PURIFICATION OF *p*-DICHLOROBENZENE AND *m*-CHLORONITROBENZENE CRYSTALLINE PARTICLES BY SWEATING

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In order to obtain highly purified organic substances, sweating of crude crystalline particles was investigated with two organics; *m*-chloronitrobenzene and *p*-dichlorobenzene. By maintaining the crude crystals at a temperature close to the equilibrium one in order to form melts and followed by rapid drainage of the melts, the crystals were found to be purified upto 99.99% within 1.5 or 2 hr. The final purity was found to depend on the sweating temperature. The rate of purification was analyzed with a model that the drainage of the melts dominated the phenomena of sweating. Empirically, the rate of removal of the melts was expressed as $k(\alpha - \alpha_\infty)^2$ where k is the coefficient for purification rates and $(\alpha - \alpha_\infty)$ denotes the free melts removable by the sweating. The values of k were found to be common to the examined two organics and α_∞ was a function of the sweating temperature. The purification rate was thus analyzed quantitatively.

1. Introduction

Demands for high purity materials have increased recently in various fields. Applications of repeated crystallization such as zone melting, or directional crystallization such as Czochralski or Bridgman-Stockberger techniques have been known successful in preparation of high-purity organic materials.^{3,5,7)}

However it is also true that organic crystals produced in a conventional crystallizer at moderate crystal growth rates are most often contaminated by some impurities. In many cases, these impurities come from the mother liquor and are present at the surface and/or within the crystals as inclusions.

Many studies on the removal of such impurities have been reported, and some have been applied to industrial purifications. Cutts and Wells¹⁾ studies purification of benzene crystalline particles by washing and found that the washing was effective to remove the surface impurities alone, therefore removal of inclusions within the crystals was not expected by washing.

Wilcox^{8,9)} critically reviewed and discussed the removal of inclusions by gradient methods by applying temperature gradients as large as 100°C/cm or pressure gradients in an ultracentrifugal field of 210,000 G and showed possibility of the removal. Practical applications of these gradients, however, seem impossible and these methods must be restricted

to specific materials.

Removal of inclusions by heating upto as high as the melting point of the crude crystals has been used in purifying a number of organics and metals.¹¹⁾ This operation is, as described below, based on the solid-liquid phase equilibrium and is sometimes called, "sweating". In the present paper the term of sweating is used with the definition as a process of partial melting of crude crystalline materials by heating followed by drainage of the resulted melts.

Murata and Matsuoka⁴⁾ applied sweating to prepare high purity organics and found significant influences of sweating temperatures, but they did not give quantitative analyses of the sweating rates. While Saxer and Papp⁶⁾ developed a purifier exploiting sweating. Their purification is semibatch, and the sequence of crystallization on an inner wall of a vertical tube and sweating was repeated by external cooling and heating.

In addition to these fundamental studies, Yamada *et al.*¹⁰⁾ studied a continuous commercial purifier in which sweating as well as recrystallization and washing occurs simultaneously.

There have been reported many other purification apparatus in which sweating is involved, however the above two processes seem to take advantage in carrying out sweating effectively, since crystals are not dispersed in melts during purification. Unfortunately, mathematical analyses of these operations are not sufficient, moreover understanding of the sweating phenomena itself is so far very poor. The present

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study aims to understand the phenomena of sweating of organic crystals and to formulate the rate of sweating to analyze the process quantitatively.

2. Preliminary Consideration

Consider a binary simple eutectic forming system as shown in **Fig. 1**. Crystalline products from a crystallizer, of which apparent composition is given as w_s at a given temperature t_0 , are mixtures of pure crystals and impure melts. The composition of the melt varies with the temperature; during crystallization it would be close to the bulk melt composition $w_{l,0}$ or its equilibrium composition $w_{l,0}^*$ while it may be w_l^* during the storage at a temperature t' . In addition, it will be w_l^* during the sweating at a temperature of t if equilibrium is assumed. Generally at higher sweating temperatures up to the liquidus point of the mixture, the amount of the melt is larger in accordance with the phase diagram and the lever rule. Therefore the rate of purification by sweating must be connected with the rate of generation of the melt, i.e. the rate of heat transfer at which melting inside of the crystals occurs.

Imagine that a single spherical crystal of temperature t_1 with diameter of 1 mm is suddenly placed in air at temperature t_2 ($> t_1$). Then heat is transferred by convection from the air and by conduction in the sphere. By providing appropriate physical properties of the typical organics and typical value of heat transfer coefficient one finds that after about 20 seconds the temperature at the center of the sphere has experienced 90% of the final temperature change i.e., $(t_2 - t_1)$. Hence even when one takes into account the latent heat of fusion during the sweating, a few minutes are enough to establish an almost uniform temperature profile inside of the crystal. This conclusion suggests that rapid purification by sweating is expected.

3. Experimental

3.1 Preparation of crude crystals

The simple eutectic systems of *m*-chloronitrobenzene(CNB)-*o*-CNB and *p*-dichlorobenzene(DCB)-*o*-DCB were used. Major experiments were made with the DCB system. The individual organics of the former system (Tokyo Chemical Industry Co., Ltd., Reagent grade) were purified by recrystallization three times from acetone solutions while the latter organics were used without further purification.

