

The Complex Formation in the Lead(II) Ethoxyacetate System

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The formation of complexes between the lead(II) ion and the ethoxyacetate ion in aqueous solution has been studied at 25.0°C by two independent experimental methods, *viz.* determination of the concentration of free central ion and of free ligand.

Both methods showed the formation of three mononuclear complexes. No polynuclear complexes were found. The following gross stability constants were calculated: central ion measurements: $\beta_1 = (52 \pm 1) \text{ M}^{-1}$, $\beta_2 = (440 \pm 40) \text{ M}^{-2}$, $\beta_3 = (530 \pm 260) \text{ M}^{-3}$, ligand measurements: $\beta_1 = (53 \pm 1) \text{ M}^{-1}$, $\beta_2 = (460 \pm 20) \text{ M}^{-2}$, $\beta_3 = (400 \pm 200) \text{ M}^{-3}$.

The constants refer to an ionic strength of 1.0 M (sodium perchlorate).

In an earlier investigation¹ it was found that the copper(II) ion forms stronger complexes with the methoxyacetate and the ethoxyacetate ions than with the acetate ion. Since these alkoxyacetate ions are considerably weaker bases than the acetate ion, it should be reasonable to ascribe the greater stability of the alkoxyacetate complexes to a certain degree of chelation. The same conclusion is drawn by Dillon and Rossotti² from the results of investigations of quite different character.

The investigations^{3,4} of the lead(II) acetate system seem to show that the complex formation in this system is comparatively strong, the first mononuclear complex having a stability constant of about 10^2 M^{-1} . No investigation, however, seems to have been published so far on the complex formation in the lead(II) ethoxyacetate system.

In the present investigation the complex equilibria between the lead(II) ion and the ethoxyacetate ion have been studied by means of two electrometric methods. One method is based on direct determination of the concentration of free lead(II) ion in the complex solutions by means of lead amalgam. The other method involves indirect determination of the concentration of free ligand by measuring the hydrogen ion concentration in ligand buffer solutions. These methods are well established and are applied here following closely the principles proposed by Leden⁵ and Fronæus.⁶

CALCULATIONS

The stability constants have been calculated from the experimental data by the graphical method of Fronæus,⁶ as summarized in Refs. 1 and 7. The data from the central ion measurements were also treated by the fast computer method earlier presented.⁸

The following notations are used in the present paper.

C_M	= total concentration of Pb^{2+} -ion
$[M]$	= concentration of free Pb^{2+} -ion
α	= proportionality factor. The concentration of perchloric acid in the lead(II) perchlorate solution is $\alpha \cdot C_M$
C_L'	= stoichiometric total concentration of ligand L
C_L	= corrected total concentration of ligand L
δ	= buffer quotient in the ligand buffer. The stoichiometric concentration of the acid HL is $\delta \cdot C_L'$
$[L]$	= concentration of free ligand
K_a	= $[H_3O^+] \cdot [L]/[HL]$
N	= maximum coordination number
β_n	= $[ML_n]/[M][L]^n$ = gross stability constant
K_n	= $[ML_n]/[ML_{n-1}][L]$ = stepwise stability constant
X	= $C_M/[M] = 1 + \sum_{n=1}^N \beta_n [L]^n$
X'	= $dX/d[L]$
\bar{n}	= $(C_L - [L])/C_M$ = the ligand number
$\bar{n}/[L]$	= X'/X
$\ln X([L]_j)$	= $\int_0^{[L]_j} (\bar{n}/[L]) \cdot d[L]$
X_i	= $(X_{i-1} - \beta_{i-1})/[L]$; ($1 \leq i \leq N$; $X_0 = X$; $\beta_0 = 1$)
h_m and h_0	= $[H_3O^+]$ in solutions with the same C_L' -value, h_0 referring to a solution with $C_M = 0$
h_R	= $[H_3O^+]$ in a reference buffer
E_0	= $59.16 \log (h_0/h_R)$ mV
E_m	= $59.16 \log (h_m/h_R)$ mV
E_L	= $E_m - E_0 = 59.16 \log (h_m/h_0)$ mV
E'	= emf in mV of cell (1) with $C_L' = 0$
E''	= emf in mV of cell (1) with $C_L' > 0$
E_M	= $E'' - E' = 29.58 \log X$
RE	= Ag/AgCl reference electrode with $I = 1.000$ M ($NaClO_4$) including a salt bridge with 1.000 M $NaClO_4$.

