Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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To cite this Article Shinagawa, Hideo , Hamada, Takuya , Miyamoto, Ken-Ichi and Okuyama, Kikuo(1994) 'Heterogeneous Nucleation Characteristics of a Eutectic-Forming Vapor Mixture on a Cold Substrate', Separation Science and Technology, 29: 14, 1823 — 1840

To link to this Article: DOI: 10.1080/01496399408002175

URL: http://dx.doi.org/10.1080/01496399408002175

SEPARATION SCIENCE AND TECHNOLOGY, **29**(14), pp. 1823–1840, 1994

Heterogeneous Nucleation Characteristics of a Eutectic-Forming Vapor Mixture on a Cold Substrate

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ABSTRACT

The formation of solid condensates by heterogeneous nucleation from a mixture of *p*-xylene and water vapor onto a cold substrate was observed by slowly cooling the substrate under reduced pressure conditions. The results from binary experiments were compared to those for the pure vapors. Two critical substrate temperatures, corresponding to the onset of nucleation, were determined experimentally at a given initial vapor pressure by observing a rapid decrease in the vapor pressure. A mixed vapor with a water content greater than 85% formed ice at the first critical point, and the critical partial vapor pressure agreed well with that for pure water. For mixed vapors in which the *p*-xylene content was greater than 30%, *p*-xylene crystals formed at the first critical point, but the critical vapor pressure tended to decrease with decreasing *p*-xylene content. For mixed vapors with a composition close to the eutectic, it was unclear which crystal formed at the first critical point. The relationship between the logarithm of the critical vapor pressure and the inverse of the critical temperature at the second critical point showed good linearity and was close to that at the eutectic condition. Using these experimental results, we discuss the conditions required for separating binary eutectic-forming vapors by sublimation.

Key Words. Heterogeneous nucleation; *p*-Xylene; Water; Sublimation; Supersaturation; Binary vapor separation

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INTRODUCTION

The heterogeneous phase transition initiated when a condensable vapor encounters a cold substrate is important in such processes as vapor recovery, drying, and separation.

Most previous studies of heterogeneous nucleation have looked at the formation of liquid water from water vapor (1, 2). We recently measured the critical supersaturation ratios required for heterogeneous nucleation of solid condensates (crystal) for pure water and organic vapors onto a cold substrate, and we discussed their dependence on the critical temperature and interfacial energy (3–5). However, no investigations of the heterogeneous nucleation for vapor mixtures have been reported despite their practical importance.

The objective of the present work is to examine experimentally the heterogeneous nucleation characteristics of *p*-xylene and water vapor mixtures. These species form a simple eutectic mixture in the vapor–solid system. The advantage of using this system to understand the fundamental physics of separating a eutectic-forming vapor mixture include (i) the mixture composition is relatively easy to control because there are only small difference in the equilibrium vapor pressures of both liquids, (ii) the eutectic composition is not too close to either pure component because the equilibrium vapor pressures of both solids are comparable, and (iii) we understand the heterogeneous nucleation characteristics of both pure vapors from our single-component experiments (4, 5). The critical vapor pressure–critical temperature relationships were determined by changing the composition of the binary vapor mixture. These results were compared with those generated in the single-component experiments. Using all of the experimental results, we discuss sublimation as a technique for separating vapor mixtures.

EXPERIMENTAL

Experimental Apparatus and Procedure

A schematic diagram of the experimental apparatus used in the heterogeneous nucleation experiments for mixed vapors is shown in Fig. 1. It is similar to that used in previous single-component nucleation studies (3) but with the addition of a second vapor feeder. Experiments were conducted for pure *p*-xylene or water vapor and binary mixtures. The experimental procedures are described only briefly here because they are the same as in our previous studies (4, 5).

The test chamber was first evacuated to a negligibly small residual gas pressure (1.5×10^{-3} Pa). Vapors from both feeders were combined and

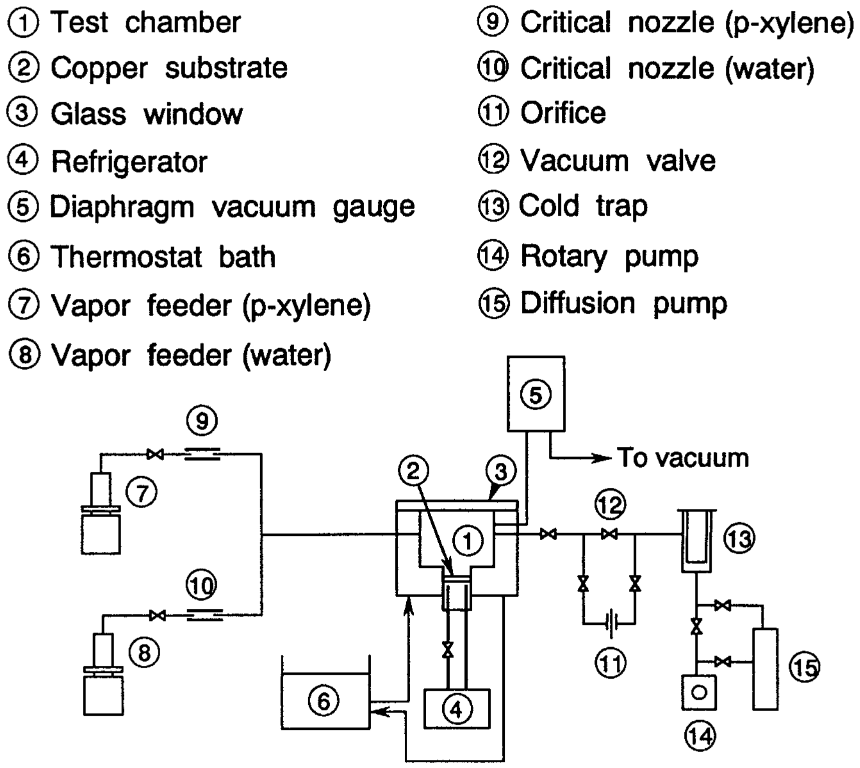


FIG. 1 Schematic diagram of the experimental apparatus.

introduced into the test chamber at a low flow rate while the coolant was circulated through the cooling cylinder below the substrate. The coolant was maintained at a constant temperature a few K higher than the expected temperature of first crystal formation. Both the total vapor pressure and the mixing ratios were adjusted by controlling a vacuum valve and the temperatures of the feeders.

