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APPLICATION OF THE METHOD OF CONTINUOUS VARIATION TO A SOLID-LIQUID REACTION

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A method has been developed for the identification of all the insoluble complexes formed in a solid-liquid reaction of an insoluble Lewis acid with a soluble Lewis base by extending the method of continuous variation to such a heterogeneous system. It was applied to the reaction of PbI_2 with pyridine(py) in ethanol solution. Two insoluble complexes, $PbI_2 \cdot py$ and $PbI_2 \cdot 2py$, were identified.

In a previous paper,[1)] we developed a method for the identification of all the insoluble complexes formed in a solid-liquid reaction by extending the mole ratio method[2)] to such a heterogeneous system. The method was found to be applicable to solid-liquid reactions of PbI_2 with ethylenediamine[1)] and with 1,3-propanediamine.[3)] In the present paper, we wish to describe another method for the identification of insoluble complexes by extending the method of continuous variation[4)] to a solid-liquid reaction instead of the mole ratio method.

Let us assume that an insoluble Lewis acid, A, reacts with a soluble Lewis base, B, in a solution according to Eqs.1 and 2 to yield two insoluble complexes;

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

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

Suppose that A and B are allowed to react with each other in varying proportions at a constant temperature and pressure in a fixed volume of a reaction solution so that the sum of the total amounts of A and B is kept constant and that the concentration of B(=[B]) remaining in each solution is determined in some way after equilibrium has been reached. The relations between [B]'s and the amounts of B taken at the beginning of the reaction are depicted by a curve in Fig.1 which is tentatively termed a "concentration curve".

As discussed in detail on the basis of the phase rule in a previous paper,[1)] two regions of II and IV where the concentration curve is flat represent two invariant states, one of which corresponds to the coexistence of A and A•mB in the solid phase, and the other, A•mB and A•(m+n)B. On the other hand, three regions of I, III, and V where the curve has certain slopes represent three univariant states, each of which corresponds to the presence of A, A•mB, and A•(m+n)B in the solid phase, respectively.

Let us consider how the value of the slope on the concentration curve changes in each univariant region. If the volume of the reaction solution, V dm^3, remains unchanged during the reaction and the species containing A dissolve negligibly in the solution, [B] is given by:

$$[B] = \frac{X - YZ}{V}, \tag{3}$$

where X and Z are the amounts of B and A in mol taken at the beginning of the reaction, respectively and Y is the mole ratio of B/A in the solid phase. Let D be the sum of the total amounts of A and B in mol:

$$X + Z = D = \text{constant}. \tag{4}$$

Equation 3 is converted to Eq.5 by using Eq.4;

$$[B] = \frac{X - Y(D - X)}{V} = \frac{(1 + Y)}{V}X - \frac{YD}{V}. \tag{5}$$

The value of the slope equals 1/V in the region of I where only A is present in the solid phase, since Y=0:

$$[B] = \frac{1}{V}X. \tag{6}$$

Similarly, the values of the slope are (1+m)/V and (1+m+n)/V in the regions of III and V, respectively, since Y=m and Y=m+n;

$$[B] = \frac{(1 + m)}{V}X - \frac{mD}{V} \tag{7}$$

and

$$[B] = \frac{(1 + m + n)}{V}X - \frac{(m + n)D}{V}. \tag{8}$$

Therefore, it is possible to identify insoluble complexes formed in such a solid-liquid reaction by determining the values of the slope on the concentration curve.

The method developed above was applied to the solid-liquid reaction of PbI_2 with pyridine in ethanol solution. Various amounts of finely powdered PbI_2 were suspended in 10.0 cm^3 of ethanol solution containing the desired amount of pyridine in each ampoule so that D equaled 3 mmol. Each ampoule was sealed and kept at 24.3 ± 0.2 °C for about three weeks. It was shaken mechanically for about 9 hours a

