[Contribution from the Sterling Chemistry Laboratory of Yale University]

Polarographic Studies of Metal Complexes. IV. The Lead(II) Tartrates and Oxalates

By Thelma Meites and Louis Meites

Lead(II) forms a hydrogen tartrate complex, $Pb_2(HTart)_3^+$, in acidic solutions, and, in strongly alkaline solutions, a complex containing two tartrate ions per lead atom. The latter complex is transformed at the dropping electrode surface into colloidal lead hydroxide which is then reduced. In 1 *F* potassium hydroxide solutions there is some evidence for the existence of a third complex in which the tartrate:lead ratio is 1. In strongly alkaline solutions containing oxalate, the biplumbite ion predominates. At *p*H values below about 12 a basic oxalate, $3Pb(OH)_2 \cdot PbC_2O_4$, precipitates from 0.05 *F* oxalate solutions. At higher oxalate concentrations the $Pb(C_2O_4)_2^=$ ion predominates between *p*H 7.5 and 10.5.

The polarography of lead in tartrate media was first studied by Suchy,[1] who reported a well-defined wave for which $E_{1/2} = -0.60$ v. *vs.* S.C.E. in an 0.5 *F* potassium sodium tartrate medium of unspecified *p*H. Lingane[2] gave $E_{1/2} = -0.50$ v. in 0.5 *F* potassium tartrate, and −0.48 v. and −0.75 v. for the half-wave potentials in 0.5 *F* tartrate media of *p*H 4.5 and 13, respectively. Pyatnitskii[3] found that in strongly alkaline solutions the rate of change of $E_{1/2}$ with *p*H indicated that two hydrogen ions were involved in the reduction of one lead atom. He gave the formula of the complex as $Pb(OCHCOO^-)_2$, and its association constant as 3.2×10^{14} from polarographic data, or 2.1×10^{13} from potentiometric studies.

No previous studies of the polarography of lead in oxalate media have been published.

Experimental

Measurements were made with the polarographic apparatus previously described,[4] using the techniques discussed in earlier papers of this series.[5-7]

For this work the half-wave potentials were measured by a simplified modification of a very precise method recently described.[8] The residual current at the half-wave potential was secured by extrapolation from the preceding "zero-current" portion of the wave, and the half-wave potential was found by interpolation between measurements made at 5-mv. intervals along the rising portion of the wave. By this technique, results apparently precise to 2 mv. are easily secured.

Data and Discussion

The Lead(II) Tartrates.—The half-wave potential of lead has been studied as a function of *p*H in 0.050, 0.20 and 0.50 *F* tartrate solutions. For *p*H values below about 9, tartaric acid solutions were titrated with sodium hydroxide; higher *p*H values were secured with potassium tartrate solutions titrated with potassium hydroxide. The results, shown in Fig. 1, are generally similar to those found with the copper(II) tartrates.[5] In strongly acidic solutions, where undissociated tartaric acid predominates, $E_{1/2}$ approaches that for the aquo-plumbous ion in media of comparable ionic strength.[9]

As the *p*H is raised, $E_{1/2}$ becomes more negative, and finally becomes constant at *p*H values between about 4.5 and 6, where it is equal to −0.440 v. in 0.05 *F* tartrate, −0.465 v. in 0.2 *F* tartrate and −0.482 v. in 0.5 *F* tartrate. From the fundamental equation for the reduction of a metal complex, then, assuming that the hydrogen tartrate ion is the complexing species

$$\Delta E_{1/2}/\Delta \log [\mathrm{HTart}^-] = -0.042 = -0.0591(p/n)$$

where *p* is the number of hydrogen tartrate ions per lead atom in the complex and *n* is 2 for the reduction of lead(II) to lead amalgam. This gives $p = 1.42$, so that the complex is presumably $Pb_2(HTart)_3^+$. Comparing $E_{1/2}$ for this complex in 0.05 *F* tartrate with the value found by Lingane[9] in 0.1 *F* potassium nitrate, for which the ionic strength is about the same, we calculate a value for the formal dissociation constant of this complex of about 3×10^{-5}.

