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Effect of Adsorption on Crystal Nucleation in Binary Droplets: Implication for the Formation of Nitric Acid Hydrate Particles

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The adsorption of surfactant molecules at the droplet−vapor interface can affect the droplet surface tension and thus alter the rate of surface-stimulated crystal nucleation. Recently, we have shown that if the condition of partial wetting holds for at least one crystal facet then the crystallization process is most likely to initiate at the droplet surface. Here, we outline an adsorption model to determine the main physical characteristics of the interior and surface layer of a binary droplet. The theoretical model is illustrated by numerical calculations for aqueous nitric acid droplets. As expected, an increase in the surfactant concentration in the droplet interior lowers the droplet surface tension, which has an impeding effect on the surface-stimulated crystallization. However, we show that an increase in the surface-to-volume ratio of a droplet favors crystal nucleation at the surface not only kinetically but also thermodynamically. This occurs because for a given droplet composition smaller droplets have a higher surface tension. Thus, the impeding effect of a soluble surfactant on the surface mode of crystal nucleation becomes weaker as the droplet size decreases. Our results also show that for a fixed overall droplet composition the excess surface coverage decreases with decreasing droplet radius. The effect of organic contaminants on crystallization in aqueous nitric acid droplets is also qualitatively studied.

1. Introduction

The physical state of aerosol and cloud particles influences the earth's climate and atmospheric composition.[1] Therefore, it is important to understand fundamental physical processes by which atmospheric particles change their phase. Although many phase transformations in aqueous and cloud droplets occur as a result of heterogeneous nucleation on preexisting solid particles,[2] in a number of important cases, atmospheric particles appear to freeze homogeneously.[3−7]

Recently, we have studied the thermodynamics of homogeneous crystal nucleation in both single-component[8] and multicomponent[9] liquids. We showed that in both cases if the crystal form has at least one facet only partially wettable by its melt then the pseudoheterogeneous formation of a crystal nucleus (with this facet as a vapor−solid interface) is thermodynamically favored over the homogeneous process (with all crystal facets within the liquid). In support of this theory, we provided experimental evidence for the surface crystallization of ice in supercooled water droplets[10] and hydrates of nitric acid in aqueous nitric acid droplets.[11]

Clearly, crystal nucleation in a multicomponent system involves several phenomena that are nonexistent in a unary system: dissociation of molecules, their adsorption into the interfaces present, and formation of a solid phase of fixed composition from a nonstoichiometric solution.[9] Although these effects do not alter the form of the condition of surface-stimulated crystallization, they play an important role in determining the liquid−vapor and liquid−solid surface tensions and the mode of crystal nucleation. In the present paper, we explore how the droplet size can affect adsorption at the droplet−vapor interface and, consequently, the thermodynamics of crystal nucleation. Our theoretical results are then applied to aqueous nitric acid droplets. Their freezing behavior has important implications for the springtime ozone chemistry in the polar regions.[6]

2. Adsorption Aspects of Surface-Stimulated Crystal Nucleation

Let us denote the surface tension by σ and use the superscripts α, β, and δ to indicate the liquid, vapor, and solid phases, respectively, and a double superscript for a corresponding interface. The thermodynamic condition for surface-stimulated crystal nucleation in both unary and multicomponent liquids has the form of the condition of partial wetting of at least one crystal facet by its melt:[8,9]

$$\sigma_\lambda^{\beta\delta} - \sigma^{\alpha,\beta} < \sigma_\lambda^{\alpha\delta} \tag{1}$$

(here λ indicates a particular facet of the crystal nucleus). When this condition is satisfied, the work of formation of a critical crystal with one facet (λ) as a vapor−solid boundary is lower than the work of formation of a critical crystal with all of its facets immersed in the liquid.

The surface tension $\sigma^{\beta\delta}$ in eq 1 is hardly affected by the composition of the liquid solution. However, the surface tensions $\sigma^{\alpha\beta}$ and $\sigma_j^{\alpha\delta}$ (j marks some arbitrary facet of the crystal) can strongly depend on the solution composition. ($\sigma_j^{\alpha\delta}$ can also depend on the solid-phase composition.) Usually, an increase in the concentration of a soluble surfactant causes a decrease in the surface tension $\sigma^{\alpha\beta}$. Thus, one might conclude that surface-stimulated crystallization would be less likely in a

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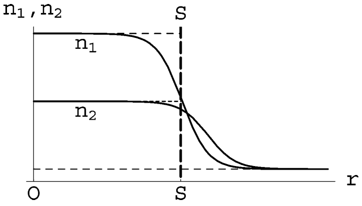

Figure 1. Scheme of density profiles for a binary droplet in a vapor mixture: n_1 and n_2 are densities of components 1 and 2, *SS* is the dividing surface, *O* is the center of the droplet, and *r* is the distance from the center.