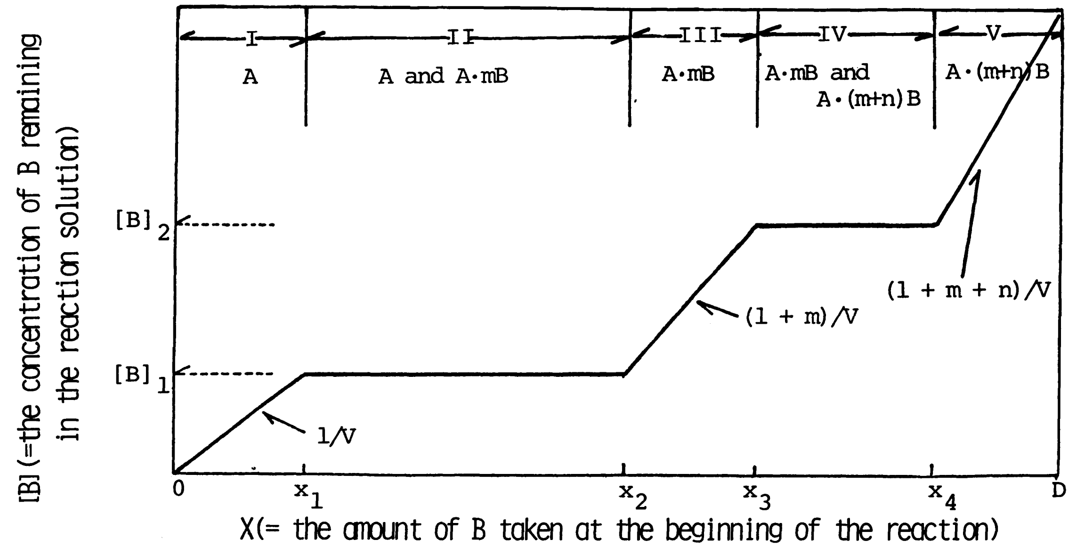

Fig.1. A typical phase diagram for a binary system consisting of A and B where two insoluble complexes, A·mB and A·(m+n)B, form. The values of the slope on the concentration curve equal 1/V, (1+m)/V, and (1+m+n)/V in the regions of I, III, and V, respectively. The values of x_1, x_2, x_3, and x_4 on the abscissa are $[B]_1V$, $(mD+[B]_1V)/(m+1)$, $(mD+[B]_2V)/(m+1)$, and $((m+n)D+[B]_2V)/(m+n+1)$, respectively, where D is the sum of the total amounts of A and B in mol.

day to promote the reaction. The concentrations of pyridine(=[py]) remaining in the reaction solutions were determined by measuring the absorbance at 256.4 nm. The concentration of Pb^{2+} ion(=$[Pb^{2+}]$) dissolved in each solution was also determined by complexometric titration.5)

The findings on the reaction are shown in Fig.2 in the same manner as in Fig.1. $[Pb^{2+}]$'s at points of 1, 2, and 3 as indicated in Fig.2 were 5.0, 2.0, and 1.8 x 10^{-5} M(1 M= 1 mol dm^{-3}), respectively. This means that the amounts of PbI_2 dissolved in the reaction solutions are negligibly small with those of PbI_2 taken at the reaction. Therefore, it is unnecessary to consider the effect of the solubilities of the species containing PbI_2 on the values of the slope in the concentration curve. Since [py]'s in the regions of II and IV were nearly constant, the reaction attained equilibrium. The formation of two kinds of complexes can be pointed out on the basis of the discussion described above, since the concentration curve has two plateaus in Fig.2. The values of the slope on the curve which are determined with least-squares method were 98.5, 199, and 296 dm^{-3}, respectively. Since the value of 98.5 dm^{-3} equals nearly that of the coefficient of X in Eq.6, namely, 100 dm^{-3}(=1/V=1/0.01 dm^{-3}), only PbI_2 was present as a solid phase in the region of I, even if any complex forms in the reaction solutions. The values of m=0.99 and m+n= 1.96 are obtained by substituting 199 and 296 dm^{-3} in Eqs.7 and 8. This indicates the formation of $PbI_2 \cdot py$ in the region of III and $PbI_2 \cdot 2py$ in the region of V.

The concentration of pyridine in each invariant region is related to the formation constants, K_1 of Eq.1 and K_2 of Eq.2:

$$K_1 = \frac{a_{A \cdot mB}}{a_A \, a_B^m} \qquad (9)$$

$$K_2 = \frac{a_{A \cdot (m+n)B}}{a_{A \cdot mB} \, a_B^n} \qquad (10)$$

where a means the activity. Since the activity of a solid is constant, Eqs.9 and 10 become Eqs. 11 and 12, respectively;

$$K_1' = \frac{1}{a_B^m} \qquad (11)$$

$$K_2' = \frac{1}{a_B^n} \; . \qquad (12)$$

If the activity of B equals the concentration of B, K_1' and K_2' are given in Eqs.13 and 14;