A mixture with known composition was placed in a batch stirred crystallizer of 250 ml made of glass, and its equilibrium temperature (liquidus point) was determined by confirming no size changes of a crystal particle thrown in the melt for at least one hour. Then the melt was slowly supercooled by 1°C by controlling the bath temperature, and spontaneously nucleated

Fig. 1. Phase diagram of a simple eutectic system and schematic representation of sweating operation.

and grown crystal particles were quickly separated from the melt by vacuum filtration. The crystals thus obtained were stored as the crude crystals.

The composition of the prepared crude *p*-DCB crystals w_s were found to be ranged in 0.978–0.985 for those prepared from the melt of $w_l = 0.70$ –0.75 at the supercooling of 1°C. The most of the crude crystals of *p*-DCB were agglomerates consisting of several rod-like elementary particles, while the crude *m*-CNB crystals were rectangular when prepared from the melt of $w_l = 0.892$ at a supercooling of about 2°C.

3.2 Sweating

About one gram of the crude crystals were placed in a glass tube of 15 mm in diameter after precisely weighed. The tube was made of a thick centrifuge tube with steel screen to hold the crystals in the middle of it. Then the tube was sealed and immersed in a constant temperature bath maintained at the sweating temperature t for a determined sweating period, and was transferred in a centrifuge, of which rubber holders had been kept at about the same temperature t with hot water. The centrifugal separation was carried out at a fixed condition of 5000 rpm for 5 minutes. Then the weights and compositions of the separated crystals and melts were measured. With this separation all the melts except occluded inclusions deep inside of the crystals were regarded to be completely removed. As experimental variables the sweating period, defined as the period when the tube was held in the bath, was varied from 5 minutes to 4 hours, and the sweating temperature was also varied from 1 to 4°C below the melting points of the pure organics.

3.3 Analysis

All the compositions of the crude and purified crystals and the melts were quantitatively analyzed with an FID gas chromatograph (Hitachi 163 with Thermon 1000 as a liquid phase) and were automatically processed and converted into the weight fractions with a data processor (Shimadzu C-R1B) with the calibration curves prepared for each system.

4. Results

4.1 Temperature change

The temperature at the center of the crystal bed was found to change as shown in **Fig. 2** for the *p*-DCB system. The crystals were initially at room temperature, and almost attained the sweating temperature about ten minutes later after the immersion of the tube in the bath. The temperature in the crystal was therefore regarded to attain its sweating temperature a few minutes later, i.e., about 15 or 20 minutes are enough for the crystals to be in equilibrium with the surroundings and thereafter the sweating proceeds isothermally.

4.2 Increase of purity of crystals

The observed relations between the purity of the crystals after the centrifuge and the sweating period are shown in **Fig. 3-a** for the *p*-DCB and in **Fig. 3-b** for the *m*-CNB systems. These curves show strong dependence on the sweating temperature as well as rapid increases in purity in the initial periods and existence of asymptotic purity levels for given sweating temperatures. Moreover it can be seen that 1.5 or 2 hours are needed to obtain about 99.99% purity products at elevated temperatures and that two or three hours are necessary to attain the final asymptotic purities for each sweating temperature. All of these facts were found to be common to the two organics of which apparent crystal shapes were remarkably different one another as described earlier.

4.3 Yield of crystals

Figure 4 shows the changes of the crystal yields defined as the ratio $(w_{s,0} - w_l^*) / (w_s - w_l^*)$. Though as mentioned above the crystal temperature attained the sweating temperature within about 15 or 20 minutes, continuing decrease in the crystal yields or corresponding increase in the amount of melts was observed for the periods as long as those corresponding to the purity changes (**Fig. 3**). This suggests that drainage of the melt is a governing factor in the purification by the sweating operation.

4.4 Compositions of the melt

The average composition of the melt w_l formed in the sweating period was plotted against the time in **Fig. 5** for the *p*-DCB crystals. A rapid increase in compositions at the beginning of the sweating is seen for each run, followed by the gradual approach to a specific value which was found to coincide with the equilibrium composition at the sweating temperature.

5. Discussion

5.1 Modelling of sweating mechanism

As described in the previous sections, the purification of the crystals and the changes of the melt compositions continued for a long period even after the crystal temperature attained the sweating tem-

Fig. 2. Temperature change in crystal beds during sweating for *p*-DCB crystals.

Fig. 3. Increase in crystal purities with sweating time. a: *p*-DCB crystals with *o*-DCB impurity. b: *m*-CNB crystals with *o*-CNB impurity.

perature. In addition, the melt composition attained to its final value much faster than the yield did. From these facts one can suppose the sweating mechanism other than those described in the preliminary consideration simply on the basis of the phase equilibrium and the lever rule.

As depicted schematically in **Fig. 6**, the crude crystals are regarded to contain the melt on the

Fig. 4. Changes of crystal yield with sweating time for *p*-DCB crystals.

