

Adsorption and Nucleation on Smooth Surfaces

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The nucleation and growth of condensate nuclei on smooth surfaces, e.g., an immiscible liquid or a smooth solid, can occur both by the direct addition of molecules from the vapor and from those adsorbed on the substrate. We show how to generalize nucleation theory to allow for the simultaneous occurrence of both mechanisms. The vapor–condensate–substrate interfacial forces, the contact angle, the critical supersaturation, and the coefficient in the adsorption isotherm are different ways of expressing the affinity between vapor molecules and the substrate surface. The critical supersaturations for nucleation on the surface of an immiscible liquid and nucleation on the surface of a perfectly smooth solid are predicted in terms of these parameters and the relationships among them. For most values of these parameters we find that adsorbed molecules are usually far more important to the nucleation process than those in the vapor phase.

KEY WORDS: Nucleation; adsorption; vapor condensation; vapor deposition; homogeneous nucleation.

1. INTRODUCTION

Vapor deposition on substrate surfaces has become a very important technique in many manufacturing processes, especially the electronics industry. Understanding the mechanism of the vapor–substrate interactions is therefore increasingly important. This paper is a study of adsorption and nucleation on substrate surfaces, which are the initial steps of the deposition process.

Nucleation and condensation take place when a vapor contacts a substrate surface of sufficiently low temperature. On solids such condensation occurs at preferred sites. However, if the concentration of preferred sites is

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low or if the supersaturation is sufficiently high, nucleation on solid surfaces also will occur at randomly distributed locations, i.e., homogeneously. Condensation of the supersaturated vapor on the substrate can occur by different paths. It can condense directly from the vapor or it can adsorb on the surface and then migrate by two-dimensional diffusion until it condenses (see Figs. 1 and 2). The relative importance of these two routes depends on the vapor–condensate–substrate interfacial free energies and on the film pressure of the adsorbed molecules. In this paper we show how to generalize homogeneous nucleation theory to allow for both processes simultaneously, and present sample calculations for the nucleation and condensation of an ideal gas vapor on the surface of an immiscible liquid or on a perfectly smooth solid (i.e., no preferred sites).

2. MODEL

When a vapor condenses on the surface of an immiscible liquid substrate^(1,2) the condensate nuclei have the shape shown in Fig. 1. One can express the cosines of angles θ_1 and θ_2 in term of σ_{vc} , σ_{cs} , and σ_{vs} , the vapor–condensate, condensate–substrate, and vapor–substrate interfacial tensions, respectively (see Fig. 1), i.e.,

$$\cos \theta_1 = \frac{\sigma_{vc}^2 + \sigma_{vs}^2 - \sigma_{cs}^2}{2\sigma_{vc}\sigma_{vs}} \quad (1)$$

$$\cos \theta_2 = \frac{\sigma_{cs}^2 + \sigma_{vs}^2 - \sigma_{vc}^2}{2\sigma_{cs}\sigma_{vs}} \quad (2)$$

The circumference of a nucleus containing i condensate molecules is $l_0 i^{1/3}$. The vapor–condensate and condensate–substrate interfacial areas of this

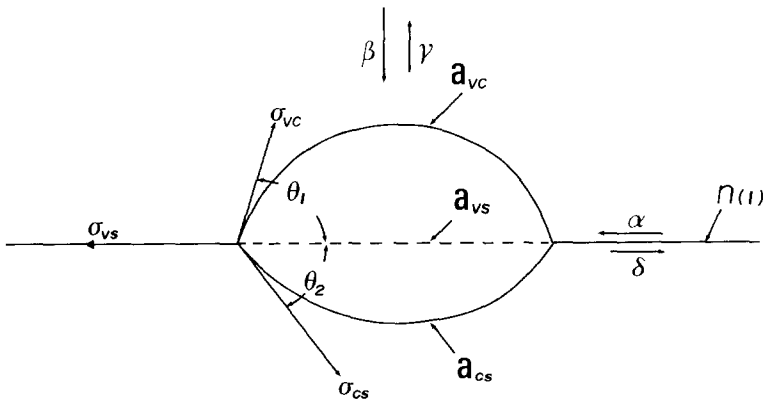


Fig. 1. Condensation on an immiscible liquid substrate.