The flow rates of *p*-xylene and water vapor were 2.7×10^{-6} to 1.5×10^{-5} mol/s and 1.5×10^{-5} to 4.5×10^{-5} mol/s, respectively. After the total vapor pressure P and substrate temperature T_s attained steady state, the substrate was cooled at a slow cooling rate (9.2×10^{-3}–1.5×10^{-2} K/s) by operating a refrigerator under a fixed total vapor pressure. Since the decreasing rate of substrate temperature is found to be almost constant and very small, the nucleation phenomena can be approximated to the pseudo-steady-state ones. The experiments were conducted under P = 30–300 Pa. The temperatures of the substrate, water, and liquid *p*-xylene in the feeders, and the vapor pressure in the test chamber were recorded continuously throughout the experimental runs. The surface of the substrate was observed visually during the experimental runs, and the number of crystals formed on the substrate was counted visually at given time intervals. The experiments lasted for some time after the second critical point was reached. The liquid *p*-xylene used was reagent grade, and the water used was prepared by distillation followed by ion exchange. Prior to the experiments, the flow rate through the critical nozzle was calibrated by storing the vapor flowing from the constant temperature feeder in a 22.9-L closed vacuum tank.

Flow Rates through Critical Nozzle

The linear relationship between the feed rate G and the equilibrium vapor pressure corresponding to the temperature of the liquid in the feeder, p_{ef}, is shown in Fig. 2. The accuracy of this relationship was ±2%. The composition of the mixed vapor was determined from the ratio of the two flow rates.

Determination of Critical Point for Heterogeneous Nucleation

We observed two types of time-dependent phase transitions on the substrate depending on the total vapor pressure, P, supplied: 1) Direct formation of a solid condensate from the vapor in one or two stages, which occurred at lower values of P (two stage solidification); and 2) formation of a solid condensate followed by freezing of a liquid condensate from the vapor, which occurred at higher P (solidification, subsequent liquefaction and freezing).

Figure 3 shows typical variations in the total vapor pressure P and the substrate temperature T_s with time. As observed during nucleation from the one component vapor (3–5), P started to decrease at the point labeled FBP (first breaking point) when crystals first appeared on the substrate. The crystals continued to grow after the first breaking point, and tended to be transparent and dendritic in shape. Some time later, at the point labeled SBP (second breaking point, Fig. 3a), P decreased more rapidly and a second opaque, white crystal appeared adjacent to the initial crystals. This was assumed to be a crystal corresponding to the eutectic composition, and the second critical point is thought to be the result of eutectic crystal formation. In some experimental runs for mixed vapor compositions with mole fractions of *p*-xylene in the range of y = 0.20–0.26, the FBP almost coincided with the SBP. This may be due to the appearance

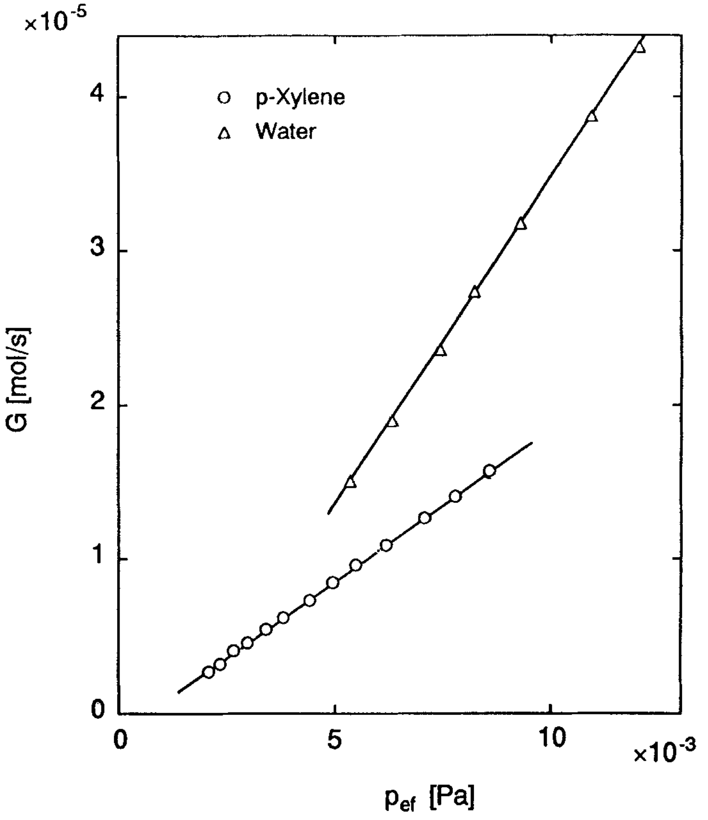
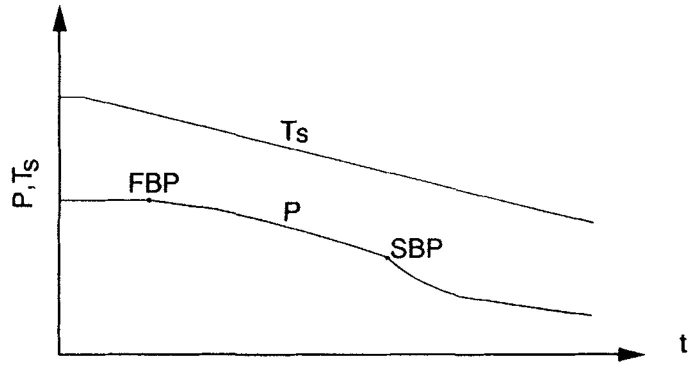


FIG. 2 Flow rate through the critical nozzle. The solid lines represent the flow rates determined by least-squares fits of the data.

