unsaturated hydrocarbon is produced in a yield in excess of the saturate. Hydrogen and small amounts of other products are also formed. It is evident that, while a large fraction of the decomposition does proceed in a manner analogous to that of the photolysis, there are other reactions of varying importance that do contribute. One must be careful not to overgeneralize the similarities that do exist.

The predominant effect of the radiolysis of the alkyl iodides is the rupture of the C–I bond. This occurs in spite of the fact that an appreciable fraction of the energy is initially absorbed by the hydrocarbon part of the molecule. It appears, therefore, that absorbed energy is rapidly distributed over the whole molecule and results in primary chemical dissociations which are characteristic of the activated species. In the present case preferential rupture is expected to occur upon localization of energy in the weaker carbon–iodine bond. Exclusive rupture of this bond in the alkyl iodides is of course known for low energy quanta from spectroscopic[18] and photochemical[8] considerations. In a similar manner organic acids are known to undergo preferential decarboxylation.[19] McDonell and Newton[20] have found that in the high energy irradiation of the aliphatic alcohols the energy is directed to the α carbon atom.

There is one other very important aspect to the present work. McCauley, Williams and Hamill have reported that in the photolysis of *n*-propyl iodide at 3261 Å. there is very little isomerization ($\sim$ 3%) of the *n*-propyl radical. Under more energetic conditions at 2537 Å. there is observed an appreciable yield of isomer ($\sim$ 28%). In the present work isomerization amounts to only about 4%. This very strongly indicates that a large majority of the radicals result from processes in which barely sufficient energy is given to the molecule to rupture the C–I bond. This contrasts with the assumption frequently made that since ionizing radiation is very energetic, a very drastic effect upon the system is produced. As is of course evidenced by the formation of minor products, some reactions do occur which involve a considerable amount of energy. In a large majority of the cases, however, the processes represent a minimum of energy in the reacting system.

[18] G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

[19] I. A. Breger, *J. Phys. Colloid Chem.*, **52**, 551 (1948).

[20] W. R. McDonell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

BUFFALO 8, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Acetato Complexes of Lead in Aqueous Solution

BY EUGENE A. BURNS[1] AND DAVID N. HUME

RECEIVED FEBRUARY 17, 1956

The existence of three complex ions, $Pb(OAc)^+$, $Pb(OAc)_2$ and $Pb(OAc)_3^-$ has been shown in perchlorate solutions of lead containing excess sodium acetate and acetic acid. By the use of polarographic, potentiometric and solubility techniques successive "over-all" formation constants have been evaluated at an ionic strength of 1.98 *M*. The average values of the "over-all" formation constants obtained by the three techniques for the mono-, di- and tri-acetato complexes are 145, 810 and 2950, respectively. The presence of anionic species was confirmed by means of an anion-exchange technique.

The formation of complex ions by lead salts in acetate media has been investigated in the past by several authors.[2–8] The striking disagreement among them both as to the number and stability of the complexes formed is illustrated by the results summarized in Table I. In almost every instance there has been some evident source of potential error: the use of nitrate media, which have recently been shown to cause complex formation with lead,[9,10] variable ionic strength or standard state, insufficient range of acetate concentrations to show the existence of higher complexes or *p*H so high as to introduce the possibility of forming hydroxo-lead-(II) ions. This unsatisfactory state of affairs prompted the present study in which we have investigated the reactions between lead and acetate ions in a buffered perchloric acid medium of constant ionic strength by three independent methods: potentiometric, polarographic and solubility.

Experimental

Polarography.—Measurements were made with a Sargent Recording Polarograph Model XXI. Corning marine barometer tubing was used for the capillary, which had a value of 1.36 mg.$^{2/3}$ sec.$^{-1/2}$ for $m^{2/3}t^{1/6}$ in 2.0 *M* sodium perchlorate at the potential of the saturated calomel electrode. The temperature was maintained at 25.0 ± 0.3°. No maximum suppressor was found to be necessary.

