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Single Crystal Growth of Sparingly Soluble Adducts of Lewis Acids with Bases

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A method is described for growing single crystals from a solution where a base's concentration is controlled so that an adduct to be grown is equilibrated with the solution. A slight difference in its solubilities at two different temperatures is responsible for their growth process. The technique is valuable for adducts which cannot readily be grown in other ways owing to their low solubilities.

In a previous paper,[1)] we have developed a method for confirming the compositions of all the sparingly soluble adducts of Lewis acids with bases formed in solid-liquid reactions by extending the mole ratio method[2)] to such heterogeneous reactions, when proper solvents are unavailable which dissolve Lewis acids. We wish to report a method for growing single crystals of sparingly soluble adducts on the basis of information obtained when the developed method is applied to solid-liquid reactions.

The process of single crystal growth will be at first discussed from a theoretical point of view by citing a solid-liquid reaction of PbI_2 with pyridine (=py). Formation of two adducts, $PbI_2 \cdot py$ and $PbI_2 \cdot 2py$, was already confirmed in the reaction.[3)] Figure 1 shows the findings on the reaction of PbI_2 with py in ethanolic solutions at 25 °C and 15 °C, when the mole ratio method was applied; the amount of powdered PbI_2 taken at the beginning of the reactions was 1.00 mmol and the volume of reaction solution was 10 cm^3. As discussed in detail previously[1)] on the basis of the phase rule, two regions II and IV , where the concentrations of pyridine(=[py]) become fixed, represent invariant states. Accordingly, PbI_2 and $PbI_2 \cdot py$ coexist in region II and $PbI_2 \cdot py$ and $PbI_2 \cdot 2py$,in region IV in each solid phase. On the other hand, three regions I, III, and V where [py] increases represent monovariant states and correspond to the presence of PbI_2, $PbI_2 \cdot py$, and $PbI_2 \cdot 2py$ in the solid phase, respectively. Figure 1 indicates that $PbI_2 \cdot py$ is present as only one solid phase when [py] is between 0.04 - 0.18 M (1 M = 1 mol dm^{-3}) at 25 °C and between 0.03 - 0.14 M at 15 °C and that $PbI_2 \cdot 2py$ is present when [py] is more than 0.18 M at 25 °C and more than 0.14 M at 15 °C. Therefore, if $PbI_2 \cdot py$ is kept with a solution which has [py] in the range of 0.04 - 0.14 M where monovariant region III overlaps at both temperatures,

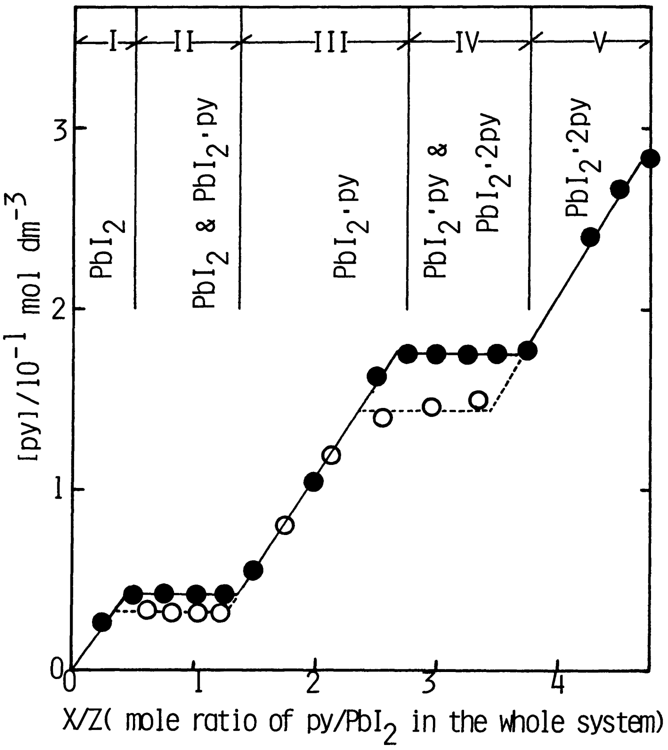

Fig.1. Phase diagram of PbI_2-py-ethanol system at 25 °C(●) and 15 °C(○).

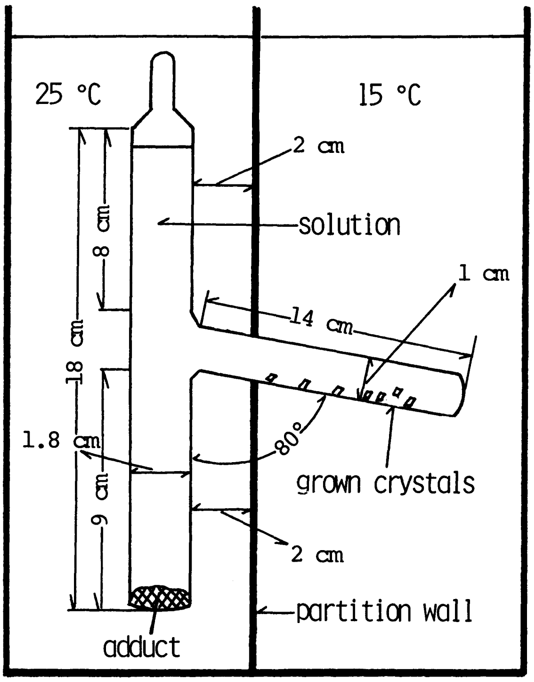

Fig.2. Size of branched ampoule and setting situation of it.

