
REACTIONS BETWEEN Pb^{2+} AND $(I^- + I_3^-)$ IN
ACIDIC SILICA GELS¹

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ABSTRACT

In this work it was found that reactions between Pb^{2+} and $(I^- + I_3^-)$ in acidic silica gels are limited to the formation of PbI_2 from $Pb^{2+} + 2 I^-$ and from $Pb^{2+} + 2 I_3^-$, the latter occurring with the coincident formation of I_2 crystals. There was no evidence of pseudomorphic conversion of I_2 to PbI_2 , even by the presence of large excesses of Pb^{2+} , in contrast to reactions in acidic gels between excess Hg^{2+} , Ag^+ , or Tl^+ and I_2 , in which instances these metal cations convert I_2 pseudomorphically to the respective iodides. When a deficiency of Pb^{2+} existed, there was no zone separation of PbI_2 and I_2 , as occurs with HgI_2 , AgI , or TlI and I_2 in metal-ion deficient systems, and the distributions of PbI_2 and I_2 crystals were random.

Reactions between Pb^{2+} and I^- in acidic and slightly basic silica gels have been described by Holmes (1917, 1934). In sufficiently acidic gels, Holmes found that the normal iodide, PbI_2 , formed, whereas in only slightly acidic and in basic gels, a basic iodide resulted, presumably $Pb(OH)I$ or $PbI_2 \cdot PbO$. Holmes (1917, 1934)

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also describes the formation of HgI_2 in gels. The present investigator has repeated and extended Holmes' work and has found that, when acidic silica gels containing $(\text{I}^- + \text{I}_3^-)$ are reacted with excess Hg^{2+} , Ag^+ , or Tl^+ , all of the iodine, as well as all of the iodide, is converted to the respective heavy-metal iodide (Kurz, 1966 and unpublished results). With excess Hg^{2+} crystals of red HgI_2 , some of which are pseudomorphs, are the single visible, ultimate reaction product in a slightly cloudy but otherwise colorless gel, indicating the absence of I_3^- and I_2 .

Similarly, with excess Ag^+ , yellow microcrystals of AgI and larger yellow pseudomorphs originally formed as I_2 are the sole visible end products in an otherwise color-free gel. With excess Tl^+ , glistening clusters of lemon-yellow needles and long, lustrous black needles coexist in an otherwise color-free gel at the conclusion of the reaction. The yellow needles presumably are TlI , and the black needles probably represent a higher-valence thallium iodide. In $(\text{I}^- + \text{I}_3^-)$ -bearing gel systems treated with only enough Hg^{2+} or Ag^+ to react with the excess I^- and to rob I_3^- of its I^- , crystals of HgI_2 and I_2 or of AgI and I_2 , respectively, form in distinctly separate zones in the gel and coexist permanently. The metal halide crystals form nearest the gel surface and the I_2 crystals are segregated in the zone farthest from the gel surface. The gel background and the supernatant liquor are light yellow brown in color and probably represent aqueous media saturated with I_2 .

Reactions between Pb^{2+} and acidic gels containing $(\text{I}^- + \text{I}_3^-)$ were investigated because lead is another heavy metal whose iodide, like HgI_2 , AgI , and the thallium iodides, is relatively insoluble in water. As mentioned above, it has been known for many years that crystals of PbI_2 can be grown in acidic silica gels using I^- as the internal reagent and Pb^{2+} as the external reagent, or vice versa. Both methods were tried before reacting Pb^{2+} with $(\text{I}^- + \text{I}_3^-)$, to which no reference has been found.

When $(\text{I}^- + \text{I}_3^-)$ -bearing gels were reacted with Pb^{2+} supplied from a supernatant solution of lead nitrate, interesting and, in the light of earlier experience with Hg^{2+} and Ag^+ , somewhat unexpected results were obtained.

