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Solubility of Lead Iodate in Aqueous Systems

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Two forms of lead iodate, with different crystalline structures and solubilities in water, have been reported. Previous workers have found that when the compound is prepared from dilute solution with a slight excess of lead nitrate one form is produced at 25 °C and the other at 60 °C. In this study, relative excesses of lead nitrate or potassium iodate during precipitation were found to have more influence than temperature on the form produced. Solubilities in water at various temperatures and in several aqueous systems at room temperature have been determined. Photomicrographs and X-ray data have also been obtained.

Introduction

Systems containing lead iodate were first studied in detail by Harkins and Winninghoff,[1] who prepared the salt by precipitation from very dilute solution at room temperature. Their solubility in water was 30.7 mg/L at 25 °C. Later La Mer and Goldman[2] prepared lead iodate at 60 °C and found a considerably lower solubility of 20.1 mg/L at 25 °C; this appeared to be roughly confirmed by a single value of 4.13×10^{-5} M (23 mg/L) at 25.8 °C from Kohlrausch.[3a] Another paper by the same author[3b] gave values equivalent to 17.3 mg/L at 17.1 °C and 13.4 mg/L at 9.2 °C. Earlier Böttger[4] gave a value of 18.3 mg/L at 19.95 °C, calculated from conductivity data. Geilmann and Höltje[5] found a solubility equivalent to 24 mg/L at "common temperature". Polesitzkii[6] determined solubilities from (0 to 100) °C. His result of 5.25×10^{-5} M (29.2 mg/L) at 25 °C is closer to that of Harkins and Winninghoff. Edmonds and Birnbaum[7] found a value of 3.58×10^{-5} M (19.9 mg/L) at 25 °C, very close to that of La Mer and Goldman.

Keefer and Reiber[8] prepared lead iodate in both cold and hot solutions. The solubility of each product agreed with the corresponding value in refs 1 or 2. They attributed the difference in the results as being due at least partially to a difference in particle sizes of the two preparations. La Mer and Goldman[2] had suggested this, as well as the possibility of trace impurities affecting the solubility.

Solubility at 35 °C has been reported by Mohanty and Aditya[9] and by Misra and Pani.[10] The figure given by the latter corresponds to 28.3 mg/L, which would appear to represent the La Mer form. Misra and Pani also determined solubilities in potassium nitrate solutions.

X-ray data on hot-precipitated lead iodate have been given by Staritzky and Walker,[11] who described the crystals as orthorhombic bipyramidyl. The cold form was studied by Kellersohn, et al.[12] Data on the hot form are also available from the National Institute of Standards and Technology.[13]

Experimental Section

Lead iodate in each form was prepared by adding small volumes of 0.05 M $Pb(NO_3)_2$ and 0.10 M KIO_3 alternately to two liters of water at room temperature (22 to 23) °C or at 60 °C, with stirring. Both products are formed without water of crystallization. After filtration and washing they were dried in air, without heating. Several different lots of each were prepared. Assay values were (99.9 ± 0.05) %. The raw materials, as well as the potassium nitrate used in some of the tests, were all of ACS reagent grade.

After the bulk of this study was completed, new preparations of lead iodate were made using a large excess of either lead nitrate at 60 °C or potassium iodate at 22 °C. A solubility test was also run on the hot form of $Pb(IO_3)_2$ in 0.2 M KIO_3 solution.

Solutions for solubility measurements were prepared by placing about 1 g of either product in a 473 mL (16-oz.) square glass bottle, with about 400 mL of water or appropriate solution, and mixing well several times during two or more days at the desired temperature. Then, each mixture was allowed to settle for at least 2 days, at the same temperature, after which 25- or 50-mL samples were pipetted (with preheated or cooled pipets as needed) from the upper one-third of the solution with precautions to avoid any fine particles floating on the surface. Iodate was determined by iodometric titration with 0.01 M thiosulfate, standardized against 0.01 M KIO_3 with an uncertainty of about 0.2%. When nitrate was present, the samples were diluted with 100 mL or more of water and bubbled with nitrogen or carbon dioxide to avoid oxidation of iodide by air or nitrate when acidified. When lead nitrate was present, the samples were treated with excess sodium sulfate, allowed to stand overnight, and filtered with washing before titration of the filtrate. For the solubility in potassium iodate solution, lead was determined polarographically.

For the settling tests shown in Table 2, larger volumes of mixtures were prepared as described and then sampled from the top levels after standing for the indicated time intervals.

