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Separation of Acetic Acid from Acetic Acid-Water Mixture by Crystallization

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Separation of acetic acid from acetic acid and water mixture was carried out by melt crystallization. The effect of the cooling rate, the amount of seeds, the seeding temperature, the sweating rate, and the sweating fraction on the distribution coefficient was investigated. The acetic acid was successfully separated by single-stage melt crystallization. As the sweating fraction is increased, the crystalline layers grown at lower cooling rates are purified more highly. Eventually, the crystallization rate is much more important than the sweating rate. The effective distribution coefficient ranges from 0.01 to 0.25 for the crystal growth rates of 1.2×10^{-6} m/s to 4×10^{-6} m/s.

Keywords acetic acid; crystallization; separation; sweating

INTRODUCTION

The technique for purification and separation is an increasingly important subject in chemical processes. Crystallization of organic materials from the melt is also a separation technique to enable the purification of chemicals at a lower energy cost compared to conventional separation technique like evaporation. The use of melt crystallization for separation has increased rapidly in the chemical industry over the past few years. In melt crystallization, the purified compounds as well as the impurities are recovered in molten form and can be recycled, incinerated, or treated in some other way without an intermediate solvent removal step. From this point of view, melt crystallization is a clean technology for the separation of organics without using a solvent (1).

Separation of acetic acid from acetic acid-water mixture was mainly tried by membrane technology (2), distillation (3), and liquid-liquid extraction technology (4). They required big energy consumption and additional chemicals. As an alternative process to those technologies, melt crystallization technology was studied in this paper.

Acetic acid-water mixture is a simple eutectic mixture with eutectic point of −26.5°C at the concentration of 60 wt% acetic acid. Therefore, pure acetic acid can be separated thermodynamically at above the eutectic point. In the melt crystallization operations, the inclusion entrapped inside crystals is inevitable and cannot be removed by a purification method like washing (5–7). Therefore, an additional purification is essentially required for upgrading the crystal to ultra-purity after crystallization. Washing and sweating are used as additional purification methods. In purification of crystalline layers by washing, the washing was found to be effective in removing the impurity on the surface. The removal of inclusions in the crystals is not expected by washing. Sweating is desirable for upgrading the purity of crystalline layers after crystallization operations. Thus, the sweating process is effective for purification of crystals obtained in crystallization in industrial processes (7–10). Although many previous works presented purification of crystals by sweating, most studies concentrated on the influences of sweating temperature and temperature gradient (7,8,11).

In this study, melt crystallization and sweating operations were carried out for separation of acetic acid from acetic acid-water mixtures. The operating parameters investigated were cooling temperature, cooling rate, seeding temperature, seed amount, and sweating rate. Acetic acid-water was separated by layer crystallization combined with the sweating. Separation efficiency was compared for crystallization and sweating processes.

EXPERIMENTAL SECTION

Acetic acid (reagent grade, purity > 99.5 wt%) was purchased from Duksan Chemical Co. (Kyungkido, Korea). Ultrapure deionized water was used.

In the layer crystallization, 85 wt% acetic acid and 15 wt% water mixture was fed into the crystallizer (glass column) at 20°C and cooled until −10°C. The column was covered with a plug. The crystallization was conducted by following a linear cooling rate in the cylindrical column from 0.1 K/min to 5 K/min by means of internal control of

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the linear cooling ramp in thermostatic bath. Seed crystal of acetic acid was added in crystallizer at the various cooling temperatures within metastable zone width. The seed crystals of acetic acid were obtained by immersing the acetic acid solution into the cooling bath of −20°C. The mean crystal size of seed was about 15 µm.