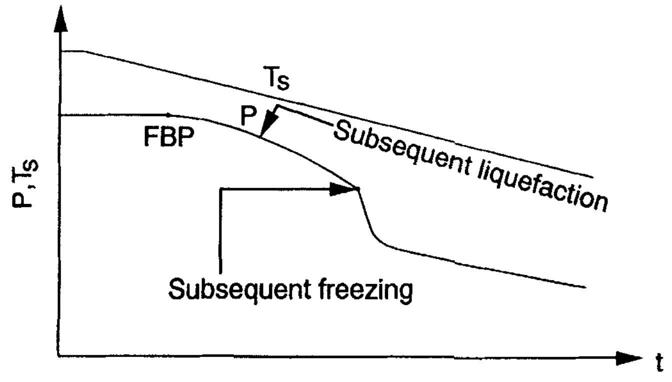
of the eutectic crystal at the first critical point. This phenomenon was observed when the initial value of P was lower than about 150 Pa.

In several experimental runs at total vapor pressures initially greater than about 150 Pa, condensation of a liquid and subsequent freezing of the liquid condensate was observed after the formation of a crystal of one component. This is illustrated in Fig. 3(b). In these cases, an SBP did not appear as P decreased.

The P and T_s corresponding to sudden changes in pressure were assumed in the same manner as in previous works (3–5) for the single component vapors to be the critical total vapor pressure and the critical temperature, P_c and T_{sc} at the FBP, and P'_c and T'_{sc} at the SBP. Hereafter, we



(a) Two stage solidification



(b) Solidification, subsequent liquefaction and freezing

FIG. 3 Typical changes in total vapor pressure and substrate temperature with time. FBP and SBP represent first and second breaking points, respectively.

denote FBP and SBP as the first and second critical points, respectively. The critical partial vapor pressure at the first critical point was determined from P_c and the feed rate of both components. The equilibrium vapor pressures of both pure solids, as described in later sections, are cited from References 8 and 9.

EQUILIBRIUM PHASE DIAGRAM

No data for the vapor–solid phase equilibrium of the *p*-xylene–water binary system are available. It is known that the liquids are immiscible (6), and that the crystalline forms of *p*-xylene and ice are monoclinic and hexagonal (7), respectively. Because the affinity between molecules of *p*-xylene and water is low and the crystalline forms are different, it is probable that this binary mixture forms a eutectic in the vapor–solid system.

Figure 4 illustrates the equilibrium temperature–composition diagram at $P = 100$ Pa for the *p*-xylene and water system. It was calculated using the equilibrium vapor pressure–temperature relationships for the vapor–solid system of both components (8, 9). The mixed vapor forms *p*-

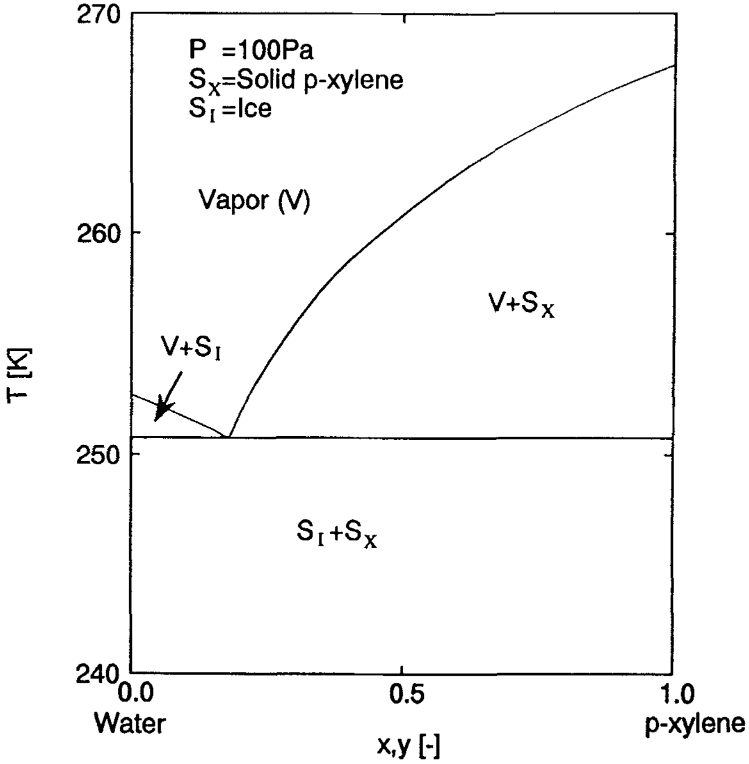


FIG. 4 Equilibrium phase diagram of *p*-xylene–water system. *V*, S_I, and S_X represent vapor phase, ice, and solid *p*-xylene, respectively.

xylene crystals over a wide range of composition, and forms ice in a narrow region near pure water vapor.

