

On the Complex Formation in the Lead(II) (Ethylthio)acetate System

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The complex formation in aqueous solution between the lead(II) ion and the (ethylthio)acetate ion has been studied at 25.0°C by central ion measurements and by ligand measurements.

Both methods indicated the formation of at least two mononuclear complexes, for which the following gross stability constants were calculated:

from the central ion measurements: $\beta_1 = (52.5 \pm 0.7) \text{ M}^{-1}$,
 $\beta_2 = (670 \pm 30) \text{ M}^{-2}$;

from the ligand measurements: $\beta_1 = (52.7 \pm 0.4) \text{ M}^{-1}$,
 $\beta_2 = (670 \pm 10) \text{ M}^{-2}$.

The constants refer to an ionic strength of 1.0 M (NaClO_4).

The existence of anionic complexes could not be established with any certainty.

A sparingly soluble phase separated from solutions with large central ion concentration.

A comparison is made between the complex formation in the present system and in the lead(II) ethoxyacetate system.

Investigations of the formation of ethoxyacetate and (ethylthio)acetate complexes of bivalent nickel,¹ copper,² zinc,³ and cadmium⁴ have been reported earlier. The results indicate that the (ethylthio)acetate ion in forming mononuclear complexes in aqueous solution acts mainly bidentately with copper(II), but mainly monodentately with the other metal ions.

In this paper, an investigation of the complex formation in the lead(II) (ethylthio)acetate system is reported. As in an earlier investigation of the lead(II) ethoxyacetate system,⁵ two independent electrometric methods have been used, *viz.* (1) indirect determination of the concentration of free ligand in buffer solutions by means of a glass electrode, and (2) direct determination of the concentration of free central ion by means of a lead amalgam electrode.

The formation of lead(II) (ethylthio)acetate complexes in 50 % dioxane at 30°C has earlier been studied by Irving and Fernelius.⁶

CALCULATIONS AND NOTATIONS

The stability constants have been obtained by graphical treatment of the data according to Fronæus.⁷ A numerical method⁴ has also been used with the data from the central ion measurements.

In this paper, the following notations are used:

- C_M = total concentration of Pb^{2+} -ion
 $[M]$ = concentration of free Pb^{2+} -ion
 C_L' = stoichiometric total concentration of ligand L
 C_L, C_{HL} = corrected total concentration of ligand L, acid HL
 δ = buffer quotient in the ligand buffer. The stoichiometric concentration of the acid HL is $\delta C_L'$
 $[L]$ = concentration of free ligand
 $K_a = [H_3O^+][L]/[HL]$
 N = maximum coordination number
 $\beta_n = [ML_n]/([M][L]^n)$ = 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
 $X_i = (X_{i-1} - \beta_{i-1})/[L]$; ($1 \leq i \leq N$; $X_0 = X$; $\beta_0 = 1$)
 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_M = emf of cell (1) = $29.58 \log (X)$ mV
 D = hypothetical correction term (mV)
 I = ionic strength

EXPERIMENTAL

Chemicals. The (ethylthio)acetic acid supplied by Eastman Organic Chemicals was not pure. It was rectified by vacuum distillation. A portion constantly boiling at 122.0°C (16 mbar) had the equivalent weight 120.3 (calc. 120.2). The buffer solutions prepared from the pure acid and carbonate free sodium hydroxide were analysed with the aid of a cation exchange resin.

The lead(II) perchlorate stock solution, the sodium perchlorate, and the lead amalgam were the same as used in an earlier investigation.⁵

All other chemicals used were of *pro analysi* grade.

Methods. The same two experimental methods were applied as in the investigation of the lead(II) ethoxyacetate system. A description of these methods was given in the report of that investigation,⁵ and will not be repeated here.

To obtain favourable conditions for a comparison of the lead(II) complex formation with ethoxyacetate and with (ethylthio)acetate, the same measurement equipment and, as far as possible, the same chemicals were used in the two investigations.⁵

Table 1. Corresponding values of $[L]$ and $\bar{n}/[L]$ in the lead(II) (ethylthio)acetate system. Buffer with $\delta = 0.258$. The values of E_0 refer to $I_R = 6.0 \times 10^{-5}$ M.