EXPERIMENTAL

Chemicals

The *lead(II) perchlorate* was supplied by G. Frederick Smith. No foreign anions or cations could be detected in the preparation. By potentiometric titration, however, a certain deficit of free acid was observed. To compensate for this, a small amount of HClO_4 was added in preparing the stock solution. The concentration of Pb^{2+} -ions in the stock solution was determined to (0.333 ± 0.001) M by titration with EDTA using xylenol-orange as indicator.⁹

Sodium perchlorate was prepared from perchloric acid *p.a.*, sodium carbonate *p.a.*, and sodium hydroxide. Special care was taken to eliminate protolytic impurities. In a 1.000 M solution of the salt the concentration of protolytic impurities was found to be less than about 3×10^{-6} M. This small concentration was neglected in the calculations.

The *ethoxyacetic acid* preparation supplied by Eastman Organic Chemicals was yellow and its equivalent weight was too high. The pure substance was obtained by repeated vacuum distillation. Buffer solutions were made from the pure acid and carbonate free sodium hydroxide. The buffers were analysed by means of a cation exchange resin in the hydrogen form.

A two-phase *lead amalgam*, 3.1 % by weight, was made by electrolysing a solution of lead(II) nitrate *p.a.* with mercury *p.a.* as cathode. The amalgam was stored in a special funnel constructed to prevent lead oxide following the amalgam into the titration vessel. All other chemicals used were of analytical grade.

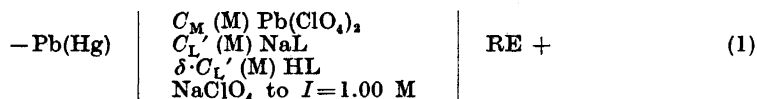
Method

At higher pH-values the hydrolysis of the lead(II) ion is considerable.¹⁰ To avoid this effect, the measurements were done in buffers of ethoxyacetate and its corresponding acid.

The measurements were carried out as potentiometric titrations. In a titration C_L' was varied and C_M was kept constant.

The temperature of the cells was kept at $(25.00 \pm 0.05)^\circ\text{C}$ by means of a water thermostat.

The central ion measurements. The emf of the following galvanic cell was measured.



The solutions were swept by a stream of oxygen-free nitrogen to prevent oxidation of the amalgam. After some of the titrations the total concentration of lead(II) in the complex solution was determined by means of EDTA.⁹ The results showed that C_M really was constant during a titration.

A Norma potentiometer with a Kipp en Zonen Galvanometer as zero instrument was used to measure the emf with a precision of 0.01 mV.

The emf reached a stable value almost instantaneously after addition of a portion of the titrant, provided the nitrogen stream was swift enough to cause thorough mixing. The difference between the E_M -values obtained in repeating the titrations had a mean value of 0.03 mV and never exceeded 0.09 mV. Occasionally the emf was checked for 2 h, during which time it remained perfectly constant.

The ligand measurements. In these measurements the complex solution had the same general composition as in cell (1). With this solution, denoted by S, the cell was

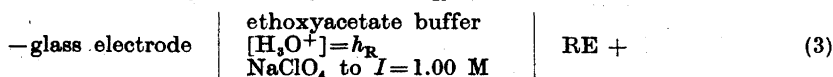


A Jena Type U glass electrode was used, which was found to have the theoretical slope in the actual pH-region. The emf was read by a Radiometer PHM 4 potentiometer.

The emf reached its final value within a few minutes after addition of titrant. The solutions were mixed by means of a magnetic stirrer. The emf was not affected by reasonable changes of the speed of the stirrer.

The maximum difference between the four emf-values obtained in solutions mixed to be identical, only seldom exceeded 0.1 mV. Thus the experimental reproducibility was the same as the precision of the voltmeter.