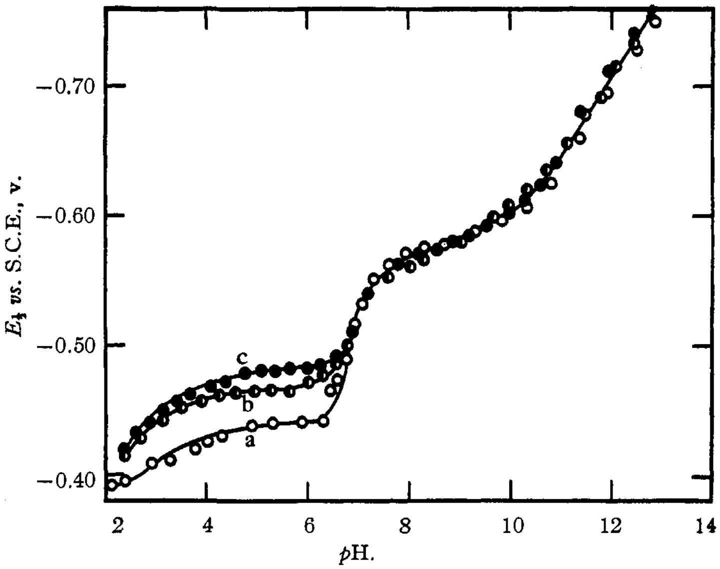

Fig. 1.—Half-wave potentials of lead(II) in (a) 0.05 *F* (open circles), (b) 0.20 *F* (half-solid circles) and (c) 0.50 *F* (solid circles) tartrate media.

We have attempted to verify the formula for this complex by an amperometric titration of a solution of lead nitrate in 0.1 *F* potassium nitrate, *p*H 3.4, with potassium hydrogen tartrate. The difference between the diffusion coefficients of the aquo- and hydrogen tartrato- complexes is, however, so small that no break could be detected in the resulting curve. The very low value found by Lingane[2] for the diffusion current constant of lead

(1) K. Suchy, *Collection Czechoslov. Chem. Communs.*, **3**, 354 (1931).

(2) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(3) I. V. Pyatnitskii, *Zhur. Anal. Khim.*, **3**, 331 (1948).

(4) L. Meites and T. Meites, This Journal, **72**, 3686 (1950).

(5) L. Meites, *ibid.*, **71**, 3269 (1949).

(6) L. Meites, *ibid.*, **72**, 180 (1950).

(7) L. Meites, *ibid.*, **72**, 184 (1950).

(8) L. Meites, *ibid.*, **72**, 2293 (1950).

(9) J. J. Lingane, *ibid.*, **61**, 2099 (1939).

in his "acid tartrate" medium is probably due to the gelatin present in his solutions.[10]

As the *p*H is raised above 6, the concentration of hydrogen tartrate ion in the solution becomes small compared to the lead concentration and, as with the copper complexes,[5] the half-wave potential shifts rapidly to more negative values. There is no well-defined region of constancy corresponding to a normal tartrate complex, but rather a fairly sharp increase between *p*H 6 and 7.5, then a slower change up to *p*H 9.5, and finally, at still higher *p*H values, a linear change of $E_{1/2}$ at the rate of -60 mv. per *p*H unit.

This last observation is in accordance with the findings of Pyatnitskii.[3] The reducible species in the strongly alkaline media cannot, therefore, be biplumbite ion, for the measured half-wave potentials are about 100 mv. more negative than those measured by Lingane[11] for this ion in sodium hydroxide solutions, and also because of the clear indication that two, not three, hydroxyl ions are liberated per atom of lead reduced. However, it also cannot be a hydroxytartrato-complex, as suggested by Pyatnitskii, because the half-wave potential is independent of the tartrate concentrations can be fitted by the equation $E_{1/2} = -0.829 + 0.060\ p\mathrm{OH}$ (for *p*OH values between 1 and 3.5) with an average error of 3 mv.