Microscopic images of the two types of lead iodate were taken after dispersing the dry $Pb(IO_3)_2$ powders onto conventional 13 mm diameter aluminum scanning electron microscope stubs using a carbon-impregnated double-sided adhesive disk. Excess powder was removed from the adhesive by tapping the inverted specimen. The specimens were sputter-coated with an AuPd target for conduction of surface charges to ground during imaging.

Initial imaging attempts in a conventional hard-vacuum scanning electron microscope (SEM) exhibited too much

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Table 1. Solubilities in Water at Various Temperatures

temp	C $Pb(IO_3)_2$/mg·L^{-1}	
°C	cold form	hot form
7 ± 1	12.1 ± 0.5	11.8 ± 0.5
22.6 ± 0.2	21.9 ± 1.0	20.0 ± 1.0
40.0 ± 1.0	23.6 ± 1.5	23.2 ± 1.0
50.0 ± 1.0	43.0 ± 1.5	41.7 ± 1.0
60.0 ± 1.0	57.0 ± 1.5	56.7 ± 1.5
70.0 ± 1.5		70.0 ± 2.0
80.0 ± 1.5		92.0 ± 2.0

Table 2. Settling Tests (at 22−23 °C)

time	C $Pb(IO_3)_2$/mg·L^{-1}	
h	cold form	hot form
6	23.3	19.6
24	22.6	19.1
48	22.6	20.9
96	21.4	20.5
14400	20.5	19.3

surface charging, so the samples were imaged on an ElectroScan E-3 environmental scanning electron microscope (ESEM). Images were collected digitally from the ESEM with a 4pi Analysis digital image acquisition system using 17.9 pixels·μm^{-1} resolution (1000× magnification on the console). The microscope was operated at 20 keV accelerating potential with 27 μA emission current, 0.886 kPa H_2O vapor pressure, and 6.8 mm working distance with the environmental secondary electron detector (ESD).

Samples were prepared for X-ray powder diffraction by lightly grinding ≈400 mg with a mortar and pestle before loading into zero-background off-axis quartz holders. The sample cavity in each holder was a circular depression 20.0 mm in diameter and 0.5 mm deep. This cavity was filled with sample and pressed flat using a glass slide. X-ray powder diffraction data were collected using a Siemens D-500 diffractometer equipped with Co tube source, primary beam monochromator, and Braun position sensitive detector. Samples were scanned from 5° 2-theta to 90° 2-theta at a rate of 0.5°/min. Samples were rotated at approximately 45 rpm during data collection. The resulting cobalt-wavelength powder diffraction patterns were converted to Cu-radiation patterns using the JADE 6.0 software package.[14]

Conductivity measurements were made on aqueous solutions at room temperature of (22.5 ± 0.5) °C, with a Fisher Scientific ACCUMET AB 30 conductivity meter equipped with a Yellow Springs Instruments K=1 conductivity probe. The probe was calibrated with a potassium chloride solution of known conductivity.

Results

The solubility data obtained at various temperatures are shown in Table 1 and Figure 1. Table 2 shows the difference in settling rates of the two products in water at room temperature. Solubilities in the presence of potassium nitrate or lead nitrate at room temperature are given in Table 3 and plotted in Figures 2 and 3. Figures 4 and 5 are photomicrographs of the two crystalline forms. Figures 6 and 7 are the corresponding X-ray diagrams.

Conductivities of saturated solutions of the two crystalline products (hot or cold forms) were roughly the same, at (15 ± 1) μS cm^{-1}.

Discussion of Results

None of the authors of references (1, 2, and 8) gave solubilities at temperatures other than 25 °C. Our data indicate differences between apparent solubilities of the cold (Harkins) and hot (La Mer) products at temperatures between 8 °C and 60 °C, but the differences were not as large as would be expected from the earlier data. The results of Polesitzkii, included in Figure 1, probably refer to the cold form. We did not make measurements of that form above 60 °C because of the difficulty in maintaining thoroughly settled solutions.