C_L' (mM)	$C_M = 60.0$ mM			$C_M = 50.0$ mM			$C_M = 40.0$ mM			$C_M = 20.0$ mM		
	E_L (mV)	$[L]$ (mM)	$\bar{n}/[L]$ (M ⁻¹)	E_L (mV)	$[L]$ (mM)	$\bar{n}/[L]$ (M ⁻¹)	E_L (mV)	$[L]$ (mM)	$\bar{n}/[L]$ (M ⁻¹)	E_L (mV)	$[L]$ (mM)	$\bar{n}/[L]$ (M ⁻¹)
1.471	65.9	0.265	52.9	60.2	0.313	53.2	53.5	0.378	54.1	34.2	0.646	52.3
1.948	62.4	0.364	53.1	56.6	0.431	52.9	50.0	0.518	53.9	31.5	0.866	53.1
2.419	59.5	0.470	52.4	53.8	0.554	52.5	47.1	0.670	52.5	29.2	1.108	51.4
2.885	57.4	0.572	52.6	51.9	0.668	53.3	45.2	0.812	52.7	27.7	1.339	51.0
3.80	54.2	0.778	52.7	48.8	0.909	53.1	42.4	1.096	52.8	25.7	1.791	50.8
5.12	50.9	1.089	52.4	45.6	1.274	52.3	39.5	1.528	52.0	23.7	2.47	49.6
6.40	48.7	1.393	52.3	43.5	1.631	51.9	37.5	1.961	51.1	22.4	3.14	48.7
8.43	46.1	1.896	51.6	41.1	2.22	51.0	35.4	2.65	50.2	21.0	4.22	47.4
10.71	44.1	2.47	50.8	39.3	2.88	50.3	33.8	3.45	49.4	19.9	5.46	46.1
13.86	42.3	3.27	50.3	37.6	3.82	49.4	32.3	4.56	48.4	18.9	7.19	44.8
17.60	40.8	4.25	49.5	36.2	4.96	48.5	31.0	5.92	47.2	17.9	9.35	42.9
22.43	39.2	5.58	48.1	34.7	6.52	46.9	29.6	7.79	45.4	16.9	12.23	40.8
28.9	37.6	7.44	46.3	32.9	8.80	44.2	28.0	10.47	42.7	15.6	16.38	37.4
35.9	36.0	9.67	43.9	31.5	11.36	42.0	26.5	13.62	40.0	14.1	21.4	33.2
42.7	34.9	11.85	42.3	30.4	13.95	40.3	25.2	16.89	37.4	13.3	26.2	31.1
55.7	32.8	16.50	38.8	28.2	19.56	36.3	23.1	23.6	33.4	11.6	36.3	26.5
68.0	31.1	21.3	35.9	26.5	25.3	33.2	21.5	30.5	30.3	10.6	45.9	23.9
84.3	29.0	28.4	32.3	24.4	33.8	29.5	19.5	40.6	26.5	9.5	59.1	21.1
103.6	26.4	38.4	28.0	22.0	45.3	25.4	17.3	54.1	22.6	8.2	76.2	17.8
128.3	23.5	52.9	23.5	19.3	62.0	21.1	15.1	72.7	18.9	7.0	98.7	14.9
157.8	20.5	72.7	19.3	16.8	83.7	17.5	13.1	96.3	15.8	6.1	125.5	12.8
198.6	17.3 ^a	103.2	15.2	14.2	116.1	14.1	10.9	131.6	12.6	5.2	163.3	10.7
245.6	^b	^b	^b	11.9	156.6	11.3	9.2	173.5	10.3	4.3	209	8.7
300	^b	^b	^b	10.0	205.5	9.1	7.6	225	8.2	3.6	262	7.2
375	7.6	^b	^b	8.2 ^a	275	7.2	6.3	296	6.7	3.0	335	5.9

^a Supersaturated solution. ^b Precipitation.

MEASUREMENTS AND RESULTS

The ligand measurements. As in the corresponding measurements with ethoxyacetate buffers,⁵ the experimental reproducibility was the same as the precision of the voltmeter, viz. ± 0.1 mV. The experimental results from the main part of the investigation, in which a ligand buffer solution with $\delta = 0.258$ was used, are collected in Table 1.