In order to obviate irreproducible results, which are found due to precipitation of potassium perchlorate at the interface when the conventional saturated calomel electrode is used in conjunction with a perchlorate medium, a calomel electrode saturated in sodium chloride rather than potassium chloride was utilized. The potential of the reference electrode was found to be within 1 mv. of the conventional electrode at 25°. The saturated calomel electrode was connected by means of saturated sodium chloride—3% agar-agar salt bridge to a reservoir of 1.98 *M* sodium perchlorate

[1] Abstracted from a thesis submitted by Eugene A. Burns in partial fulfillment of the requirements for the degree of Doctor of Philosophy from the Massachusetts Institute of Technology, 1956.

[2] A. Jacques, *Trans. Faraday Soc.*, **5**, 225 (1909).

[3] S. M. Edmonds and N. Birnbaum, THIS JOURNAL, **62**, 2367 (1940).

[4] B. C. Purkayashta and R. N. Sen-Sarma, *J. Ind. Chem. Soc.*, **23**, 31 (1946).

[5] N. K. Das, S. Aditya and B. Prasad, *ibid.*, **29**, 169 (1952).

[6] S. Aditya and B. Prasad, *ibid.*, **30**, 213 (1953).

[7] V. F. Toropova and F. M. Batyrshina, *Zhur. Anal. Khim.*, **4**, 337 (1949).

[8] S. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Section*, **74**, 531 (1953).

[9] H. M. Hershenson, M. E. Smith and D. N. Hume, THIS JOURNAL, **75**, 507 (1953).

[10] A. I. Briggs, H. N. Parton and R. A. Robinson, *ibid.*, **77**, 5846 (1955).

TABLE I

COMPARISON OF REPORTED FORMATION CONSTANTS OF THE LEAD–ACETATE SYSTEM

Investigator	Method	Ionic strength	K_1	$K_2 \times 10^{-4}$	$K_3 \times 10^{-3}$	K_4
Jacques[2]	Potentiometric	0.00	480	1.44	40.0	..
Edmonds and Birnbaum[3]	Solubility	1.00	104	....	...	..
Purkayashta and Sen-Sarma[4]	Conductometric	Vary	25	....	...	..
Aditya and Prasad[5,6]	Potentiometric	0.00	270	0.89	...	..
Toropova and Batyrshina[7]	Polarographic	2.00	170	....	0.15	125
Suzuki[8]	Potentiometric	?	..	44.0	...	..
This work	Polarographic	1.98	150	0.084	3.00	..
	Potentiometric	1.98	155	0.082	3.35	..
	Solubility	1.99	130	0.077	2.45	..

$$K_n = \frac{[\mathrm{Pb(OAc)}_n{}^{+2-n}]}{[\mathrm{Pb}^{++}]\,[\mathrm{OAc}^-]^n}$$

in which the polarographic cell was placed. The polarographic cell consisted of a 10 cm. length of 25 mm. glass tubing with a semi-permeable membrane (Celon Cap) at the interface. The resistance of the cell system was found to be 1040 ohms, as measured by a 1000 cycle a.c. bridge. This resistance did not change noticeably as the composition of the acetate–perchlorate mixture was altered. The usual volume in the polarographic cell was 10–15 ml. The solution was deaerated with purified nitrogen for 15 minutes and a nitrogen atmosphere was maintained over the solution while the polarogram was run.

The half-wave potentials were measured by use of the technique described by Hume, DeFord and Cave.[11] The plots of the potential (corrected for iR drop) *vs.* log $[(i_d - i)/i]$ gave straight lines whose average slope was 30.7 mv. with a coefficient of variation of 1.4%. It was possible to evaluate the half-wave potential to 0.1 mv. in any given experiment, and duplicate experiments showed that the reproducibility was of the order of 1 mv. and often well within 1 mv.