EXPERIMENTAL RESULTS AND DISCUSSION

As in a previous paper (3), heterogeneous nucleation in this study is thought to proceed under pseudo-steady-state conditions because of the very slow cooling rate employed. We assume that the mixed p-xylene–water vapor does not form solid-solution crystals, thus the equilibrium vapor pressure above a crystal of one component is not changed by the presence of a crystal of the second component.

Critical Vapor Pressure–Critical Temperature Relationship for Pure Vapor

The relationship between the logarithm of the critical vapor pressure p_{cX}°, p_{cW}°, and $1/T_{sc}$ observed for pure p-xylene and water vapors was linear and in very good agreement with the results of our previous work (4, 5). The critical vapor pressures in the nucleation from pure vapors, p_{cX}° and p_{cW}°, should be discriminated from the critical vapor pressures in the nucleation from mixed vapors, p_{cX} and p_{cW}, because p_{cX} and p_{cW} are affected by the presence of another component as described in later sections. The experimental relationships obtained by the least square fits in the present work are given below.

For pure p-xylene:

$$p_{cX}^{\circ} = 1.01 \times 10^{13} \exp(-6.64 \times 10^{3}/T_{sc}) \tag{1}$$

For pure water:

$$p_{cW}^{\circ} = 1.23 \times 10^{12} \exp(-5.82 \times 10^{3}/T_{sc}) \tag{2}$$

Assuming that p-xylene and ice crystals are formed independently, the condition for eutectic formation in terms of the critical vapor pressures is given by the following equations:

$$P_c y = p_{cX}^{\circ} \tag{3}$$

$$P_c(1 - y) = p_{cW}^{\circ} \tag{4}$$

In these equations, P_c denotes the total vapor pressure at the first critical point and y is the mole fraction of p-xylene. It should be noted that the eutectic composition derived from Eqs. (3) and (4) varies from 0.20 to 0.26 with a change in P_c from 30 to 300 Pa. Similarly, the eutectic composition based on the equilibrium vapor pressure–temperature relationship varies from 0.17 to 0.20 with the same variation in total pressure.

Critical Vapor Pressure and Critical Temperature at the First Critical Point

In the experiments we could not discriminate visually which crystal was formed because all the mixed vapors formed transparent dendritic crystals at the first critical point. We drew the equilibrium vapor pressure of each pure solid in the figures in this section for reference because the heterogeneous nucleation from the vapor is affected significantly by the supersaturation with respect to the equilibrium vapor pressure corresponding to the substrate temperature.

Figures 5 and 6 show the relationships between ln p_{cX} and ln p_{cW} vs $1/T_{sc}$ for mixed vapors with compositions far from the eutectic compositions ($y = 0.17$–0.26). In these figures the solid lines are the equilibrium vapor pressure–temperature relationships and the broken lines are the critical pressure–temperature relationships for the pure vapor. Crystals of *p*-xylene formed from the mixed vapor with the compositions in Fig. 5 because the partial vapor pressure for water was lower than the equilibrium vapor pressure of ice, p_{eI}. Several data points in Fig. 5 are appreciably lower than the relationship for pure *p*-xylene vapor. Most of these are for the mixed vapor with $y = 0.32$–0.33. This suggests that the nucleation rate of *p*-xylene is enhanced by the existence of the water vapor

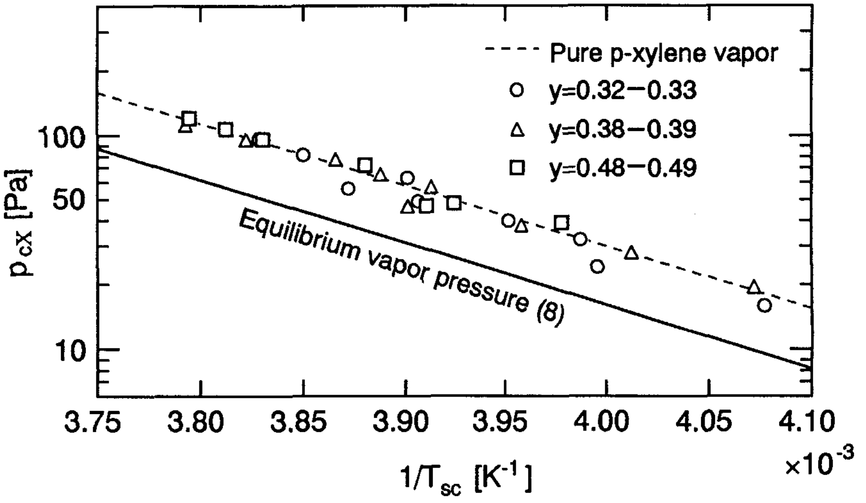


FIG. 5 Critical partial vapor pressure as a function of critical temperature for the formation of *p*-xylene crystals at the first critical point. The solid and broken lines represent the equilibrium vapor pressure of pure *p*-xylene solid cited from Reference 8 and the critical vapor pressure in the nucleation from pure *p*-xylene vapor, respectively.