An amperometric titration of 1.6 m*M* lead in *ca.* 0.02 *F* potassium hydroxide–0.05 *F* potassium nitrate with 0.050 *F* potassium sodium tartrate (Fig. 2a) shows a fairly well defined break at a solution composition corresponding to 1.9 moles of tartrate per mole of lead. The same result is also secured in similar titrations in 0.02 *F* potassium hydroxide–1 *F* potassium nitrate, and in 1.5 *F* potassium hydroxide–1 *F* potassium nitrate. (In the latter medium there is a second end-point at a tartrate:lead ratio of 1; *cf.* Fig. 2b.) Therefore there must actually be a reaction in the body of the solution involving two tartrate ions per lead atom. It may be mentioned that in the 0.02 *F* potassium hydroxide–0.05 *F* potassium nitrate solution the half-wave potential of lead was -0.716 v.: this value was shifted to -0.728 v. by the addition of 0.3 mole of tartrate per mole of lead, and was -0.735 v. when the tartrate:lead mole ratio was 11.3.

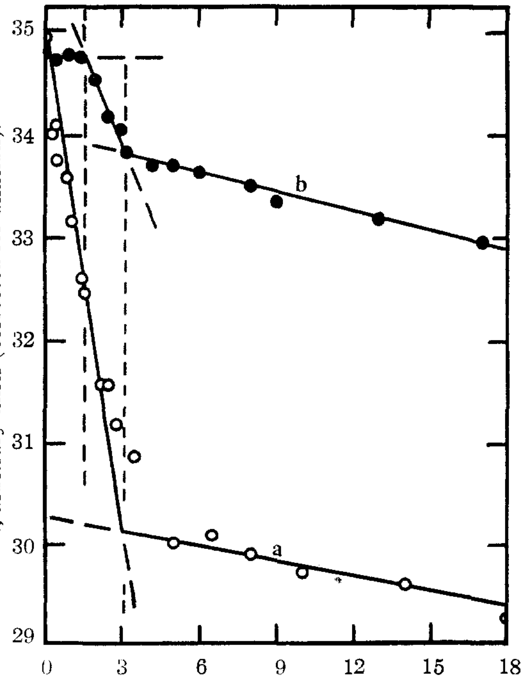

Fig. 2.—Amperometric titrations with 0.050 *F* potassium sodium tartrate of 50.0-ml. portions of 1.59 m*M* lead(II) in (a) *ca.* 0.02 *F* potassium hydroxide–0.05 *F* potassium nitrate and (b) 1.5 *F* potassium hydroxide–1 *F* potassium nitrate. The dashed vertical lines correspond to tartrate:lead ratios of 1.0 and 2.0.

These facts seem to indicate that the complex containing two (or one) tartrate groups per lead atom, formed in the body of the solution, dissociates rapidly at the electrode surface to give colloidal lead hydroxide, which is then reduced.[12] This assumption accounts for the influence of tartrate on the diffusion current *via* the larger size and consequently smaller diffusion coefficient of the tartrato- or hydroxytartrato- complex compared to the biplumbite ion. It also accounts for the fact that the tartrate concentration in the bulk of the solution is without effect on the half-wave potential, and for the dependence of $E_{1/2}$ on the *p*H of the solution.

The effect of Triton X-100 on this wave is shown in Fig. 3. Curves secured at Triton concentrations up to $1.05 \times 10^{-3}\%$ are completely superimposable. A further increase to $1.4 \times 10^{-3}\%$, however, clearly alters the shape of the top of the wave, and this effect increases at higher Triton concentrations up to about 0.2%. Drop time data show a discontinuity at a Triton concentration of $1.10 \times 10^{-3}\%$; this value for the polarographic critical concentration of this material is in good agreement with the value found earlier in an alkaline copper(II) tartrate solution.[13]

The effect of gelatin (Fig. 4) is different from any previously observed. Below the polarographic critical concentration from drop time data ($4.6 \times 10^{-3}\%$), no change in the wave form takes place, but at higher concentrations the curve is shifted to more negative potentials to an extent which increases continually from zero at the foot of the wave to as much as—in an extreme case—1.1 v. near its peak. This suggests the effect of a superimposed external resistance.[14] And it is actually found that near the foot of the wave the displacement along the potential axis is proportional to the current. The apparent resistance thus added is approximately 2500 ohms with $7.5 \times 10^{-3}\%$ gelatin, and it increases up to 60,000 ohms with $9.3 \times 10^{-2}\%$ gelatin. However, this simple proportionality is valid only at potentials more positive than $E_{1/2}$ in each case, for at higher cur-

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(10) J. K. Taylor and R. E. Smith, *Anal. Chem.*, **22**, 495 (1950).