Potentiometry.—Potential measurements were made with a Rubicon portable potentiometer sensitive to 0.05 mv. From previous work[12] performed in this Laboratory, it was found that lead amalgam electrodes were quite difficult to work with and often gave erratic and irreproducible results. To facilitate the potential measurements, solid electrodes in the form of sticks similar to those used by Hershenson, Smith and Hume[9] were employed. Concentration cells of the type

$$\mathrm{Pb}\left|\begin{array}{ll}\mathrm{Pb(ClO_4)_2} & 1.00\ mM\\ \mathrm{HOAc} & 1.96\ M\\ \mathrm{HClO_4} & 0.0100\ M\\ \mathrm{NaClO_4} & 1.98\ M\end{array}\right\|\begin{array}{ll}\mathrm{Pb(ClO_4)_2} & 1.00\ mM\\ \mathrm{HOAc} & 1.97\ M\\ \mathrm{NaOAc} & \mathrm{x}\ M\\ \mathrm{NaClO_4} & (1.98-\mathrm{x})M\end{array}\right|\mathrm{Pb}$$

were set up and the potential measured as a function of the acetate concentration. The salt bridge was a solution of 1.98 M sodium perchlorate in Tygon tubing bisected by a T-joint, by which the bridge was filled, with $^1/_2$ inch Vycor plugs inserted in each end of the bridge. The Vycor plugs had been previously leached with 1.98 M sodium perchlorate to remove a trace of iron that was found to be present.

The electrodes were rubbed to shiny surface with sandpaper and rinsed in dilute perchloric acid before use. The solutions were deaerated 15 minutes prior to placing the electrodes in the solution and a stream of nitrogen was maintained over the solutions throughout the determinations (*i.e.*, 2 hr.). Two electrodes were placed in each solution and the potentials corresponding to the four possible combinations of electrodes were read and the average value taken. This procedure was repeated at 15-minute intervals for a period of 2 hr. The potentials of the four combinations agreed to within ±0.4 mv. each time, and the 15 minute averages were reproducible to ±0.2 mv. After prolonged use, *i.e.*, from 4 to 10 hr., an oxide film appeared on the electrodes and they became passive and insensitive.

Solubility Measurements.—Lead sulfate was equilibrated with various concentrations of sodium acetate in 1.96 M acetic acid, maintained at a constant ionic strength of 1.98 M with sodium perchlorate. The mixtures were shaken for one week at room temperature (26–27°) and then allowed to stand in a constant temperature water-bath held at 25.00 ± 0.03° for 2 days. The supernatant liquid was twice filtered through S and S 589 Blue Ribbon filter paper and aliquots of these solutions were adjusted to be 1.00 M in sodium acetate, 0.99 M in sodium perchlorate and 1.96 M in acetic acid. A polarographic method for the determination of lead in these aliquots had been devised and standardized utilizing these conditions. For the range 4.00×10^{-4} to 2.00×10^{-3} M lead perchlorate, the diffusion current constant was 3.04 ma. l./mole mg.$^{2/3}$ sec.$^{-1/2}$ with a coefficient of variation of 0.6%.

Lead iodate was prepared in a manner similar to that of LaMer and Goldman.[13] Samples dried at 105° were analyzed iodometrically for iodate, and the average percentage of lead iodate thus calculated was 99.89%.

The polarographic determination of lead in the lead iodate solubility experiments involved the removal of the acetic acid by evaporation to dryness and adjustment of the acetate and perchlorate concentration to be 1.00 and 0.99 M, respectively, by the addition of either solid sodium perchlorate or sodium acetate. The pH was adjusted to 7.1 with a few drops of 1.0 M perchloric acid or 0.5 M sodium hydroxide so that the iodate present in the solution would not obscure the lead wave. The diffusion current constant for the determination of lead in the presence of iodate under the above circumstances was calculated to be 3.18 ma. l./mole mg.$^{2/3}$ sec.$^{-1/2}$ with a coefficient of variation of 0.5% in the range 10^{-3} to 5×10^{-5}. These calibrations were performed with iodate present, to correspond to the actual conditions in the solubility determination.