Before and after each titration the constancy of the asymmetry potential of the glass electrode was checked by measuring the emf E_R of the cell



MEASUREMENTS AND RESULTS

The lead(II) perchlorate. The concentration of perchloric acid in the lead(II) perchlorate stock solution was determined by the experimental technique described earlier.¹ The calculation of α , however, was done by plotting $\exp(E/25.69)$ against c^{-1} . (The notations are the same as in Ref. 1 and the measurements were performed at 25°C.) In agreement with theory, this plot was found to be a straight line. By application of the least squares principle, α was found to be

$$\alpha = (1.70 \pm 0.01) \times 10^{-2}$$

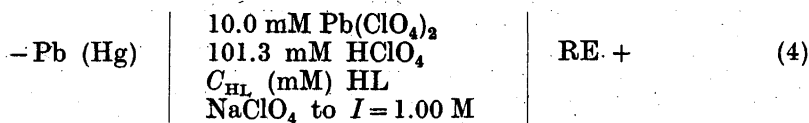
where the stated error is 3 times the calculated estimate of the standard deviation.

The central ion investigation. To check the amalgam the emf of the cell (1) was measured with $C_L' = 0$. C_M had the values to be used in the main investigation. E° was calculated from $E^\circ = E' + 29.58 \log C_M$ (C_M in M). The variation of the E° -values was not greater than the corresponding uncertainty of the C_M -values.

Results: C_M (mM), pH, E° (mV); 5.0, 3.2, 489.74; 10.00, 3.2, 489.78; 15.00, 3.2, 489.80; 5.0, 4.1, 489.69; 10.00, 3.8, 489.78; 15.00, 3.6, 489.77.

During the main part of the investigation the amalgam storage vessel was air thermostated at 24.5°C. The E° -value from these investigations was 489.84 mV with a maximum deviation of 0.05 mV. Heating the amalgam storage vessel to secure two-phase amalgam in the electrode vessel resulted in $E^\circ = (490.00 \pm 0.04)$ mV.

To find out if the emf was dependent on the concentration of free ethoxyacetic acid, the emf of the cell (4) was measured.



For 9 different C_{HL} -values in the region $0 \leq C_{\text{HL}} \leq 207$ mM the emf-readings were scattered at random within an interval of 0.04 mV. The same result was obtained by repeating the titration. Thus it was found that the emf of the cell was independent of the concentration of free ethoxyacetic acid.

In the calculations the value $K_a = 3.08 \times 10^{-4}$ M was used for the acid constant of the ethoxyacetic acid.⁸

Table 1. Corresponding values of C_L and E_M (mean value) in the lead(II) ethoxyacetate system.

$C_M=15.00$ mM		$C_M=10.00$ mM		$C_M=5.00$ mM	
C_L (mM)	E_M (mV)	C_L (mM)	E_M (mV)	C_L (mM)	E_M (mV)
2.95	1.20	3.03	1.40	3.10	1.66
5.17	2.06	5.25	2.38	5.33	2.80
8.71	3.40	8.79	3.88	8.87	4.50
12.04	4.64	12.12	5.24	12.20	6.00
15.17	5.78	15.25	6.48	15.33	7.35
18.69	7.02	18.78	7.81	18.86	8.77
21.98	8.18	22.07	9.04	22.68	10.24
26.06	9.55	26.15	10.46	26.23	11.54
29.81	10.78	29.90	11.74	29.98	12.83
34.1	12.14	34.2	13.14	34.3	14.23
38.0	13.33	38.1	14.34	38.2	15.47
41.9	14.48	42.6	15.69	42.4	16.74
47.8	16.18	47.9	17.22	48.0	18.34
52.4	17.46	52.5	18.56	53.2	19.91
57.6	18.86	57.7	19.94	59.1	21.44
63.4	20.32	63.5	21.40	65.6	23.00
70.4	21.98	70.5	23.04	72.5	24.56
76.5	23.40	77.3	24.56	79.8	26.18
82.6	24.70	83.8	25.97	87.5	27.76
89.6	26.18	90.9	27.42	95.5	29.32
97.0	27.68	98.8	28.92	103.9	30.89
104.8	29.16	107.6	30.54	112.5	32.39
112.8	30.62	116.5	32.13	121.8	33.96
121.1	32.08	125.7	33.64	131.7	35.57
129.6	33.49	135.5	35.24	142.2	37.18
138.7	34.98	145.4	36.74	153.1	38.78
148.4	36.48	155.7	38.28	164.4	40.35
158.6	37.98	166.4	39.79	175.9	41.90
169.2	39.51	177.4	41.28	187.9	43.43
180.0	40.97	188.9	42.79	200.7	45.00
191.1	42.42	201.3	44.32	214.4	46.60
202.3	43.84	214.6	45.91	228.1	48.16
213.9	45.24	227.4	47.36	242.9	49.74
226.4	46.70	239.9	48.76	259.1	51.40
239.8	48.21	253.7	50.24	273.9	52.89
256.3	49.98	266.6	51.56	287.5	54.18
270.1	51.42	278.5	52.74	300	55.37
284.0	52.80	289.6	53.82	317	56.88
299.8	54.35	300	54.82	335	58.40
321	56.32	317	56.34	353	59.96
342	58.17	335	57.90	372	61.56
366	60.19	353	59.48	391	63.03
390	62.11	372	61.07	411	64.52
413	63.93	391	62.62	431	65.97
435	65.58	411	64.12	452	67.52
459	67.38	431	65.60	476	69.18
484	69.11	452	67.18	500	70.76
511	70.96	476	68.88	523	72.29
542	72.96	500	70.50	549	73.93
573	74.94	523	72.05	573	75.48

