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A Polarographic, Potentiometric and Spectrophotometric Study of Lead Nitrate Complexes

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Lead has been found to form a mononitrate complex, $PbNO_3^+$, in solutions of moderate nitrate concentration. The formation constant of this complex has been determined by polarographic, potentiometric and spectrophotometric methods, and the values obtained were, respectively, 2.8 ± 0.5, 3.3 ± 0.5 and 1.6 ± 1.0 at 25° and an ionic strength of 2.00. The ratio of the components in the complex was verified by application of the method of continuous variations.

It has customarily been taken for granted in polarographic work, and by chemists in general, that no complexes of appreciable stability are formed between lead and nitrate ions in aqueous solution. We were, therefore, surprised to observe a very marked displacement of the reversible half-wave potential of the lead ion to more negative values at high nitrate ion concentrations. This could hardly be explained except in terms of complex formation: by analogy with cadmium in nitrate medium[1] and lead in perchlorate medium, the shift should have been in the other direction. A search of the literature revealed that a number of workers have attempted to interpret the behavior of lead nitrate solutions in terms of complex formation (or "incomplete dissociation") with varying degrees of success. Righellato and Davies[2] by conductivity measurements and Plake[3] and Zirkler[4] from heats of dilution deduced degrees of dissociation of lead nitrate corresponding to formation constants for the $PbNO_3^+$ ion of the order of 6–15. These results are unconvincing, however, because the methods used give similar orders of magnitude for the degree of dissociation of such manifestly strong electrolytes as the alkaline earth nitrates and complexes known to be appreciably stable such as $PbCl^+$ and $CdCl^+$. Redlich[5] has since pointed out the theoretical shortcomings of the above methods and has emphasized the difficulty of interpreting results in solutions where the concentrations are so high that specific ionic interactions become very significant before appreciable complex formation takes place.

Nasanen[6] was able to interpret the potentiometrically measured solubility of lead iodide in sodium and barium nitrate solutions with the aid of the Debye–Hückel theory and the assumption of the partial formation of $PbNO_3^+$ ions. He obtained an equation for the relationship between the apparent formation constant of the ion and ionic strength which, unfortunately, contained constants depending greatly on the particular supporting electrolyte used, the estimated formation constants at an ionic strength of 2 varying from 3.5 to 16. In order to determine conclusively whether peculiarities in the chemical behavior of lead in nitrate medium should be attributed to complex formation or changes in activity coefficients alone, we have studied the apparent reaction of lead and nitrate ions at constant ionic strength in nitrate–perchlorate mixtures over a wide range of concentration by three independent methods.

Experimental

Polarographic Measurements.—Measurements were made with a Sargent Recording Polarograph, Model XXI. Corning marine barometer tubing was used for the capillary which had a value of 1.65 for $m^{2/3}t^{1/6}$ at the potential of the S.C.E. A constant temperature water-bath, held at 25 ± 0.2° was used for all measurements. The water-bath, dropping mercury cathode and one side of the 115 a.c. input to the polarograph were all grounded for stable operation.

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[1] D. D. DeFord and D. L. Anderson, THIS JOURNAL, **72**, 3918 (1950).

[2] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[3] E. Plake, *Z. physik Chem.*, **A162**, 257 (1932).

[4] J. Zirkler, *ibid.*, **A163**, 1 (1932).

[5] O. Redlich, *Chem. Revs.*, **39**, 333 (1946).

[6] R. Nasanen, *Ann. Acad. Sci. Fennicae A II Chem.*, No. 13, 1 (1945).

In order to avoid the irreproducible results which are found when the conventional saturated calomel electrode is used in conjunction with a perchlorate medium and which are probably due to the precipitation of potassium perchlorate at the interfaces, two other types of reference electrodes were used. The first of these was a large calomel electrode made up with a solution of 1.00 *M* in sodium perchlorate and 0.100 *M* in sodium chloride. This was used with a 1.0 *M* sodium perchlorate salt-bridge, and had a potential of +0.100 v. *vs.* the S.C.E.