Ion-exchange Measurements.—The anion and cation exchange resins were Dowex 1X2 and Dowex 50X4 that had been transferred to the acetate and sodium forms, respectively, and air-dried. Fifty milliliters of the solution under investigation was added to the resin under investigation and the mixture shaken for three days. The supernatant liquid was filtered and aliquots were taken for analysis. The lead was determined polarographically after the supporting electrolyte had been adjusted to be 1.00 M in sodium acetate, 0.99 M in sodium perchlorate and 1.96 M in acetic acid.

Thermometric Measurements.—Thermometric titrations were performed using the detection apparatus of Keily,[14] consisting of a thermistor in a d.c. bridge circuit. The unbalance of the bridge was fed into a Speedomax recording potentiometer which had been calibrated in degrees centigrade. The titration was performed in a Dewar flask and the titrant was added in increments rather than a continuous flow.

pH Measurements.—The pH was determined by means of a Leeds and Northrup line-operated, continuous-reading pH meter. The electrodes of the manufacturer were used with one alteration; the calomel electrode was saturated in sodium chloride rather than potassium chloride.

Materials.—Reagent grade chemicals were used at all times. A stock solution of lead perchlorate in perchloric acid was prepared by dissolving a known amount of reagent lead oxide in a known amount of perchloric acid. The molarity of the lead was checked gravimetrically by precipitation as the sulfate. A stock solution of sodium acetate was

---

(11) D. N. Hume, D. D. DeFord and C. C. B. Cave, THIS JOURNAL, **73**, 5323 (1951).

(12) H. M. Hershenson, unpublished results, 1951

(13) V. K. LaMer and F. H. Goldman, THIS JOURNAL, **52**, 2791 (1930).

(14) H. J. Keily, Ph.D. Thesis, Mass. Inst. of Technology, 1956.

standardized by potentiometric titration with perchloric acid. The ammonium salt solutions were standardized by the Kjeldahl method. Stock sodium perchlorate solutions were standardized gravimetrically by precipitation with potassium chloride. Iodate was determined iodometrically by means of the starch end-point using thiosulfate that had been standardized *vs.* iodate.

Results

Polarographic.—The polarographic results were interpreted by the method of DeFord and Hume.[15] This method consists of the graphical differentiation of the $F_0(X)$ term which can be obtained from polarographic data

$$F_0(X) = \text{antilog}\left\{\frac{n}{0.0591}\left[(E^{1/2})_s - (E^{1/2})_c\right] + \log\frac{I_s}{I_c}\right\} \qquad (1)$$

at 25.0°, where n is the number of faradays of electricity required per mole of electrode reaction, $E_{1/2}$ refers to the half-wave potential, I is the diffusion current constant and the subscripts s and c refer to the simple (aquo) ion and the same ion in complexing media, respectively. In solutions with excess ligand present and a constant ionic strength, it is known that

$$F_0(X) = 1 + K_1X + K_2X^2 + K_3X^3 + \ldots + K_n X^n \qquad (2)$$

where $K_1 \ldots K_n$ are the different "over-all" concentration constants and X is the equilibrium concentration of the ligand (which closely approximates the analytical concentration when an excess is present).

TABLE II

EFFECT OF ACETIC ACID ON THE DIFFUSION CURRENT AND HALF-WAVE POTENTIAL

NaOAc, M	HOAc, M	pH	I^a	$E_{1/2}$, v. *vs.* SCE
0.493	0.0100	6.42	3.88	−0.4475
	.0199	6.61	3.75	.4476
	.1078	5.39	3.71	.4474
	.499	4.71	3.63	.4460
	.988	4.43	3.48	.4455
	1.966	4.05	3.25	.4431
0.0000	.000^b	1.93	4.62	.3686
0.0028^c	1.954	1.67	3.92	.3644

^{a} Diffusion current constant in ma. l./mole $\text{mg.}^{2/3}$ $\text{sec.}^{-1/2}$. ^{b} 0.0100 M $HClO_4$ present in solution. ^{c} Calculated from dissociation of acetic acid.