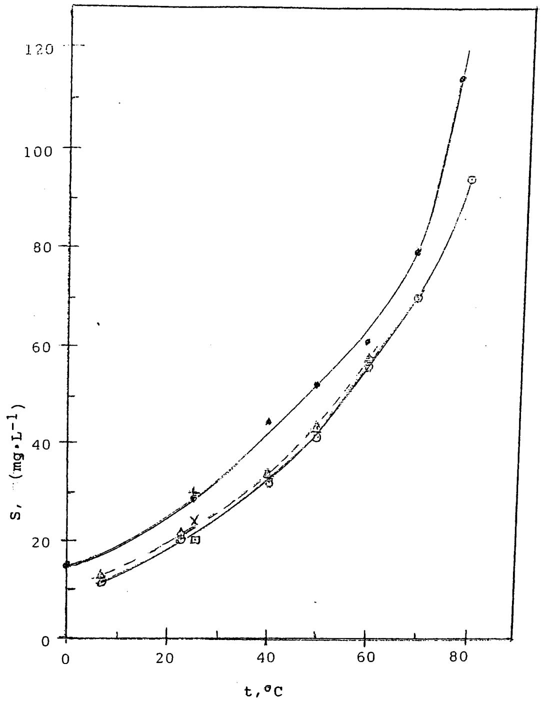

Figure 1. Solubility of lead iodate in water. (Dot in circle) this work, cold form; (triangle) this work, hot form; (solid dot) Polessetski; +, Harkins, cold; (dot in square) La Mer, hot; + Keefer, cold; ×, Geilman

Table 3. Solubilities in Salt Solutions (at 22−23 °C)

C	C $Pb(IO_3)_2$/mg·L^{-1}	
mol·L^{-1}	cold form	hot form
	KNO_3	
0	21.9 ± 1.0	20.0 ± 1.0
0.05	32.5 ± 1.0	30.3 ± 1.0
0.125	40.0 ± 1.5	38.5 ± 1.0
0.25	49.8 ± 1.5	46.4 ± 1.5
0.50	70.0 ± 2.0	65.0 ± 1.5
	$Pb(NO_3)_2$	
0.005	3.0 ± 0.8	1.7 ± 0.3
0.010	2.6 ± 0.4	2.2 ± 0.4
0.025	3.4 ± 0.3	2.7 ± 0.4
0.050	3.5 ± 0.5	2.8 ± 0.3
0.125	4.3 ± 0.7	3.8 ± 0.3
0.250	5.6 ± 0.7	4.8 ± 0.5

The previously mentioned authors relied upon filtration through tubes containing cotton or asbestos plugs. These do not completely remove very fine particles. Filtration through paper for the finest precipitates (Whatman No. 42) yielded a solution of the Harkins (cold) material with 22.4 mg of $Pb(IO_3)_2$ per liter at 22.5 °C as compared with 20.5 mg/L after very long settling.

Our data confirm the assumption of Keefer and Reiber,[8] that the apparent difference in solubilities of the two products is due to a difference in particle sizes. The photomicrographs support this observation. As shown by the X-ray diagrams, the two products have different crystalline forms, but this would not necessarily lead to

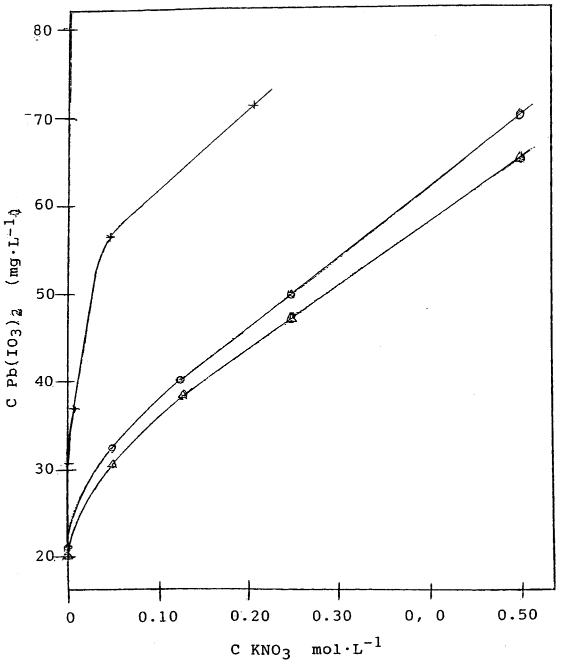

Figure 2. Solubility of lead iodate in potassium nitrate solutions. + Harkins, (cold form), 25 °C; (dot in circle), current, cold form, 22–23 °C; (dot in triangle), current, hot form, 22–23 °C.