(11) J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

(12) In other words, the reduction probably proceeds according to the equations $\mathrm{Pb(OH)_2(Tart)_2^{-4}} \rightleftarrows \mathrm{Pb(OH)_2} + 2\mathrm{Tart}$ and $\mathrm{Pb(OH)_2} + 2e^- \rightleftarrows \mathrm{Pb\ (Hg)} + 2\mathrm{OH}^-$, and the second of these is the rate-determining step.

(13) L. Meites and T. Meites, THIS JOURNAL, **73**, 177 (1951).

(14) J. J. Lingane, *ibid.*, **62**, 1665 (1940).

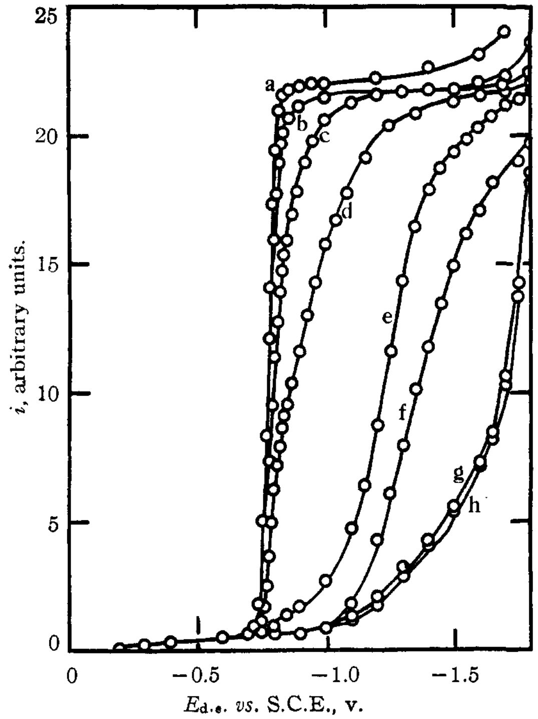

Fig. 3.—Polarograms of 1.6 mM lead(II) in 0.2 F potassium sodium tartrate–0.5 F potassium hydroxide with (a) 0, (b) 1.39, (c) 1.88, (d) 2.85, (e) 6.75 × 10^{-3}, (f) 1.96 × 10^{-2}, (g) 0.19 and (h) 1.03% Triton X-100.

rents the calculated resistance begins to increase again and may finally amount to several times the values given.

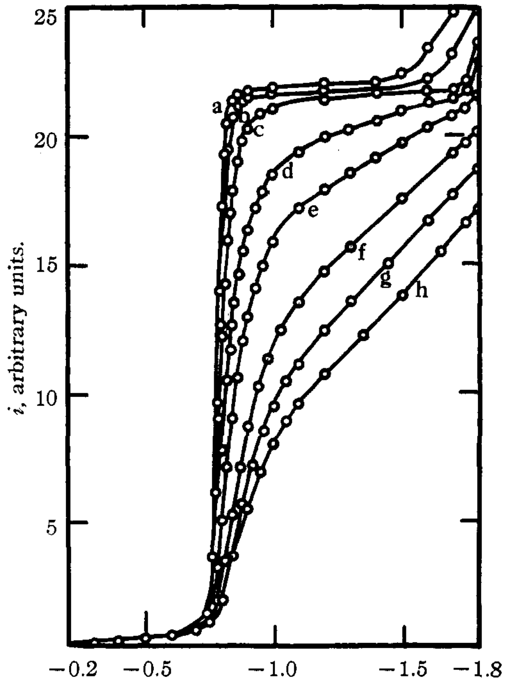

Fig. 4.—Polarograms of 1.6 mM lead(II) in 0.2 F potassium sodium tartrate–0.5 F potassium hydroxide with (a) 0, (b) 5.1, (c) 7.5, and (d) 9.9 × 10^{-3}, (e) 1.5, (f) 2.6, (g) 5.0 and (h) 9.3 × 10^{-2}% gelatin.