droplet that has a higher concentration of a soluble surfactant than in a droplet that has a lower concentration of the same surfactant. However, a change in the droplet composition can affect both sides of the inequality in eq 1. The left side of eq 1 increases as the surfactant concentration increases; therefore, the inequality can break down. However, the right side of eq 1 can also change: it may increase for some facets but decrease for others. Although not a general rule, it is clear that the surface tension of a crystallographic plane exposed to the solution can nonmonotonically depend on the difference between the packing composition of that plane and the composition of the solution. One can expect that the more the solution composition differs from the packing composition of a given facet, the greater the surface tension of that facet. As the droplet composition changes, inequality 1 can break down for some facets but may begin to hold for others for which it did not hold before composition changes occurred. For example, let χ' be an arbitrary solution composition such that facet 1 is partially wettable, whereas facet 2 is completely wettable by the solution, that is, $\sigma_1^{\beta\delta} - \sigma^{\alpha\beta} < \sigma_1^{\alpha\delta}$ and $\sigma_2^{\beta\delta} - \sigma^{\alpha\beta} = \sigma_2^{\alpha\delta}$. Under such conditions, facet 1 will tend to replace the liquid−vapor interface, whereas facet 2 will tend to remain within the solution. Now let χ'' be another solution composition (corresponding to a higher surfactant concentration) such that, because of changes in $\sigma^{\alpha\beta}$ and $\sigma_{1,2}^{\alpha\delta}$, facet 1 is completely wettable, whereas facet 2 is only partially wettable, that is, $\sigma_1^{\beta\delta} - \sigma^{\alpha\beta} = \sigma_1^{\alpha\delta}$ and $\sigma_2^{\beta\delta} - \sigma^{\alpha\beta} < \sigma_2^{\alpha\delta}$. Under such conditions, facet 1 will tend to remain within the solution, but facet 2 will tend to replace the liquid−vapor interface. Thus, surface-stimulated crystallization may remain an important mechanism for freezing of atmospheric droplets even at high concentrations of soluble surfactant molecules. This is corroborated by the analysis of Tabazadeh et al.,[10] suggesting that even in very concentrated aqueous nitric acid droplets crystallization appears to be initiated at the droplet surface.

3. Adsorption of a Soluble Surfactant at the Surface of a Binary Droplet

Consider a liquid particle of binary solution in the corresponding vapor mixture. The temperature *T* in the system (of total volume *V*) is assumed to be uniform. The subscript *i* will indicate quantities attributed to component *i* ($i = 1, 2$).

The density profiles in such a system can be schematically represented as shown in Figure 1. The center of the spherically symmetric liquid particle is placed in the point O. The low density part corresponds to the vapor mixture. There is an interfacial layer between relatively uniform (bulk) liquid and relatively uniform (bulk) vapor. In this interfacial layer, the density smoothly changes from that of the bulk liquid to that of the bulk vapor. We will define a droplet as the part of the system where the density is different from that of the bulk vapor.

According to the principles of Gibbsian thermodynamics, our system can be regarded as consisting of three distinct parts: (a) a liquid sphere of radius *R* and of uniform densities of both components, (b) a vapor mixture of uniform densities of both components, and (c) a dividing surface. The choice of the dividing surface is arbitrary.

The vapor mixture is assumed to be ideal and is characterized by the partial saturation ratios ζ_1 and ζ_2 defined as

$$\zeta_i = \frac{P_i}{P_{ie}} \qquad (i = 1, 2)$$

where P_i and P_{ie} are the partial and equilibrium vapor pressures (at given *T*) of component *i* of the vapor mixture. The pure vapor of component *i* of pressure P_{ie} would be in equilibrium with the planar surface of its liquid phase at a given temperature *T*.

By definition, the droplet consists of a liquid sphere of radius *R* and of uniform density (interior), plus the dividing surface (surface layer). The composition of the droplet interior can be characterized, for example, by the mole ratio

$$x = \frac{n_2}{n_1} \tag{2}$$

where n_i ($i = 1, 2$) is the number of molecules of component *i* in the droplet interior. The approach adopted here is similar (but not identical) to that used by Rusanov et al.[12] and Kuni et al.[13] to study an aqueous droplet containing soluble involatile surfactants. (A more detailed description of the model is given elsewhere.[14])

We denote the total number of molecules of component *i* in the droplet, including both the interior and surface layer, by ν_i ($i = 1, 2$). If we choose the equimolar (with respect to component 1) surface as a dividing surface, then the total number of molecules of component 1 in the droplet equals the number of molecules in its interior, that is, $\nu_1 = n_1$. However, for component 2, the relation between the total number of molecules in the droplet, ν_2, and the number of molecules in its interior, n_2, is

$$\nu_2 = n_2 + 4\pi R^2 \Gamma_2 \tag{3}$$

where Γ_2 is the adsorption of component 2 at the dividing surface.

The physical meaning of Γ_2 can be clarified according to Adamson.[15] Consider the cross section of the real surface region by the dividing surface (*S* in Figure 1), chosen so that $\Gamma_1 = 0$. Γ_2 represents the (algebraic) excess number of molecules of component 2 per unit area of that cross section over the number of molecules that would be present in a bulk region containing the same number of molecules of component 1 as does the section of the surface region.

We introduce the variable *y* and parameter λ as

$$y = \frac{\nu_2}{\nu_1} \tag{4}$$

and $\lambda = (3v_1/4\pi)^{1/3}$, where v_i ($i = 1, 2$) is the volume per molecule of component *i* in its pure liquid phase. Note that *y* is the overall mole ratio of the second component to the first (in the whole droplet) and λ is the effective radius of a molecule of component 1 in its pure liquid.

Equation 3 can be rewritten in variables x and y as

$$x = y - s_2(1 + \upsilon_{21}x)^{2/3}y^{1/3}\nu_2^{-1/3} \tag{5}$$

where $s_2 = 4\pi\lambda^2\Gamma_2$ is the dimensionless adsorption and $\upsilon_{21} = \upsilon_2/\upsilon_1$.