nucleus are $a_{vc} = a_0 i^{2/3}$ and $a_{cs} = a'_0 i^{2/3}$, respectively. The vapor-substrate interfacial area covered by this nucleus is $a_{vs} = a''_0 i^{2/3}$. Using trigonometry, one can express all quantities in terms of the interfacial tensions and the contact angles,

$$l_0 = 2\pi\Omega \sin \theta_1 \tag{3}$$

$$a_0 = 2\pi\Omega^2(1 - \cos \theta_1) \tag{4}$$

$$a'_0 = 2\pi\Omega^2(\sigma_{cs}/\sigma_{vc})^2 (1 - \cos \theta_2) \tag{5}$$

$$a''_0 = \pi\Omega^2 \sin^2 \theta_1 \tag{6}$$

where

$$\Omega = \left(\frac{3V_c \sigma_{vc}^3}{4\pi[\sigma_{vc}^3 \Phi(\theta_1) + \sigma_{cs}^3 \Phi(\theta_2)]} \right)^{1/3} \tag{7}$$

$$\Phi(\theta) = (2 - 3 \cos \theta + \cos^3 \theta)/4 \tag{8}$$

and V_c is the molecular volume of the condensate.

When a vapor condenses on the surface of a smooth solid substrate, the condensate nuclei have the shape shown in Fig. 2. Calculations similar to those used above lead to the equations

$$a_{vs} = a_{cs} \tag{1'}$$

$$\cos \theta = (\sigma_{vs} - \sigma_{cs})/\sigma_{vc} \tag{2'}$$

$$l_0 = 2\pi\Omega \sin \theta \tag{3'}$$

$$a_0 = 2\pi\Omega^2(1 - \cos \theta) \tag{4'}$$

$$a'_0 = \pi\Omega^2 \sin^2 \theta \tag{5'}$$

$$a''_0 = a'_0 \tag{6'}$$

where

$$\Omega = [3V_c/4\pi\Phi(\theta)]^{1/3} \tag{7'}$$

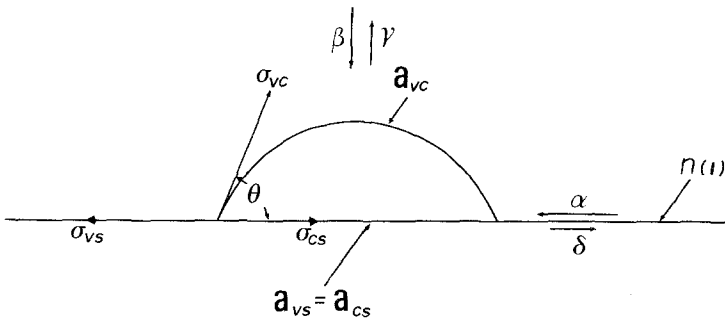


Fig. 2. Condensation on a smooth solid substrate.

3. ADSORPTION ON AN IMMISCIBLE LIQUID OR A SMOOTH SOLID

When a vapor is in contact with an immiscible liquid or a smooth solid, the relationship between $n(1)$, the number of vapor molecules adsorbed on a unit area of this substrate surface, and P , the pressure of the vapor, usually can be accurately represented⁽³⁾ by the equation

$$\frac{P}{P_e} = \frac{k_a n(1)}{(1/b_2) - n(1)} \exp \left[\frac{n(1)}{(1/b_2) - n(1)} - \frac{2a_2 n(1)}{kT_s} \right] \quad (9)$$

where P_e is the saturation vapor pressure at T_s , the temperature of the substrate surface, k is Boltzmann's constant, a_2 and b_2 are the two-dimensional van der Waals constants, and k_a is a constant related to the strength of adsorption. At low partial pressures of the vapor, $n(1)$ is small and Eq. (9) simplifies to

$$P/P_e = k_a b_2 n(1) \quad (10)$$

Hence, strong adsorption implies small values of k_a . Since, at equilibrium, the concentration of adsorbed molecules is related to the derivative of the vapor-substrate interfacial tension,⁽⁴⁾ i.e.,

$$n(1) = -\frac{P}{kT_s} \frac{\partial \sigma_{vs}}{\partial P} \quad (11)$$

one can use Eqs. (11) and (10) to eliminate P and thus obtain a relationship for the constant k_a at low partial pressure of the vapor. One can also use the Gibbs equation⁽⁵⁾ to obtain a relationship for π , the film pressure due to the adsorbed molecules, i.e.,

$$\pi = \sigma_s - \sigma_{vs} = kT_s \int_0^P n(1) (d \ln P) \quad (12)$$

where σ_s is the surface free energy of a substrate without any adsorbed vapor molecule on it. Obtaining $d(\ln P)/dn(1)$ from Eq. (9) and using it to change the variable of integration, one obtains

$$\pi = \frac{F}{b_2} \left(\frac{kT_s}{1-F} - \frac{a_2 F}{b_2} \right) \quad (13)$$

where F , the fraction of the surface covered with adsorbed molecules, is equal to $b_2 n(1)$.

