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THE IDENTIFICATION OF THE COMPOSITION OF THE INSOLUBLE ADDITION COMPOUND

Goro HIHARA*, Hiroshi MIYAMAE, and Miharu NAGATA
Department of Chemistry, Faculty of Science, Josai University,
Sakado-shi, Saitama 350-02

A method has been developed for ascertaining the compositions of the insoluble compounds which may be grown by addition reactions of an insoluble substance with a soluble substance in a solution. This method was applied to the addition reaction of lead(II) iodide with ethylenediamine(en) in a ternary system of PbI_2-en-ethanol, and three addition compounds are identified as $3PbI_2 \cdot 2(en)$, $PbI_2 \cdot en$, and $PbI_2 \cdot 2(en)$.

In the study of a series of addition compounds of lead(II) iodide with some kinds of organic Lewis bases$^{1)}$, it becomes important to ascertain the compositions of the whole compounds that may be grown by the reaction of an organic base upon PbI_2. In the cases where all of the materials that concern in an addition reaction are fairly soluble in a common solvent, there have already been some elegant methods such as the continuous variation method$^{2,3,4)}$ and the mole ratio one$^{5)}$ to search for the compounds. But these methods are not available for the study of the addition compounds of PbI_2, because of the scarce solvability of PbI_2 and its compounds in solvents. In this paper, an effective method to work out this problem is offered.

Providing that an insoluble substance A reacts with substance B, which is dissolved in a solvent, to grow two kinds of insoluble addition compounds as follows,

$$A(s) + mB(l) = A \cdot mB(s) \qquad (1)$$

$$A \cdot mB(s) + nB(l) = A \cdot (m+n)B(s) \qquad (2)$$

where l and s in the parentheses represent liquid and solid phase respectively. The degree of freedom of this ternary system can be shown in the equation 3,

$$F = C + 2 - P = 5 - P \qquad (3)$$

where F is the number of the degrees of freedom, C the number of the components, and P the number of phases.

Under the atomospheric pressure, F comes to $(3-P)$ at a fixed temperature since the participation of the air upon the degrees of freedom of this equilibrium compensates for the subsistence of a gaseous phase.

$$F = 3 - P. \qquad (4)$$

When the equilibrium is established between one solid phase and the solution, the freedom of the system becomes univariant, and the concentration of B in the solution is capable of variation within definite ranges, as the solid phase is dominated by one of A, $A \cdot mB$, or $A \cdot (m+n)B$. In the case where the equilibrium is arranged among two solid phases and the solution, there appears the invariant state, and the concentration of B in the solution falls immutable according as either A and $A \cdot mB$ or $A \cdot mB$ and $A \cdot (m+n)B$ coexist in the solid phase.

Provided that every fixed amount of substance A is put in every fixed amount of the solution containing the various quantities of substance B, and is allowed to stand until the addition reaction of A with B has reached to an equilibrium. The relation between the amounts of B introduced into this system at the beginning of the reaction and the concentration of B remaining in the solution at the end of the reaction, should be drawn as a graph as shown in Fig.1. Two plateaus on the stepped diagram in Fig.1 correspond to the invariant states, one of which contains two solid phases of A and $A \cdot mB$, and the other $A \cdot mB$ and $A \cdot (m+n)B$. The composition of each sediment which is equilibrated with the solution, can be also plotted on the graph against the introduced amount of B. As shown in Fig.1, this diagram should reveal three plateaus, each of which corresponds to the composition of A, $A \cdot mB$, and $A \cdot (m+n)B$ in the solid phase.