There are three independent variables in eq 5 because the variables x and s_2 can be related to each other by an adsorption isotherm. The composition of the droplet interior is a single-valued function of the excess surface coverage. The inverse is not in general true because of the existence of 2D phase transitions in adsorption layers of soluble surfactants.[16]

Hereafter, we will limit our consideration to equilibrium droplets. In a binary system, equilibrium conditions require the chemical potential in a droplet to be equal to that in the vapor phase for either component,[17]

$$\mu_i(T, P, x) = \mu_i'(T, P_i) \qquad (i = 1, 2) \tag{6}$$

where μ_i and μ_i' are the chemical potentials of component i in the droplet interior and vapor mixture, respectively, and P is the pressure within the droplet. These chemical potentials can be written in the form

$$\mu_i(T, P, x) = \mu_i(T, P) + kTz_i \ln[a_i(x)] \qquad (i = 1, 2) \tag{7}$$

$$\mu_i'(T, P_i) = \mu_i'(T, P_{i\infty}) + kT \ln \zeta_i \qquad (i = 1, 2) \tag{8}$$

where z_i denotes the number of ions into which a molecule of component i dissociates in a solution, $a_i(x)$ is the mean ionic activity of component i in a solution of composition x, and $\mu_{i0}(T, P)$ is the chemical potential of component i in a standard state (depending on the choice of the basis for activities). Note that z_i may differ from the corresponding quantity in the surface layer. For example, in an aqueous nitric acid solution, a nitric acid molecule dissociates into H^+ and NO_3^- ions within the bulk, whereas at the surface, nitric acid is mostly adsorbed in a molecular form.[18,19] In what follows, we will assume that component 1 does not dissociate so that $z_1 = 1$. This limitation is quite acceptable in atmospheric studies because the main constituent of atmospheric droplets is water. In the rational system of activities,[15] $a_1(x)$ and $a_2(x)$ can be written as

$$a_1(x) = \frac{1}{1 + z_2x}f_1(x) \qquad a_2(x) = \frac{x}{1 + z_2x}f_2(x) \tag{9}$$

where $f_1(x)$ and $f_2(x)$ are the activity coefficient of component 1 and the mean ionic activity coefficient of component 2, respectively, in a solution of composition x.

Assuming the vapor mixture to be ideal and the droplet to be incompressible, one can rewrite the equilibrium conditions in eq 6 as

$$\ln\frac{(1 + z_2x)\zeta_1}{f_1(x)} = \frac{2\upsilon_1 y^{1/3}\gamma(x)\nu_2^{-1/3}}{4\pi\lambda^3(1 + \upsilon_{21}x)^{1/3}} \tag{10}$$

$$z_2 \ln\frac{(1 + z_2x)\zeta_2^{1/z_2}}{xf_2(x)} = \frac{2\upsilon_2 y^{1/3}\gamma(x)\nu_2^{-1/3}}{4\pi\lambda^3(1 + \upsilon_{21}x)^{1/3}} \tag{11}$$

where $\gamma(x) = 4\pi\lambda^2\sigma(x)/kT$ is a dimensionless surface tension, with $\sigma \equiv \sigma^{\alpha\beta}$. These are just the well-known Kelvin equations (relating the saturation ratios to the radius of an equilibrium droplet) in variables ν_2, x, and y. Because now the dividing surface does not coincide with the surface of tension, in eqs 10 and 11, we assumed that the Tolman length (i.e., the distance between the dividing surface and the surface of tension) is much smaller than the droplet radius. This allows one to use experimental data on the surface tension of bulk solutions for the droplet surface tension, which is acceptable for large droplets (at least several nanometers in radius).

At a given T, the quantities s_2 and x are related by an adsorption isotherm.[15] As mentioned above, x is a single-valued function of s_2, although the inverse is, in general, not true. We assume that this relationship can be written in one of two explicit forms:

$$x = x(s_2) \qquad s_2 = s_2(x) \tag{12}$$

Either of these explicit functions along with the Gibbs adsorption equation can be used to find the surface tension as a function of either the internal composition (x) or excess adsorption (s_2). Actually, for a given choice of the dividing surface at constant temperature and pressure, the Gibbs adsorption equation relates the dimensionless surface tension γ to the dimensionless (in units kT) chemical potential μ_2 in the bulk solution

$$d\gamma = -s_2\, d\mu_2 \tag{13}$$

If the adsorption isotherm can be written in the form $s_2 = s_2(x)$, then the integration of the Gibbs adsorption equation provides the surface tension as a function of internal composition, that is, a generalized Szyszhkowski equation.[20,21] If the adsorption isotherm can be written in the form $x = x(s_2)$, then the integration of the Gibbs adsorption isotherm can be carried out with respect to s_2, which provides the surface tension as a function of adsorption. Thus, eqs 5, 7, and 8 can be solved with respect to three independent variables: either x, y, and ν_2 or s_2, y, and ν_2. For concreteness, assume that the adsorption isotherm is given in the form $s_2 = s_2(x)$. It is more convenient to rewrite the set of eqs 5, 7, and 8 as

$$\ln\frac{(1 + z_2x)\zeta_1}{f_1(x)} = \upsilon_{21}^{-1}z_2 \ln\frac{(1 + z_2x)\zeta_2^{1/z_2}}{xf_2(x)} \tag{14}$$