At equilibrium, i.e., when $P/P_e = 1$, the concentration of the adsorbed vapor molecules $n_e(1)$ can be computed using Eq. (9). Using this value, one can find the number of clusters containing i molecules per unit area of substrate surface at equilibrium, using the assumption implicit in all the present versions of nucleation theories, i.e.,

$$n_e(i) = n_e(1) \exp(-W/kT_s) \quad (14)$$

where W is the minimum reversible work required to form such a cluster on the substrate surface. Using thermodynamic arguments,^(1,2,6,7) one obtains

$$n_e(i) = n_e(1) \exp[-(\sigma_{vc}a_{vc} + \sigma_{cs}a_{cs} - \sigma_{vs}a_{vs})/kT_s] \quad (15)$$

4. GROWTH OF CLUSTERS

A condensate cluster can grow by direct condensation from the vapor at a rate of β molecules per unit interfacial area per unit time and by condensation from the adsorbed molecules at a rate of α molecules per unit circumferential length per unit time. If we restrict ourselves to pressures such that the vapor is an ideal gas, then

$$\beta = P/(2\pi mkT_v)^{1/2} \quad (16)$$

where m is the molecular mass and T_v is the temperature of the vapor. If the adsorbed vapor molecules behave as a two-dimensional ideal gas,⁽⁸⁾ then

$$\alpha = n(1)(\pi kT_s/32m)^{1/2} \quad (17)$$

Condensate clusters can shrink by evaporation of molecules to the vapor and by evaporation of molecules to the adsorbed layer at rates γ and δ , respectively. Thus, the net rate at which clusters containing i molecules become clusters containing $i + 1$ molecules is^(6,7)

$$J(i) = (\beta a_0 i^{2/3} + \alpha l_0 i^{1/3}) n(i) - [\gamma a_0 (i+1)^{2/3} + \delta l_0 (i+1)^{1/3}] n(i+1) \quad (18)$$

Note that even though Eq. (18) appears complicated, it is in reality of the form

$$J(i) = f(i) n(i) - b(i+1) n(i+1) \quad (19)$$

where $f(i)$ is the forward rate, i.e., the rate at which molecules are added to the cluster, and $b(i)$ is the backward rate, i.e., the rate at which molecules

leave the cluster. When the partial pressure of the condensate molecules in the vapor phase equals its equilibrium vapor pressure P_e (i.e., the partial pressure of such molecules if a thick film of them were condensed on the substrate surface at a temperature T_s), the system is at equilibrium. Therefore, $J \equiv 0$ for all i , β and α become, respectively,

$$\beta_e = P_e / (2\pi mkT_s)^{1/2} \tag{20}$$

$$\alpha_e = n_e(1) (\pi kT_s / 32m)^{1/2} \tag{21}$$

and Eq. (18) provides a relationship for γ and δ in terms of α_e and β_e and the equilibrium distribution $n_e(i)$, i.e.,

$$\gamma a_0(i+1)^{2/3} + \delta l_0(i+1)^{1/3} = (\beta_e a_0 i^{2/3} + \alpha_e l_0 i^{1/3}) n_e(i) / n_e(i+1) \tag{22}$$

Using it, one obtains

$$b(i) = [\beta_e a_0(i-1)^{2/3} + \alpha_e l_0(i-1)^{1/3}] n_e(i-1) / n_e(i) \tag{23}$$