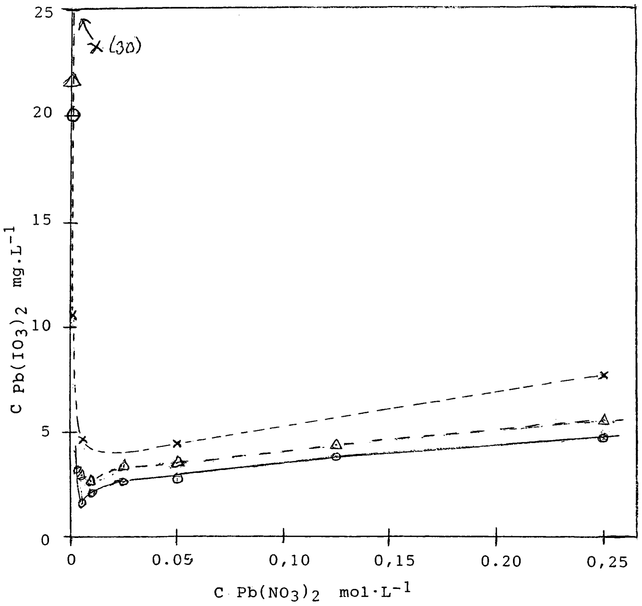

Figure 3. Solubility of lead iodate in lead nitrate solutions. ×, Harkins, (cold form), 25 °C; (dot in triangle), current, cold form, 22–23 °C; O, current, hot form, 22–23 °C.

different solubilities. One would expect that dissolved lead iodate would have only one dissociation constant, and this is indicated by the conductivity data.

Harkins and Winninghoff[1] also determined apparent solubilities in potassium nitrate and lead nitrate solutions. Our results parallel theirs but are lower, as would be expected from the difference in particle size and our use of long settling rather than filtration. The effect of potassium nitrate in greatly increasing the apparent solubility of lead iodate may possibly be due to the formation of the double salt lead nitrate–iodate, $Pb(NO_3)(IO_3)$. If this is the case, we and others have really reported the lead iodate equivalent of this salt in solution. The effect of lead nitrate on the solubility of the iodate is due to the common ion (lead) at low concentrations but probably more to the nitrate ion at higher levels.

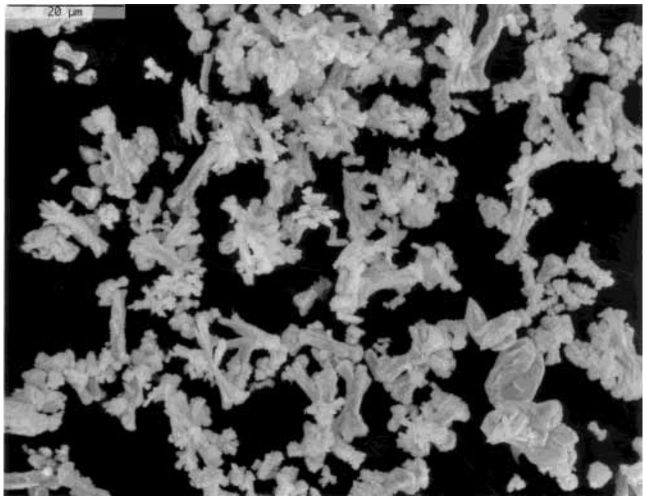

Figure 4. Lead iodate crystals (Harkins cold form).

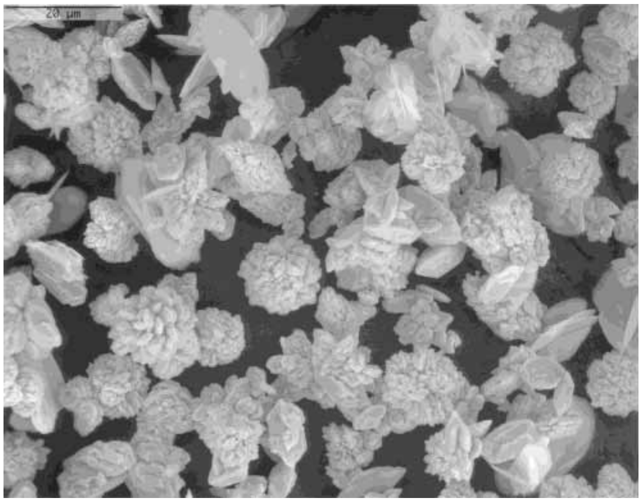

Figure 5. Lead iodate crystals (La Mer hot form).

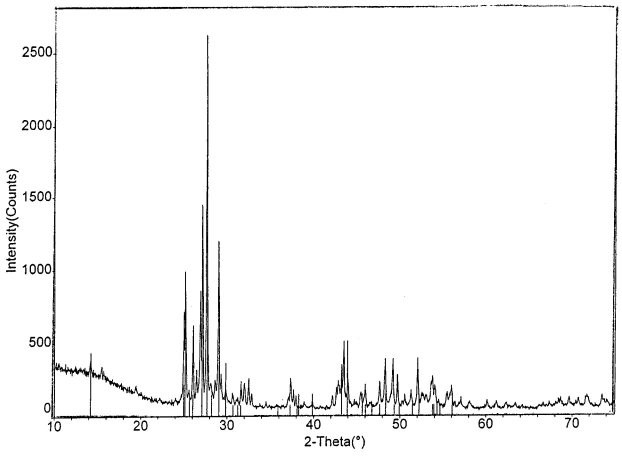

Figure 6. X-ray spectrum, lead iodate (Harkins cold form)

