The Identification of the Compositions of the Compounds Formed in an Addition Reaction Involving Insoluble Substances

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A method has been developed for the identification of the compositions of all the insoluble compounds which are formed in the reaction of an insoluble substance (A) with a soluble one (B). It consists of allowing a fixed amount of A to react with various amounts of B in a fixed volume of a solution, determining the concentrations of B(=[B]) remaining unreacted after the equilibrium is reached, and then finding the number of the formed compounds and their compositions from the variations in [B] on the basis of the phase rule. This method was applied to the reactions of PbI_2 with diethylenetriamine (dien) and with 1,3-propanediamine (pren); the presence of the following addition compounds was found: $PbI_2 \cdot Y$(dien) (Y=1/2 and 1) and $PbI_2 \cdot Y$(pren) (Y=4/5, 1, and 2).

In studying coordination compounds, the first step is to determine the compositions of the complexes formed in the reaction. When all of the species involved are soluble in a common solvent, there have already been developed several useful methods, such as the continuous variation[1—3] and the mole ratio methods.[4] However, they can not be used when some of the species concerned are insoluble. A method which is applicable to such a case was reported in a previous paper.[5] It consists, essentially, in pursuing the variations in the concentrations of a soluble substance [B] in equilibrium with the insoluble ones.

In the present study, this method was applied to the reactions of PbI_2 with diethylenetriamine and with 1, 3-propanediamine; it will be pointed out that the examination of the powder X-ray diffraction patterns of the insoluble compounds is very helpful in confirming the presence of complexes formed in the reaction, especially when such complexes are otherwise apt to be overlooked.

Theoretical

Let us assume that an insoluble substance, A, reacts with a soluble one, B, in a solution according to Eqs. 1 and 2 to yield two insoluble addition compounds;

$$\text{A(solid)} + m\text{B(soln.)} = \text{A}\cdot m\text{B(solid)} \qquad (1)$$

$$\text{A}\cdot m\text{B(solid)} + n\text{B(soln.)} = \text{A}\cdot(m+n)\text{B(solid)}. \qquad (2)$$

The degree of freedom of this system, f, is given on the basis of the phase rule by:

$$f = c + 2 - p, \qquad (3)$$

in which c is the number of the components, and p, the number of phases. Since the system is composed of A, B, and a solvent, c equals 3. Therefore,

$$f = 5 - p. \qquad (4)$$

Under a constant temperature and pressure, f becomes $(3-p)$:

$$f = 3 - p. \qquad (5)$$

When the equilibrium is established between the solution and one of three solid phases, A, A·mB, or A·(m+n)B, the system becomes univariant and the concentration of B in the solution is capable of variation within a definite range. On the other hand, when two solid phases and the solution are in equilibrium, there appears an invariant state and the concentrations of B remain fixed, as long as either A and A·mB or A·mB and A·(m+n)B coexist in the solid.

When a fixed amount of A is put in a fixed volume of a solution containing various quantities of B and each mixture is allowed to stand until an equilibrium is established, the concentration of B remaining in each solution is determined in some way. The relations between the amounts of B taken at the beginning and the concentrations of B remaining at the end of the reaction are depicted by the solid curve in Fig. 1, which is tentatively termed a "concentration curve."

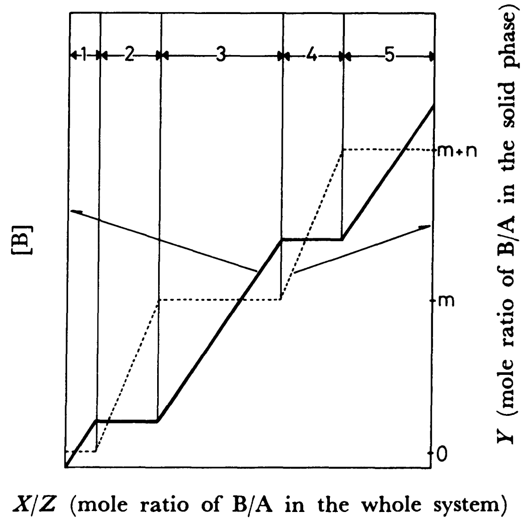

Fig. 1. A typical phase diagram for a ternary system where two insoluble addition compounds, A·mB and A·(m+n)B form.

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The two plateaus on the concentration curve represent two invariant states, one of which corresponds to the coexistence of A and A·mB, and the other, A·mB and A·$(m+n)$B. Each incline on the curve is related to each univariant state.