Even though both $J(i)$ and $n(i)$ are in principle functions of time, in most cases a steady state is rapidly set up and both become constant. Elsewhere we have shown^(6,7,9) that Eq. (19) can be solved in steady state by defining an intermediate variable

$$Z(i) \equiv \prod_{j=1}^i b(j) / f(j) \tag{24}$$

where

$$Z(1) \equiv 1 \tag{25}$$

Doing so, one obtains

$$J = f(1) n(1) \left/ \sum_{i=1}^{\bar{i}} Z(i) \right. \tag{26}$$

where \bar{i} is any sufficiently large number. Substituting Eqs. (23)–(25) into Eq. (26), we obtain

$$J = \frac{(\beta a_0 + \alpha l_0) n(1)}{\sum_{i=1}^{\bar{i}} \frac{n_e(1)}{n_e(i)} \prod_{j=2}^i \frac{\beta_e a_0 (j-1)^{2/3} + \alpha_e l_0 (j-1)^{1/3}}{\beta a_0 j^{2/3} + \alpha l_0 j^{1/3}}} \tag{27}$$

We have thus obtained an expression for the rate of nucleation of droplets of the condensing material in terms of the arrival rates of

molecules from the vapor and from the adsorbed surface phase and in terms of the concentration of clusters that would exist on the surface if the partial pressure of the condensing material were equal to its equilibrium vapor pressure.

5. THE CRITICAL SUPERSATURATION

The nucleation flux J for the condensation of a vapor on the surface of an immiscible liquid or on a smooth solid is a function of the substrate–vapor, vapor–condensate, and condensate–substrate interfacial tensions, the film pressure π of the adsorbed vapor molecules on the substrate surface, and $1/k_a$, the strength of adsorption. As is typical of nucleation processes, this condensation process has a critical supersaturation $(P/P_e)_c$. The rate of nucleation is negligibly small at supersaturations below this critical value and increases explosively beyond it.

The contact angle θ , or the ratio of interfacial tensions, the coefficient k_a in the adsorption isotherm, Eq. (9), and the π , F , $n(1)$, and P/P_e values

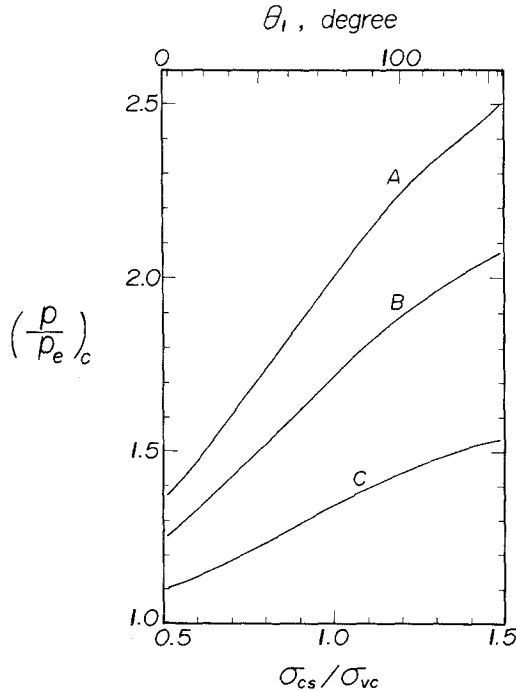


Fig. 3. Critical supersaturation $(P/P_e)_c$ as a function of σ_{cs}/σ_{vc} or θ_1 for condensation on an immiscible liquid substrate. For these calculations $\sigma_{vs}/\sigma_{vc} = 0.5$ and curves A, B, and C are for $\pi/\sigma_{vc} = 0.02, 0.04, \text{ and } 0.06$, respectively.

when the system is critical are all different ways of expressing the affinity between the vapor molecules and the substrate surface. The lower the values of θ , k_a , and $(P/P_e)_c$ and the higher the critical values of π , F , and $n(1)$, the more hydrophilic is the substrate surface. Relationships among them can be obtained by solving of the equations mentioned above.

As an example, we calculate the critical supersaturations $(P/P_e)_c$, defined here as the supersaturations at which the rate of nucleation equals one cluster per square centimeter per second, for the condensation of water vapor at 50°C. In the case of condensation on the surface of an immiscible liquid, the angle θ_1 (see Fig. 1) can go from $\theta_1 = 0$, i.e., condensate droplets nucleate submersed under the surface of the immiscible liquid, to $\theta_1 = \pi$, i.e., the substrate is so hydrophobic that nucleation occurs only in the vapor phase. For condensation on the surface of a smooth solid, possible contact angles (see Fig. 2) range from $\theta = 0$, i.e., the substrate is so hydrophilic that no supersaturation is necessary for the onset of condensation, to $\theta = \pi$, i.e., nucleation occurs only in the vapor phase.