$$y = x + 2\pi\lambda^3 s_2(x)\frac{[1 + \upsilon_{12}x]}{[\gamma(x)\,\beta(x)]} \tag{15}$$

$$\nu_2 = \frac{[\gamma(x)\,\beta(x)]^3 y}{8\pi^3\lambda^9(1 + \upsilon_{21}x)} \tag{16}$$

where

$$\beta(x) = \frac{\left[\dfrac{\upsilon_1}{1 + z_2x} + \dfrac{\upsilon_2 x}{1 + z_2x}\right]}{\left[\dfrac{1}{1 + z_2x}\ln\dfrac{(1 + z_2x)\zeta_1}{f_1(x)} + \dfrac{z_2x}{1 + z_2x}\ln\dfrac{(1 + z_2x)\zeta_2^{1/z_2}}{xf_2(x)}\right]}$$

Consider, for example, the Langmuir adsorption isotherm in the case where component 2 dissociates in the bulk and is adsorbed at the interface in a molecular form:

$$s_2 = s_\infty\frac{\dfrac{a_2^{z_2}}{a_1}}{b + \dfrac{a_2^{z_2}}{a_1}} \tag{17}$$

Here $a_1(x)$ and $a_2(x)$ are the activity of component 1 and the mean ionic activity of component 2, respectively, in a solution of composition x. The parameter b is related to the rate constants for the adsorption and desorption from the surface into the two bulk phases, and s_∞ is the saturation value of the dimensionless adsorption s_2.

Substituting eqs 7 and 17 into eq 13 and integrating, we obtain the dimensionless surface tension γ as a function of x:

$$\gamma(x) = \gamma_0 - z_2 s_\infty \int_0^x \frac{\dfrac{[a_2(x)]^{z_2}}{a_1(x)}}{\mathrm{b} + \dfrac{[a_2(x)]^{z_2}}{a_1(x)}} \cdot \frac{\mathrm{d}\ln a_2(x)}{\mathrm{d}x}\mathrm{d}x \qquad (18)$$

where $\gamma_0 = \lim_{x\to 0}\gamma(x)$ is the surface tension of pure water (solvent, component 1). Thus, all of the necessary constituents of eqs 14−16 are determined, and they can be solved in variables x, y, ν_2. Equation 18 is a generalized Langmuir−Szyszhkowski equation.

4. Adsorption Isotherm and Its Parameters

There are several kinds of adsorption isotherms, differing in the analytic relationship between the excess surface coverage and the characteristics of the bulk phases involved. Any adsorption isotherm contains parameters that are specific for every given system. For example, the Langmuir adsorption isotherm describes adsorption in systems where the excess surface coverage is limited to one monolayer of adsorbate, and it has two system-specific parameters. Unlike the Langmuir model, the Frumkin adsorption isotherm[12,15] involves three system-specific parameters and takes the lateral interaction of adsorbate molecules into account, although it is also limited to monolayer adsorption. The well-known Brunauer−Emmett−Teller (BET) adsorption isotherm describes multilayer adsorption on a solid surface from the gas phase and contains two system-specific parameters.[15] Thus, two problems may arise when studying adsorption phenomena in a particular system.

First, it is necessary to identify what kind of adsorption isotherm best fits the real process. Then, it is necessary to determine its parameters for a system of interest. For example, the Langmuir adsorption isotherm, eq 17, contains two parameters that need to be known. A usual method[15,22] to find these parameters for adsorption at a liquid−vapor interface is to determine s_2 as a function of bulk composition x experimentally (by using eq 13) and to plot the data for dilute solutions as $x^{z_2}(1 + z_2x)^{1-z_2}/s_2$ versus $x^{z_2}(1 + z_2x)^{1-z_2}$. According to eqs 9 and 17, this dependence should follow a straight line of slope $1/s_\infty$ and intercept b/s_∞.

In the case where the adsorption isotherm is expected to be of a known type, say $s_2(x, a, b, ...)$ with unknown parameters a, b, ..., these can be easily found if there are reliable experimental data (not necessarily extensive) on the composition dependence of the surface tension. Substituting the adsorption isotherm $s_2(x, a, b, ...)$ into eq 13 and integrating the result, one can find the corresponding Szyszhkowski equation $\gamma = -\int \mathrm{d}x\, s_2(x, a, b, ...)(\mathrm{d}\mu_2/\mathrm{d}x)$ with unknown adsorption parameters a, b, ... The experimental data on the surface tension γ can then be fit by this equation upon (presumably) a unique choice of adsorption parameters. This procedure, unlike the commonly adopted one (described above), does not involve numerical differentiation of a large amount of surface tension experimental data and hence should provide more accurate values for the adsorption parameters.

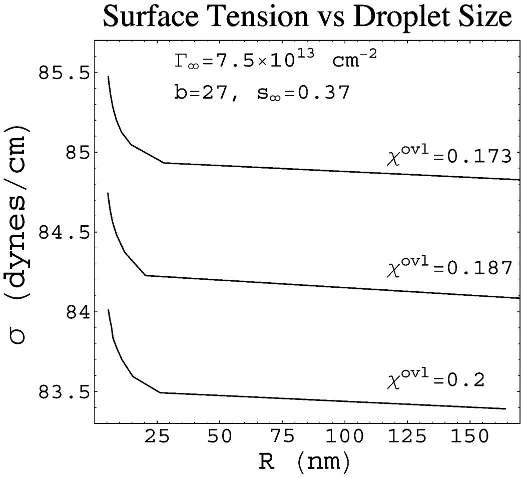

Figure 2. Dependence of the droplet surface tension, σ, on its radius, R. Each curve corresponds to a fixed overall mole fraction of nitric acid, χ^{ovl}, as indicated. The parameters of the Langmuir adsorption isotherm are also shown.