The composition of each sediment which is equilibrated with the solution can be calculated from Eq. 6;

$$Y = (X - V[\mathrm{B}])/Z, \tag{6}$$

where Y is the mole ratio of B/A in the sediment; X, the amount of B in mol taken at the beginning; [B], the concentration of B in mol/dm^3 in the final solution; V, the volume of the solution in dm^3, and Z, the total amount of A in mol taken at the beginning. The composition of each sediment calculated is also plotted by the dashed curve in Fig. 1, which is tentatively termed a "composition curve." The curve should reveal three plateaus, which correspond to the compositions of A, A·mB, and A·$(m+n)$B in the solid phase.

Experimental

Apparatus. A Toa Denpa HM-5H pH meter was used to determine the concentration of amines in the solution and the content of amines in the sediments. When it was necessary to characterize the sediments, use was made of powder X-ray diffractometry with a Rigaku Denki Geigerflex Diffractometer.

Reagents. PbI_2 was prepared by mixing a solution of KI with that of $Pb(NO_3)_2$ in a stoichiometric ratio. The diethylenetriamine (dien) (99.0% pure) was obtained from Wako Pure Chemical Industries, Ltd. The 1, 3-propanediamine (pren) (99.0% pure) was obtained from Tokyo Kasei Co., Ltd. These amines were used without any further purification. The ethanol was dehydrated with molecular sieves (4Al/16) and then distilled.

The Addition Reaction of PbI_2 with dien. One g (2.17 mmol) of finely powdered PbI_2 was suspended in an ampoule with 10.0 ml of an ethanol solution containing the desired amount of dien. The mole ratio of dien/PbI_2 was varied in the range of 0.3—3.0. Then each ampoule was sealed and kept at 20.0±0.2 °C for about two months. For the smooth progress of the reaction, each ampoule was shaken violently for 10 min twice 1 d. The sediments were separated from the solutions and then subjected to chemical analysis and powder X-ray diffractometry. The concentration of dien in each solution was also determined. A similar treatment was done in the case of the reaction of PbI_2 with pren.

Analysis of the Solutions and the Sediments. Five ml of each solution separated from the sediment was diluted with about 35 ml of water, and the amine was potentiometrically titrated with 0.1 M (1 M=1 mol dm^{-3}) HCl. The content of Pb^{2+} in the solution was determined by titrating with 0.01 M EDTA, using xyrenol orange as an indicator.[6] For the determination of the amine content in the sediments, about 10—20 mg of the sediment was dissolved in 10.00 ml of 0.1 M HCl. After 30 ml of water had been added, the excess of HCl back-titrated potentiometrically by 0.1 M NaOH. The Pb content of the sediments was determined by the complexometric titration described above after about 10—20 mg of each sediment had been dissolved into 40 ml of water containing 0.5 ml of 1 M HNO_3.

Results and Discussion

Preliminary experiments confirmed that PbI_2 does not react with ethanol and is scarcely soluble in it, even in the presence of pren or dien. The direct reactions of PbI_2 with dien were made in various mole ratios of dien/PbI_2, 0.5, 1, 2, and 3. The unreacted dien was removed by pressing the products with a filter paper. The diffraction patterns of the products were similar to those of the products formed in the ethanolic solution containing the amine. These facts show that the net reactions in the ethanolic solutions are the addition reactions of PbI_2 with the amines and that ethanol acts merely as a diluent.

The findings on the reaction of PbI_2 with pren are shown in Fig.2 in the same manner as in Fig. 1. The concentration curve ascends from about 0.8 of X/Z(=pren/PbI_2) on the abscissa, and the composition curve becomes flat at Y=0.8 in the range of about 0.75—1.35 of X/Z. This shows the presence of an addition compound, PbI_2·4/5(pren). The occurrence of two other compounds, PbI_2·pren and PbI_2·2pren, can be pointed out in a similar way.