Figure 3 shows the critical supersaturation $(P/P_e)_c$ as a function of σ_{cs}/σ_{vc} for three different π/σ_{vc} values and $\sigma_{vs}/\sigma_{vc} = 0.5$ for nucleation of water vapor at 50°C on a liquid substrate. The left ends of these curves

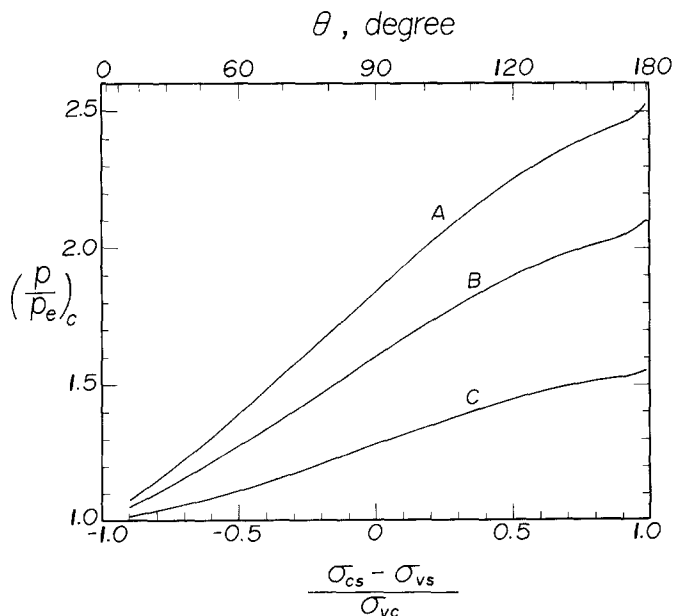


Fig. 4. Critical supersaturation $(P/P_e)_c$ as a function of $(\sigma_{cs} - \sigma_{vs})/\sigma_{vc}$ or θ for condensation on a smooth solid substrate. Curves A, B, and C are for $\pi/\sigma_{vc} = 0.02, 0.04,$ and 0.06 , respectively.

terminate when $\sigma_{cs} = \sigma_{vc} - \sigma_{vs}$, i.e., where $\theta_1 = 0$ and the condensate nuclei start to be covered completely by the liquid substrate. When this happens the radii of the critical nuclei are nonetheless finite, and consequently values for $(P/P_e)_c$ are larger than unity. For $\theta_1 < 0$, i.e., $\sigma_{cs} < \sigma_{vc} - \sigma_{vs}$, any condensate droplet would be completely submerged under the liquid substrate and the mechanism of condensation would be different from that considered here. When $(\sigma_{cs} - \sigma_{vs})/\sigma_{vc}$ approaches unity, i.e., when θ_1 approaches 180° , the liquid substrate is not wetted by the condensate nuclei. Thus, $(P/P_e)_c$ increases abruptly to the value appropriate for homogeneous nucleation in the vapor phase (approximately 2.9 for the conditions used in this figure).

Figure 4 shows the critical supersaturation as a function of $(\sigma_{cs} - \sigma_{vs})/\sigma_{vc}$ for three different π/σ_{vc} values for the nucleation of water vapor at 50°C on a smooth solid substrate. Since σ_{cs} and σ_{vs} pull in opposite directions and act in the plane of the rigid substrate surface, only their difference is important (and σ_{vs}/σ_{vc} is not an independent parameter). Because the contact angle is another way of expressing the balance of the

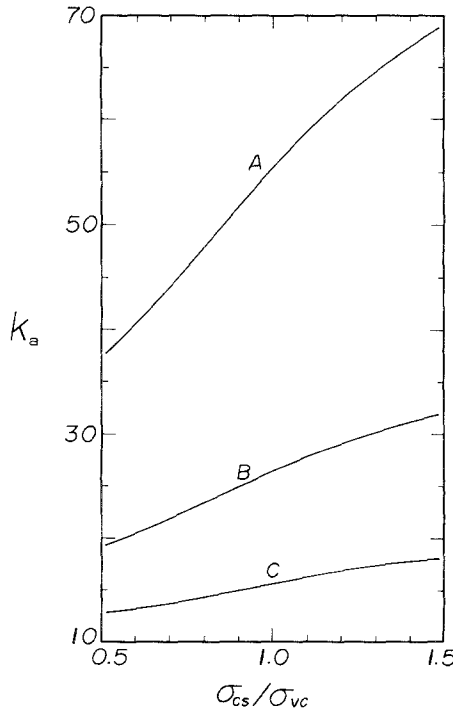


Fig. 5. The adsorption constant k_a as a function of σ_{cs}/σ_{vc} for condensation on an immiscible liquid substrate. For these calculations $\sigma_{vs}/\sigma_{vc} = 0.5$ and curves A, B, and C are for $\pi/\sigma_{vc} = 0.02, 0.04, \text{ and } 0.06$, respectively.