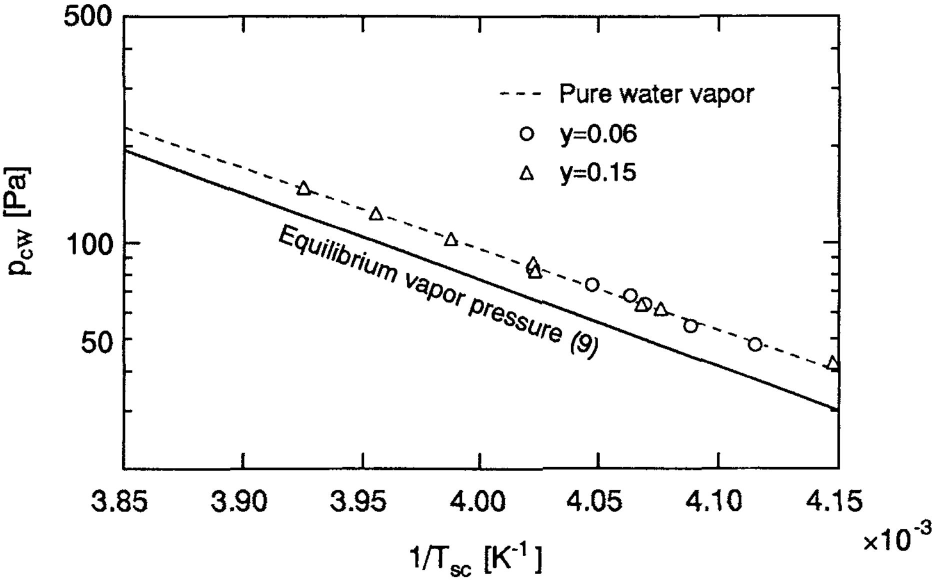


FIG. 6 Critical partial vapor pressure as a function of critical temperature for the formation of ice crystals at the first critical point. The solid and broken lines represent the equilibrium vapor pressure of ice cited from Reference 9 and the critical vapor pressure in the nucleation from pure water vapor, respectively.

even when the mixed vapor composition deviates appreciably from the eutectic. In Fig. 6 the data for mixed vapors that are largely water vapor are well described by the relationship for pure water vapor. In the mixed vapor with $y = 0.06$, ice crystals formed the condensed phase because the partial vapor pressure of p-xylene was lower than the equilibrium vapor pressure of p-xylene, p_{eX}. The formation of pure ice crystals when $y = 0.15$ is not assured because the mixed vapor was also supersaturated with respect to solid p-xylene. However, we believe that only ice crystals formed because the critical partial vapor pressure agrees with that for pure water vapor.

Figures 7 and 8 show the partial vapor pressure–critical temperature relationships of each component when the composition of the mixed vapor was near the eutectic composition. These results were obtained by changing the initial total vapor pressure P while holding the mixing ratio y constant. In contrast, Fig. 9 shows the results from experiments in which the mixed vapor always had the eutectic composition corresponding to the total initial pressure calculated using Eqs. (3) and (4). As before, the solid and broken lines in these figures represent the equilibrium vapor pres-

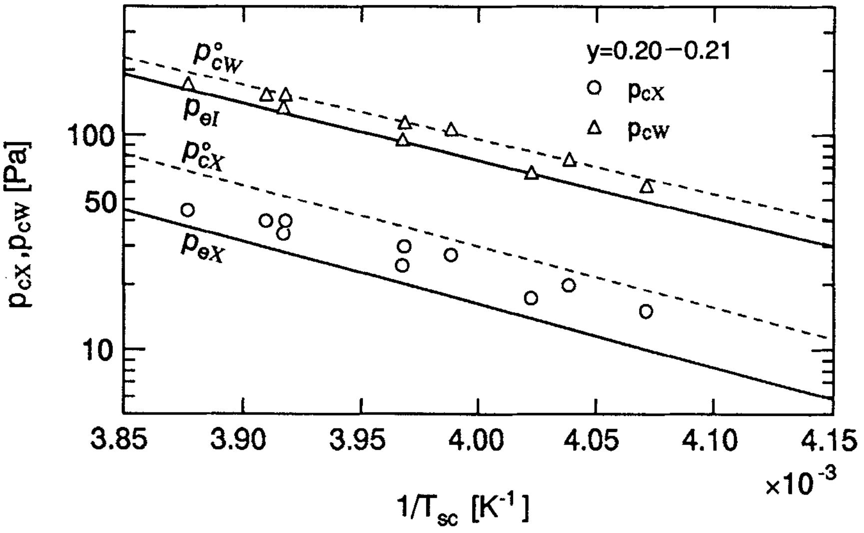


FIG. 7 Partial vapor pressure as a function of critical temperature for *p*-xylene and water at the first critical point, $y = 0.20$–0.21. The upper and lower solid lines, respectively, represent the equilibrium vapor pressures of pure ice and *p*-xylene solids cited from References 9 and 8, respectively. The upper and lower broken lines represent the critical vapor pressures in the nucleation from pure water and *p*-xylene vapors, respectively.

sure–temperature relationships and the critical vapor pressure–critical temperature relationships for both pure components. It can be seen from Figs. 7, 8, and 9 that the partial vapor pressures for both components at the first critical point are lower in almost all cases than the critical vapor pressures for both pure components except for the cases undersaturated with respect to ice, and the corresponding vapor pressure of *p*-xylene in the undersaturated cases is lower than the critical vapor pressure in the nucleation from pure *p*-xylene while the formation of *p*-xylene crystal is evident. It is apparent in most cases that the crystal forms at lower supersaturation from the mixed vapor than from the pure vapor. This behavior indicates that the nucleation rate is enhanced for binary vapors close to the eutectic composition, but the component of the crystals formed is unknown in almost all cases.