The above equations can be easily extended to the case when a multicomponent droplet is in equilibrium with the corresponding vapor mixture. First, the addition of a new component k to the system results in one additional equation of type 5. Next, for an equilibrium droplet an additional condition of type 6 takes place, and only one additional independent variable appears (say, x_k, the concentration of component k in the droplet interior) because an additional adsorption Γ_k will be again related to the internal composition by an adsorption isotherm. Note that now the adsorption of all components at the droplet surface will be a competitive process so that every adsorption Γ_i (i = 1, 2, ...) will be a function of all of the independent concentrations $\{x_k\}$ (k = 1, 2, ...) in the droplet interior.[15] Clearly, technical problems will arise related to the necessity to know the activity coefficients in multicomponent solutions and the adsorption isotherm parameters for a competitive adsorption model. This, however, will be the subject of future research.

5. Numerical Results for Aqueous Nitric Acid Droplets

As an illustration of the above adsorption model, we carried out numerical calculations for aqueous nitric acid droplets at T = 193.15 K. The activity coefficients and densities were taken from Clegg and Brimblecombe.[23] The surface tension of pure liquid water at this temperature was set equal to σ_0 = 89 dynes/cm.[2] There is experimental evidence for the adsorption of molecular nitric acid (mainly in the form of the monohydrate) at the liquid−vapor interface.[18,19] The composition dependence of the surface tension of aqueous nitric acid was previously experimentally studied.[18,24,25] In our calculations, we used the Langmuir adsorption isotherm, eq 17, to find the function $\gamma(x)$ that is needed to solve eqs 14−16. The parameters Γ_∞ and b in eq 17 were chosen so that $\gamma(x)$ fits experimental data[24] on the surface tension extrapolated down to T = 193.15 K in the range of $0 \lesssim x \lesssim 1$. These parameters were set equal to x_0 = 0.27 and s_∞ = 0.37 (the latter corresponds to $\Gamma_\infty = 1.0 \times 10^{14}$ cm^{-2}). The main results of the calculations are shown in Figures 2−5.

Figure 2 shows the droplet surface tension $\sigma^{\alpha\beta}$ as a function of the droplet radius R. Each curve corresponds to a fixed overall mole fraction of nitric acid in the droplet, $\chi^{\mathrm{ovl}} = y/(1 + y)$, indicated over the curve. As expected, for a fixed droplet of radius R, the surface tension decreases as the overall concentration of nitric acid in solution increases. However, for a fixed χ^{ovl}, the surface tension increases as droplet size decreases, and

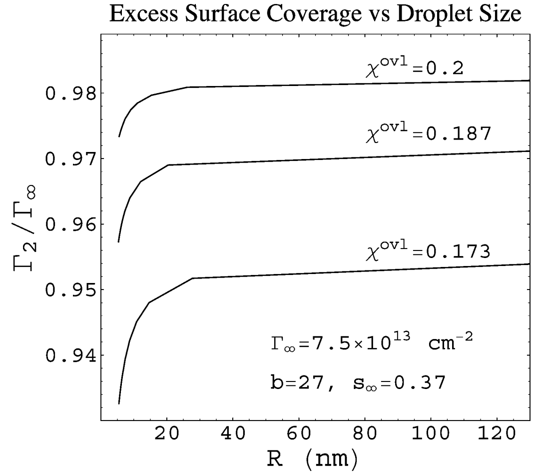

Figure 3. Dependence of the excess surface coverage, Γ_2, on the droplet radius, *R*. Each curve corresponds to a fixed overall mole fraction of nitric acid, χ^{ovl}, as indicated. The parameters of the Langmuir adsorption isotherm are also shown.

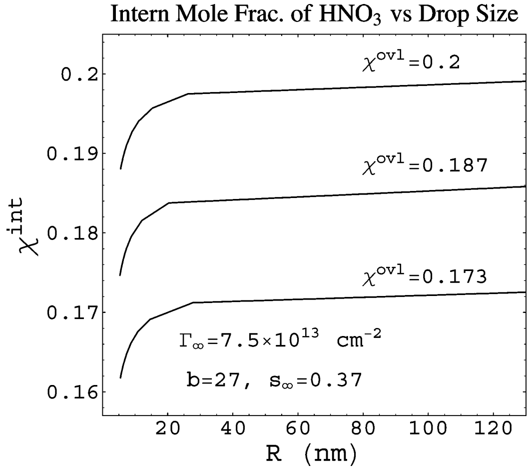

Figure 4. Dependence of the interior mole fraction of nitric acid in the droplet, χ^{int}, on its radius, *R*. Each curve corresponds to a fixed overall mole fraction of the solute, χ^{ovl}, as indicated. The parameters of the Langmuir adsorption isotherm are also shown.

this increase is particularly sharp for $R \lesssim 30$ nm. Thus, for droplets of a fixed overall composition the condition of surface-stimulated crystallization is more likely to hold for smaller droplets than for larger ones.