interfacial forces, in Figs. 3 and 4, $(P/P_e)_c$ values are also shown as functions of θ and θ_1 , respectively.

Figure 5 shows the theoretical relationship between the interfacial forces and the coefficient k_a for adsorption and nucleation on the surface of an immiscible liquid. Figure 6 presents a similar relationship for adsorption and nucleation on a smooth solid substrate. Figure 7 indicates that when the value of the σ/σ_{vc} ratio or the fractional surface coverage F is fixed, the $(P/P_e)_c/k_a$ ratio is also fixed, i.e., it is not a function of the other interfacial forces, as indicated by Eq. (9).

It is also interesting to note that the curve in Fig. 7 has a point of inflection at point C, where $F=0.332$, $(P/P_e)_c/k_a=0.0880$, and $\pi/\sigma_{vc}=0.0638$. These are the critical values beyond which two-dimensional condensation of the adsorbed vapor molecules may occur,⁽³⁾ and consequently a computation based on the assumption of a two-dimensional gas is no longer realistic.

In order to investigate the relative importance of the addition of the adsorbed molecules to the critical nuclei by two-dimensional migration and the direct addition of the vapor molecules, we define

$$R = (\alpha l_0 i^{*1/3}) / (\beta a_0 i^{*2/3}) \quad (28)$$

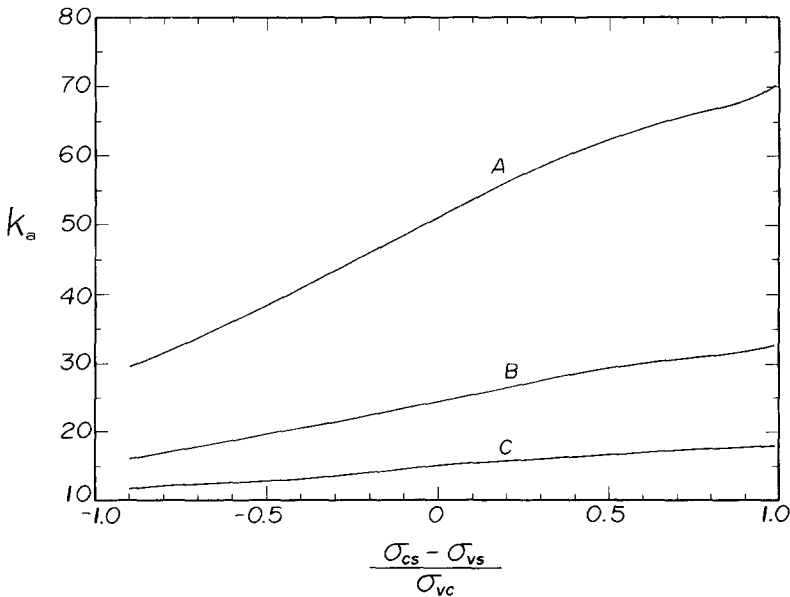


Fig. 6. The adsorption constant k_a as a function of $(\sigma_{cs} - \sigma_{vs})/\sigma_{vc}$ for condensation on a smooth solid substrate. Curves A, B, and C are for $\pi/\sigma_{vc}=0.02$, 0.04, and 0.06, respectively.

