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A Polarographic Study of Lead Fluoride Complexes and Solubility

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Polarographic studies of lead in fluoride media have shown the homogeneous solution equilibria between lead and fluoride ions to be rapidly established and measurable despite the simultaneous slow precipitation of lead fluoride. The method of DeFord and Hume was applied in sodium perchlorate–sodium fluoride mixtures of ionic strength 2.0 at pH 4.0, and the over-all formation (stability) constants β_1 and β_2 for PbF^+ and PbF_2 were found to be 18.0 and 356 at 25°. From the polarographically determined solubility of lead fluoride in sodium perchlorate and in sodium perchlorate–sodium fluoride mixtures, the concentration solubility product of lead fluoride, corrected for complex ion formation, was found to be 2.5×10^{-7} at 25° and an ionic strength of 2.0.

The existence of lead fluoride complexes is to be expected by analogy with the behavior of lead with the other halides. The weakness of the complexes formed and the relative insolubility of lead fluoride makes the study of the system by most means a difficult matter. The only prior work reported seems to be that of Connick and Paul,[1] who by an indirect potentiometric method estimated the formation constant of the PbF^+ ion as less than 2. The necessity of working in solutions so dilute that lead fluoride did not precipitate unfortunately confined the study to a concentration range in which almost no complex formation took place. The polarographic method has the advantage, for systems such as lead fluoride, that the measurements and their interpretation need not be interfered with by the gradual precipitation of one component and therefore more concentrated solutions can be studied. The half-wave potential of a reversibly reduced species, in a given environment, is independent of its concentration. The diffusion current, simultaneously measured, is at the same time a convenient measure of the concentration, whether it be constant or changing. In the present investigation, the polarographic characteristics of lead in fluoride-containing media have been utilized to determine the formation constants of the first two mononuclear lead fluoride complexes and the solubility of lead fluoride.

Experimental

The chief difficulty involved was the fabrication of capillaries which were satisfactory for use in acidic fluoride solutions. Ordinary Corning marine barometer tubing was found to be attacked in fluoride media of pH 4.0 or less at a rate sufficient to give a readily observable wave due to lead ions leached from the glass. Attempts to make acceptable capillaries out of materials such as Teflon, Lucite, or polyethylene were not successful. A thoroughly satisfactory dropping electrode which gave no difficulties in fluoride solutions with pH values as low as 2.5 was obtained by coating the outside of Corning marine barometer tubing with Tygon in the following manner.

Tygon primer (Code No. T.P. 1078, U. S. Stoneware Co., Akron, Ohio), a lacquer-like product, was thinned with an equal volume of ethyl ether. The clean, dry capillary with mercury flowing through it was immersed for a few moments in the thinned primer and air-dried overnight. The coating thus formed was found to remain adherent for months if the capillary was kept in water when not in use. The capillary used in the quantitative measurements in the present study had m and t values of 1.505 mg./sec. and 4.2 sec./drop at a column height of 110 cm. of mercury, in 0.1 M potassium chloride at the potential of the s.c.e.

Polarograms were recorded on a Sargent Model XXI recording polarograph without damping. The reference electrode was a saturated sodium chloride calomel connected to the polarographic cell by a short, large diameter bridge of 2.0 M sodium perchlorate and a Celon diaphragm. The internal resistance of the cell system as measured with a General Radio Co. Type 1650A impedance bridge was always less than 100 ohms. The cell itself, as were all vessels used to contain fluoride solutions, was constructed of polyethylene or similar fluoride-resistant plastic material. Potential measurements were made with a calibrated Sargent Model MFD potentiometer, and pH values were determined with a glass electrode–sodium chloride calomel pair.

Current measurements were made at the point of maximum drop size. Half-wave potentials were determined graphically or from the plots of log $[(i_d - i)/i]$ *vs.* E, and corrected for iR drop in the cell.[2] Reproducibility was of the order of ±1 mv. or better.

All chemicals used were of C.P. or Analytical Reagent grade. Ten-min. purging with prepurified nitrogen was used to remove and exclude oxygen and carbon dioxide. The use of a maximum suppressor was found unnecessary. All solutions in the polarographic studies were millimolar in lead perchlorate and the total ionic strength was adjusted to 2.0 M with sodium perchlorate. The pH was adjusted to 4.0 ± 0.2 by addition of sodium hydroxide or perchloric acid, as needed.

Results and Discussion

Complexes.—Preliminary runs showed that at the concentration of lead and fluoride ions needed to form significant amounts of complexes, lead fluoride would precipitate. However, the precipitate formed relatively slowly (a few minutes to 1 or 2 hr.) while the solution equilibria were established rapidly, so the system was suitable for study by the polarographic method. The polarographic wave of lead in pH 4.0 sodium perchlorate medium as in pH 4.0 sodium fluoride–sodium perchlorate medium was well defined. The slope of plots of $-E_{\text{d.e.}}$ *vs.* log $[i/(i_d - i)]$ for reduction of lead in sodium perchlorate and sodium fluoride–sodium perchlo-

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[1] (a) R. E. Connick and A. D. Paul, *J. Am. Chem. Soc.*, **80**, 2069 (1958); (b) A. D. Paul, Thesis, University of California, Berkeley, 1955; UCRL 2926.