Table 2. Some values from the graphical determination of [L] in the lead(II) ethoxyacetate system.

E_M (mV)	C_L (mM) for $C_M =$			
	15.00 mM	10.00 mM	5.00 mM	0
3	7.64	6.67	5.74	4.78
6	15.75	14.02	12.20	10.44
9	24.40	21.98	19.43	16.99
12	33.7	30.7	27.5	24.4
15	43.6	40.2	36.7	33.3
18	54.4	50.5	46.6	42.7
21	66.2	61.8	57.4	53.0
24	79.3	74.8	70.0	65.4
27	93.6	88.9	83.7	78.9
30	109.4	104.6	99.0	94.0
33	126.7	121.7	116.0	110.7
36	145.2	140.4	134.5	129.5
39	165.7	160.7	154.7	149.5
42	188.0	183.0	177.0	172.0
45	212.0	207.0	201.0	196.0
48	238	233	227	222
51	266	261	256	250
54	296	292	286	282
57	329	324	319	314
60	364	360	354	349
63	401	396	390	386
66	440	436	431	427
69	482	478	474	470
72	527	522	518	514

The experimental results are collected in Tables 1 and 2.

The stability constants were calculated both graphically and numerically.⁸ In the graphical determination the errors were estimated subjectively. The errors assigned to the numerically calculated constants are 95 % confidence limits.

	Graphical	Numerical
β_1 (M ⁻¹)	53 ± 1	52 ± 1
β_2 (M ⁻²)	430 ± 20	440 ± 40
β_3 (M ⁻³)	550 ± 200	530 ± 260
β_4 (M ⁻⁴)	800 ± 400	800 ± 400

The ligand investigation. The main part of this investigation was performed with a buffer with $\delta = 0.215$. The experimental results are collected in Table 3.

Measurements were also made at $C_M = 40$ mM with a buffer with $\delta = 0.492$ in order to find out whether $\bar{n}/[L]$ was dependent on the concentration of free ethoxyacetic acid. As can be seen from Fig. 1 no such dependence was found. This indicates that no complexes are formed between the lead(II) ion and the free ethoxyacetic acid.

Table 3. Corresponding values of [L] and $\bar{n}/[L]$ in the lead(II) ethoxyacetate system. The values of E_0 refer to $h_R = 6.0 \times 10^{-5}$ M.