The second reference electrode used was a large "H" cell with a very fine sintered glass disk separating the two arms containing the solution to be polarographed in one arm and a saturated quinhydrone solution in the other arm. Except for the 0.0001 *M* lead nitrate in the d.m.e. arm, and the quinhydrone in the reference arm, the solutions in both arms were the same. A cylindrical platinum mesh electrode (0.5 × 2 inches) was dipped into the quinhydrone solution to give a large platinum surface area. The polarographic assembly was fitted with a nitrogen supply introduced through a two-way stopcock so that the lead-containing solution could be first deaerated, following which a stream of nitrogen was passed through the quinhydrone arm during the polarographic measurement to provide a stirring effect. This method of stirring was found to be more satisfactory than mechanical stirring because the excessive vibrations introduced by the latter affected the dropping electrode and caused irregular curves.

The half-wave potentials were measured by use of the technique described in an earlier communication.[7] The plots of log $[(i_d - i)/i]$ *vs.* *E* were good straight lines of slope 30 ± 1 mv. It was found possible to estimate the half-wave potential in any given experiment to 0.1 mv., and duplicate experiments showed that the reproducibility was of the order of 1 mv. The observed half-wave potentials are corrected for *iR* drop but still involve junction potentials of unknown value. These junction potentials should be small for the sodium perchlorate–calomel electrode and nearly zero for the quinhydrone cell.

Potential Measurements.—Potential measurements were made with a Rubicon portable potentiometer sensitive to 0.05 mv. Amalgam pool measurements were made in a large "H" cell of the same type used in the polarography. One arm of the cell contained a sodium perchlorate solution while the other held an equal concentration of sodium nitrate or an equivalent mixture of sodium nitrate and sodium perchlorate. In addition, each solution contained lead ion and dilute perchloric acid. Enough lead amalgam to cover the bottom of the cell was added to each arm. The amalgam was about 0.1% lead and was made by adding the appropriate amount of pure lead to mercury and heating. The amalgam was kept from exposure to air to prevent the formation of oxide scum.

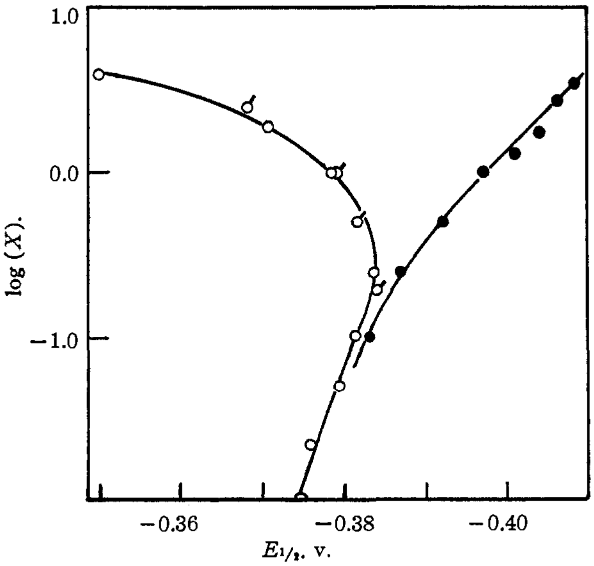

Fig. 1.—Half-wave potential of lead as a function of concentration of supporting electrolyte: open circles, perchloric acid; tailed circles, sodium perchlorate; solid circles, sodium nitrate.

Solid lead electrodes in the form of sticks were used in some experiments. These were rubbed to a shiny surface with sandpaper and rinsed in dilute perchloric acid before use. Each stick was fitted with a copper wire contact fitted into a groove at one end and sealed with "Apiezon W" sealing compound to prevent moisture from reaching the junction. Since the junction is the same for each electrode, any contact potentials which are developed ought to be cancelled out by the use of opposing electrodes. Electrodes prepared in this manner showed differences of less than 0.5 mv. among themselves when placed in the same solution.