[2] D. N. Hume, D. D. DeFord, and G. C. B. Cave, *J. Am. Chem. Soc.*, **73**, 5232 (1951).

rate supporting electrolytes at 25° was very close to the theoretical value of 29.6 mv. for reversible two-electron reduction. The method of DeFord and Hume[3] was used to interpret the change in half-wave potential of lead as a function of fluoride ion concentration in terms of the formation of a series of consecutively formed mononuclear lead fluoride complexes. Table I summarizes the results of a typical series, in which the concentration of sodium fluoride was varied from 0.05 to 0.7 M and an ionic strength of 2.0 held constant by addition of sodium perchlorate. Gradual precipitation of lead fluoride occurred, but as the half-wave potential is not a function of concentration and because the relative amounts of the various lead species in the series is fixed at a constant fluoride concentration, the precipitation does not affect the interpretation of the results. It was necessary only to assume the diffusion current constants of the simple lead ion and of the complex species to be the same. Because of the nature of the equation involving the diffusion current constants[3] a considerable deviation from equality would result only in a small error which would not significantly affect the interpretation. In solutions as acidic as pH 4.0 it is necessary to correct for the portion of the total fluoride which is bound as undissociated hydrofluoric acid and as the HF_2^- ion. The free fluoride ion concentrations given in Table I were obtained by solution of the appropriate quadratic equation using 1.0×10^{-3} and 3.0 as the best estimates available for the dissociation constant of hydrofluoric acid and the formation constant of HF_2^- from un-ionized hydrofluoric acid and fluoride ion in a medium of 2.0 M sodium perchlorate at 25°. Any error introduced in the estimation of these constants from values given in the literature for other temperatures and ionic strengths should be negligible inasmuch as neglecting the association of hydrogen and fluoride ions entirely was found to result in only a 10% increase in the value of β_1 calculated below.

Table I

Analysis of $E_{1/2}$ of Lead in Fluoride Medium

Ionic strength 2.0 M; pH 4.0 ± 0.2

NaF, M	(F^-), M	$E_{1/2}$	$F_0(X)$	$F_1(X)$
0.00	0.00	−0.363	1.00	[18.0]
.05	.043	.376	2.75	35.0
.10	.089	.386	5.98	49.8
.15	.132	.393	10.3	60.2
.20	.172	.401	17.8	84.1
.25	.215	.404	24.3	93.3
.30	.253	.408	33.2	107.
.40	.333	.414	55.4	136.
.50	.408	.420	84.1	166
.60	.482	.424	115.0	190
.70	.551	.428	152.	216

Conventional plots of $F_0(X)$ and $F_1(X)$ as a function of free fluoride ion concentration, Fig. 1, showed good linearity for $F_1(X)$, indicating the only species present in significant amounts up to 0.6 M fluoride to be the free lead ion, PbF^+, and PbF_2. The over-all formation constants, $\beta_1 = [PbF^+]/[Pb^{++}][F^-]$ and $\beta_2 = [PbF_2]/[Pb^{++}][F^-]^2$, were determined from the intercept and the slope, respectively, of the $F_1(X)$ plot and found to be 18.0 and 356. Efforts to verify the result by independent methods (solvent extraction, potentiometry, and light absorption) were thwarted by the precipitation which took place whenever concentrations sufficient for the formation of the complex species were obtained.

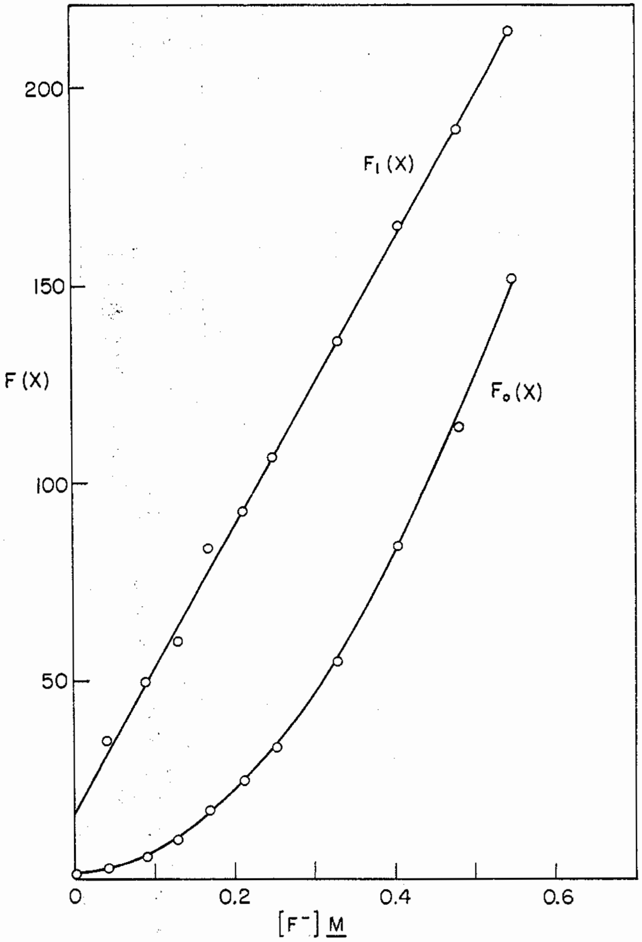

Fig. 1.—Analysis of half-wave potential of lead in fluoride–perchlorate mixtures.