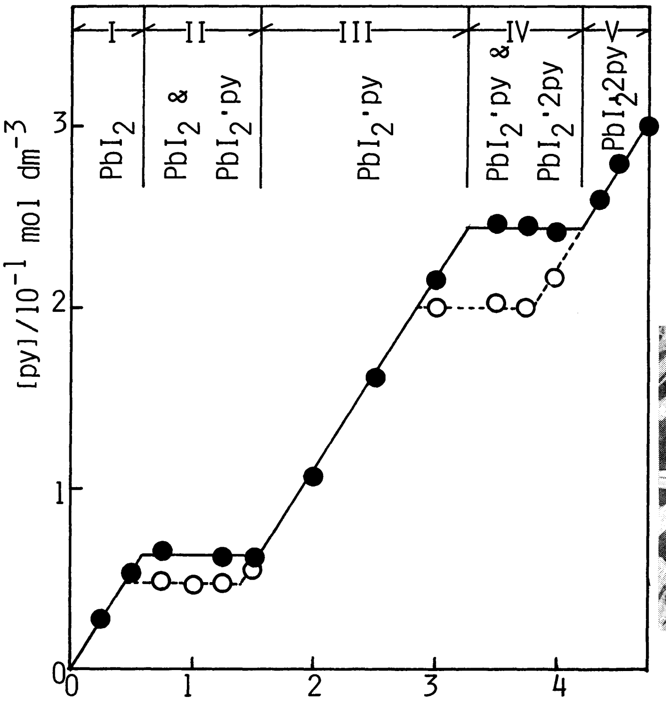

Fig.3. Phase diagram of PbI_2-py-methanol system at 25 °C(●) and 15 °C(○) where 1.08 mmol of PbI_2 was taken in the reaction.

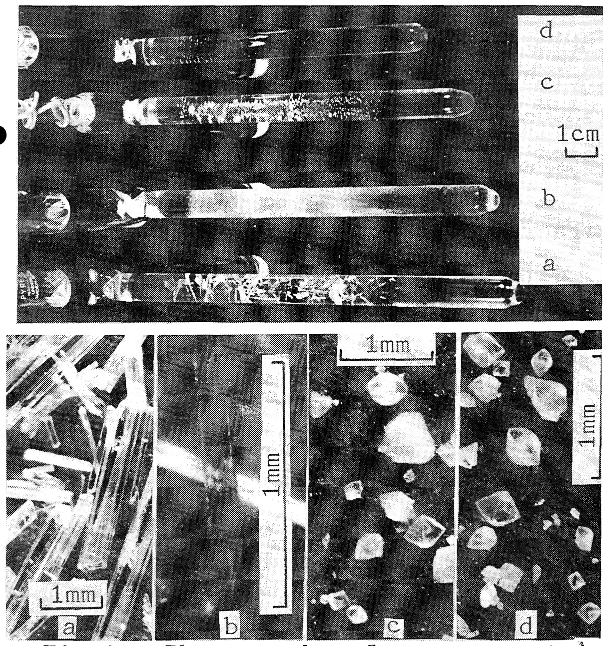

Fig.4. Photographs of grown crystals in the ampoules.
a:$PbI_2\cdot py$ in methanolic solution,
b:$PbI_2\cdot py$ in ethanolic solution,
c:$PbI_2\cdot 2py$ in methanolic solution,
d:$PbI_2\cdot 2py$ in ethanolic solution.

it changes to neither PbI_2 nor $PbI_2 \cdot 2py$, but remains intact between both temperatures. Similarly, $PbI_2 \cdot 2py$ remains unchanged when [py] is higher than 0.18 M. In addition, if their solubilities increase as an increase in temperature, it is expected that adducts which are placed at a high temperature side are transferred through the solution to a low temperature side due to thermal diffusion of them and deposit there in single crystals due to a slight difference in the solubilities between both temperatures. Table 1 shows the solubilities of Pb^{2+}ion at 25 °C and 15 °C in the solutions which are in equilibrium with either $PbI_2 \cdot py$ or $PbI_2 \cdot 2py$; its concentrations were determined by measuring the absorbance at 357 nm after 1 cm^3 of a sample solution had been mixed with 4 cm^3 of 4 M KI solution.[4] It is seen from Table 1 that their solubilities are slightly smaller at 15 °C than at 25 °C. Therefore, transport to the lower temperature side occurs in this system.