Potential measurements using the solid electrodes were made in two ways. The first consisted of measuring the difference in potential of two solutions directly in an "H" cell using two electrodes in each arm. The four possible different readings of the potential were made with the electrodes and the average value taken. The second method was to measure the potential of each solution in question against a suitable reference electrode, such as the quinhydrone–quinone electrode, and then to calculate the potential difference between any two solutions. In the former case, one measures directly potential differences on the order of 20 mv. while in the latter one subtracts two measured potentials of about 800 mv. to obtain a difference of about 20 mv. The former method is to be preferred.

Spectrophotometric Measurements.—All absorbancy measurements were made using the Beckman model DU spectrophotometer with 1.000-cm. silica cells. These were compared against each other using 0.1 *M* sodium nitrate at 300 mμ and the appropriate correction was applied to the observed absorbancy in each cell.

Materials.—Reagent grade chemicals were used without further purification. Lead perchlorate was prepared by adding yellow lead oxide (PbO) to 72% perchloric acid until no further reaction took place. When an excess of the oxide had been added, the hot solution was allowed to cool to room temperature and stand overnight. It was then filtered through a fine sintered glass filter to give a clear, colorless, viscous solution. The lead content of this solution was determined gravimetrically by precipitation as lead sulfate. Prepurified nitrogen was used to remove oxygen from solutions before polarographic or potentiometric measurement.

Polarographic Determination.—Polarograms of 0.001 *M* lead perchlorate in various concentrations of slightly acidified (*p*H 3) sodium perchlorate were taken using the sodium perchlorate–calomel electrode. The results, together with those of a similar series using 0.0001 *M* lead perchlorate in perchloric acid and quinhydrone reference electrodes containing perchloric acid of the same composition are shown in Fig. 1. All potentials refer to the saturated calomel electrode as 0.000 v. The striking shift of half-wave potential to more positive values at high ionic strengths observed by DeFord and Anderson with cadmium in nitrate media is equally apparent here. Their interpretation of the phenomenon as the effect of medium on the activity coefficient of the metal ion is given additional support by our results in perchloric acid which were obtained without the usual large uncertainty due to unknown liquid junction potentials. Data on the half-wave potential of lead with sodium nitrate as the supporting electrolyte, plotted on the same axis, show strong indication of complex formation.

In order to gain some idea as to the possible magnitude of specific ionic activity effects at an ionic strength of 2.00 in the absence of complex formation, experiments were made with mixtures of perchloric acid and sodium perchlorate. The half-wave potential of lead *vs.* the quinhydrone electrode in the same medium was determined over the range of compositions given in Table I. For each mixture, the half-wave potential *vs.* the S.C.E. was then computed as before using the value of Hovorka and Dearing[8] for the standard potential of the quinhydrone electrode and assuming the activity coefficient of hydrogen ion to be a function of ionic strength alone in these mixtures. The salt effect difference between perchloric acid and sodium perchlorate was estimated to be within experimental error of the measurements and was, therefore, neglected.

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[7] D. N. Hume, D. D. DeFord and G. C. B. Cave, THIS JOURNAL, **73**, 5323 (1951).

[8] F. Hovorka and W. C. Dearing, *ibid.*, **57**, 446 (1935).

From the data in Table I it was concluded that sodium perchlorate and perchloric acid are alike in their effect upon the half-wave potential of lead ion and that specific univalent cation effects on the activity coefficient of lead ion are not great at an ionic strength of 2.

TABLE I

COMPARISON OF $NaClO_4$ AND $HClO_4$ AT IONIC STRENGTH = 2.0

Concn. $HClO_4$, moles/liter	$E^1/_2$ *vs.* QH. mv.	$E^1/_2$ *vs.* S.C.E., mv.
0.40	−802	−371
0.70	−819	−372
1.00	−826	−371
1.30	−833	−371
1.60	−839	−372
1.90	−843	−371

The half-wave potential of 0.0001 *M* lead ion was then determined in solutions 0.001 *M* in perchloric acid and containing varying amounts of sodium perchlorate and sodium nitrate at a constant ionic strength of 2.0. Two separate series of experiments were made, using in the first the sodium perchlorate–calomel reference electrode and in the second the quinhydrone reference electrode. These were in good agreement except at the very lowest nitrate concentrations.