Consider droplets of mole fraction $\chi^{ovl} = 0.2$. The left side of inequality 1 is $\sigma_\lambda^{\beta\delta} - 84.1$ (dynes/cm) for droplets of radius 5 nm, whereas it is $\sigma_\lambda^{\beta\delta} - 83.4$ (dynes/cm) for those of radius 100 nm. Assuming that for some particular facet $\sigma_\lambda^{\alpha\delta}$ is nearly the same in both droplets, the contact angles Θ for this facet in two droplets would be such that $\cos(\Theta_5) = 0.99 \times \cos(\Theta_{100})$. (The contact angle Θ is defined as $\cos\Theta = (\sigma^{\beta\delta} - \sigma_\lambda^{\alpha\delta})/\sigma^{\alpha\beta}$, and the subscript of Θ indicates the droplet size.) If for a large droplet $\Theta_{100} = 0.1°$ (almost complete wetting), then for a small droplet $\Theta_5 = 8°$ (clear partial wetting). Consequently, at a given temperature the condition of partial wetting is more likely to be satisfied in smaller droplets, and they are more likely to crystallize in a surface-stimulated mode. Therefore, a decrease in the droplet size favors the surface-stimulated mode of crystallization not only kinetically but also thermodynamically. In unary systems or systems with no soluble surfactants, the role of surface-stimulated crystallization increases with decreasing droplet size only because of the kinetic effect,that is, via an increase in the number of surface-located crystal nucleation sites.

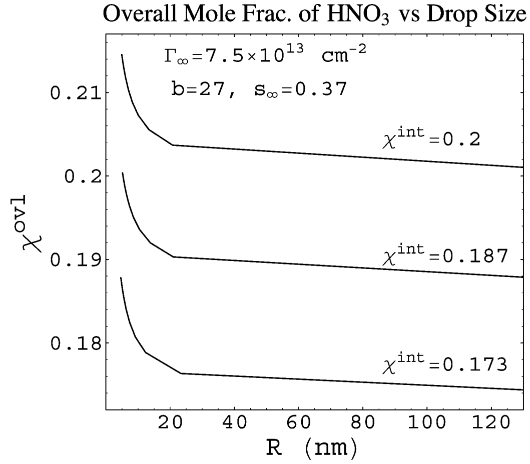

Figure 5. Dependence of the overall mole fraction of nitric acid in the droplet, χ^{ovl}, on its radius, *R*. Each curve corresponds to a fixed internal mole fraction of nitric acid, χ^{int}, as indicated. The parameters of the Langmuir adsorption isotherm are also shown.

The above effect carries important consequences for laboratory investigations. The rates of crystal nucleation, inferred from experiments, depend on what crystallization mode is thermodynamically favored (either surface-stimulated or volume-based).[10,11] In multicomponent droplets, this mode is determined not only by the temperature but also by the droplet size, whereas in unary systems, it is determined only by temperature. Furthermore, according to Pruppacher and Klett,[2] present atmospheric studies assume that crystal nucleation in droplets occurs within the volume. As our results show, the crystallization of droplets may occur in different modes (and hence with different rates) depending on their sizes.

Clearly, quantitative studies of the surface-stimulated crystal nucleation and its contribution to the rate of crystal nucleation in droplets require much more information than the present model contains. The overall crystal nucleation rate, *J*, in a droplet consists of two terms, one of which, J_v, is due to the volume-based process and the other, J_s, is due to the surface stimulated mode: $J = J_v + J_s$. The structure of J_v is well known.[2] According to classical nucleation theory,[2] J_s can also be represented as a product $K_s \exp(-W_s)$, where K_s is the kinetic factor whose structure remains to be rigorously studied. A general expression for W_s, the reversible work of formation of a crystal nucleus in a surface-stimulated mode, was derived in refs 8 and 9. Qualitatively, W_s decreases (hence J_s increases) with increasing $\sigma^{\alpha\beta}$, that is, with decreasing droplet size (provided that the composition of the droplets is the same). However, the quantitative application of the expression for W_s requires detailed knowledge of the surface tension of all of the facets of a crystal nucleus in solution as well as in vapor. Thus, an accurate calculation of W_s depends greatly on how well the structure of the nascent crystal phase is known.

Figures 3 and 4 show the excess surface coverage Γ_2 (in units Γ_∞) and the internal droplet composition χ^{ovl}, respectively, as functions of droplet radius *R*. Each curve corresponds to a fixed overall droplet composition χ^{ovl} (indicated over the curve). For a given *R*, the greater χ^{ovl}, the greater the excess surface coverage Γ_2 and internal mole fraction $\chi^{int} = x/(1 + x)$. However, for a given χ^{ovl}, the quantities Γ_2 and χ^{int} decrease as the droplet size decreases, and this decrease in Γ_2 and χ^{int} is particularly sharp for $R \lesssim 30$ nm. This can be explained by the fact that the surface-to-volume ratio of a droplet goes as $^{1}/_{R}$. Thus the smaller a droplet, the higher the fraction of surfactant molecules that can relocate to the droplet surface. For very small droplets ($R \lesssim 30$ nm), there are not enough surfactant molecules in the droplet to ensure surface coverage, which is characteristic of the bulk solution (Figure 3). The same phenomenon reveals itself as the surface layer depletes surfactant molecules from the droplet interior (Figure 4). It should be noted that for a water-*n*-propanol system the effects shown in Figures 2 and 4 were earlier predicted by Bianco and Marmur[26] and Laaksonen.[27]