Figure 3 represents the findings on the reaction of

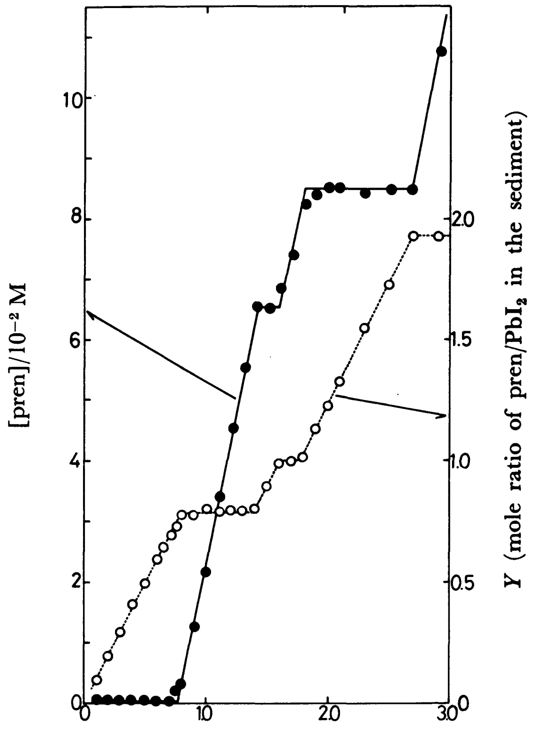

Fig. 2. The relation between the concentration of 1,3-propanediamine (pren) remaining in the solution and the composition of the sediments at 20 °C.

PbI_2 with dien. The concentration curve ascends from 0.5 and becomes flat at 0.55 of X/Z (=dien/PbI_2). The value of Y in the region of 0.5—0.55 of X/Z can be read as 0.5 from the composition curve, although it does not seem to have the corresponding plateau because of the narrow range. This is considered to imply the presence of $PbI_2 \cdot 1/2$(dien) according to the phase rule. The presence of $PbI_2 \cdot 1/2$(dien) can be confirmed from the powder X-ray diffraction patterns of the sediments, which are shown in Fig. 4. When the patterns are examined, it can be seen that the characteristic peak of 9.4°(=2θ) has a maximum intensity at Y=0.5 and that it disappears at Y=0.0 and 1.0. This fact indicates the presence of $PbI_2 \cdot 1/2$(dien). The presence of one more compound, $PbI_2 \cdot$dien, can be pointed out, since the concentration curve ascends from about 1.1 of X/Z(=dien/PbI_2) and the composition curve becomes flat at Y=1.0 in the range of 1.1—2.3 of X/Z in Fig. 3. Table 1 lists the data on the compositions of some sediments found by chemical analysis. The values of Y of $PbI_2 \cdot Y$(dien) obtained by substituting the equilibrated concentrations of dien for [B] in Eq. 6 agree very closely with those found by chemical analysis.

If a compound forms over a wide range of X/Z (=B/A), its presence can be confirmed on the basis of the resulting slope of the concentration curve and the corresponding plateau of the composition curve. This is the case with such compounds as $PbI_2 \cdot 4/5$ (pren) and [Ag(thiopyrine)$_3$]ClO_4.[8] However, if a compound forms in a narrow range of X/Z, its presence is liable to be overlooked because the corre-

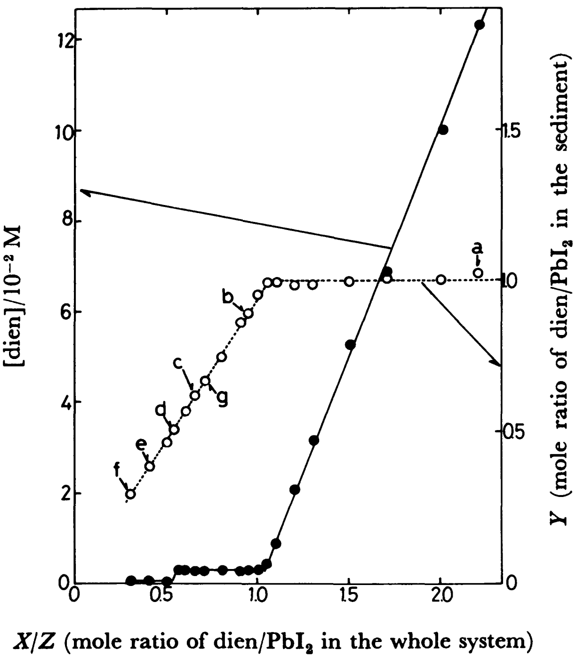

Fig. 3. The relation between the concentration of dien remaining in the solution and the composition of the sediments at 20 °C. The range of the mole ratio over 2.3 was omitted since the concentrations increased monotonously and the mole ratio of the sediments was equal to nearly 1.