Adopting the observed value in the pure perchlorate medium as the half-wave potential of the simple ion, the value of the formation constant K_1 for the complex $PbNO_3^+$ was calculated by the method of DeFord and Hume.[9] In Table II are listed the values for $F_j(X)$ as calculated from the data obtained with the quinhydrone reference electrode, which were considered more reliable. These data are plotted in Fig. 2. The plot of $F_0(X)$ is a curve, but the plot of $F_1(X)$ approaches the horizontal at lower nitrate concentrations, indicating that in this region only the mononitrate complex is present. The curvature at high nitrate concentration indicates that there is a small contribution due to unionized lead nitrate in this region. Extrapolation of a plot of $F_1(X)$ to zero nitrate concentration yielded a value of 3.4 for K_1. Substitution of this value and calculation of $F_2(X)$ resulted in a curve which on extrapolation leads to a value of less than unity for K_2. Measurement of the limiting slopes of the previous $F(X)$ curves give a value of 3.4 for K_1 and about 0.8 for K_2. The application of the same method to the data from measurements against the sodium perchlorate–calomel reference electrode (involving somewhat greater uncertainty due to junction potentials) gave a value of 2.3 for K_1 and again slightly less than unity for K_2.

TABLE II

ANALYSIS OF DEPENDENCE OF $E^1/_2$ ON NITRATE CONCENTRATION

$\mu = 2.0, t° = 25°, I_s = 4.30, K_1 = 3.4, K_2 = \sim 0.8$

(NO_3^-), m./l.	$\Delta E^1/_2$, mv.	*I*c	$F_0(X)$	$F_1(X)$	$F_2(X)$
0.30	9.2	4.25	2.1	3.6	0.7
.60	14.8	4.28	3.2	3.7	0.5
.90	19.3	4.08	4.8	4.2	0.9
1.20	24.0	3.98	7.0	5.0	1.3
1.50	29.5	4.13	10.4	6.3	2.0
1.80	32.9	3.99	14.1	7.2	2.1
2.00	35.3	3.94	17.2	8.1	2.4

Potentiometric Determination

The formation constant for the $PbNO_3^+$ complex is calculated from the difference in potential of identical lead electrodes in nitrate and perchlorate solutions equal concentration with the aid of the relation (for 25°)

$$\Delta E = \frac{0.0591}{2} \log \frac{(Pb^{++})_p}{(Pb^{++})_n}$$

activity coefficients are assumed to be equal at the same ionic strength; ΔE is the potential difference between the solutions; $(Pb^{++})_p$ is the lead ion concentration in the perchlorate solution, which is, on the assumption of no complexing, equal to the amount added; and $(Pb^{++})_n$ is the lead ion concentration in the nitrate-containing solution. The latter is calculated and then the value of K_1 is found by substituting into the usual relation for the formation constant, assuming only $PbNO_3^+$ to be formed.

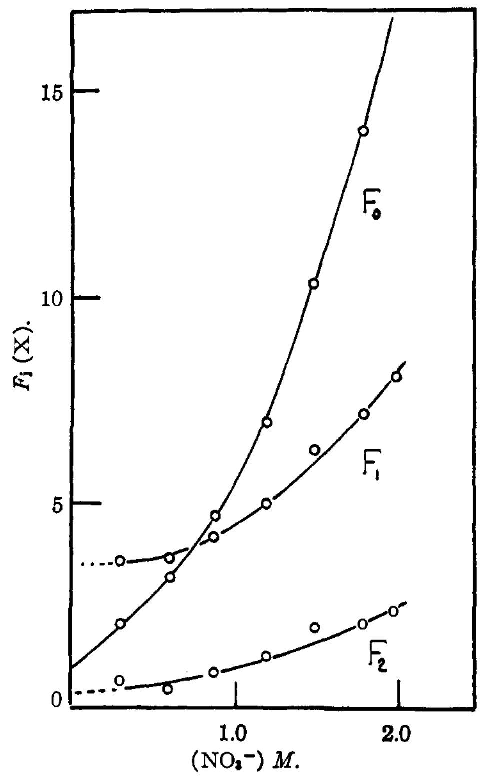

Fig. 2.—Analysis of shift of half-wave potential as a function of nitrate ion concentration.