Table I summarizes the composition of the gels and the concentrations of reactants used in these experiments. In one gel system, the amount of Pb^{2+} ultimately placed on the gel was only slightly in excess of that required to react

TABLE I
Composition of gel systems for reactions between Pb^{2+} and $(\text{I}^- + \text{I}_3^-)$

Sodium silicate solution		Acetic acid		Potassium iodide		Iodine (dissolved in KI)			Total I^-	Lead nitrate (external reagent)								
Undiluted silicate. ^a ml	Water, ml	OH^- in silicate milli- equiv- alents	ml	N	Milli- equiv- alents	ml	N	Equiv- alents I^-	gm	Milli- equivalents I_3^-	I ⁰	I ^{-b}	Available as I^- or in I_3^- + poten- tial (in I_2) milliequiv- alents	ml	N	Milliequivalents		
																Used	Excess avail- able	Excess over total I^-
1.67	8.33	6.7	5	1.5	7.5	5	1	5	0.4	3.2	2.7	7.7	3 x 5	2	30	25	22.3	
8.3	41.7	33.3	25	1.5	37.5	25	1	25	2.4	16.6	13.8	38.8	2 x 20	1	40	15	1.3	
20.0	100.0	80.0	60	1.5	90.0	60	0.5	30	2.4	16.6	13.8	43.8	(1 x 16+ 3 x 10)	2	92	62	48.2	

^aPhiladelphia Quartz Company's N Sodium Silicate ($\text{SiO}_2/\text{Na}_2\text{O}=3.22/1$ by weight).

^bOnly 5/6 of I_2 goes to I^- on hydrolysis and disproportionation.

with both the available I^- (present as I^- or complexed in I_3^-) and the potential I^- (obtainable from I_2 by promotion of its hydrolysis to $I^- + IO_3^-$). In the other gel systems, approximately 2- to 4-fold excesses of Pb^{2+} , based on available plus potential I^- , were used.

The sketches in figure 1 show typical formations of PbI_2 and I_2 crystals in two of the gel-reaction systems described in table 1. In both gel systems, crystals of the two species coexisted permanently at the conclusion of the reaction and no indication of pseudomorphic formations of PbI_2 , at the expense of I_2 , was evident.

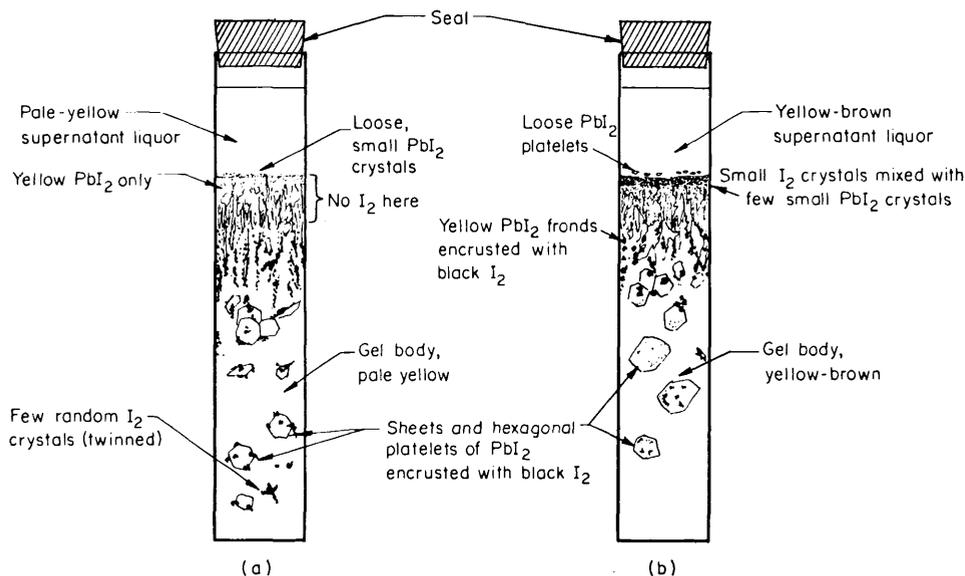


FIGURE 1. SKETCHES OF FORMATIONS OF PbI_2 AND I_2 IN ACIDIC ($I^- + I_3^-$) -BEARING GELS REACTED WITH Pb^{2+}

The first gel system described in table 1 initially contained 1.6 millimols of I_3^- (from $I^- + I_2 \rightarrow I_3^-$) and 3.4 milliequivalents of excess I^- . It was reacted at approximately bimonthly intervals with three successive 5-ml portions of 2N $Pb(NO_3)_2$ solution. Each 10-milliequivalent-portion of lead nitrate solution contained more than enough Pb^{2+} to react with all of the I^- , available plus potential, in the gel. The reaction:



is possible and occurs because the gel contains free I^- .

The reaction:



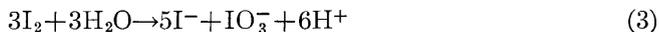
apparently occurs also because, in addition to golden-yellow hexagonal platelets of PbI_2 , black, usually twinned crystals of I_2 form as encrustations on the yellow fronds or hexagonal platelets of PbI_2 . The black crystals are dispersed randomly on the yellow ones. In the presence of excess Pb^{2+} , as was used in this system, it is reasonable to believe that reactions (1) and (2) are essentially complete. Together they can consume 5 milliequivalents of Pb^{2+} , leaving an excess of 5 to

25 milliequivalents of Pb^{2+} (after first and third additions of Pb^{2+}) to react with I^- , or IO_3^- that may form from I_2 by hydrolysis. The background color of the gel and the supernatant liquor were light yellow brown, approximating the color of a saturated aqueous solution of I_2 , after the first 10 milliequivalent portion of Pb^{2+} had reacted and paled only slightly as the second and third portions of Pb^{2+} were used. The only noticeable effect of using successive portions of $\text{Pb}(\text{NO}_3)_2$ solution was to dissolve some of the PbI_2 crystals initially formed near the top of the gel. This may have been a result of equilibration of PbI_2 between the gel and the supernatant liquor which initially contained no PbI_2 , but only $\text{Pb}(\text{NO}_3)_2$. It appears unlikely that the disappearance of some of the PbI_2 was an acidification effect, because PbI_2 crystals will form in gels prepared with glacial acetic acid (16N) and which are approximately 7N in acetic acid after neutralization of the silicate (Kurz, unpublished results).

The second gel system described in table 1 initially contained 8.3 millimols of I_3^- and 16.7 milliequivalents of uncomplexed I^- . It was reacted with two 20 ml portions of 1N $\text{Pb}(\text{NO}_3)_2$, added about 1 year apart. Reactions (1) and (2) apparently proceed in this system also, as indicated by the formation of crystals of PbI_2 and I_2 , which coexist in the gel as shown in figure 1. In this instance reactions (1) and (2) require 25 milliequivalents of Pb^{2+} . There was no excess Pb^{2+} until the second 20 milliequivalent portion of Pb^{2+} was placed on the gel. Yet, as evidenced by the formation of I_2 during the first "half" of the reaction, Pb^{2+} successfully robbed I_3^- of its I^- . The background color of this gel system was a deep yellow brown, indicating the presence of I_3^- , as would be expected in the absence of excess Pb^{2+} addition. Likewise, as expected, the gel and supernatant assumed light yellow brown colors after the second 20-milliequivalent portion of Pb^{2+} had reacted.

Crystal distribution of both species is random in both gels. However, the bulk of the growth occurs in the half of the gel nearest the external reactant. This suggests that I^- and I_3^- migrate toward the supernatant source of Pb^{2+} faster than Pb^{2+} infuses into the gel.

It is apparent, because I_2 coexists with PbI_2 in the presence of large excesses of Pb^{2+} , that, unlike Hg^{2+} and Ag^+ under similar conditions, Pb^{2+} does not promote reactions between I_2 and H_2O which would produce I^- and IO_3^- as follows:



Hence, apparently only reactions (1) and (2) occur in $(\text{I} + \text{I}_3^-)$ -bearing gels reacted with Pb^{2+} .

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