TABLE III

ANALYSIS OF $E_{1/2}$ OF LEAD IN ACETATE MEDIUM WITH $\mu = 1.98$

NaOAc, M	$E_{1/2}$, v.	I^a	$F_0(X)$	$F_1(X)$	$F_2(X) \times 10^{-3}$	$F_3(X) \times 10^{-3}$
0.0000	−0.3630^b	3.99^b	(1.00)	...	..	..
.0028^c	.3644	3.92	....	...	..	..
.0394	.3895	3.66	8.59	193	1.09	..
.0893	.4029	3.55	25.1	270	1.34	..
.1896	.4176	3.40	82.4	429	1.47	3.32
.290	.4282	3.37	189.4	649	1.72	3.03
.391	.4368	3.29	379	968	2.09	3.19
.493	.4431	3.25	627	1268	2.26	2.88
.695	.4534	3.16	1436	2065	2.75	2.75
.997	.4655	3.03	3850	3860	3.72	2.89
1.424	.4772	2.79	10360	7270	5.00	2.92
1.901	.4875	2.66	24350	12660	6.66	3.06
				K_1 = 150	K_2 = 840	K_3 = 3000

^{a} Diffusion current constant in ma. l./mole $\text{mg.}^{2/3}$ $\text{sec.}^{-1/2}$. ^{b} Extrapolated value. ^{c} Calculated from dissociation of acetic acid.

Initial experiments when no acetic acid was present gave irreversible waves in which case the above method is not applicable. It was felt that in these experiments a competition for the lead, between hydroxide and acetate ions (the pH range was 3.22–8.06), was responsible for the irreversibility. To obviate this effect the solutions were made 1.96 M in acetic acid, which in turn caused a junction potential effect to appear in the comparison of solutions with and without acetic acid. It was also noticed that the diffusion coefficient of the lead ion was not the same in solutions with and without acetic acid present. Table II shows the results of a study made on the effect of acetic acid on this system. The shift of the half-wave potential toward more negative values at higher pH when acetate is present appears to indicate the presence of hydroxide competition. An even more striking effect was evident in the absence of acetate as would be expected from the known tendency of lead ions to hydrolyze in the absence of complex forming anions.[16]

The diffusion current constant and half-wave potential in 1.96 M acetic acid were plotted as a function of acetate concentration and extrapolated to zero acetate concentration and these values were used for I_s and $(E_{1/2})_s$ in eq. 1, respectively. In Table III, experimentally determined half-wave potentials and diffusion current constants are given, together with the calculated values of $F(X)$. When these were plotted against acetate ion concentration, $F_2(X)$ and $F_3(X)$ were found to be straight lines, demonstrating the existence of $PbOAc^+$, $Pb(OAc)_2$ and $Pb(OAc)_3^-$ in this range of acetate concentrations with clear evidence against the existence of any significant amount of higher complexes. The extrapolation of the $F(X)$ curves to zero acetate ion concentration gave values for the successive "over-all" formation constants which were 150, 840 and 3000 for K_1, K_2 and K_3, respectively.

Potentiometric.—Employing Leden's[17] method, the potentiometric determination of successive formation constants was performed at an ionic strength of 1.98 M. In this method

$$\log F_0(X) = \frac{n}{0.0591}\,\Delta E \qquad \text{at } 25° \qquad (3)$$

where $F_0(X)$ and n have the same meaning as before, and ΔE is the potential difference of concentration cells in which one half-cell contains no acetate and the other a varying known concentration of acetate. As in the polarographic solutions, 1.97 M acetic acid was present in all the solutions, and thus there was not a solution that contained absolutely no acetate. To take this into account, the potential differences were extrapolated to zero acetate ion concentration, the extrapolated ΔE being −1.8 mv.; then ΔE in eq. 3 was equal to ΔE observed +1.8 (in mv.).

Table IV gives the experimentally determined potential differences corrected to zero acetate concentration together with the calculated values of $F(X)$. Once again, only three complexes were

---

[15] D. D. DeFord and D. N. Hume, THIS JOURNAL, **73**, 5321 (1951).

[16] G. Mattock, *Acta Chem. Scand.*, **8**, 777 (1954).

[17] I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

shown to be present and the values obtained for K_1, K_2 and K_3 are 155, 820 and 3350, respectively.