A number of measurements were made with amalgam electrodes at both variable and constant ionic strength and with stick electrodes at a constant ionic strength of 2.00. Each solution was

TABLE III

POTENTIOMETRIC DETERMINATION OF FORMATION CONSTANT OF $PbNO_3^+$ ION

(NO_3^-) *M*	μ	Electrode[a]	ΔE, mv.	K_1
0.10	0.11	A	4.2	3.8
0.50	0.51	A	12.3	3.2
1.00	1.0	A	21.3	4.2
0.10	2.00	A	4.2	3.8
0.50	2.00	A	11.2	2.8
1.00	2.00	A	19.5	3.6
1.00	2.00	S	16.9	2.7
1.00	2.00	S	19.9	3.7
1.00	2.00	S	17.5	2.9
1.00	2.00	S	20.8	4.1
1.00	2.00	S	18.2	3.1
1.00	2.00	S	17.1	2.8
1.00	2.00	S	17.9[b]	3.0

[a] A = amalgam pool, S = stick. [b] Measured indirectly with a quinhydrone reference electrode.

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

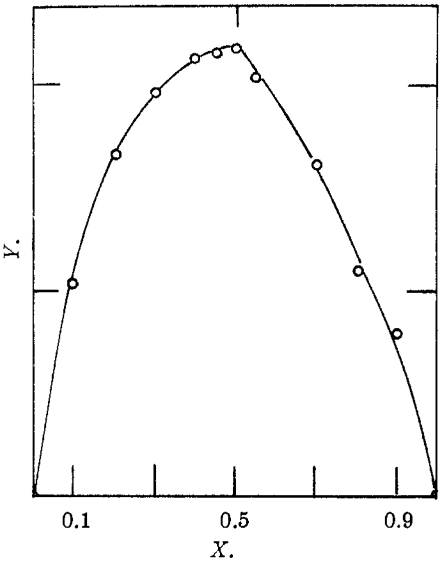

Fig. 3.—Method of continuous variations: Y = change in absorbancy; X = mole fraction of lead perchlorate in lead perchlorate–sodium nitrate mixtures.

0.001 M in lead ion and 0.01 M in perchloric acid, and the remainder sodium perchlorate and/or nitrate. The results, shown in Table III, confirm the polarographic findings at the same ionic strength. It was necessary to assume in these calculations that the junction potential between a 1.00 M $NaClO_4$, 1.00 M $NaNO_3$ solution and 2.00 M $NaClO_4$ was negligible, and the correctness of this assumption, within experimental error, appears to be borne out by the last run where no junction potential was involved. The best value of K_1 for ionic strength of 2.00 was selected as 3.3 with a standard deviation of 0.5.

Spectrophotometric Determination

Although the agreement found between the polarographic and potentiometric methods was gratifying, we were not convinced that the two methods provided a truly independent check on the value of the formation constant, or for that matter even the existence of the ion $PbNO_3^+$. Both are limited in application to the same sort of solution: low lead and high nitrate concentration; and both measure what is fundamentally the same electrochemical property of the system. We, therefore, cast about for an entirely different method of approach, and soon found that absorption spectrophotometry offered one.

Nitrate ion, as is well known, absorbs in the ultraviolet, an absorption maximum occurring at about 300 mμ in water. Preliminary experiments showed that lead perchlorate, itself transparent in this region, resulted in an increase in the absorption of nitrate solutions.

The method of continuous variations[10] was then applied to the lead perchlorate–sodium nitrate system at a wave length of 300 mμ in order to find the ratio of the lead and nitrate ions in the complex. Solutions of sodium nitrate and lead perchlorate each 0.10 M were prepared and a series of mixtures containing x ml. of the lead solution and $10 - x$ ml. of the nitrate solution were made up in 10-ml. volumetric flasks. The absorbancy of each solution was measured with respect to water. Figure 3 shows the result obtained when the increase in absorbancy over that predicted for no reaction, y, was plotted against mole fraction, x, of lead. The peak occurs at a mole fraction of 50% lead ion and indicates that the ratio of lead ion to nitrate ion in the complex is unity, as would be expected for the ion $PbNO_3^+$. The curve shows skewness toward higher nitrate fractions, indicating some contribution from a species containing a larger nitrate to lead ion ratio, such as un-ionized lead nitrate.