For $C_M = 60.0$ mM and 50.0 mM, measurements could be made in the slightly supersaturated solutions at $C_L' = 198.6$ mM and 375 mM, resp. At higher C_L' -values, precipitation occurred immediately. The precipitate was not dissolved, at least not completely, at $C_L' = 750$ mM. The precipitate was a heavy, viscous, greyish liquid, forming large drops on standing. An estimate of the lead content of the substance was obtained in the following way. The precipitate was washed with water and kept at 80°C for 1 h. The drops were then transparent and very viscous. After some weeks in a desiccator over silica gel, the substance was light brown and had a horny consistence. Samples were dissolved in very dilute nitric acid and titrated with EDTA with xylenol-orange as indicator.⁸ (Found: Pb 47.0 ± 0.5 . Calc. for $\text{Pb}(\text{C}_2\text{H}_5\text{S.CH}_2\text{COO})_2$: Pb 46.5.)

With $C_M = 40.0$ mM and 20.0 mM, the measurements were extended to $C_L' = 750$ mM, without precipitation being observed. The E_L -values obtained at $C_L' > 375$ mM, however, were too small to allow calculation of reliable $[\text{L}]$ -values, and were not used in the calculation of the stability constants.

Titration curves were also made at $C_M = 40.0$ mM with a ligand buffer with $\delta = 0.418$. The results showed that, within the experimental reproducibility, $\bar{n}/[\text{L}]$ was independent of δ . Hence it is likely that the hydrolysis of the lead(II) ion is negligible under the present experimental conditions, and that no complex formation occurs between the lead(II) ion and the free (ethylthio)-acetic acid.

As can be seen in Fig. 1, $\bar{n}/[\text{L}]$ was not quite independent of C_M . A limiting curve representing $\bar{n}/[\text{L}]$ at $C_M = 0$ as a function of $[\text{L}]$ was obtained by linear

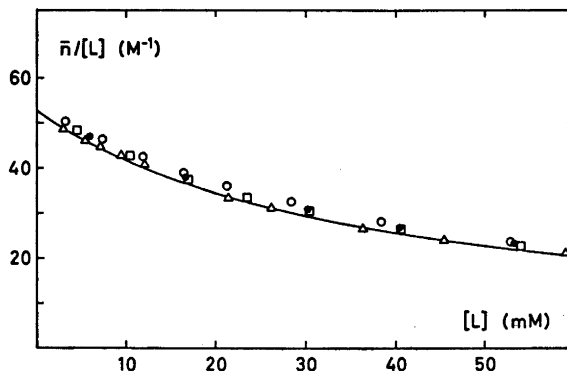


Fig. 1. Some $\bar{n}/[\text{L}]$ -values from the ligand measurements. The main investigation, $\delta = 0.258$: $C_M = 60$ mM (○), $C_M = 40$ mM (□), $C_M = 20$ mM (△). Buffer with $\delta = 0.418$, and $C_M = 40$ mM (●). The full-drawn curve is calculated from the β_n -values obtained in the ligand investigation.

Table 2. Corresponding values of [L] and $\bar{n}/[L]$ in the lead(II) (ethylthio)acetate system. $C_M = 40.0$ mM. Buffer with $\delta = 0.418$. The E_0 -values refer to $h_R = 6.0 \times 10^{-5}$ M.

C_L' (mM)	E_0 (mV)	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M ⁻¹)	C_L' (mM)	E_0 (mV)	E_L (mV)	[L] (mM)	$\bar{n}/[L]$ (M ⁻¹)
1.471	7.3	45.6	0.405	52.9	28.9	11.8	27.1	10.52	42.7
1.948	8.6	42.8	0.552	52.5	35.7	11.7	26.0	13.46	40.5
2.419	9.2	41.1	0.692	53.2	42.6	11.7	24.8	16.74	38.0
2.885	9.8	39.6	0.840	52.8	55.8	11.5	22.9	23.5	34.0
3.80	10.4	37.5	1.134	52.3	68.0	11.2	21.4	30.2	30.9
5.12	11.0	35.5	1.568	51.6	84.2	10.9	19.3	40.4	26.8
6.40	11.3	34.2	1.995	51.1	103.5	10.5	17.4	53.3	23.3
8.43	11.6	32.7	2.69	50.1	128.3	9.9	15.2	71.9	19.5
10.71	11.7	31.6	3.48	49.3	157.8	9.3	13.2	95.3	16.2
13.86	11.8	30.5	4.60	48.3	198.6	8.4	11.0	130.5	12.9
17.60	11.8	29.5	5.98	47.0	245.6	7.2	9.3	172.1	10.6
22.43	11.8	28.4	7.85	45.2	300	5.9	7.8	223	8.6