A reviewer of this paper suggested that increased solubility in solutions of fairly high nitrate content may be due to decreased activity coefficients. To test this hypothesis, we determined the solubility in the presence of 0.2 M potassium iodate, by polarographic analysis for lead. The concentration found was less than 0.1 mg Pb per liter. Because the effect of KIO_3 on activity coefficient should be as great as that of KNO_3 or $Pb(NO_3)_2$, it is

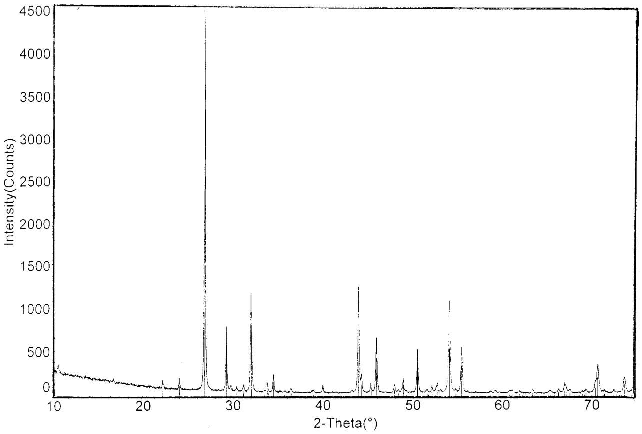

Figure 7. X-ray spectrum, lead iodate (La Mer hot form).

evident that some other effect is responsible for the increases in solubility reported in Table 3. Without it, $Pb(NO_3)_2$ should lower the solubility as much as KIO_3.

When lead iodate was prepared at 60 °C with a large excess of lead nitrate, the crystals obtained were of the "cold form". Conversely, when the preparation was done at room temperature with a large excess of potassium iodate, the product was the "hot form". Evidentially temperature determines the result only when limited amounts of either reagent are present. When a large excess of one reagent is used, that reagent determines which type of precipitate is formed.

We postulate that with either a small or a large excess of lead nitrate, the precipitate formed intermediately consists of the double salt lead iodate–nitrate which then is converted to the "cold form" of lead iodate. When a large excess of iodate is used at either temperature, or only a small excess of nitrate at 60 °C, the "hot form" is precipitated directly, probably because the double salt is more soluble or is not formed at all.

We conclude that the two crystalline forms would have identical solubilities if the finest particles of the "cold form" could be eliminated by complete settling or filtration.

Literature Cited

(1) Harkins, W. D.; Winninghoff, W. J. *J. Am. Chem. Soc.* **1911**, *33*, 1827–1836.
(2) La Mer, V. K.; Goldman, F. H. *J. Am. Chem. Soc.* **1930**, *52*, 2791–2793.
(3) Kohlrausch, F. *Z. Phys. Chem.* **1903**, *44*, 226; **1908**, *64*, 51.
(4) Böttger, W. *Z. Phys. Chem.* **1903**, *46*, 521–619.
(5) Geilmann, W.; Höltje, *R. Z. Anorg. Allgem. Chem.* **1926**, *152*, 59–72.
(6) Polesitzkii, A. *Compt. Rend. Acad. Sci. URSS* **1935**, *4*, 197–200; *Chem. Abstr.* **1936**, *30*, 3700.
(7) Edmonds, S. M.; Birnbaum, N. *J. Am. Chem. Soc.* **1940**, *62*, 2367–2369.
(8) Keefer, R. M.; Reiber, H. G. *J. Am. Chem. Soc.* **1941**, *63*, 689–692.
(9) Mohanty, R. C.; Aditya, S. *J. Indian Chem. Soc.* **1955**, *32*, 234–251; *Chem. Abstr.* **1955**, *49*, 15390g.
(10) Misra, R. N.; Pani, S. *J. Indian Chem. Soc.* **1957**, *34*, 387–398; *Chem. Abstr.* **1958**, *52*, 840b.
(11) Staritzky, E.; Walker, D. I. *Anal. Chem.* **1956**, *28*, 914.
(12) Kellersohn, T.; Alici, E.; Esser, D.; Lutz, H. D. *Z. Kristallogr.* **1993**, *203(2)*, 225–233.
(13) National Bureau of Standards U.S., 1980; Monograph 25, p 1745.
(14) *JADE* 6.0 for Windows 2001; Materials Data, Inc.: Livermore, CA, 2001.

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