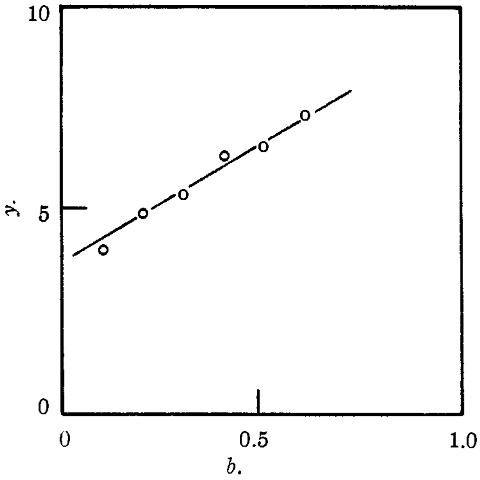

Fig. 4.—Plot of $y = ab/(D - D')$ vs. b for nitrate and lead in McConnell-Davidson equation.

In order to determine the formation constant of the complex ion, the absorbancies of a series of solutions, each 0.05 M in sodium nitrate and containing varying amounts of lead perchlorate and sodium perchlorate, were measured at 300 mμ against reference solutions of the same composition as the samples except that the nitrate was absent. The ionic strength, as usual, was held at 2.00 M. Previous experiments had shown that the extinction coefficient of 0.05 m nitrate ion was the same in 1.95 M sodium perchlorate as in water so that it could be assumed that any "medium effect" was negligible. The data (Table IV) when treated by the method of McConnell and Davidson[11] gave a value of K_1 equal to 1.6. A run at μ = 6.0 led to a slightly higher result, 3.3.

Table IV

Absorbancy of $Pb(ClO_4)_2$–$NaClO_4$–$NaNO_3$ Mixtures

Ionic strength = 2.0; 0.05 M sodium nitrate in each solution = a; wave length = 300 mμ; D' = absorbancy of 0.05 $NaNO_3$ = 0.348

Lead added (b), moles/liter	Absorbancy (D)	$(D - D')$	ab	$ab/(D - D')$
0.10	0.472	0.125	0.005	0.0400
.20	.550	.202	.010	.0495
.30	.630	.282	.015	.0532
.40	.665	.317	.020	.0630
.50	.730	.382	.025	.0653
.60	.757	.409	.030	.0733

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[10] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

[11] H. McConnell and N. Davidson, This Journal, **72**, 3164 (1950).

Discussion

The spectrophotometric results show beyond question that the $PbNO_3^+$ ion is actually present in these solutions. The formation constant so obtained, although differing by a factor of two from the results of the electrical methods is actually not in bad agreement when it is considered that the lead-to-nitrate ratio differs by a factor of 20,000. Furthermore, it would be surprising indeed if the specific effects on individual activity coefficients of lead, nitrate and lead mononitrate ions were the same in 2.0 *M* sodium perchlorate as in 0.67 *M* lead perchlorate, even though the ionic strengths of the two are the same.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF ETHYL CORPORATION]