The mass of the ice layer formed was around 400 g. When the temperature of the cylindrical tube reached the final crystallization temperature, the residual solution was drained through the bottom draw-off tap. After crystallization, the temperature of the crystallizer was increased to induce a partial melting of solid. The melted liquid was drained gradually until the crystalline layers were entirely molten. The desired sweating temperature was controlled by the cooling fluid circulating inside the jacket. The sweating rate was adjusted. The temperature was progressively increased from the final temperature of the crystallization step towards the chosen final temperature of sweating. The melt draining out during the sweating step was collected for its analysis. At the end of the sweating step, the remaining acetic acid layer was completely molten and the resulting solution was analyzed. The crystal and the molten liquid were sampled with respect to the sweating fraction. The concentrations in liquid and solid were measured by gas chromatography. Figure 1 shows a schematic drawing of equipment of layer crystallization.

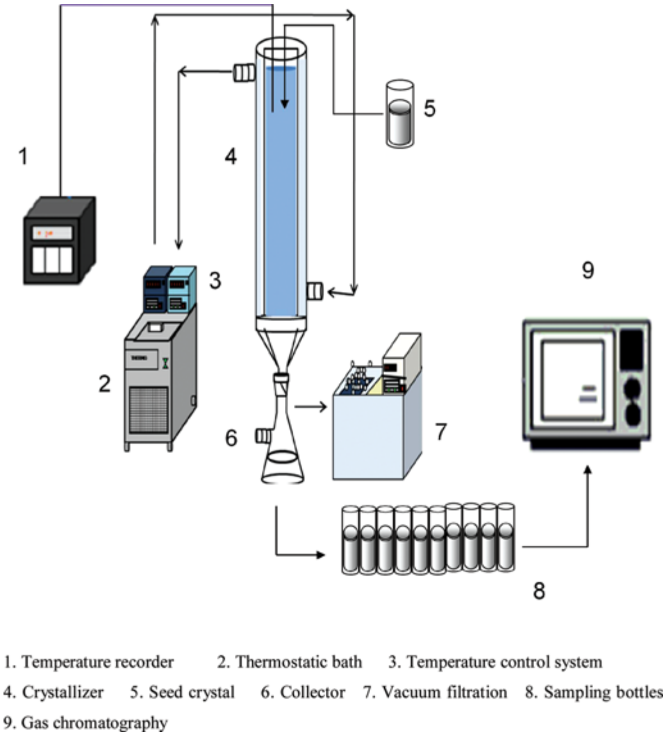

FIG. 1. Schematic drawing of experimental apparatus. (Color figure available online)

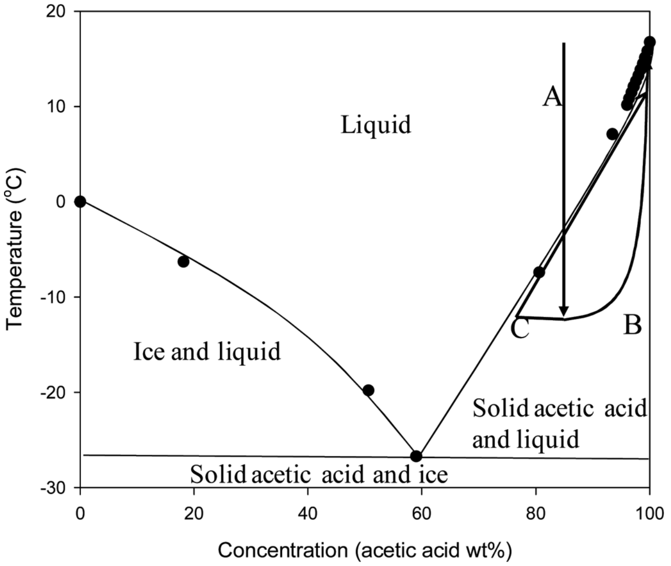

FIG. 2. Solid-liquid equilibrium of acetic acid and water mixture and experimental paths.

Figure 2 shows the solid-liquid phase diagram for acetic acid and water mixture. It is a typical single eutectic mixture. In this diagram, there are four sections for liquid, ice and liquid, solid acetic acid and liquid, and solid acetic acid and ice. Acetic acid can be separated at the above eutectic temperature (about −26.5°C) in the section of solid acetic acid and liquid. Paths A, B, and C are carried out by crystallization, solid purified by sweating and melt drained-out by sweating, respectively. The seeding was carried out in the range of −2 to −7°C in path A.