Table 3. Calculation of the X-function and the stability constants from $\bar{n}/[L]$ at $C_M = 0$.

[L] (mM)	\bar{n} (M ⁻¹)	X	X_1 (M ⁻¹)	X_2 (M ⁻²)	[L] (mM)	\bar{n} (M ⁻¹)	X	X_1 (M ⁻¹)	X_2 (M ⁻²)	X_3 (M ⁻³)
0	52	1	52.7	670						
5	46.6	1.280	55.9		70	18.5	7.98	99.7	670	
10	41.5	1.595	59.5		80	16.8	9.52	106.5	675	
15	38.0	1.946	63.0		90	15.8	11.21	113.4	675	
20	33.5	2.326	66.3		100	14.8	13.06	120.6	680	
25	31.1	2.734	69.4	670	120	12.9	17.23	135.3	690	
30	29.0	3.18	72.6	665	140	11.5	22.0	150.0	695	
35	27.0	3.66	75.8	660	160	10.7	27.5	165.4	705	
40	25.5	4.17	79.2	665	180	9.8	33.7	181.7	715	250
45	24.0	4.72	82.6	665	200	8.7	40.6	197.8	725	280
50	22.5	5.30	86.0	665	225	7.8	49.9	217.1	730	270
60	20.5	6.57	92.8	670	250	7.2	60.1	236.5	735	260

extrapolation of $\bar{n}/[L]$ as a function of C_M at constant [L]. From this curve, X-values were obtained by graphical integration.

The variation of $\bar{n}/[L]$ with C_M may indicate the existence of polynuclear complexes. By extrapolation of the different $\bar{n}/[L]$ -plots to [L] = 0, the stability constant $\beta_{12} = [M_2L]/([M]^2[L])$ could be estimated^{2,7} to about 40 M⁻². However, the effect is very small and might as well be attributed to variations in the liquid junction potential and in the activity coefficients.

The maximum value of \bar{n} , obtained directly from the measurements, was about 2. As can be found from Table 3, \bar{n} calculated from $\bar{n}/[L]$ at $C_M = 0$ reached a value of 1.8. Thus it is likely that at least two mononuclear complexes are formed.

The X_1 -plot was linear for [L] ≤ 70 mM (corresponding to $\bar{n} \leq 1.4$). Applying the least squares principle in this region resulted in the estimates of β_1 and

Table 4. Corresponding values of C_L and E_M (mean values) for $C_L' < 50$ mM.

$C_M = 15.00$ 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)
1.307	0.54	1.376	0.68	1.447	0.79
2.242	0.90	2.317	1.09	2.393	1.28
4.06	1.60	4.14	1.90	4.22	2.24
6.63	2.60	6.71	3.02	6.79	3.54
8.63	3.33	8.71	3.88	8.79	4.50
10.89	4.23	10.97	4.85	11.05	5.59
13.32	5.14	13.41	5.84	13.49	6.68
15.59	5.98	15.68	6.78	15.76	7.75
18.55	7.07	18.64	7.96	18.72	9.02
21.98	8.32	22.07	9.30	22.15	10.45
25.46	9.56	25.55	10.61	25.63	11.83
28.66	10.68	28.75	11.80	28.83	13.06
33.0	12.29	33.1	13.52	33.2	14.74
37.3	13.75	37.4	15.02	37.5	16.22
41.5	15.13	41.6	16.42	41.7	17.63
46.3	16.68	46.4	17.98	46.5	19.20

Table 5. Corresponding values of C_L' and E_M (mean values) for $C_L' > 50$ mM ($C_L \approx C_L'$).