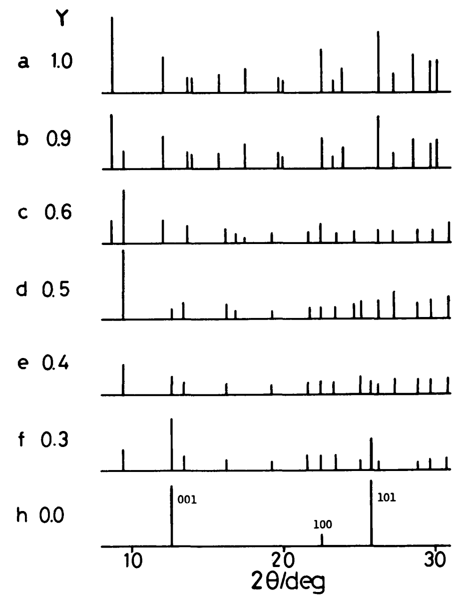

Fig. 4. The powder X-ray diffraction patterns of $PbI_2 \cdot Y$ (dien) where Y represents the mole ratio of dien/PbI_2 found by chemical analysis. The marks a—f are shown in Fig. 3 and h is the pattern of the sediment obtained by immersing PbI_2 in ethanol. Its peaks are the same as those of PbI_2 and are indexed.[9]

TABLE 1. THE COMPOSITION OF SOME SEDIMENTS GROWN IN THE PbI_2-dien-ETHANOL SYSTEM

Sediment[a]	Found by chemical analysis					Determined from dien concn.[c]
	Pb %	PbI_2[b] %	dien %	Recovery %	Y(mole ratio of dien/PbI_2)	
a	37.3	83.0	18.7	102	1.01	1.03
f	42.9	95.5	6.7	102	0.31	0.30
g	39.0	86.8	14.2	101	0.73	0.67

a) The sediments analyzed are shown in Fig. 3. b) The weight percentage of PbI_2 was calculated from the content of lead. c) These mole ratios were evaluated from Eq. 6, using the concentration of dien in the solution after the equilibration.

sponding plateau does not always appear in the composition curve, even though the concentration curve ascends. This is the case with such compounds as $PbI_2 \cdot 1/2$(dien) and $PbI_2 \cdot 2/3$(en) (en=ethylenediamine). In a previous paper[5] on the reaction of PbI_2 with en, spectrophotometry[7] could follow the minute variations in the concentrations of en in the vicinity of the range where $PbI_2 \cdot 2/3$(en) formed, and its presence was pointed out clearly, although the plateau did not appear in the composition curve. Since the minute variations in the concentrations of dien could not be followed accurately in the range where $PbI_2 \cdot 1/2$(dien) formed, X-ray powder diffractometry was used instead of spectrophotometry in order to confirm its presence. X-Ray powder diffractometry as well as spectrophotometry was found to be helpful in confirming the presence of the compounds which formed in a narrow range of X/Z.

When the present method is compared with the mole ratio and continuous variation methods, it is found to be more similar to the former than to the latter, since a fixed amount of one of two substances is allowed to react with various amounts of the other. The present method is applied to a heterogeneous system, while the mole ratio method is applied to a homogeneous system. Therefore, the method described here may be taken as a substitute for the mole ratio method in a heterogeneous system.

The method for the identification of the insoluble addition compounds was found to be applicable to the reactions of PbI_2 with pren and dien. The following addition compounds were confirmed: $PbI_2 \cdot Y$(pren) (Y=4/5, 1, and 2) and $PbI_2 \cdot Y$(dien) (Y=1/2 and 1). Many compounds have been reported of PbI_2 with Lewis bases, such as aniline,[10] thiourea,[11] and *N*,*N*-dimethylformamide.[12] Since most of them have the composition of 1:1 or 1:2 (=PbI_2:base), $PbI_2 \cdot 4/5$(pren) and $PbI_2 \cdot 1/2$(dien) have unusual compositions. On the other hand, there have been few reports on crystal structures of compounds of PbI_2 with Lewis bases: $PbI_2 \cdot 2$(dimethylsuloxide),[13] $PbI_2 \cdot 2$(pyridine),[14] and $PbI_2 \cdot 2$(en).[15] An X-ray study of $PbI_2 \cdot 2$(pren) and $PbI_2 \cdot$dien is now in progress in our laboratory.

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