RESULTS AND DISCUSSION

Effect of Seeding Temperature during Crystallization

In this study, seeded crystallization and sweating processes were discussed for upgrading the purity of crystalline layers. Six types of crystalline layers made at the seeding temperature of −2 to −7°C, were sweated by applying a temperature increase in the column, from the final temperature of crystallization (263.15 K) to the same final temperature of sweating (293.15 K). Figure 3 shows the effect of the sweating fraction on the concentration of acetic acid in the crystalline layers with respect to various seeding temperatures. Sweating fraction means the ratio of the amount of the melt drained out to the total amount of crystalline mass after crystallization. Eventually the sweating fraction is the same as the yield of crystallization. Crystalline layers were formed at a feed composition of 85 wt% acetic acid and a cooling rate of 0.1 K/min. Seeding was carried out within the metastable zone width. The metastable temperature at which nuclei are formed spontaneously without seeding is −7.8°C. The sweating rate was set as 0.1 K/min. The purity of the crystalline layer increases with increasing

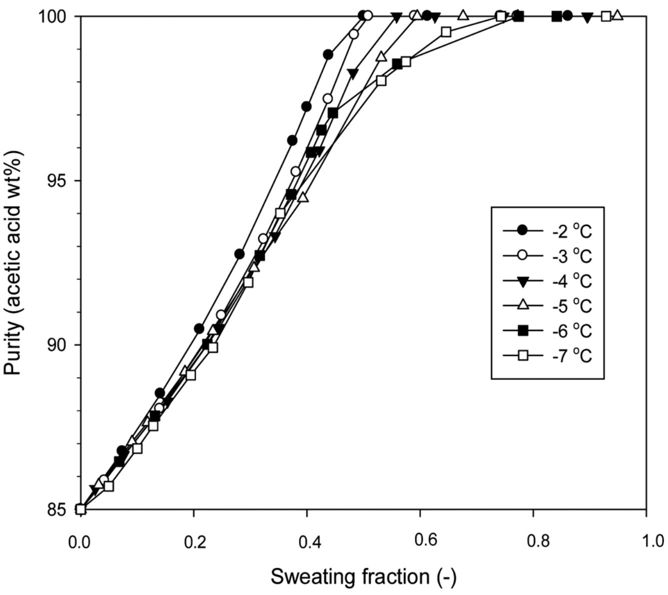

FIG. 3. Effect of seeding temperature on the purity.

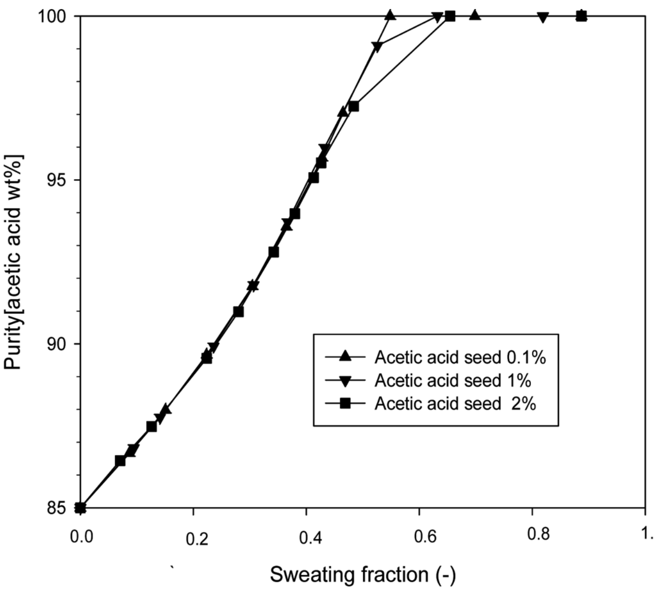

FIG. 4. Effect of seed amount on the purity.

the sweating fraction. Especially purity increases linearly at the beginning of sweating process below a sweating fraction of 0.4. This means that the impurity formed on growing crystals is mostly located on the surface of the crystalline layer. Impure inclusions occluded on the outside of the layer are easily drained away at the beginning of the sweating operation. This indicates that the impure crystalline layer begins melting from the surface of the layer.