C_L' (mM)	D (mV)	E_M (mV) for $C_M =$			C_L' (mM)	D (mV)	E_M (mV) for $C_M =$		
		15.00 mM	10.00 mM	5.00 mM			15.00 mM	10.00 mM	5.00 mM
52.6	0.1	18.51	19.85	21.06	156.7	2.3	41.58	42.42	43.12
59.8	0.3	20.66	21.96	23.14	169.4	2.5	43.68	44.45	45.05
67.5	0.4	22.80	24.08	25.22	181.4	2.8	45.52	46.28	46.81
74.9	0.6	24.77	26.02	27.14	194.6	3.1	47.47	48.16	48.72
82.2	0.7	26.61	27.82	28.90	208.7	3.4	49.44	50.09	50.54
91.5	0.9	28.84	30.00	31.04	223.4	3.7	51.40	52.01	52.48
100.0	1.1	30.77	31.88	32.87	240.0	4.1	53.51	54.08	54.55
110.9	1.3	33.10	34.14	35.06	256.5	4.4	55.52	56.02	56.46
121.3	1.5	35.20	36.20	37.07	272.7	4.8	57.39	57.86	58.30
131.2	1.7	37.08	38.06	38.84	287.5	5.1	59.04	59.47	59.84
143.1	2.0	39.26	40.17	40.88	300	5.4	60.37	60.79	61.11

β_2 given below, with 99 % confidence limits. The slope of the X_2 -graph indicated the existence of a very weak third complex. The stability constant of this third complex could be estimated only within wide limits of error. The following stability constants were obtained:

$$\begin{aligned}\beta_1 &= (52.7 \pm 0.4) & \text{M}^{-1} \\ \beta_2 &= (670 \pm 10) & \text{M}^{-2} \\ \beta_3 &= (200 \pm 100) & \text{M}^{-3}\end{aligned}$$

A check with the experimental data obtained at $C_L' > 375$ mM showed these to be consistent with the results obtained at lower C_L' -values. The preci-

Table 6. Some values from the graphical treatment of the data from the central ion measurements.

E_M (mV)	C_L (mM) for $C_M =$				X_1 (M^{-1})	X_2 (M^{-2})	X_3 (M^{-3})
	15.00 mM	10.00 mM	5.00 mM	0			
				0	52.5	670	900
1.5	3.78	3.20	2.79	2.29	54.1		
3.0	7.72	6.70	5.73	4.73	55.6		
4.5	11.59	10.16	8.75	7.30	57.5		
6.0	15.61	13.79	11.91	10.09	59.0		
7.5	19.72	17.48	15.19	12.92	61.4		
9.0	23.90	21.28	18.66	16.03	63.3	670	
10.5	28.1	25.3	22.3	19.3	65.6	680	
12.0	32.2	29.2	26.1	23.0	67.2	640	
13.5	36.6	33.0	29.9	26.4	70.5	680	
15.0	41.1	37.4	33.9	30.2	73.3	690	
16.5	45.7	41.9	38.3	34.6	75.5	660	
18.0	50.7	46.5	42.8	38.8	78.9	680	
21.0	60.8	56.4	52.4	48.0	86.0	700	
24.0	71.8	67.1	62.9	58.3	93.9	710	
27.0	83.6	78.8	74.3	69.5	103	730	
30.0	96.4	91.4	86.9	82.0	114	750	
33.0	110.1	105.2	100.7	95.8	126	770	
36.0	125.2	120.2	115.8	110.9	140	790	
39.0	141.5	136.4	132.1	127.2	156	810	
42.0	159.1	154.0	149.5	144.5	175	850	
45.0	178.0	173.0	169.0	164.3	196	870	
48.0	198.1	193.5	189.5	185.0	221	910	
51.0	220	216	212	208	250	950	1340
54.0	244	239	236	231	285	1010	1460
57.0	269	265	261	257	325	1060	1520
60.0	297	292	289	285	372	1120	1590

Table 7. The stability constants K_n calculated from the β_n -values.