$$K_1' = \frac{1}{[B]^m} \qquad (13)$$

$$K_2' = \frac{1}{[B]^n} \; . \qquad (14)$$

K_1'=23.4 and K_2'=4.57 are obtained

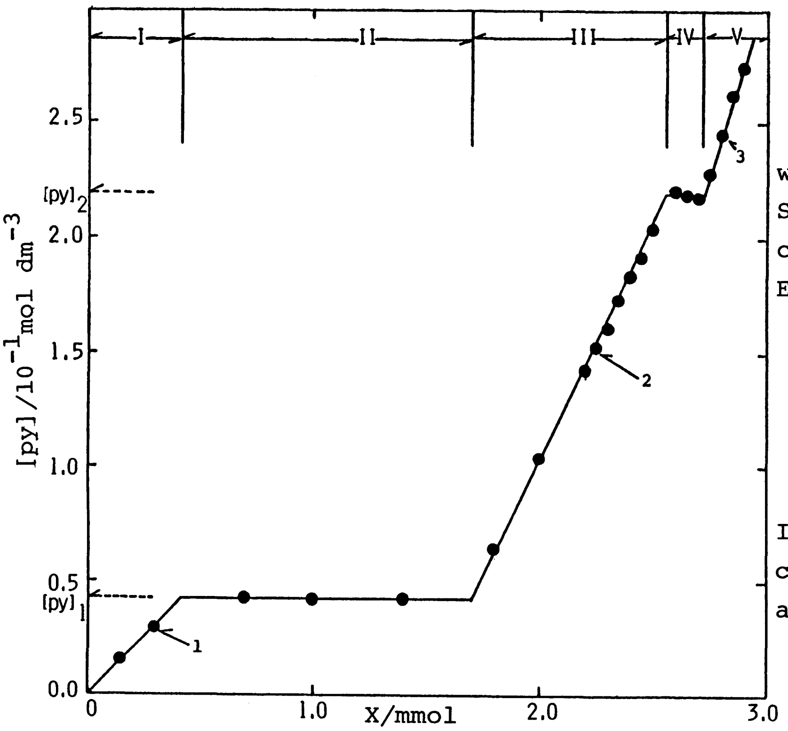

Fig.2. The relations between the amounts of pyridine taken at the reaction and the concentrations remaining in the solutions.

by substituting $[py]_1=4.28 \times 10^{-2}$M and $[py]_2=2.19 \times 10^{-1}$M, respectively.

Miyamae et al. reported the X-ray crystal structure of $[Pb_2I_4(py)_4]$.[6] The X-ray powder diffraction patterns of any sediment obtained in the region of V are the same as that of the single crystal, $[Pb_2I_4(py)_4]$ and show no peak shifts. The patterns of the sediments in the region of III are different from that of PbI_2 and of PbI_2·2py and show no peak shifts. These facts indicate that both solid phases in the regions of III and V are not the mixed crystals.

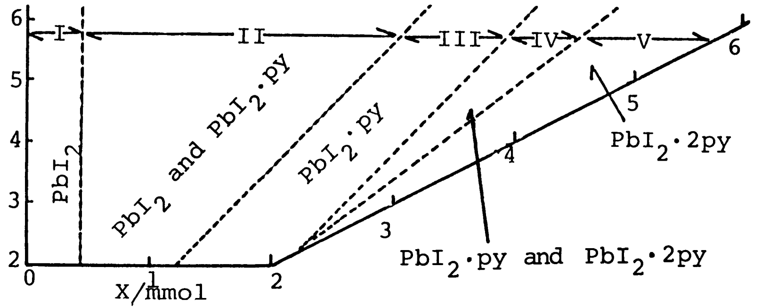

Fig.3. The phase diagram for the PbI_2-pyridine system when D is varied. The dashed line(-----) indicates a phase boundary.

Wharf et al. reported the preparation of PbI_2·py and PbI_2·2py in benzene or ethanol solution,[7] but did not cite their formation constants. Since the present method gives not only the information on the formation of complexes but also the formation constants, it is useful in estimating roughly the intensity of the interaction between Lewis acid and base when proper solvents are not available which dissolve Lewis acid. Figure 3 shows how the width of each state changes as D is varied by using $[py]_1$ and $[py]_2$ in Fig.2. The invariant region becomes wide as D increases. Therefore, the formation constants can be always obtained if a proper value of D is selected.

When the mole ratio method was applied to a solid-liquid reaction,[1] the value of the slope on the concentration curve becomes a certain constant value in all univariant regions according to the experimental conditions used. The compositions of complexes formed must be calculated from the resulting concentrations of the Lewis base. In the present method, the value of the slope is different in each univariant state and depends on the composition of complexes formed. Therefore, the present method is superior to that applying the mole ratio method from the viewpoint of obtaining directly the composition of the formed complexes without calculating it.

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