TABLE IV

POTENTIOMETRIC ANALYSIS OF LEAD IN ACETATE MEDIA WITH $\mu = 1.98$

NaOAc, M	E,[a] mv.	$F_0(X)$	$F_1(X)$	$F_2(X) \times 10^{-3}$	$F_3(X) \times 10^{-3}$
0.0028[b]	1.8	......	...	..	..
.0394	27.9	8.78	197	1.07	..
.0893	41.8	25.9	279	1.39	..
.1896	58.0	91.4	476	1.69	..
.290	67.4	190	652	1.71	3.07
.391	77.0	401	1024	2.22	3.58
.493	83.9	687	1390	2.50	3.40
.695	95.2	1656	2380	3.20	3.42
.997	107.3	4250	4260	4.12	3.31
1.424	120.1	11500	8080	5.57	3.33
1.901	130.7	26250	13800	7.17	3.34
			$K_1 = 155$	$K_2 = 820$	$K_3 = 3350$

[a] Potentials referred to extrapolated zero acetate. [b] Calculated from dissociation of acetic acid.

Solubility.—The fact that the general principles of Leden's method may also be applied to solubility data has been known and used by previous investigators.[18,19] It is not generally known, however, that solubility data may be used to give $F(X)$ functions of exactly the same form as in the potentiometric and polarographic methods. These functions may be derived readily for the general case of the solubility of the compound M_pA_q in complexing media (ligand X). The following equilibria need to be considered

$$\mathrm{M}_p\,\mathrm{A}_q = p\mathrm{M}^{+a} + q\mathrm{A}^{-(pa/q)} \tag{4}$$

$$\mathrm{M}^{+a} + \mathrm{X}^{-r} = \mathrm{MX}^{+a-r} \tag{5}$$

$$\mathrm{M}^{+a} + 2\mathrm{X}^{-r} = \mathrm{MX}_2^{+a-2r} \tag{6}$$

$$\mathrm{M}^{+a} + n\mathrm{X}^{-r} = \mathrm{MX}_n^{+a-nr} \tag{7}$$

In this case $(m/m_0)^{(p+q)/p} = F_0(X)$ where $F_0(X)$ has the same meaning as in the previous sections, and m_0 and m are the solubilities of the compound in the absence and presence of complexing ligand, respectively. The slightly soluble compound chosen in this work was lead sulfate, and here there is also the possibility of hydrogen sulfate ion formation. It can be shown that in this case

$$F_0(X) = \left[\frac{m}{m_0}\right]^2 \frac{(H_0 + K_a)}{(H + K_a)}$$

where K_a is the ionization constant of the hydrogen sulfate ion at an ionic strength of 1.99 and H_0 and H are the equilibrium hydrogen ion concentrations in the presence and absence of complexing ligand (acetate), respectively. Since junction potentials would not be a factor in this case, the experiments with zero acetate also contained no acetic acid but instead were 1.00 millimolar in perchloric acid. Using a value of 0.084 for the dissociation constant of hydrogen sulfate ion at an ionic strength of 1.99 M[20] and assuming the activity coefficient of hydrogen ion to be unity in this medium, it was found that the correction factor, $(H_0 + K_a)/(H + K_a)$, is practically constant and is equal to 1.007 ± 0.007, over the pH range of 3 to 5 which was used here.

Table V gives the experimentally determined solubilities as a function of the acetate concentration together with the calculated values of $F(X)$. Three complexes are again shown to be present, the successive "over-all" formation constants K_1, K_2 and K_3, being 130, 770, 2350, respectively. Although they are slightly lower than the constants obtained by potentiometry and polarography, the agreement is quite good.