As a result, pure acetic acid was obtained at the sweating fraction >0.8 for all cases. It indicates that the yield decreases and the purity increases as increasing the sweating fraction. The results, therefore, show that crystal purity could be improved by operating sweating. The crystalline layer obtained by seeding at −2°C was highest in purification rate by the sweating. It means the state of the layer formed in crystallization process is important in the sweating process. Higher seeding temperature leads to lower supersaturation. In general, the lower supersaturation results in the higher purity (12).

Figure 4 shows the effect of the amount of seeding on the purity of the crystalline layer. Crystalline layers were formed at a feed composition of 85 wt% acetic acid and a cooling rate of 0.1 K/min. Seeding was carried out at a cooling temperature of −4°C. As can be seen in Fig. 4, the purity is almost the same in the range of seeding amount from 0.1 wt% to 2.0 wt%. Seeding amount was therefore selected as 0.1 wt% of the feed amount.

Effect of Cooling Rate

Three types of crystalline layers made at the cooling rate of 0.1 to 5 K/min, were sweated by applying a temperature increase in the column, from the final temperature of crystallization (263.15 K) to the same final temperature of sweating (293.15 K).

The separation of acetic acid from acetic acid-water mixture is characterized by the effective distribution coefficient. The effective distribution coefficient k_{eff} is defined by the ratio of mass fractions of impurity in the feed x_{if} and in the crystal x_{ic} (1,7).

$$k_{eff} = \frac{x_{ic}}{x_{if}} \tag{1}$$

The effective distribution coefficient k_{eff} close to 1 means that in a binary system almost no separation occurs while k_{eff} close to 0 means an almost perfect separation. Here $0 < k_{eff} < 1$ is an essential condition of purification.

Figure 5 shows that, for the three types of crystalline layer, the purity of the sweated crystalline layer increases with increasing sweating fraction. The crystalline layers were prepared at cooling rates of 0.1, 1, and 5 K/min for 85 wt% acetic acid and 15 wt% water mixture by seeding acetic acid solid at −2°C. Purity after sweating is also higher for the layer crystallized at lower cooling rate. Obviously, the purity improvement was accompanied by an increase of the sweating fraction.

Figure 6 shows the distribution coefficient with respect to the sweating fraction for three crystalline layers. The distribution coefficient decreases with increasing the sweating fraction. In comparison to the initial k_{eff} at a sweating fraction of about 0.3, its value decreases with decrease in cooling rate. As the sweating fraction is increased, the crystalline layers prepared at lower cooling rate lead to the lower distribution coefficient. At the constant sweating

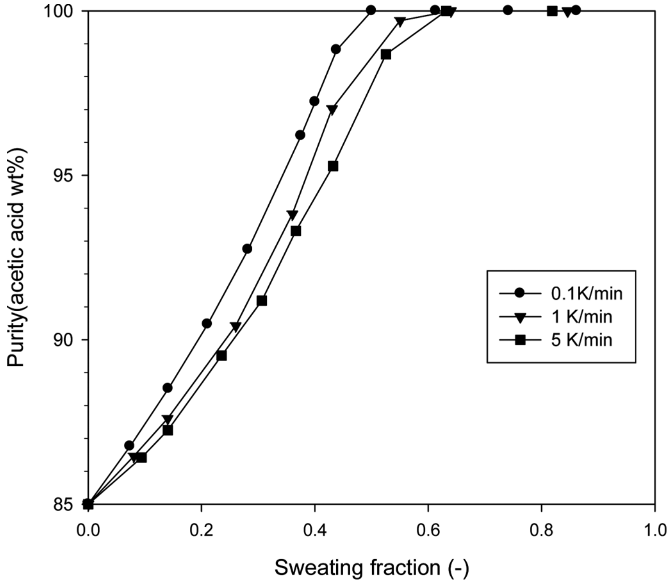

FIG. 5. Effect of cooling rate on the purity.