Fig. 5. Changes of melt composition with sweating time for *p*-DCB crystals.

Fig. 6. Schematic drawing to illustrate sweating phenomena.

surface as the adhered melt and within the crystal as inclusions. The composition of the melt at the beginning of sweating is expected to be close to $w_{i,0}^*$ since adhesion or trapping accompany the existing melt at the interface when it occurs. During the sweating the melt with the equilibrium composition w_i^* continues to appear and gradual mixing within the melt causes the average composition to approach to the final value in equilibrium at the sweating temperature as seen in Fig. 3. Then the drainage or phase separation would leave some inclusions of the equilibrium melt composition.

At the same time gradual increase in the amounts of the separated melt occurs in a different manner. Every crude crystal must possess in its interior domain some defects originated from the inclusion in the course of growth, and they continue from the inclusion site to the surface. Hence heating such a crude

crystal causes partial melting around the inclusion and along the defects selectively.

After initial heating periods, the droplet of the melt within the crystal gradually alters its shape to open a channel as its way to the surface. The driving force for this change must be either curvature-dependent phase equilibria or pressure forces arising from the volume increase on the melting. Since the inclusion is surrounded by facets initially, there are positions with infinitesimal curvatures at the corners of the inclusion where melts with higher compositions are present. Accordingly the diffusion caused by the resultant concentration gradient in the inclusion as well as the flows due to the pressure difference enlarges the channel, leading to make drainage of the inclusion easy.

Consequently the rate of purification is suggested to be proportional to the rate of removal of the melt, in other words the rate of channel formation governs the purification rate in the operation of sweating.

5.2 Formulation of sweating rates

Since the crude crystals as well as crystals during or after sweating are regarded to consist of pure crystals and inclusions, their apparent composition w_s can be written in terms of the inclusion coefficient α , defined as a fraction of the included melt²⁾ with the assumption of isothermal and equilibrium sweating, as

$$w_s = \alpha w_i^* + (1 - \alpha) w_s^* \quad (1)$$

where w_i^* and w_s^* denote equilibrium compositions of the melt and the crystal at a given sweating temperature t . Then the rate of purification at a constant temperature is expressed as

$$\frac{dw_s}{d\theta} = -(w_s^* - w_i^*) \frac{d\alpha}{d\theta} \quad (2)$$

Consequently the rate of purification is assumed to be proportional to the rate of drainage, i.e. the rate of removal of the inclusions. Since the purity attainable at a given temperature is limited, it is clear that even after long sweating time persistent inclusions (α_∞) remain inside of the crystal. The rate of removal of the inclusion is therefore assumed to be a function of the amount of free inclusions, which is defined as inclusions removable by the sweating ($\alpha - \alpha_\infty$), i.e.,

$$-\frac{d\alpha}{d\theta} = f(\alpha - \alpha_\infty) \quad (3)$$

The right hand side was then assumed to be of the form of $k(\alpha - \alpha_\infty)^n$, and by the least squares method the following equation was found to correlate the purification rate well on the whole,

$$-\frac{d\alpha}{d\theta} = k(\alpha - \alpha_\infty)^2 \quad (4)$$

In the above equation, the values of α_∞ were first

estimated from those at about four hours sweating. The determined values of the coefficient k were found to be 160 [1/h] common to the examined two substances though considerable scatters were observed. In addition to this, the pertinent inclusions in terms of α_∞ were correlated as a function of the sweating temperature as shown in Fig. 7.

Since α_∞ is finite for the sweating below its melting point, complete removal of inclusions by sweating can hardly be expected, i.e. obtaining a completely pure substance is possible only when the sweating is carried out at a temperature infinitely close to its melting point.

The curves in Fig. 3 were those calculated from Eq. (4) with the above described values of k and α_∞ . They showed good agreements with experimental data, particularly after 20 minutes where isothermal sweating was probably held as estimated previously in 4.1.

Conclusion

High purification of the *p*-DCB and the *m*-CNB crystal particles by sweating was experimentally investigated. The purities of the crystals were found to increase rapidly in the initial periods and to approach to finite purities which were dependent on the sweating temperature. The purity of 99.99% was obtained by a single sweating stage at temperatures about 1°C below the melting points of the pure crystals after the duration of 1.5 or 2 hours of sweating.

The purification rate was formulated with the assumption that drainage of the inclusions governs the rate. The measured purification rates were well explained by this model, and the constants in the equation determined from the experimental data were well correlated with the sweating temperature.

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Nomenclature

k	= coefficient for purification rate	[h ⁻¹]
t	= temperature	[°C]
w_i	= melt composition in weight fraction	[—]
w_s	= crystal composition in weight fraction	[—]
α	= inclusion coefficient	[—]

Fig. 7. Pertinent inclusion coefficient as a function of sweating temperatures. Abscissa is difference from melting point of pure organic crystals.

θ = time [h]

<Superscript and subscript>

0 = crude crystals

*

' = arbitrary temperature

m_p = melting point

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