Figure 10 shows the critical temperature–composition relationship for the mixed vapor at constant $P_c = 116$ Pa. The solid and broken curves in Fig. 10 represent the critical temperature–composition relationship given by Eqs. (3) and (4) and the equilibrium temperature–composition relationship, respectively. Again, data points ($y < 0.20$, $y > 0.26$) far from

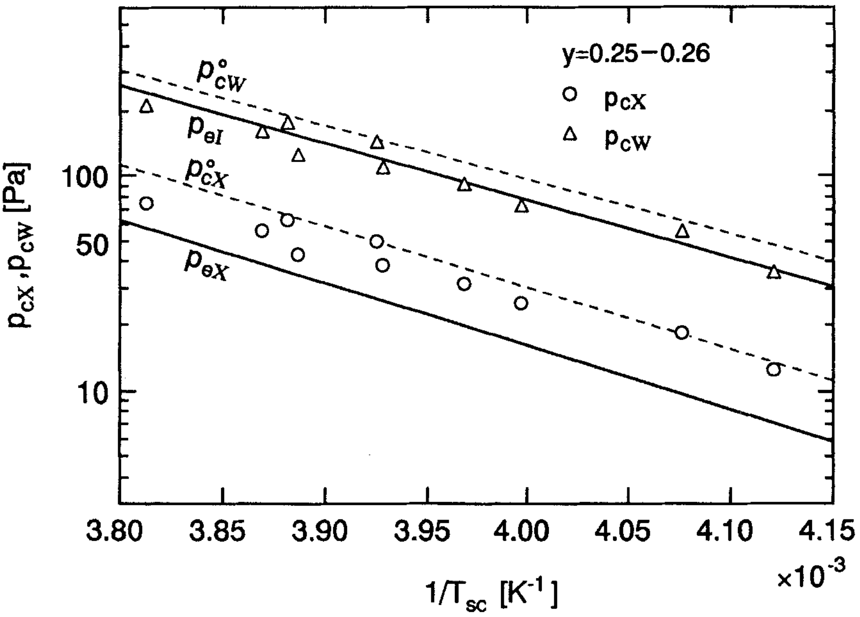


FIG. 8 Partial vapor pressure as a function of critical temperature for *p*-xylene and water at the first critical point, $y = 0.25$–0.26. The upper and lower solid lines, respectively, represent the equilibrium vapor pressures of pure ice and *p*-xylene solids cited from References 9 and 8, respectively. The upper and lower broken lines represent the critical vapor pressures in the nucleation from pure water and *p*-xylene vapors, respectively.

the eutectic composition lie on the solid curves, but those near the eutectic composition depart to the less supercooled side.

Summarizing the experimental results shown in Figs. 7–10, it is obvious that the nucleation rates for a mixed vapor with a composition near and equal to the eutectic are enhanced considerably. The reason for this behavior is discussed below. We observed that subsequent liquefaction and the formation of white crystals after the second critical point occurred in the spot adjacent to the preexisting crystal. This may indicate that nucleation of one component is enhanced by the presence of another crystal. This enhanced phase transition may be caused by a decrease in the interfacial energy or contact angle due to the preexisting crystal as estimated using classical nucleation theory. If the decrease in interfacial energy or contact angle is assumed to extend to extremely small clusters compared to the visible crystal, the decrease in critical partial vapor pressure and the enhanced nucleation rate may be due to mutual contact of the growing clusters of each component.

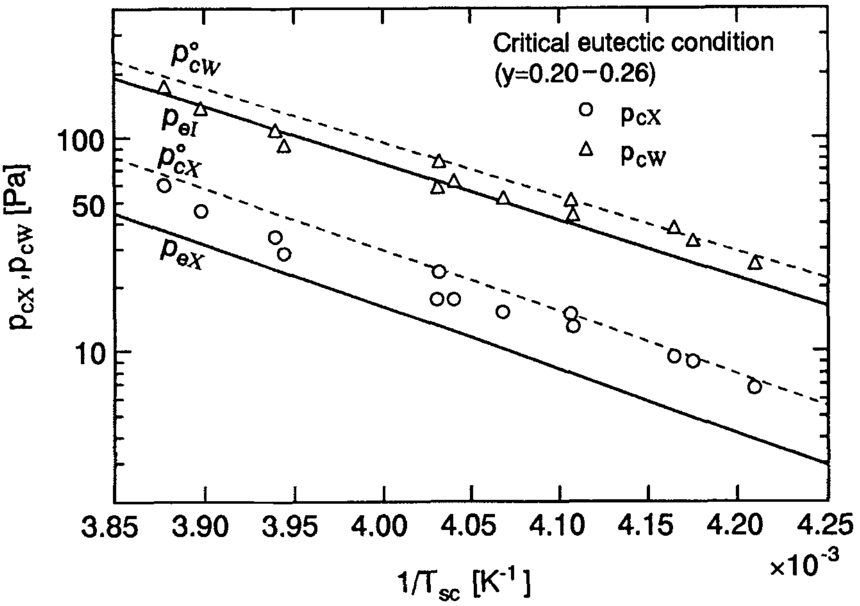


FIG. 9 Partial vapor pressure as a function of critical temperature for *p*-xylene and water at the first critical point, $y = 0.20–0.26$ (critical eutectic condition). The upper and lower solid lines, respectively, represent the equilibrium vapor pressures of pure ice and *p*-xylene solids cited from References 9 and 8, respectively. The upper and lower broken lines represent the critical vapor pressures in the nucleation from pure water and *p*-xylene vapors, respectively.

Figure 11 shows the critical total vapor pressure–composition relationship for all mixed vapors. The solid curve calculated by Eqs. (3) and (4) represents the critical total vapor pressure–composition relationship in the eutectic condition, and the broken curve represents the equilibrium vapor pressure–composition relationship in the eutectic condition. The open, filled, and half-filled symbols represent the formation of ice crystals, *p*-xylene crystals, and unknown crystals (either ice or *p*-xylene), respectively. The type of crystal formed was determined based on the criteria mentioned previously. It should be noted that liquid condensate formed at the first critical point at the high *P* conditions for which data points are not presented. Figure 11 shows that the experimental data seem to agree with the solid boundary curve for the formation of *p*-xylene crystals, while the unknown crystals form between the broken boundary curve and the solid one. Separation by sublimation is possible for mixed vapors with a water content higher than 85% or a *p*-xylene content higher than 30%.