Finally, Figure 5 presents the size dependence of the overall mole fraction of soluble surfactant in the droplet at fixed internal composition. As expected, the greater χ^{int}, the greater χ^{ovl} for a given R. However, for a fixed χ^{int}, there is a clear increase in χ^{ovl} with decreasing R, especially for droplets with radii $R \lesssim 30$ nm. Again, this can be accounted for by an increase in the surface-to-volume ratio of a droplet as R decreases. Actually, for a fixed internal composition, an increase in the surface-to-volume ratio leads to an increase in the relative quantity of surface-located molecules, which leads to a greater overall surfactant concentration in the droplet.

As our results show, because of the adsorption of molecular nitric acid at the droplet surface, the surface thermodynamic properties and hence freezing behavior of small aqueous nitric acid droplets ($R \lesssim 30$) nm can drastically differ from those of bulk solutions under the same conditions. However, this effect becomes negligible for large aqueous acid droplets ($R \gtrsim 1$ μm) whose surface properties should be expected to coincide roughly with those of bulk samples. Thus, an increase in the surface-to-volume ratio of droplets enhances the freezing propensity of droplets both kinetically (i.e., by increasing the available surface area where nucleation can initiate) and thermodynamically (i.e., by increasing the droplet surface tension).[8−11] Note that although the thermodynamic (adsorption) effect becomes negligible for droplets with sizes $R \gtrsim 1$ μm the kinetic effect continues to favor the crystallization of droplets in the whole range of stratospherically relevant sizes.

The formation of stratospheric NAD/NAT particles is believed to occur as a result of the freezing of ternary $H_2O-HNO_3-H_2SO_4$ droplets rather than binary H_2O-HNO_3 droplets.[6] Although the amount of sulfuric acid in droplets is usually very small (less than 5 wt %),[28] its presence can significantly change droplet surface properties such as the surface coverage and surface tension. Actually, in ternary droplets the adsorption of nitric acid at the droplet surface is likely to occur as a competitive process affected by the adsorption (or desorption) of sulfuric acid molecules. Thus, additional work needs to be done to take into account the possibility of competitive adsorption, and more experimental work is needed to determine the corresponding adsorption parameters. This will be the subject of future research.

5.1. Contamination of the Droplet Surface by Organics. Another factor that can affect the adsorption of molecular nitric acid is the contamination of the droplet surface by organic molecules. Even in the stratosphere, this effect can be expected not to be negligible but particularly important; it can be in laboratory experiments where droplets are exposed to tropospheric air, and organic contamination can occur if special care is not taken to prevent it.[29] Here, we present rough quantitative estimates to demonstrate how the contamination of the surface of aqueous nitric acid droplets by trace amounts of organic molecules can influence the adsorption of nitric acid at the droplet surface.

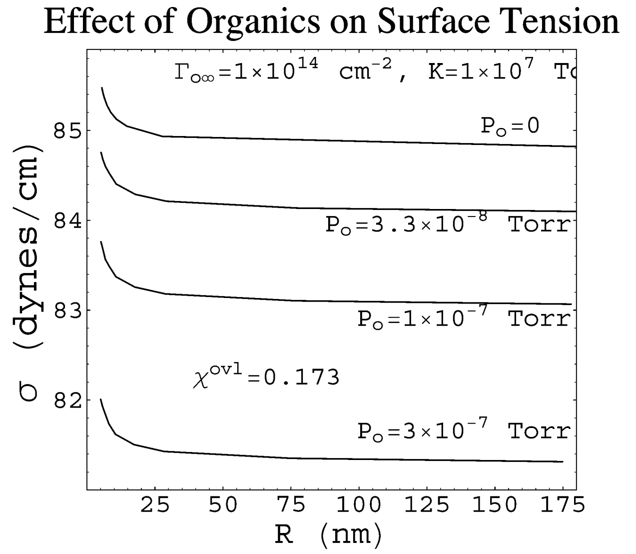

Figure 6. Effect of contamination of the droplet surface by organic molecules on the droplet surface tension. Each curve corresponds to a fixed pressure of the organic gas P_o as indicated. The overall mole fraction χ^{ovl} of nitric acid in droplets and Langmuir adsorption isotherm parameters $\Gamma_{o\infty}$ and K for the trace gas are shown. (Other adsorption parameters are the same as in Figures 2−5.)

Suppose there is a trace gas of some organic species in the vapor mixture of water and nitric acid. If the organic species is insoluble in aqueous nitric acid, then its presence does not affect the equilibrium conditions in eq 6 so that the set of eqs 14−16 will still determine the variables x, y, and ν_2 of the droplet. However, insoluble organic molecules can adsorb at the droplet surface and change its surface tension. The droplet surface tension will now depend not only on x (or s_2) but also on the surface coverage of organic species, Γ_o (we attribute the subscript o to this organic species), which is related to the organic gas pressure P_o (or concentration) by an adsorption isotherm.[15] Therefore, the solution of eqs 14−16 will give y and ν_2 depending on the organic gas content in the system, although the internal composition x will not be affected.