rate, k_{eff} decreases more rapidly in the crystalline layer formed in lower cooling rate. This means that lower growth rate induces higher purity of crystal in the sweating process. Thus, the crystallization conditions may be considered as an important factor in the purification of the layer by a sweating operation.

As the cooling rate affects the crystal growth rate, the crystalline layer formed at the higher cooling rate has more inclusion amounts in the layer. k_{eff} at the sweating is higher in the crystalline layer obtained at higher cooling rate. The purity is nearly 100 wt% at the sweating fraction >0.8 for all types of crystal. A control of the crystallization process rather than the sweating process is, therefore, necessary for an optimization of the process and for an upgrading of the purity of crystalline layer. To compare a sweating efficiency of the crystalline layers, k_{eff50} was shown in Fig. 6. k_{eff50} means the value of k_{eff} at a sweating fraction of 0.5. It was found that k_{eff50} was 0.02, 0.12, and 0.19 for the layers prepared at cooling rate of 0.1, 1.0 and 5.0 K/min, respectively. It is interesting to know that crystallization condition affects the purity despite of the same sweating conditions.

Effect of Heating Rate during Sweating

Different sweating rates were tested in the range of 0.1 to 5 K/min. Figure 7 shows the plot of purity against sweating fraction at various heating rates in the sweating process. A crystalline layer prepared at a feed composition of 85 wt% acetic acid, a cooling rate of 1 K/min and a cooling temperature of −10°C was used. The crystalline layer was heated in the range from −10°C to 20°C after crystallization. It was found that the purity of crystals has a strong dependence on the sweating fraction in the heating process. The purity increases with decrease in the heating rate.

The heating rate affects the sweating rate of the crystalline layer. Increasing sweating rate induces decreasing the sweating effect. The partial melting of the crystal surface in the sweating process is desirable for increasing the purification effect by sweating. Increasing the sweating rate leads to retard in partial melt of the layer due to channel effect of the melt draining-out.

Separation Efficiency

To grasp the efficiency of the sweating process, k_{eff50} was defined in this study. k_{eff50} means the value of k_{eff} at a

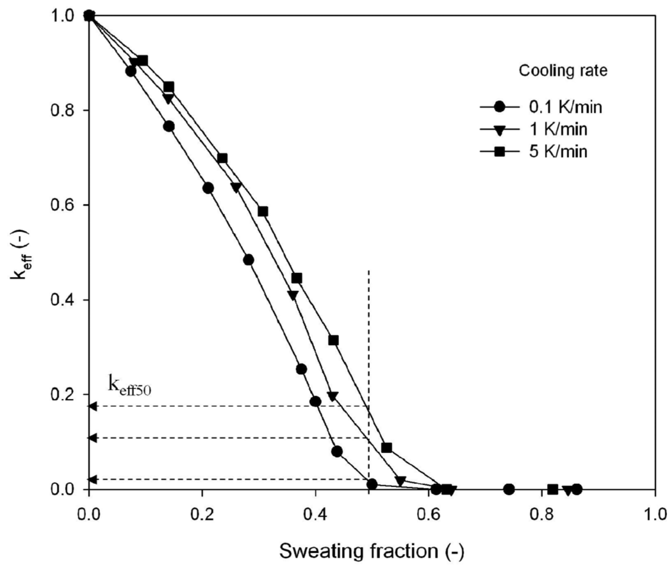

FIG. 6. Effect of cooling rate on the k_{eff}.