TABLE V

SOLUBILITY ANALYSIS OF LEAD IN ACETATE MEDIA WITH $\mu = 1.99$

NaOAc, M	$M \times 10^3$, M	$F_0(X)$	$F_1(X)$	$F_2(X) \times 10^{-3}$	$F_3(X) \times 10^{-3}$
0.0000	0.604	(1.00)	..	...	..
.0504	1.912	10.0	179	0.913	2.84
.1007	3.01	24.8	236	1.02	2.51
.2014	5.40	79.9	392	1.29	2.56
.3021	7.92	172	566	1.43	2.20
.504	14.05	541	1070	1.86	2.16
.705	22.2	1354	1920	2.53	2.50
1.007	35.5	3450	3420	3.27	2.48
1.511	60.8	10120	6700	4.34	2.36
			$K_1 =$ 130	$K_2 =$ 770	$K_3 =$ 2450

Discussion

It has been shown by three independent methods that there are three acetato complexes, Pb(OAc)$^+$, Pb(OAc)$_2$ and Pb(OAc)$_3^-$ whose "over-all" formation constants are 145, 810 and 2950, respectively. Averaging the values of the three methods with equal weight was felt to be justified, for although the potentiometric and polarographic determinations essentially measure the same quantity, the solubility determination is not necessarily as accurate. Figure 1 shows the distribution of lead in its various forms at an ionic strength of 1.98 M as a function of the free acetate ion. That these values do not confirm those of earlier investigators is obvious, and the reasons are undoubtedly the same as were suggested in explanation of why previous workers disagreed so radically among themselves. The discovery that the carefully planned and executed work of Edmonds and Birnbaum, long ad-

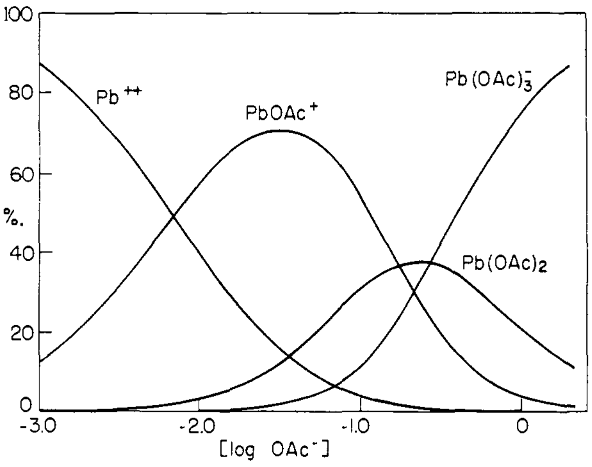

Fig. 1.—Percentage of lead in its various forms as a function of the free acetate ion concentration.

---

[18] E. L. King, THIS JOURNAL, **71**, 319 (1949).

[19] G. C. B. Cave and D. N. Hume, *ibid.*, **75**, 2893 (1955).

[20] E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

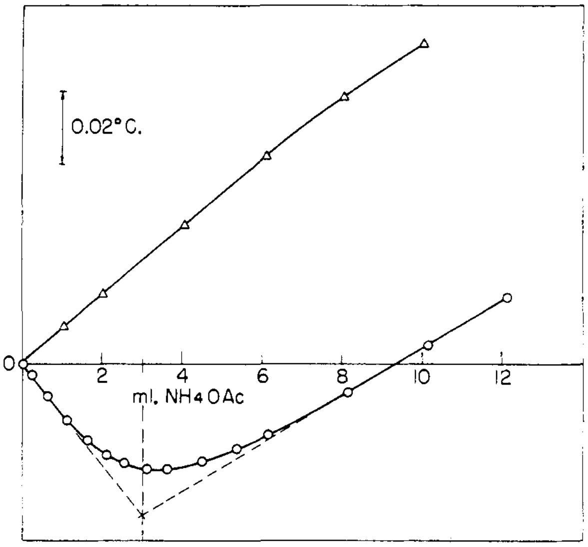

Fig. 2.—Thermometric titration curves with 0.990 *M* ammonium acetate. Circles, titration of 50.0 ml. of 0.0600 *M* lead nitrate; triangles, blank titration of 50.0 ml. of water.

mired as a classic, had failed to reveal the higher complexes came as a surprise, however. The most likely explanation probably lies in the fact that lead ion is extensively hydrolyzed and polymerized as the *p*H is increased.[16] Reaction of hydroxide ions with lead iodate may produce a solid phase in which the lead to iodate ratio is no longer 1:2. This would mean that the iodate concentration in solution could not be used to calculate the solubilities of lead iodate directly, as in their experiments. Some spot checks were made of the solubility of lead iodate in various solutions (Table VI), and it was evident that the lead to iodate ratio in solution differed appreciably from the theoretical in a number of instances. When it is remembered that the solubility values were cubed in the subsequent calculations, it is not unreasonable that the accumulated errors might obscure the presence of the relatively weak higher complexes.

