3.95	888.88	23.19	908.69	47.9	920.17	3.64	851.44	4.74	841.89
6.35	892.22	30.9	913.27	63.7	925.79	8.38	853.76	9.34	843.12
8.70	895.06	46.0	920.29	94.5	934.20	12.94	856.14	11.60	843.70
13.20	899.77	60.5	925.64	124.6	940.51	17.34	858.54	16.00	844.98
17.66	903.51	88.0	933.49	153.6	945.50	25.67	863.21	20.24	846.26
21.90	906.62	113.5	939.22	181.9	949.67	27.66	864.31	24.33	847.52
25.99	909.27	137.4	943.69	209.3	953.20	33.4	867.51	28.27	848.82
29.93	911.54	159.7	947.33	248.9	957.71	40.7	871.30	32.1	850.11
33.7	913.58	200.3	952.97	286.9	961.46	47.4	874.62	39.3	852.66
41.0	917.01	218.8	955.25	335	965.71	53.8	877.55	46.1	855.11
47.7	919.85	236.2	957.22	381	969.28	59.7	880.10	52.4	857.48
54.1	922.26	268.3	960.58	424	972.36	65.3	882.33	58.7	859.81
60.0	924.31	297.0	963.30	486	976.25	70.6	884.33	69.3	863.75
65.7	926.11	323	965.60	542	979.50	80.4	887.73	79.0	867.31
70.9	927.72	347	967.54	595	982.30	89.1	890.48	87.7	870.32
80.7	930.42	368	969.20	645	984.74	97.0	892.84	95.6	872.89
89.4	932.65	406	971.94	706	987.52	104.1	894.81	102.7	875.14
97.3	934.50	438	974.10	775	990.49	110.6	896.50	109.3	877.08
104.4	936.12	465	975.88	850	993.43				
110.9	937.50	489	977.35	927	996.28				
		510	978.57	1021	999.51				
				1102	1002.10				
				1202	1005.08				
				1284	1007.38				

$$E_{\text{calc}} = E_0 + 29.577 \log \left( 1 + \sum_1^4 \beta_n [\text{Ac}^-]^n \right)$$

and the error square sum

$$U = \sum_i (E_{\text{calc}} - E_{\text{exp}})^2 \tag{14}$$

is calculated for all points.

$U$  is approximated to a second degree function of the  $\beta_n$ . Inserting  $x_n = \beta_n - \beta_n'$ , where  $\beta_n'$  ( $n = 1, 2, 3, 4$ ) denotes a fixed set of the constants — in the first run the graphically estimated values — and  $\beta_n$  the constants now considered as variables,  $U$  may be written

$$U = c_0 + 2 \sum_n c_{0n} x_n + \sum_n \sum_m c_{nm} x_n x_m, \quad (n, m = 1, 2, 3, 4) \tag{15}$$

Eqn. (15) contains  $(N + 1)(N + 2)/2$  unknown constants  $c_0$ ,  $c_{0n}$  and  $c_{nm}$ , where  $N$  is the number of variables. To calculate these fifteen constants, as many values of  $U$  were calculated from (14), by varying the  $x_n$  in steps of  $h_n$ . In the first run the  $h_n$  values were guessed, after that the steps were changed to a fourth of the calculated "standard deviation" of the constants. The set of constants,  $\beta_n = \beta_n''$ , that minimizes  $U$  is searched for. This is equivalent to  $x_n = x_n''$ . The conditions for  $U$  to have a minimum are

$$\frac{\partial U}{\partial x_n} = 0 \text{ or } \sum_m x_n'' c_{nm} + c_{0n} = 0 \quad (n, m = 1, 2, 3, 4)$$

From this linear equation system the computer calculates the "best" values

$$x_n'' = -\sum_m c_{0m} C_{nm} C^{-1}; \quad \beta_n'' = \beta_n' + x_n''$$

$C$  is the determinant of the matrix  $[c_{nm}]$ , and  $C_{nm}$  the subdeterminant of  $c_{nm}$ .