Phase Study of the $PbO–PbBr_2$ System by X-Ray Diffraction

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The binary system $PbO–PbBr_2$ has been investigated by X-ray diffraction. The results confirm the existence of the four intermediate compounds, $PbO·PbBr_2$, $2PbO·PbBr_2$, $3PbO·PbBr_2$ and $7PbO·PbBr_2$, previously demonstrated by thermal analyses, all except the dibasic compound exhibit polymorphism. The monobasic compound exists in four polymorphic forms, each of which reacts with water to produce the same hydrate, $PbO·PbBr_2·H_2O$. Thermal relationships are given for these four forms and for the hydrate. The significance of the preferential production of one of the crystalline modifications of $PbO·PbBr_2$ by a low temperature solid state reaction is discussed. The tribasic compound exists in two crystalline forms, each of which combines with one molecule of water to produce a different crystalline modification of the hydrate $3PbO·PbBr_2·H_2O$. The thermal relationships of the two forms of $3PbO·PbBr_2$ and of the hydrate are given. The heptabasic compound exists in two forms, a high temperature and a low temperature form. The latter combines with water to produce two hydrates, $7PbO·PbBr_2·5H_2O$ and $7PbO·PbBr_2·7H_2O$. On dehydration by heating, each of these undergoes successive phase changes and finally, at 500°, reverts to the original low temperature form of the heptabasic compound. Heating either of the heptabasic compounds above 600° in the presence of SiO_2 results in formation of a basic bromosilicate. The interplanar spacing values are given for the major reflections of the four intermediate compounds (including their various polymorphic forms), the hydrates and the silicate.

Introduction

During the course of an extensive investigation in these laboratories[1] of the formation and composition of engine-deposit compounds, it has become necessary to make a phase study of the binary systems of several lead compounds. The present paper gives the results of the X-ray diffraction study of the $PbO–PbBr_2$ system, the thermal analysis data for which are given in a preceding paper.[2] The X-ray diffraction data previously reported for this system are very limited. Although Baroni[3] supplemented his thermal analysis of the $PbO–PbBr_2$ system by crystallographic and X-ray diffraction observations of the various compounds formed, he stated that the photographs were complicated and difficult to interpret, and no data[1] were included in his publication. The only published X-ray data found, aside from those for the two components, PbO and $PbBr_2$, were the interplanar spacing values given in the ASTM Index File[4] for the compound, $PbO·PbBr_2$. The results from the present study show that these data are in error, since they were found to correspond to the values obtained for $3PbO·PbBr_2·H_2O$ and not for $PbO·PbBr_2$.

Experimental Method

Powder patterns were obtained for the various preparations by means of a Norelco Geiger Counter X-ray Spectrometer using CuKα radiation. The methods used for mounting the specimen and for angular calibration of the goniometer are described in an earlier publication.[5] The so-called "thermal analysis preparations" used in this study were the samples resulting from the thermal measurements previously described.[2] The fused and quenched preparations were obtained by melting mechanical mixtures of appropriate amounts of the two components, PbO and $PbBr_2$, in magnesium oxide crucibles, mixing well, and quenching by pouring on the flat surface of a large block of copper.

The method for preparing the monobasic hydrate $PbO·PbBr_2·H_2O$ has been described previously.[1] The tribasic hydrate, $3PbO·PbBr_2·H_2O$, was prepared by slowly adding with mechanical stirring 10 g. of 200-mesh PbO (yellow orthorhombic) to 250 ml. of CO_2-free, 80° distilled water containing 39 g. of NaBr. The yellow precipitate formed was filtered, washed with 95% ethyl alcohol and dried in an oven at 70° for 24 hours. Chemical analyses and X-ray diffraction examination indicated a purity of 98% or better for various preparations of the two hydrates.

Results and Discussion

Thermal Analysis Preparations.—An X-ray diffraction study was made of the numerous preparations resulting from the thermal measurements. Each of these preparations had been fused and then allowed to cool very slowly through the primary crystallization point and, also, through its peritectic and eutectic temperatures before removing it from the furnace and allowing to cool to room temperature. The X-ray diffraction data obtained from the powder patterns of these preparations confirmed the results obtained by thermal analyses. They showed the existence of intermediate compounds corresponding to the compositions: $PbO·PbBr_2$, $2PbO·PbBr_2$, $3PbO·PbBr_2$ and $7PbO·PbBr_2$. The phase diagram obtained from the thermal analysis

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(1) F. W. Lamb and L. M. Niebylski, *Anal. Chem.*, **23**, 1388 (1951).

(2) L. M. Knowles, *J. Chem. Phys.*, **19**, 1128 (1951).

(3) A. Baroni, *Atti accad. Lincei*, **20**, 384 (1934).

(4) ASTM X-Ray Diffraction Index Card No. II, 1399.

(5) G. Calingaert, F. W. Lamb and F. Meyer, THIS JOURNAL, **71**, 3709 (1949).