$C_{L'}$ mM	E_0 mV	$C_M = 60$ mM			$C_M = 40$ mM			$C_M = 20$ mM		
		E_L mV	[L] mM	$\frac{\bar{n}}{[L]}$ M ⁻¹	E_L mV	[L] mM	$\frac{\bar{n}}{[L]}$ M ⁻¹	E_L mV	[L] mM	$\frac{\bar{n}}{[L]}$ M ⁻¹
1.471	-2.5	66.1	0.277	53.4	53.9	0.395	53.1	35.3	0.651	53.5
1.948	-1.1	62.6	0.379	53.0	50.4	0.539	52.8	32.2	0.884	52.4
2.419	-0.2	60.1	0.479	53.6	47.9	0.681	53.0	30.1	1.114	51.9
2.885	0.4	58.0	0.583	53.3	45.8	0.831	52.2	28.5	1.347	51.3
3.80	1.1	54.8	0.794	52.8	42.9	1.122	51.9	26.3	1.807	50.5
5.12	1.8	51.4	1.113	51.9	39.8	1.570	50.5	24.1	2.50	48.9
6.40	2.1	49.2	1.420	51.7	37.9	2.00	50.1	22.8	3.16	48.3
8.43	2.6	46.4	1.942	50.4	35.5	2.72	48.6	21.0	4.30	45.8
10.71	2.7	44.4	2.52	49.8	33.8	3.54	47.7	19.7	5.60	44.0
13.86	2.9	42.2	3.38	48.4	31.9	4.73	45.8	18.4	7.44	41.8
17.60	3.0	40.3	4.44	46.8	30.2	6.23	43.8	17.2	9.72	39.5
22.43	3.0	38.4	5.88	44.8	28.6	8.23	41.7	16.0	12.78	36.9
28.86	3.0	36.4	7.94	42.4	26.8	11.12	38.8	14.7	17.09	33.8
36.2	3.0	34.4	10.53	39.4	24.9	14.77	35.4	13.4	22.3	30.5
42.4	2.9	33.0	12.87	37.3	23.7	17.99	33.3	12.5	27.0	28.2
55.6	2.8	30.4	18.30	33.2	21.3	25.5	29.0	10.9	37.4	24.1
68.2	2.6	28.3	24.1	30.0	19.4	33.4	25.6	9.9	47.4	21.7
84.3	2.4	25.9	32.3	26.3	17.4	44.3	22.2	8.8	60.9	19.0
03.4	2.1	23.4	43.4	22.8	15.6	58.0	19.3	7.8	77.5	16.6
28.5	1.7	20.7	59.4	19.1	13.4	78.1	16.0	6.8	99.8	14.2
57.9	1.2	18.2	80.0	16.0	11.8	101.7	13.7	6.0	126.3	12.4
98.5	0.7	15.3	112.0	12.7	10.0	136.6	11.2	5.0	164.7	10.2
45.5	-0.1	13.0	150.8	10.4	8.5	178.6	9.3	4.2	209.8	8.4
00	-1.1	11.2	197.0	8.6	7.2	229	7.7	3.7	261	7.4
75	-2.2	9.2	265	6.8	5.9	301	6.1	3.1	334	6.1
21	-3.0	8.4	307	6.1	5.5	342	5.7			
73	-4.0	7.7	354	5.6	5.1	390	5.2			
31	-5.0	7.0	408	5.0	4.6	447	4.7			
95	-6.2	6.3	469	4.4	4.2	508	4.3			
70	-7.5	5.6	543	3.9	3.6	585	3.4			
50	-8.9	4.9	624	3.3	3.0	670	3.0			

The hydrolysis of the lead(II) ion seemed to be negligible under the conditions of the present investigation, since $\bar{n}/[L]$ was independent of both C_M and δ .

Upper and lower limiting curves were drawn in the plot of $\bar{n}/[L]$ against [L]. The graphical procedure was executed on both these curves. Thus two sets of stability constants were obtained, interpreted as estimates of the upper and lower limits of the stability constants.

The determination of the stability constants gave the following results.

$$\begin{aligned}\beta_1 &= (53 \pm 1) \text{ M}^{-1} \\ \beta_2 &= (460 \pm 20) \text{ M}^{-2} \\ \beta_3 &= (400 \pm 200) \text{ M}^{-3}\end{aligned}$$

DISCUSSION

As illustrated in Fig. 1, $\bar{n}/[L]$ was independent of C_M in the ligand measurements. This is in accordance with theory if only mononuclear complexes are formed in the system.