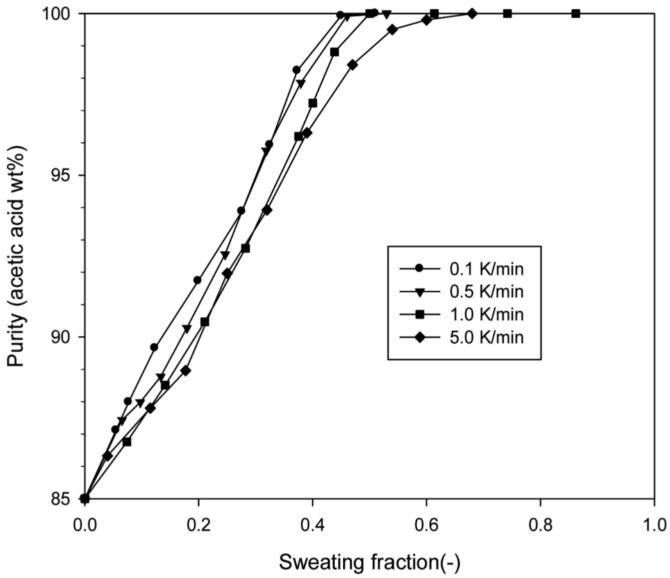

FIG. 7. Effect of heating rate on the purity.

sweating fraction of 0.5, which means the total yield of 50 wt%.

Figure 8 shows the effect of seeding temperature on k_{eff50} and supersaturation in the layer crystallization. The metastable temperature, whose nuclei were formed spontaneously without seeding was −7.8°C. The seeding temperature was in the range −7°C to −2°C. The value of k_{eff50} increases with decreasing the seeding temperature. The value of k_{eff} was found to be 0.12 to 0.02 in the range of −7°C to −2°C in seeding temperature. The supersaturation decreases with increasing the seeding temperature. The lower seeding temperature leads to the higher metastable zone width, which induces the higher supersaturation. Thus, the seeding temperature can control the supersaturation.

Figure 9 shows effect of cooling rate and heating rate on k_{eff50}. The distribution coefficient increases with increasing the cooling rate and the heating rate. Cooling rate is a key operating condition in crystallization process, while the heating rate is that in the sweating process. The distribution coefficient increases with increase in the heating rate as well as the cooling rate. The tendency for purification of crystalline layer is different between cooling rate and heating rate. As can be seen in Fig. 9, the effect of the cooling rate on k_{eff50} is higher than that of the heating rate. Eventually, the crystallization rate should be controlled for the purity rather than the sweating rate.

Effect of Growth Rate on the k_{eff50}

The purity of crystal depends mainly on the crystal growth rate (11,12). Figure 10 shows a plot of k_{eff50} versus crystal growth rate. Crystal growth rates were calculated by dividing the thickness of layer by the crystallization time during layer growth. Despite data scattered, k_{eff50} increases with increasing crystal growth rate. Wintermantel determined the similar pattern for layer crystallization processes (13). It means the purity decreases with increasing the crystal growth rate. The higher growth rate results from the higher supersaturation, which leads to higher inclusions in the crystalline layer. As can be seen, k_{eff50} ranges from 0.01 to 0.25 for the crystal growth rates of 1.2×10^{-6} m/s to 4×10^{-6} m/s. The purity of crystals was upgraded by controlling the crystal growth rate.

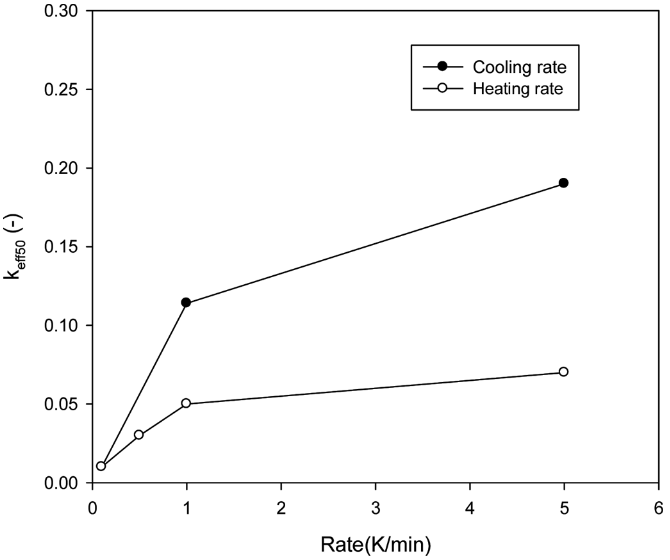

FIG. 9. Comparison between cooling rate and heating rate.