Powdered $PbI_2 \cdot py$ (about 0.5 g) separated from the solutions in region III was placed at the bottom of a branched glass ampoule which was shown in Fig.2, an ethanolic pyridine solution of 0.13 M(about 40 cm^3) was poured into it, and the top of it was sealed off. Then the ampoule was set in a thermostated vessel which was controlled at 25 °C at one side and at 15 °C at the other and was allowed to stand for about three months. In case of $PbI_2 \cdot 2py$, [py] was taken to be 0.32 M. In order to investigate solvent effects, a similar procedure described above was done by using methanol as solvent instead where [py] was taken to be 0.15 M for $PbI_2 \cdot py$ and 0.50 M for $PbI_2 \cdot 2py$. The two concentrations were adopted on the basis of the findings on the reaction of PbI_2 with py in methanolic solutions which were shown in Fig.3.

Photographs of single crystals grown in each ampoule are shown in the upper part of Fig.4 and the magnified photographs of them , in the lower part. A visual observation of the amount of crystals deposited in each ampoule indicates that for each adduct the amount of crystals grown is greater in the methanolic than in the ethanolic solutions. Most of the crystals of $PbI_2 \cdot py$ occur in columns and those of $PbI_2 \cdot 2py$ in distorted trigonal bipyramids. The powder X-ray diffraction pattern for each grown crystal was the same as that of each original adduct. Each crystal was found to be single crystal by means of the oscillation and Weissenberg method. These facts indicate that powdered adducts placed at the bottom are transferred through the solution to the branch and deposit there in single crystals. A single crystal of $PbI_2 \cdot 2py$ grown similarly as described above was

Table 1. Temperature dependence of solubilities of each adduct in solutions containing pyridine in terms of $[Pb^{2+}]$

Solvent	$[Pb^{2+}]/10^{-5}$M			[py]/M	Solid phase[2]	$[Pb^{2+}]/10^{-5}$M			[py]/M	Solid phase[2]
	25 °C	15 °C	Dif.[1]			25 °C	15 °C	Dif.[1]		
Ethanol	4	2	2	0.13	$PbI_2 \cdot py$	2	1	1	0.32	$PbI_2 \cdot 2py$
Methanol	25	16	9	0.15	$PbI_2 \cdot py$	13	5	8	0.5	$PbI_2 \cdot 2py$

1) Difference in $[Pb^{2+}]$ between 25 °C and 15 °C.

2) Composition of adducts equilibrated with solution containing py.

subjected to X-ray strcture analysis.$^{5)}$

Single crystals of complexes are usually grown by means of either (1) the evaporation of solvents or (2) slow cooling of solutions after their dissolution at a high temperature. However, both are not applicable to crystal growth for complexes having low solubilities. Crystal growth for sparingly soluble salts occurs in silica gel$^{6)}$ where ions diffuse slowly through the networks of silica gel, encounter opposite ions, and deposit there in single crystals. The method described in the present paper is based on thermal diffusion of the adducts which is caused by a slight difference in their solubilities at two different temperatures, because the end of the branch was set to be downward so that mass transport at the branch of the ampoule is caused not by convection but mainly by thermal diffusion. According to Hannay,$^{7)}$ the rate-determining step of crystal growth from solution is diffusion of solute to the crystal-solution interface. We have little information on species which are present in solution when the adducts treated here are equilibrated with the solutions. However, since the conductances of the equilibrated solutions increase as $[Pb^{2+}]$ increases, the adducts may dissociate into Pb^{2+} ion and I^- ion to some extent. If the Pb^{2+} ion is representative of the formed ions, the growth rate(=v) is given in Eq.1:

$$v \propto ([Pb^{2+}]_{25} - [Pb^{2+}]_{15})([Pb^{2+}]_{15} - C_{int})[py]_{15}, \qquad (1)$$

where C_{int} is the concentration of Pb^{2+} ion at the interface and the figure of subscript means temperature. If C_{int} and the diffusion coefficient of Pb^{2+} ion are independent of solvents, two terms of difference in $[Pb^{2+}]$ and that of [py] are larger in the methanolic than in the ethanolic solutions under the adopted conditions as Table 1 shows. Therefore, v is faster in the methanolic than in the ethanolic solutions. This conclusion agrees with the fact obtained through the visual observation described above.

Adducts of Lewis acid with liquid base are grown from liquid base itself.$^{8)}$ However, when more than one kind of adduct are formed in a certain Lewis acid-base reaction, an adduct which has an intermediate composition such as $PbI_2 \cdot py$ cannot be grown from such neat liquid base. Since the method offered here permits single crystals of adducts having the desired compositions to be grown by controlling only the concentrations of bases, the method is essential for single crystal growth of sparingly soluble adducts which have an intermediate composition.

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