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})	$\frac{K_1}{K_2}$	$\frac{K_2}{K_3}$
$Pb^{2+}/C_2H_5O.CH_2.COO^-$	53	460	(400) ^a	53	8.7	(1)	6.1	(9)
$Pb^{2+}/C_2H_5S.CH_2.COO^-$	52.7	670	(200) ^a	52.7	12.7	(0.3)	4.1	(42)
$Pb^{2+}/CH_3.COO^-$	101	1430	1900	101	14.2	1.3	7.1	11

(according to Karlsson¹¹
at 20.0°C and $I = 1$ M)

^a cf. Discussion.

sion of the value of β_3 could not be improved. Formation of a fourth complex was not indicated.

With the aid of the stability constants, the product $[M][L]^2$ was calculated to $5 \times 10^{-5} M^3$ for the two slightly supersaturated solutions mentioned above. Considering the result of the analysis of the precipitate, this value can be

regarded as a rough estimate of the solubility product of the compound ML_2 , in the medium in question.

The central ion measurements. The concentration of free (ethylthio)acetic acid did not influence E_M . This was found by measurements of the same kind as in the investigation of the ethoxyacetate complexes (see cell (4) in Ref. 5). Results: C_{HL}/mM , emf/mV - 554; 0, 0.26; 25.4, 0.26; 47.9, 0.27; 77.0, 0.25; 101.7, 0.26; 129.4, 0.26; 153, 0.29; 178, 0.28; 203, 0.27;

A ligand buffer with $\delta = 0.247$ was used in the main part of this investigation. In calculating C_L from C_L' , the earlier⁴ found value of 2.26×10^{-4} M was used for the acid constant of (ethylthio)acetic acid.

The experimental results are collected in Tables 4 and 5. The mean value of the difference between the E_M -values obtained in repeating the measurements was 0.02 mV.

Representative values from the graphical determination of the stability constants are collected in Table 6.

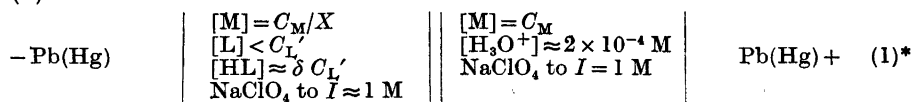
The X_1 -plot was linear only for $[L] < 35$ mM, which meant an unfavourable situation in calculating both β_1 and β_2 from this plot. The X_2 -plot, however, having no linear portion, offered still more unfavourable conditions for a determination of β_2 . Fairly reliable values of X_3 could be calculated only at $[L] > 200$ mM.

Below are stated estimates of the stability constants (with 99 % confidence limits) obtained by application of the principle of least squares; β_1 and β_2 from the linear portion of X_1 at $[L] < 35$ mM, β_3 and β_4 from X_3 at $[L] > 210$ mM:

$$\begin{aligned}\beta_1 &= (52.5 \pm 0.7) & M^{-1} \\ \beta_2 &= (670 \pm 30) & M^{-2} \\ \beta_3 &= (900 \pm 300) & M^{-3} \\ \beta_4 &= (2000 \pm 1000) & M^{-4}\end{aligned}$$

The entire experimental material was also treated by the numerical method earlier described.⁴ The result agreed well with that obtained by the graphical method.

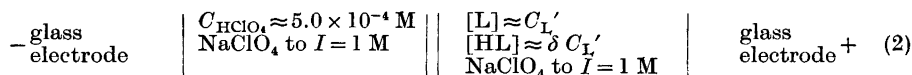
The calculations are founded on E_M , which is the emf of the galvanic cell (1).



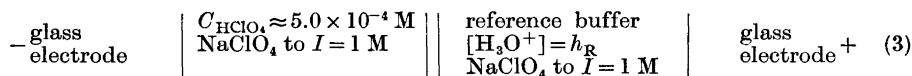
As earlier pointed out,⁵ the emf of this cell includes a liquid junction potential which is not likely to be negligible at large $[L]$ -values. Hence it is open to doubt whether useful information regarding the formation of weak complexes can be derived directly from the E_M -values obtained at high C_L' -values. An estimate of the uncertainty in this matter can perhaps be obtained with the aid of the E_0 -values from the ligand measurements. It is observed (see Table 1) that E_0 at low C_L' increases to a constant value - 0.6 mV. In this region ($0 < C_L' < 40$ mM), the K_a -value calculated from E_0 is constant, 2.3×10^{-4} M. At higher C_L' -values, both E_0 and the calculated K_a decrease.