For simplicity, consider an organic trace gas whose adsorption at the aqueous nitric acid surface is described by the Langmuir isotherm,[15] $\Gamma_o = \Gamma_{o\infty}KP_o/(1 + KP_o)$, where the parameter K is related to the rate constants for adsorption at and desorption from the surface. Both parameters $\Gamma_{o\infty}$ and K can depend on x. Substituting eq 19 into the Gibbs adsorption equation at constant T and x and integrating the resulting equation with respect to P_o leads to an expression for the surface tension as a function of internal composition and organic gas pressure:

$$\gamma(x, P_o) = \gamma(x) - s_{o\infty} \ln(1 + KP_o) \tag{19}$$

with a previous definition of the dimensionless adsorption $s_o = 4\pi\lambda^2\Gamma_o$. This equation should be an acceptable approximation up to $P_o \lesssim P_{oe}$, with P_{oe} being the equilibrium vapor pressure of organic species. The function $\gamma(x, P_o)$ should now replace $\gamma(x)$ in eqs 13−15, whose solution is illustrated by numerical calculations presented in Figure 6. The parameters K and $\Gamma_{o\infty}$ are assumed to be independent of x and are indicated in the Figure panel.

At present, there is no data on how the adsorption of organics affects the surface tension of aqueous nitric acid, so we assume that the droplet surface tension decreases as organic molecules adsorb onto the surface. With this assumption, the adsorption of organics is expected to impede the surface-stimulated mode of crystal nucleation in droplets, as is clear from Figure 6 and eq 1. For the values of P_o shown in Figure 6 (i.e., 3.3×10^{-8}, 10^{-7}, and 3×10^{-7} Torr), the mass fraction of organic molecules adsorbed at the surface of a 1-μm droplet would constitute about

0.3, 0.6, and 1%. (We assume the molecular weight of an abstract organic molecule to be on the order of 100 amu, which is typical, e.g., for C_{10} alcohols, aldehydes, and ketones.) For droplets of 100-nm radius, these mass fractions would be even higher (3, 6, and 9%, respectively). This is indirectly confirmed by laboratory measurements,[29] providing evidence for the presence of organic trace species in laboratory droplet samples. Our results may provide a possible explanation for why droplet samples in the laboratory do not freeze homogeneously, whereas droplets in the stratosphere that are less affected by organic species seem to freeze quite readily. We suggest that organic contaminants in laboratory samples may hamper the surface mode of crystal nucleation. Thus, the lack of observed nucleation in laboratory experiments may be related to organic contamination,[29] and this issue needs to be addressed by rigorous laboratory experiments.

6. Conclusions

Revisiting the thermodynamics of crystallization of atmospheric droplets, we previously showed that the higher the surface tension of a liquid droplet, the more favorable (thermodynamically) the surface-stimulated mode of crystal nucleation. In the present work, we have considered multicomponent droplets and have studied how the adsorption of soluble surfactants at the droplet surface can affect the thermodynamics of crystal nucleation.

Within the framework of Gibbsian thermodynamics, using the concept of dividing surfaces, we have proposed a model for an equilibrium binary droplet to determine the main physical characteristics of both the interior and the surface layer of the droplet. The theoretical model is illustrated by numerical calculations for aqueous nitric acid droplets.

We have shown that an increase in the surfactant concentration in the interior of the droplet causes an increase in the surfactant concentration at the surface layer. Although this leads to a decrease in the surface tension of the droplet, the condition of partial wetting may still hold because of a possible increase in the solid−liquid surface tension of some crystal facets. Thus, surface-stimulated crystallization of atmospheric droplets may dominate the volume-based process even at high concentrations of soluble surfactants. Furthermore, numerical evaluations clearly show that for a fixed overall droplet composition the surface tension increases as the droplet size decreases. This increase is related to an increase in the surface-to-volume ratio as the droplet radius decreases. For small droplets, there are not enough surfactant molecules to ensure the surface coverage characteristic of the bulk solution; that is, the impeding effect of soluble surfactants on the surface-stimulated mode of crystallization becomes weaker as the droplet size decreases. Thus, the condition of surface-stimulated crystallization is more likely to hold for droplets of smaller sizes. Therefore, a decrease in the droplet size favors the surface-stimulated mode of crystallization both kinetically and thermodynamically. Numerical calculations show that for aqueous nitric acid droplets the size dependence of the adsorption effect is important for droplets smaller than 30 nm in radius.

Our model also provides the dependence of the excess surface coverage on the droplet radius. For a fixed overall droplet composition, the surface coverage decreases with decreasing droplet radius, and this decrease becomes particularly sharp for droplets with $R \lesssim 30$ nm. This is accompanied by the depletion of surfactant molecules in the droplet interior. These effects can have significant atmospheric implications. Indeed, the rates of many heterogeneous chemical reactions on atmospheric particles depend on the droplet surface composition, which is influenced by adsorption effects. Our model can provide a simple formalism to take adsorption effects and their size dependence into account to add more rigor to quantitative studies of heterogeneous chemical reactions on atmospheric aerosols containing soluble surfactants.

Finally, we showed that the adsorption of organic trace gases onto the surface of aqueous nitric acid droplets can significantly lower the droplet surface tension and thus impede the surface-stimulated mode of crystallization. Although quite plausible, this result remains qualitative because of a lack of data on the adsorption of organics at the surface of bulk aqueous nitric acid solutions.

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