The Lead(II) Oxalates.—Addition of lead(II) to a nearly neutral 0.05–0.5 F potassium oxalate solution gives a very finely divided white precipitate, presumably normal lead oxalate.[15] This material very readily forms supersaturated solutions which are stable for increasingly longer periods of time as the oxalate concentration is increased. Thus, 1.6 mM lead gives an immediate precipitate with 0.05 F oxalate, but in 0.5 F oxalate a precipitate at this lead concentration is secured only after the solution has stood for 15 minutes or more, The precipitate, once formed, agglomerates to a dense rapidly-settling material which is slowly soluble in strongly acidic solutions. Its solubility in water and in oxalate solutions of various concentrations has been studied by Kolthoff, Perlich and Weiblen.[14]

When a more alkaline (pH 12) solution of lead(II) in dilute oxalate media is neutralized, an apparently quite different precipitate forms. Figure 5a shows the effect of pH on the half-wave potential of lead in 0.05 F potassium oxalate between pH 13.2 and 10.8: at lower pH values the concentration of dissolved lead is too small (<0.02 mM) to allow accurate measurements. The line shown has the equation $E_{1/2} = -0.799 + 0.079\ p\text{OH}$. The value of the slope is close to the expected 0.089 for a reduction liberating three hydroxyl ions per lead atom, and, considering the activity effects which may reasonably be attributed to the presence of the oxalate here,[16] this equation may be taken as identical with that established by Lingane[11] for the reduction of biplumbite ion.

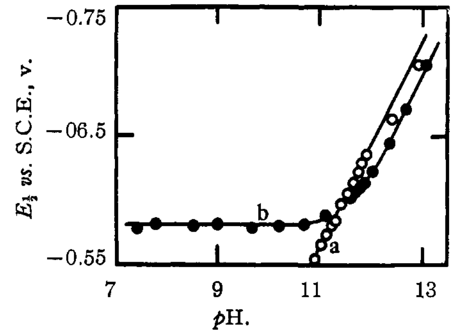

Fig. 5.—Half-wave potentials of lead(II) in (a) 0.05 F and (b) 1.0 F potassium oxalate.

Data on the diffusion current of this wave as a function of pH are presented in Table I. As in the corresponding precipitation of basic copper(II) oxalate,[7] the concentration of metal ion is governed by the 1.5 power of the hydroxyl ion concentration, as shown in the last column of Table I. Tentatively, then, we can write, as the simplest equation accounting for these facts

$$4\text{HPbO}_2^- + 4\text{H}_2\text{O} + \text{C}_2\text{O}_4^{=} \longrightarrow 3\text{Pb(OH)}_2\cdot\text{PbC}_2\text{O}_4 + 6\text{OH}^-$$

and from these data we find $K = 1.9 \times 10^3$.

A portion of the precipitate, filtered onto a sintered-Pyrex filtering crucible, washed with

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(15) I. M. Kolthoff, R. W. Perlich and D. Weiblen, *J. Phys. Chem.*, **46**, 561 (1942).

(16) D. D. DeFord and D. L. Anderson, THIS JOURNAL, **72**, 3918 (1950).

TABLE I

PRECIPITATION OF BASIC LEAD(II) OXALATE

$[OH^-]$, molar	i_d arbitrary units	$[Pb^{II}]$ molar	$[Pb^{II}]/[OH^-]^{1.5}$
4.12×10^{-2}	27.00	1.645×10^{-3}	No ppt.
8.13×10^{-3}	25.30	1.543	2.10
6.85	23.57	1.438	2.54
5.50	21.13	1.289	3.15
4.52	18.13	1.106	3.64
3.47	10.05	0.613	3.00
2.48	8.15	.497	4.01
2.00	5.17	.315	3.54
1.66	3.54	.216	3.20
1.35	2.62	.160	3.22
1.08	1.87	.114	3.21
8.22×10^{-4}	0.95	.058	2.46
5.90	.60	.036	2.50
3.16	.34	.021	3.75
		Mean	$3.1_0 \pm 0.45$