* In the present paper the double lines symbolize a salt bridge with 1.000 M $NaClO_4$.

We now make the simplifying assumptions that K_a in reality is constant also for $C_L' > 40$ mM and that the non-constancy of E_0 is due solely to the liquid junction potential. Then the variable quantity $D = (-0.6 \text{ mV} - E_0)$ should be an estimate of the liquid junction potential at high values of C_L' for the element



since h_R in the reference buffer (see cell (3) in Ref. 5) was determined by emf measurements which can be expressed by the cell



Since the solutions in the half-cells of (1) and (2) are very much alike, it is assumed that the quantity D also represents a rough estimate of the liquid junction potential of cell (1). Thus the X -values in the central ion investigation should be calculated from $E_M - D$. Values of D are inserted in Table 5.

With application of this correction term, the total experimental material was re-analysed by the computer method. It was found that the X -function in the entire $[\text{L}]$ -region ($[\text{L}] \leq 274$ mM) could be very well represented by a polynomial of the second degree, giving the stability constants (with 99 % confidence limits):

$$\begin{aligned} \beta_1 &= (52.5 \pm 0.4) & \text{M}^{-1} \\ \beta_2 &= (672 \pm 5) & \text{M}^{-2} \end{aligned}$$

The same kind of E_M -correction was applied to the data of the investigation of the lead(II) ethoxyacetate system,⁵ in which the difficulties in interpreting the central ion measurements at higher C_L' -values were similar to those encountered in the present investigation. The calculations, which were restricted to $C_L' \leq 300$ mM, showed that the X -function in this case too could be well represented by a polynomial of the second degree in $[\text{L}]$. The stability constants found in this case were (with 99 % confidence limits):

$$\begin{aligned} \beta_1 &= (52.7 \pm 0.2) & \text{M}^{-1} \\ \beta_2 &= (435 \pm 3) & \text{M}^{-2} \end{aligned}$$

The influence of the correction term upon the X_1 -functions of the two systems is illustrated in Figs. 2 and 3.

It should be emphasized that the correction of E_M made above is merely an attempt to show, by means of the data on hand, the limited possibility of drawing reliable conclusions from E_M -data at high C_L' -values in the present investigation. No systematic investigation has yet been made regarding the influence of the exchange of electrolytes upon the activity coefficients of the particles involved in the cell reactions in question.

Some support was obtained to the assumption that the liquid junction potential should be the dominating systematic error in the central ion measurements, by measuring the emf E_F (mV) of the cell (4) at 25.0°C.

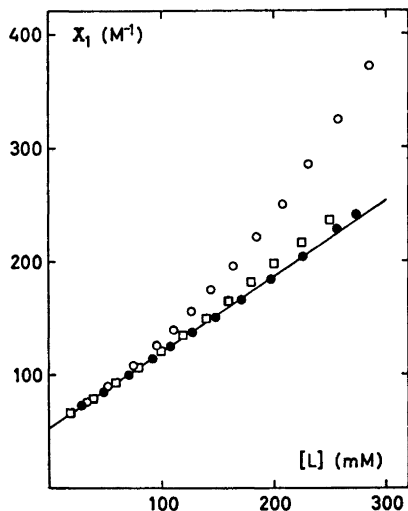


Fig. 2. The X_1 -functions for the lead(II) (ethylthio)acetate system obtained by: central ion measurements (O), ligand measurements (□), central ion measurements with application of a correction term (●). The line is $X_1/M^{-1} = 53 + 670 [L]/M$.