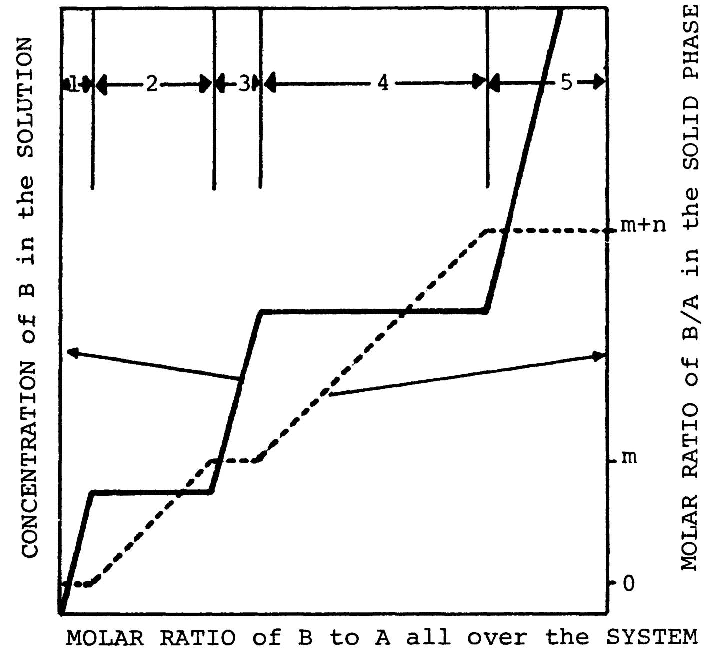

Fig.1 A typical phase diagram for the ternary system. The components are the insoluble A, the soluble B, and a solvent. The system has the growth of two insoluble addition compounds of A with B. Only A is equilibrated with the solution in the region 1, A and $A \cdot mB$ in the region 2, only $A \cdot mB$ in the region 3, $A \cdot mB$ and $A \cdot (m+n)B$ in the region 4, and only $A \cdot (m+n)B$ in the region 5.

The above discussed procedure was adopted on the addition reaction of PbI_2 with ethylenediamine(en) dissolved in ethanol. Every 1.00 g of finely powdered PbI_2 was added to each 10.0 ml of ethanol solution containing 0.039-0.390 g of en in a glass ampoule, and was kept at 25°C for about one month with 10 minutes' violent shaking two times a day. Then the solution was separated from the sediment and was examined for the concentration of en that had remained. The determination of en in the solution was carried out by the potentiometric titration and the spectrophotometry[6]. As the amount of lead(II) ion that had fled into the ethanol solution was verified to be negligible by a method of the chelate titration[7], the molar ratio of en to PbI_2 in each sediment can be easily calculated from the equation 5,

$$Y = (X - V C) / Z \qquad (5)$$

where Y is the molar ratio of en/PbI_2 in the sediment, X the amount of B in mole at the beginning of the reaction, C the concentration of B in mole/l that remained in the solution, V the volume of the solution in liter, and Z the amount of PbI_2 in mole.