Solubility Product.—The solubility of lead fluoride in sodium perchlorate at pH 5.5 was first determined as a function of sodium perchlorate concentration. The lead in the saturated solutions was determined after 3 days and again after 8 days shaking in a water bath at 25°. The solution was freed from solid lead fluoride by centrifugation and after adjusting the sodium perchlorate concentration to 2.0 M, the lead in solution was determined polarographically. The solid phases were examined by X-ray powder diffraction to verify that it was always rhombic lead fluoride present both in this and in the following series where fluoride or lead might be present in excess. The results (Table II) show good agreement between series run on analytical reagent grade solid lead fluoride and lead fluoride precipitated *in situ* from lead perchlorate and sodium fluoride. The markedly decreased solubility in sodium perchlorate solutions greater than 2 M in concentration is

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(3) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).

in agreement with the rapidly increasing activity coefficient of lead ion noted polarographically in high concentrations of sodium perchlorate.[4]

Table II

Solubility of Lead Fluoride in Sodium Perchlorate Solutions

pH 5.5 ± 0.2; 25°

$NaClO_4$, M	Solubility of PbF_2, mmoles/l. Run A[a]	Run B[b]		Average
0.0	2.69	...	...	2.69
0.1	3.80	3.90	3.84	3.85
0.5	4.42	4.72	4.60	4.58
1.0	4.64	4.88	4.80	4.77
2.0	3.96	4.05		4.01
3.0	2.80	2.86	2.84	2.48
4.0	2.02	1.96		1.99
6.0	0.80	0.70	0.81	0.77

[a] Lead fluoride added as solid salt, 0.2 g. per 50 ml. of sample. [b] Lead fluoride formed from 0.5 mM $Pb(ClO_4)_2$ and 1.0 mM NaF.

Table III

Solubility Product Data for Lead Fluoride

Initial concn., mM [Pb]	[F]	Equilibrium concn., mM [ΣPb]	$[Pb^{++}]$	$[F^-]$	$K_{sp} \times 10^7$
0.976	50.0	0.325	0.119	48.0	2.75
.976	80.0	.200	.043	78.0	2.68
.976	100.	.160	.0307	98.	2.95
.976	200.	.116	.0065	198.	2.53
.975	300.	.100	.0028	298.	2.48
1.95	100.	.165	.027	96.	2.48
4.88	100.	.170	.030	90.	2.43
4.88	[a]	8.08	7.30	5.5	2.20
[b]	100.	0.16	0.0296	100.	2.96
[b]	[b]	4.01	3.5	7.5	1.97
				Av.	2.54

[a] Excess solid PbF_2 added, no additional fluoride. [b] Excess solid PbF_2 added, no additional lead.

The solubility of lead fluoride at differing ratios of lead and fluoride ion was determined next. All solutions contained 2.0 M sodium perchlorate and were equilibrated and analyzed as before. From measurement of the total concentration of lead in solution at equilibrium and the known quantities of reactants added, it was possible to calculate the solubility product of lead fluoride utilizing the expressions $[Pb]_{total} = [Pb^{++}] + [PbF^+] + [PbF_2]$ and $[F]_{total} = [F^-] + [PbF^+] + 2[PbF_2]$ and the previously determined values for β_1 and β_2. Table III gives the results, from which it may be seen that the concentration solubility product of lead fluoride in 2.0 M sodium perchlorate corrected for complex formation and averaged from results over a considerable range of lead to fluoride ratios was satisfactorily constant and equal to 2.5×10^{-7} with a standard deviation of 0.31×10^{-7}. An estimate of the activity product may be made from the solubility determined in pure water by approximating the activity coefficients of lead and fluoride ions at the ionic strength of the saturated solution and correcting for the partial formation of PbF^+. The stability constant determined in 2.0 M sodium perchlorate probably is accurate enough for the latter calculation inasmuch as the correction to the lead ion concentration is only of the order of 10%, and the effect of PbF_2 is negligible. Taking estimates of the activity coefficients of lead and fluoride ions at ionic strength of 0.015 M from the paper by Kielland,[5] the activity product of lead fluoride was found to be 3.6×10^{-8}. This turns out to be in good agreement with the value of 4.37×10^{-8} given by Broene and DeVries[6] when the latter is corrected for the effect of the PbF^+ ion, making it 3.74×10^{-8}.

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(4) H. M. Hershenson, M. E. Smith, and D. N. Hume, *J. Am. Chem. Soc.*, **75**, 507 (1953).

(5) J. Kielland, *ibid.*, **59**, 1675 (1937).

(6) H. H. Broene and T. DeVries, *ibid.*, **69**, 1644 (1947).