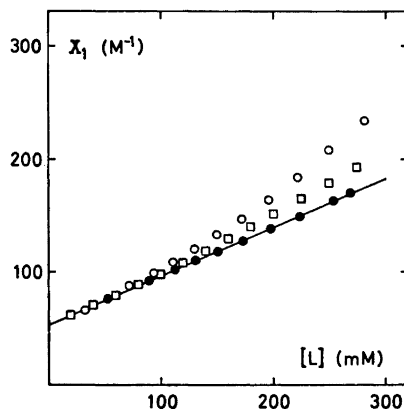
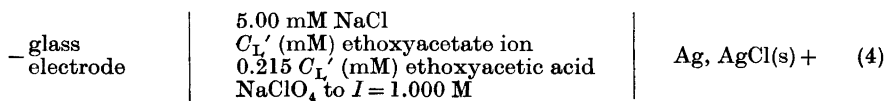


Fig. 3. The X_1 -functions in the lead(II) ethoxyacetate system⁶ as obtained by: central ion measurements (O), ligand measurements (□), central ion measurements with application of a correction term (●). The straight line is $X_1/M^{-1} = 53 + 435 [L]/M$.



With the ligand buffer replaced by 5.56 mM HClO₄, E_F was 688.0 mV. Results: C_L'/mM , $E_F/mV - 801$, $K_a \times 10^4/M$; 30.4, 0.6, 3.1; 41.0, 0.5, 3.1; 61.1, 0.5, 3.1; 79.8, 0.5, 3.1; 100.0, 0.6, 3.1; 126.3, 0.7, 3.1; 150.0, 0.8, 3.1; 175.5, 0.9, 3.1; 200.0, 1.0, 3.1; 240, 1.2, 3.0; 300, 1.5, 3.0.

Thus it was found that the change in E_0 (see Table 3 in Ref. 5) was four times as large as the change in E_F when C_L' was increased from 40 mM to 300 mM. According to Brønsted's principle of the specific interaction of ions,⁹ the activity coefficient of Cl⁻ in cell (4) should not be much influenced by the exchange of perchlorate ions against ethoxyacetate ions, since these three ions all have the same charge. However, a considerable part of the perchlorate ions are exchanged, and the experimental material is too small to justify a closer comparison of the changes in E_F and E_0 .

Similar measurements with an (ethylthio)acetate buffer could not be done, owing to the high stability of the silver (ethylthio)acetate complexes.¹⁰

DISCUSSION

Both methods used in the present investigation show that two mononuclear complexes are formed at low [L]-values. The same β_1 - and β_2 -values are obtained by both methods.

The question whether anionic complexes are formed cannot be answered with certainty, on the basis of the present experimental material. Both methods indicate the formation of a weak third complex at high [L]-values. For reasons earlier mentioned,⁵ however, this indication cannot be considered very reliable, especially as the calculations in the ligand investigation involve an extrapolation to $C_M = 0$. Formation of a third complex, with β_3 of the order of magnitude indicated by the ligand measurements, seems not to be incompatible with the fact that the sparingly soluble phase is in equilibrium with the solution in a system with $C_M = 50.0$ mM, and $C_L' = 750$ mM. A closer investigation of the solubility of the precipitate should probably give valuable information.

All the stability constants listed in Table 7 are determined by ligand measurements. The β_3 -values of the ethoxyacetate and (ethylthio)acetate systems should be considered as tentative. No thorough investigation on the complex formation in the lead(II) acetate system at 25°C and $I = 1$ M is known. The set of constants for this system, listed in Table 7, is considered to be the one offering the best conditions for a comparison with the other constants listed in the table, since the β -values of the lead(II) acetate system seem to vary more with the ionic strength^{12,13} than with the temperature.¹⁴

A comparison of the constants gives the impression that the complex formation in the three systems follows the same principal scheme, and that the two substituted acetates act mainly monodentately. Considering the fact, however, that the pK_a -values of the ethoxyacetic acid and the (ethylthio)acetic acid are 3.51 and 3.65, resp., it seems rather striking that β_1 is equal in the corresponding lead(II) systems. This relative stabilisation of the first ethoxyacetate complex may indicate that chelates are formed to a somewhat higher degree by the ethoxyacetate than by the (ethylthio)acetate. If this interpretation is correct, then the effect is a parallel to that found by other workers in investigating the formation of lead(II) complexes with potentially three- and four-dentate ligands^{15,16} containing $-C-O-C-$ and $-C-S-C-$ groups. However, the effect observed in the present investigation is small, and it seems not possible to draw a definite conclusion in this matter.

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