Table VI

Investigations of the Solubility of Lead Iodate in Acetate Media

Soln. equilibrated	(IO_3^-) $\times 10^{-4}$	(Pb^{-+}) $\times 10^{-4}$	$(IO_3^-)/(Pb^{++})$
Water	0.722	0.340	2.12
1.00 *M* NH_4ClO_4	3.95	1.74	2.27
0.99 *M* NH_4OAc	18.3	8.59	2.13
0.99 *M* $NaClO_4$ 2.00 m*H* $HClO_4$	3.64	1.81	2.01
1.00 *M* NaOAc, 0.98 *M* HOAc	13.4	6.67	2.02

The thermometric titration curve presented by Purkayastha and Sen-Sama[4] showed a very sharp end-point at the 1:1 complex which is not consistent with the results one calculates from the formation constant they gave ($K_1 = 25$), *i.e.*, at the end-point, only 64% of the lead would be complexed. We have repeated their work, titrating 50.00 ml. of 0.0600 *M* lead nitrate with 1.00 *M* ammonium acetate. Figure 2 shows the result of this titration. It is interesting that the end-point was quite rounded and the initial slope was endothermic, both observations being contrary to those of the Indian workers. One would not expect to see further changes of slope after the end-point since the higher complexes are not formed extensively at these concentrations, and the slope after the end-point should correspond to the exothermic heat of dilution of ammonium acetate as was observed in Fig. 2.

The actual presence of an anionic complex in lead acetate mixtures was demonstrated by Fronaeus' ion-exchange method.[21] Here the distribution coefficient of lead between resin and solution was measured polarographically as a function of the ligand concentration over the range of 0.02 to 1.48 *M* acetate ion. The *p*H was held constant by maintaining a 1:1 ratio of acetic acid and sodium acetate, and the ionic strength varied accordingly. In this method, the existence of negatively charged complexes is shown by the appearance of a maximum in the distribution coefficient *vs.* ligand concentration function. Although the data are not highly accurate because of the limitations of the analytical method at very low lead concentrations, the data of Table VII show clearly that such a maximum is present. The location of the maximum at approximately 0.5 *M* acetate ion corresponds closely to the acetate ion concentration where the average ligand number is 2 (Fig. 2), *i.e.*, the maximum concentration of the uncharged lead acetate molecule, as is predicted by Fronaeus' equations. The experiments with a cation-exchange resin, although highly suggestive of the presence of anionic complexes, are not as conclusive as the anion-exchange results because the low distribution coefficient at high acetate concentrations could be due to the formation of the uncharged species.

Table VII

Ion-exchange Studies on the Lead Acetate System

Initial lead $\times 10^3$, *M*	NaOAc, *M*	Final lead $\times 10^6$, *M*	Lead in resin, mole/g. $\times 10^6$	Distribution C_{MR}/C_M, l./g.
Anion exchanger				
2.00	0.020	378	8.2	0.022
2.00	.040	107	9.5	0.088
2.00	.080	20.5	9.9	0.48
2.00	.480	3.0	10.0	3.3
2.00	.980	3.7	10.0	2.7
2.00	1.480	9.4	9.95	1.1
Cation exchanger				
2.40	0.050	380	10.1	0.026
2.40	1.500	2300	0.5	0.00022

Acknowledgment.—This work has been supported in part by the U. S. Atomic Energy Commission.

Cambridge, Mass.

---

[21] S. Fronaeus, *Svensk. Kem. Tid.*, **65**, 1 (1953).