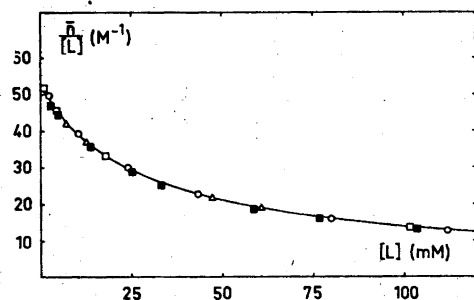


Fig. 1. Some $\bar{n}/[L]$ -values from the ligand measurements. The main investigation, $\delta=0.215$: $C_M=60$ mM (O), $C_M=40$ mM (\square), $C_M=20$ mM (\triangle). Buffer with $\delta=0.492$ and $C_M=40$ mM (\blacksquare). The full-drawn curve is calculated from the β_n -values obtained in the ligand investigation.

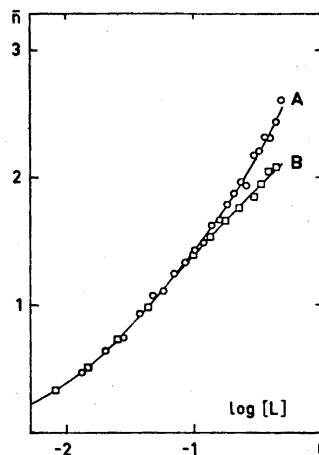


Fig. 2. The complex formation curve for the lead(II) ethoxyacetate system as obtained by the central ion investigation (A) and by the ligand investigation (B). Each of the full-drawn curves is calculated from the complete set of β_n -values obtained by the method in question. The symbol O refers to approximate \bar{n} -values obtained by means of eqn. (10) in Ref. 8. The symbol \square represents some \bar{n} -values from the ligand measurements.

In the graphical treatment of the central ion measurements it was found that, at constant E_M , C_L was a linear function of C_M . According to theory the slope of such a line is equal to \bar{n} if only mononuclear complexes are formed and if the activity coefficients of the species in the solution do not change with C_M and C_L . In the present investigation the slope was less than \bar{n} , especially at high $[L]$ -values. Such a discrepancy is often encountered in measurements of this kind and might be due to changes in the activity coefficients upon complex formation.

As shown in Fig. 2, \bar{n} reached a value between 2 and 3 in both investigations. This indicates that at least three mononuclear complexes are formed.

For $[L]>100$ mM the complex formation curves obtained by the two methods do not coincide. In this region, however, neither of the applied methods is expected to give a very accurate picture of the complex formation.

In the ligand measurements, where the systematic errors should be of minor importance, the measured emf, E_L , becomes comparatively small when

[L] increases. This results in a large random error in \bar{n} and in the quantities calculated from it.

In the central ion measurements corresponding values of [L] and X can be calculated from the emf, E_M , with small random error in the entire [L]-region. At higher C_L -values, however, when a considerable part of the perchlorate ions of the salt medium has been exchanged for ligand ions, the systematic error of the measured emf, E_M , caused by, *e.g.*, the liquid junction potential, cannot be expected to be negligible.

In the graphical determination of the stability constants it was found that β_1 and β_2 could be determined from the experimental data obtained at [L] < 100 mM. Higher complexes are not formed in sufficient amounts to allow determination of stability constants until [L] is greater than 200 mM. In this region the experimental data are less reliable, which is reflected in the wide limits of error of the calculated stability constants.

In the ligand investigation the X_2 -plot was linear over the entire [L]-region, thus indicating that three complexes are formed in the system. In the central ion investigation a stability constant of a fourth complex could be calculated at [L] > 300 mM. With respect to the difficulty of controlling systematic error at these large [L]-values, it should not be claimed, however, on the basis of this investigation, that a fourth complex really is formed in the system under investigation.

Table 4. The "most likely" complex formation constants in the lead(II) ethoxyacetate system.

β_1 (M ⁻¹)	β_2 (M ⁻²)	β_3 (M ⁻³)	K_1 (M ⁻¹)	K_2 (M ⁻¹)	K_3 (M ⁻¹)	K_1/K_2	K_2/K_3
53	450	450	53	8.5	1	6.2	8.5

An attempt has been made to estimate "most likely" stability constants, which are collected in Table 4 together with the calculated stepwise stability constants K_n . The constants seem to show that the ligand under investigation acts mainly monodentately and forms weaker lead(II) complexes than the acetate ion. A closer comparison to the acetate system can hardly be made, since the results from the numerous investigations of the lead(II) acetate system^{3,4} give the impression that the complex formation in this system is not fully known.

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