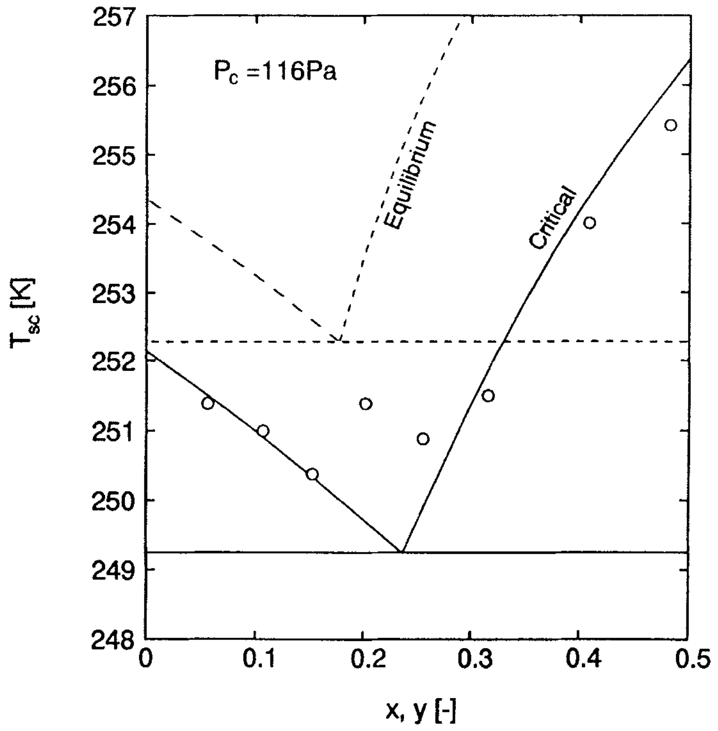


FIG. 10 Critical temperature–composition relationship. The broken curve represents the equilibrium temperature–composition relationship based on the equilibrium vapor pressure–temperature relationship.

Critical Total Vapor Pressure–Critical Temperature Relationship at the Second Critical Point

Figure 12 shows the relationship between the logarithm of the critical total vapor pressure, P_c', and the inverse of critical temperature, $1/T_{sc}'$, at the second critical point. CEC and $P_c = 116$ Pa in Fig. 12 are data for the mixed vapor with the critical eutectic composition and for the experiments at constant P_c (= 116 Pa). The solid line represents the relationship between the critical eutectic vapor pressure and the inverse of the critical eutectic temperature given by Eqs. (3) and (4). Figure 12 illustrates that the experimental data are linear and lie close to the solid line. The data are represented by the least-squares fit as

$$P_c' = 8.03 \times 10^{11} \exp(-5.66 \times 10^3/T_{sc}') \qquad (5)$$

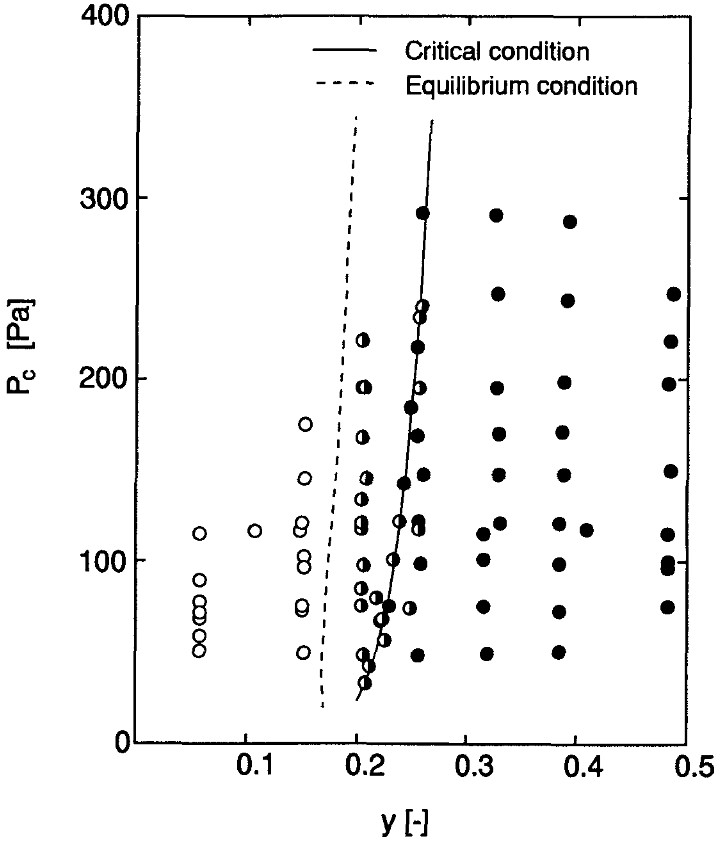


FIG. 11 Phase boundaries for the formation of *p*-xylene and ice crystals. The solid and broken curves represent the critical and equilibrium total vapor pressure–composition relationships in the eutectic condition, respectively.

The good agreement between these relationships suggests that the white crystals mentioned previously are composite crystals composed of fine *p*-xylene and ice crystals with the eutectic composition.