water and acetone and dried over anhydrous magnesium perchlorate for 2 weeks was found to weigh 0.1240 g. It was decomposed by long standing under dilute sulfuric acid, and the lead sulfate thus resulting, after drying at 105°, weighed 0.1420 g. Assuming the precipitate to have the formula given above, the calculated weight of lead sulfate is 0.1433 g. The difference between the actual and calculated weights is probably due to water retained by the basic oxalate. Had the precipitate been the normal oxalate, the calculated weight of lead sulfate would have been 0.1513 g.

In 1.0 *F* potassium oxalate solutions equilibrium in this reaction is too slowly attained to permit accurate measurement of the diffusion current by the technique here employed. A few measurements which were made after the solutions had been permitted to stand for some hours are in approximate accord with the picture outlined above, but the values of *K* secured, due to the continuing slow precipitation, are much too erratic to aid in the assignment of a more accurate value than that given.

At *p*H values above about 12.3 the half-wave potentials in 1 *F* potassium oxalate (Fig. 5b) fall on a line parallel to that representing the data in 0.05 *F* oxalate, and are about 15 mv. more positive than the latter values. The difference is probably not significant, and the slope of this section of the curve indicates that it is the biplumbite ion which is the reducible species here also.

At lower *p*H values, however, the half-wave potential values becomes more negative than would be predicted by an extrapolation of this line, and between *p*H 7.4 and 10.7 in 1 *F* potassium oxalate $E_{1/2}$ is constant at -0.581 ± 0.002 v., in very good agreement with the value of -0.59 v. calculated from the dissociation constant of the $Pb(C_2O_4)_2^{=}$ ion given by Kolthoff, Perlich and Weiblen.[15]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Raman Effect and Ultraviolet Absorption Spectra of Molybdenum and Tungsten Hexafluorides[1]

BY K. N. TANNER[2] AND A. B. F. DUNCAN

The Raman effect for MoF_6 and WF_6 has been studied and three lines were found for each molecule. Two of the lines are weak and diffuse, and the third is strong, sharp and highly polarized. This result indicates octahedral structure for these molecules. If this symmetry is assumed, the Raman inactive frequencies can be calculated from force constants obtained from the Raman active frequencies. Exploratory studies have been made on the ultraviolet absorption spectra of these molecules. A strong absorption band has been found for each, with a center probably around 1850 Å. for MoF_6 and about 1750 Å. for WF_6. This appears to represent the first allowed electronic transition. An interesting banded structure was found for this transition in MoF_6.

Introduction

Molecules of the type XY_6 are of some interest in the study of molecular structure, since symmetrical arrangements of atoms in molecules of this type may exist. The most symmetrical arrangement results when the Y atoms are located at the corners of a regular octahedron. This symmetry is characterized by several three and fourfold axes of rotation and a center of symmetry, and corresponds to the crystallographic group O_h.

A number of molecules of the type XY_6 have been studied, among them SF_6, SeF_6, TeF_6, UF_6, MoF_6 and WF_6. All have been subjected to electron diffraction experiments, and all but the last two have been studied by spectroscopic methods. All the evidence obtained so far indicates that SF_6, SeF_6 and TeF_6 have octahedral symmetry.[3] This work was undertaken to supply spectroscopic data on MoF_6 and WF_6.

In only a few cases has the electronic spectrum of molecules of cubic symmetry been studied. Since only transitions to triply degenerate excited states are allowed, the vibrational structure to be expected for such spectra would be very complicated and should appear as continuous or quasi-continuous bands.[4]

Experimental Details

The samples[5] of MoF_6 and WF_6 were prepared in metal systems and triply distilled *in vacuo* over anhydrous KF.

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(2) Part of the dissertation presented to the Faculty of the Graduate School of the University of Rochester in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

(4) H. Sponer and E. Teller, *Revs. Modern Phys.*, **13**, 92 (1941).

(5) We appreciate the kindness of Drs. Cady and Barber of the University of Washington who prepared these samples.