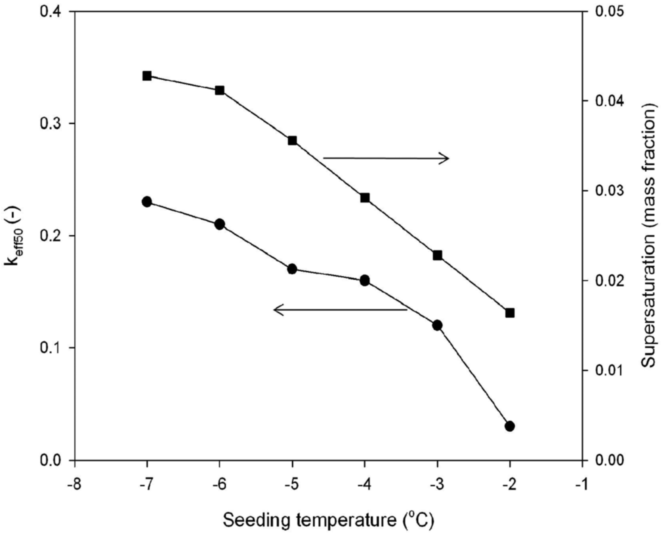

FIG. 8. Effect of seeding temperature on k_{eff50} and supersaturation.

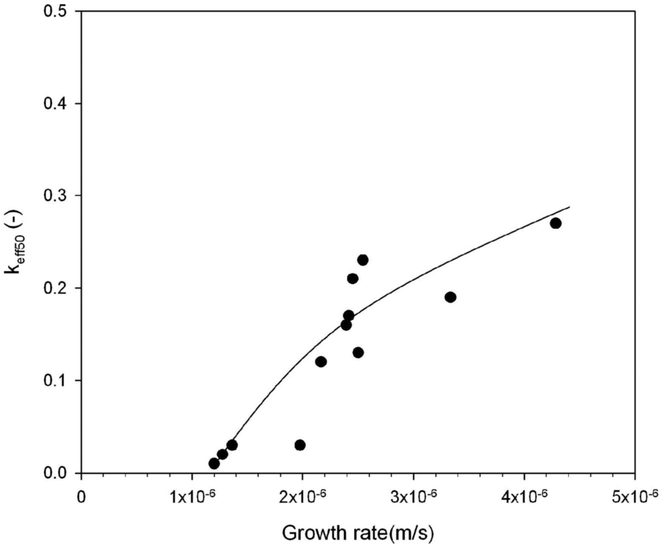

FIG. 10. Plot of k_{eff50} against growth rate.

CONCLUSIONS

In this study, the separation of acetic acid from acetic acid and water mixture was conducted by melt crystallization and sweating. Separation was carried out at various seeding temperatures, seeding amounts, sweating rates, and cooling rates. The acetic acid was successfully separated by a single-stage melt crystallization process. As the sweating fraction is increased, the crystalline layers prepared at lower cooling rate are purified higher. At the constant sweating rate, k_{eff} decreases more rapidly in case of crystalline layers formed at lower cooling rates. Eventually, the crystallization rate is much more important than the sweating rate. k_{eff50} ranges from 0.01 to 0.25 for the crystal growth rates of $1.2 \times 10^{-6}\,\mathrm{m/s}$ to $4 \times 10^{-6}\,\mathrm{m/s}$.

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