$$U_{\min} = U_0 = c_0 + \sum_1^4 c_{0n} x_n''$$

is calculated and after that the "standard deviation" of the measured emf,  $\sigma_E$ , according to

$$\sigma_E = \sqrt{\frac{U_0}{i - N}}$$

Here  $i$  denotes the number of experimental points, and  $N$  the number of unknown constants. The "standard deviations" of the complex constants,  $\sigma_{\beta_n}$ , are obtained from the maximum values of the  $x_n$  in the function

$$U = U_0 + \sigma_E^2 = U_0 + \sum_n \sum_m x_n x_m c_{nm} \quad (16)$$

Differentiating (16) and solving the obtained equation system gives

$$\sigma_{\beta_n} = (x_n)_{\max} = \sigma_E \sqrt{\frac{C_{nn}}{C}}$$

The computer calculates the  $s_{ik}$ -terms determined by the condition that the coefficients of the mixed  $x_n x_m$ -terms in (15) equal 0. After this coordinate transformation another  $\sigma_{\beta_n}$  is calculated. The unknown  $s_{ik}$ -terms are from the beginning set = 0. The computer then replaces these by the calculated values, exchanges the graphically estimated constants with the found  $\beta_n''$ , and repeats the whole procedure from (12) until constant values of the  $\beta_n''$  are obtained. Inserting the  $s_{ik}$ -terms in the variation of  $x_n$ , increases the chance to fall within the region where the approximation of  $U$  with a second-degree function is valid, and may thus lead to a quicker determination of the final  $\beta_n''$ . When these were fixed, the  $E_0$  in (4) of each titration series was regarded as a variable, and the cycle was repeated from (12). The procedure was repeated alternately with  $\beta_n$  and  $E_0$  as variables until they became constant. Finally the computer printed the difference  $E_{\text{calc}} - E_{\text{obs}}$ .

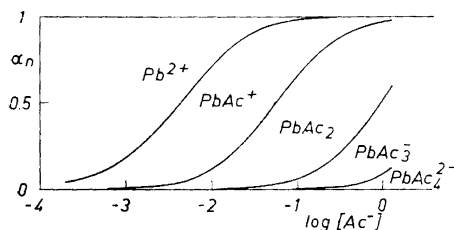


Fig. 1. The distribution of the lead in the different complexes as a function of the logarithm of the free acetate concentration. The curves have been calculated according to (18) with the potentiometric constants in (17).



The calculation gave the following complexity constants

$$\begin{aligned}\beta_1 &= (214 \pm 1) \text{ M}^{-1} \\ \beta_2 &= (3985 \pm 24) \text{ M}^{-2} \\ \beta_3 &= (3848 \pm 112) \text{ M}^{-3} \\ \beta_4 &= (736 \pm 117) \text{ M}^{-4}\end{aligned}\quad (17)$$

The assigned errors are calculated as  $3\sigma_{\beta_n}$  using the largest value of the two calculated  $\sigma_{\beta_n}$  for each constant. Only random errors and not systematical ones have been considered.  $\sigma_E = 0.06$  mM.

The maximum variation of  $E_0$  from their starting values was 0.05 mV. The distribution of the lead in the different complexes as a function of the logarithm of the free acetate concentration is shown in Fig. 1. The distribution has been calculated according to

$$a_n = \frac{\beta_n [\text{Ac}^-]^n}{1 + \sum_n \beta_n [\text{Ac}^-]^n}, \quad n = 1, 2, 3, 4 \quad (18)$$

*Acknowledgements.* I wish to express my sincere thanks to the head of this Institute, Professor Cyrill Brosset, for his great interest in this work, and for all the facilities put at my disposal. I am greatly indebted to Professor Lars Gunnar Sillén and Dr. Nils Ingri for introducing me to automatic computing, applied to the least square method, and for valuable help in carrying out the calculations. I also want to thank Professor Sillén for letting me participate in the great experience of complex chemistry in his Institute, and especially I wish to thank Docent Åke Olin for all the invaluable help he gave me in the experimental parts of this work.

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Received May 17, 1963.