Number of Formed Crystal

The number of crystal formed was counted during experimental run by visual observation as already described. In the phase transition from pure vapors, crystals were formed in most cases at the first critical point, and further crystal production was not observed during successive cooling of

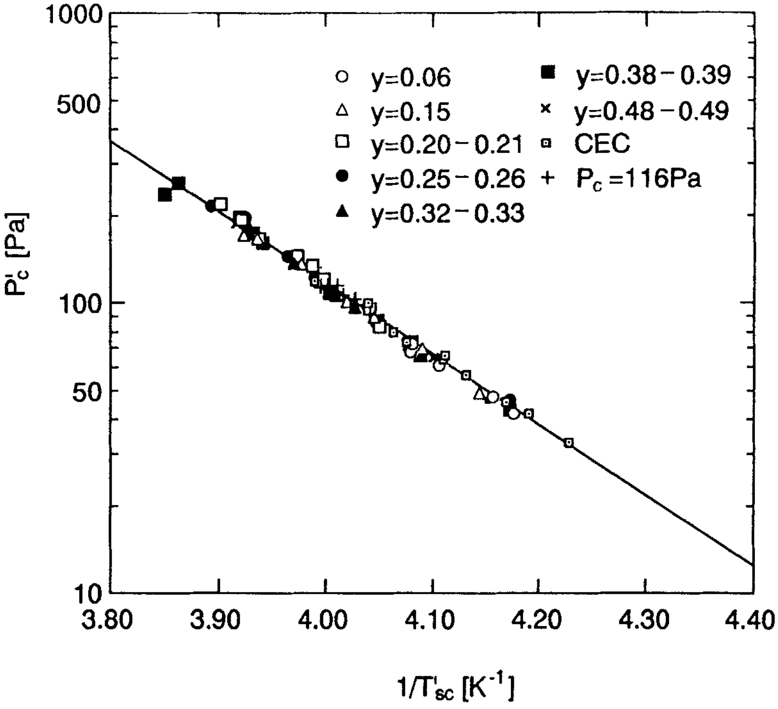


FIG. 12 Dependence of the critical total vapor pressure on critical temperature at the second critical point. CEC and P_c = 116 Pa are the data for the mixed vapor with critical eutectic composition and for the experiments at constant P_c = 116 Pa. The solid line represents the critical eutectic vapor pressure calculated using Eqs. (3) and (4).

the substrate. In contrast to the pure vapor, during phase transition from the mixed vapor, one crystal, or at best a few crystals, formed at the first critical point, but subsequent new crystals production continued until the end of the experiment. Figure 13 shows a typical variation of the number density of crystals N formed with time t. The time when the first crystal formed at the first critical point is taken as the origin of t. The formation rate of crystals is low in the first stage, increases rapidly in the middle stage, and ceases in the final stage due to vapor depletion. It is interesting that the formation behavior of crystal from the mixed vapor is different from that from the pure vapor, but a quantitative examination of the formation behavior of crystal from the mixed vapor is difficult because the total vapor pressure decreases with the elapsed time and the composition of mixed vapor in the test chamber is unknown.

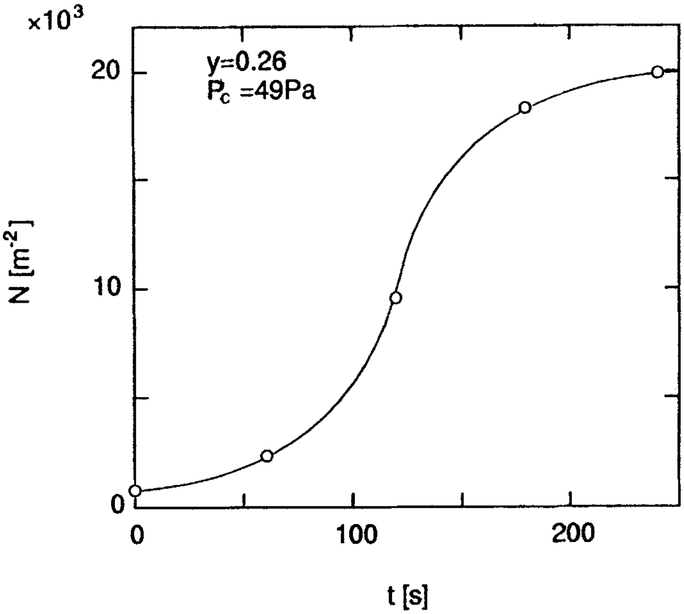


FIG. 13 Typical variation in the number density of crystals formed with time.

CONCLUSIONS

Heterogeneous nucleation of crystals from mixed *p*-xylene and water vapor onto a cold substrate under reduced pressure conditions was observed by cooling the substrate at a slow rate. The critical pressure and temperature at various mixing compositions were determined. The following conclusions were drawn from the present work.

1) Mixed vapors with a water content higher than 85% formed only ice crystal at the first critical point, and the critical partial vapor pressure agreed with that for pure water vapor. Mixed vapors with a *p*-xylene content higher than 30% formed only *p*-xylene crystals at the first critical point, and the critical partial vapor pressure tended to decrease considerably with a decrease in the *p*-xylene content of the gas.

2) The partial vapor pressures at the first critical point for the mixed vapor when *p*-xylene ranged from 20 to 26% was lower than that for either pure vapor, but the component of the crystal formed was unknown. Therefore, separation of the mixed vapor in this composition range must be avoided.

3) The relationship between the logarithm of the critical total vapor pressure and the inverse of the critical temperature at the second critical point, after the formation of the second type of crystal, was linear and in close agreement with the eutectic condition calculated from the critical vapor pressures of both pure components. This suggests that a composite crystal with eutectic composition is formed at the second critical point.

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Received by editor June 9, 1993
Revised November 12, 1993