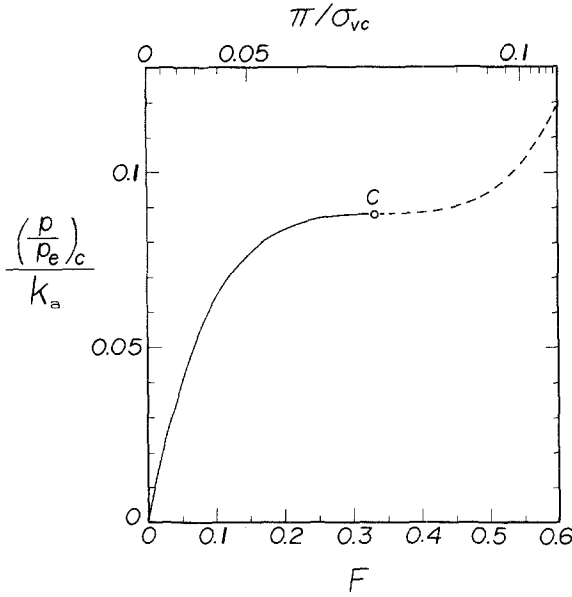


Fig. 7. Plot of $(P/P_e)_c/k_a$ as a function of F and π/σ_{vc} .

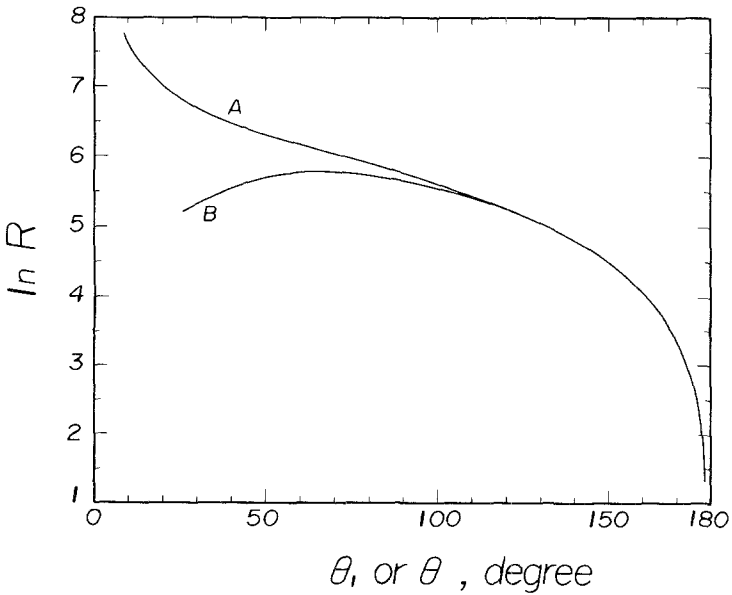


Fig. 8. Plot of $\ln R$ as a function of θ_1 or θ for $\pi/\sigma_{vc} = 0.06$, for (A) an immiscible liquid substrate with $\sigma_{vs}/\sigma_{vc} = 0.5$ and (B) for a smooth solid substrate.

where i^* is the number of molecules in a condensate nucleus of critical size. Figure 8 shows the relationship between R and the contact angle for $\pi/\sigma_{vc} = 0.06$. The value of always considerably greater than unity. In other words, the indirect addition of adsorbed vapor molecules is always more important than the direct addition of the vapor molecules, except for the extreme cases of $\theta \approx 0$, $\theta \approx \pi$, and $\theta_1 \approx \pi$. When the contact angles are larger than $\pi/2$, the geometry of the condensate droplet on a smooth solid substrate is the same as the portion of the condensate droplet on the immiscible liquid exposed to the vapor. As θ_1 increases, the portion of the condensate droplet submerged under the surface of the immiscible liquid becomes smaller and less important. Consequently, the two curves gradually coincide. The two-dimensional addition become less important when the condensate droplets have very little contact with the substrate surface as the contact angle θ or θ_1 approaches π . Below $\pi/2$, further reduction of θ makes the vapor–condensate interface of the nuclei on smooth solid substrate larger, but the reduction of θ_1 makes the vapor–condensate interface smaller because a larger portion of the condensate droplet is submerged under the surface of the immiscible liquid. Consequently, the two curves in Fig. 8 separate.

6. CONCLUSIONS

There are various ways of expressing the affinity between the molecules of a vapor and a substrate surface: the coefficient in the adsorption isotherm, the vapor–condensate–substrate interfacial forces or contact angle, and the critical supersaturation for the condensation process to begin. They are correlated and one can predict any one of them if experimental data for the others are available. In the process of nucleation and condensation of a vapor on the smooth surfaces, adsorbed vapor molecules on the substrate surface play an important role. The indirect addition of these molecules to the condensate nuclei by two-dimensional diffusion or migration is considerably more important than the direct addition of the vapor molecules except for a few extreme cases. It greatly reduces the critical supersaturation necessary for the condensation process to begin.

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