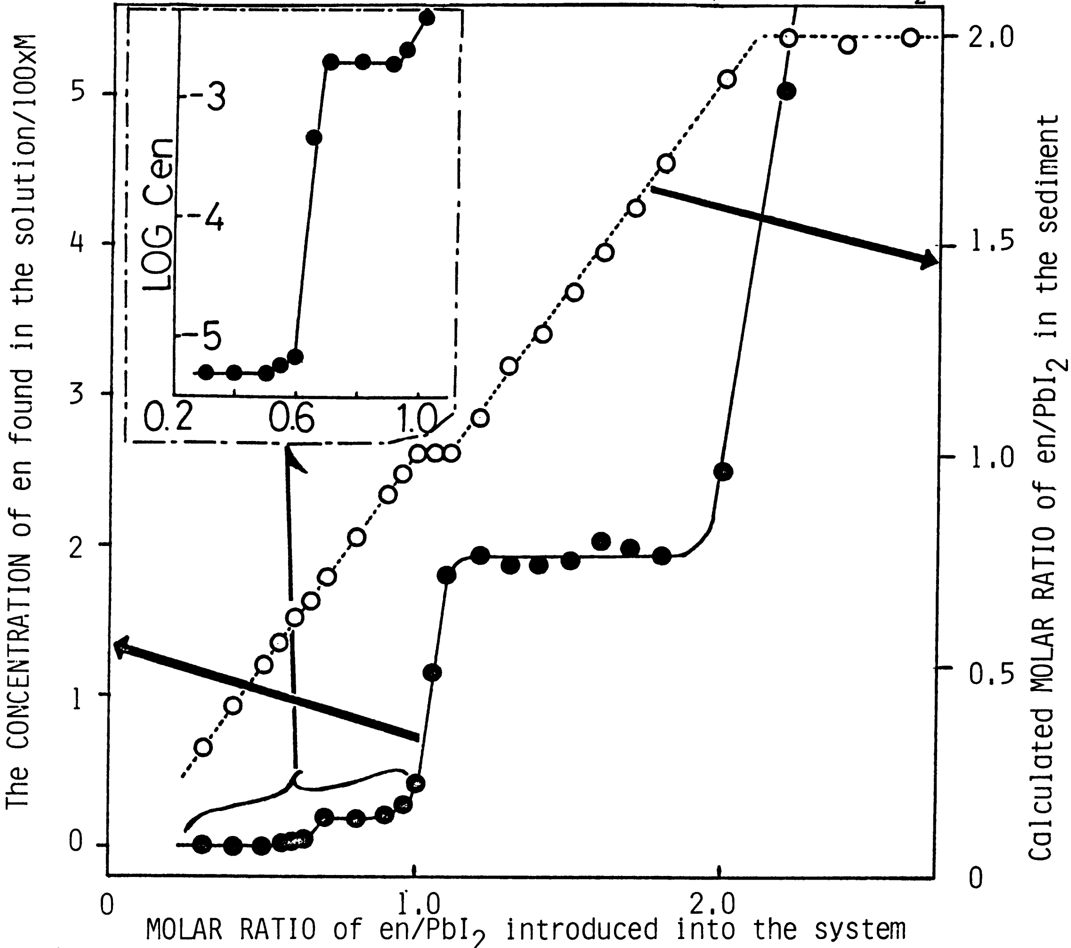

Fig.2 The relation between the composition of the sediment and the concentration (Cen) of en remaining unreacted in the PbI_2-en-ethanol system. The stability constant of Eq.1 is presented as $k = a_{(A\cdot mB)s}/(a_{As}\cdot a_B^m)$ where a is the activity. Since $a_{(A\cdot mB)s}$ and a_{As} are unit, k equals to $1/a_B^m$. Cen's of three plateaus in Fig.2 are 5.0×10^{-6}, 2.2×10^{-3}, and 1.92×10^{-2} mole/l. Each log of k is 3.5, 0.89, and 1.7 respectively.

The results in this experiment were summarized in Fig.2 in the same manner as in Fig.1. To express clearly the change of the concentration of en in the range of its lower concentration, in Fig.2 the diagram of the part of the results was also illustrated which has log of its concentration as ordinate. The diagram of the composition of the sediment in Fig.2 obviously reveals two plateaus, one of which corresponds to the composition of a compound $PbI_2 \cdot en$, and the other corresponds to that of $PbI_2 \cdot 2(en)$. A distinct difference of the concentration of en in the solution appeared between 0.6 and 0.7, suggests the existence of another addition compound, in spite of the absence of the corresponding plateau upon the "composition" diagram. The constitution of this compound is calculated as 3:2 of the molar ratio of PbI_2:en. The existence of the compound of $3PbI_2 \cdot 2(en)$ was also verified by the characteristic powder x-ray diffraction pattern of the product that can be grown by a directly absorptive reaction of en with PbI_2 at the molar ratio of 2:3. The points at which the system changes from non-variant to monovariant one took place in Fig.2 at the lower molar ratio of en/PbI_2 introduced into the system especially in case of $PbI_2 \cdot 2(en)$ than predicted theoretically. This seems that the equilibrium has not been completely established in spite of the long reaction time.

Wharf *et al*. reported that PbI_2 reacts with ethylenediamine in benzene or ethanol solution to grow $PbI_2 \cdot 2(en)$ 8), but they did not refer to other intermediate compounds. Our interest is put toward the thorough search for all of the compounds that may be produced by the addition reaction, and the method above mentioned has been found to be very useful for this purpose, especially when attended with the minute estimations for the slight fluctuations of the concentration or the composition in the phases.

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