Dipole Moment of Condensing Monomers: A New Parameter Controlling the Ion-Induced Nucleation

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Many chemically active, hazardous, and toxic substances have a high dipole moment, and they interact strongly with the charged particles and molecular ion clusters. A new nucleation model considering the contribution of the dipole-charge interaction to the ion-induced nucleation rates is developed, with the dipole moment of the condensing monomers as a new parameter. It is shown that in the polar vapors the influence of the dipole-charge interaction on the nucleation rates may be much stronger than the Thomson effect. The new model is an extension of the classical ion-induced nucleation theory, and can explain the deviation between the experimental data and the predictions of the classical ion-induced nucleation theory.

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Nucleation on ions plays an important role in the formation of atmospheric aerosols that are directly associated with the Earth's climate and air quality [1–7]. Although the relevance of the ions to the atmospheric aerosol formation and air quality was established a long time ago, the theoretical basis of the classical ion-induced nucleation (IIN) [8] has not been advanced since the late 1930s [9]. The classical IIN theory is considered as a good approximation for some practical applications [10]; however, it fails in predicting the ion-induced nucleation rates and properties of small cluster ions consisting of polar molecules [11]. It has been found [11] that below the saturation point the classical IIN theory systematically underestimates the equilibrium cluster size compared to the experimental data. Recently, the explanation of this discrepancy has been given by [12] where it has been pointed out that it is due to the dipole-charge interaction neglected in the classical Kelvin-Thomson model. Another fundamental problem of the IIN theory is its inability to predict an observed strong dependence of the nucleation rates on the ion features in polar vapors [13,14].

In this Letter we attack this problem by extending the classical IIN theory to the nucleation in the polar vapors. We develop a new theory of the ion-induced nucleation and show that the different dependence of the nucleating substances on the ambient ionization is associated with the dipole moment of condensing monomers, which is a new parameter controlling the ion-induced nucleation.

Consider the formation of a molecular cluster consisting of $i + 1$ molecules [$(i + 1)$-mer] by the attachment of a single vapor molecule (monomer) on the i-mer. For such a process the barrier-crossing or nucleation rate can be obtained using the Becker-Doring model [9,15–17] assuming the constrained equilibrium distribution [16]. Following the classical derivation, one gets the general equation for the nucleation rate valid for the arbitrary form of β_i and ΔG_i,

$$J = N\left\{\sum_{i=n_0}^{i_{\max}-1}\left[\beta_i \exp\left(\frac{-(\Delta G_i - \Delta G_{n_0})}{k_B T}\right)\right]^{-1}\right\}^{-1}, \quad (1)$$

where J is the nucleation rate, n_0 is the number of the molecules in the stable ion cluster, k_B is the Boltzmann constant, N is the ion number concentration, ΔG_i is the change in the Gibbs free energy associated with the formation of i-mer, β_i is the forward rate constant for the collision of monomers with i-mer, and $i_{\max}$ is sufficiently larger than n^*, where n^* is the number of the molecules in the critical embryo.

The classical IIN theory expresses the effect of the particle surrounding the nucleation rates in terms of the thermodynamics of the bulk gas phase that limits the number of variables entering into the problem of the ambient gas temperature and vapor concentration only [18]. However, it has recently been found that the interaction of the polar vapor monomers in the gas phase with the electrical field of the charged embryo may significantly influence both the thermodynamic properties [12] and the growth kinetics [19] of the clusters formed. In the classical IIN theory no interaction between the colliding particles is allowed, and thus the number of collisions between monomer and single i-mer per unit time $\beta_i^{(c)}$ is given by a simple kinetic theory [16]. The interaction of the condensing monomer with the charged cluster enhances the effective collision cross section that increases the growth rate accordingly $\beta_i = \mathrm{EF}_i \beta_i^{(c)}$, where EF_i is the enhancement factor [19]. Thermodynamics of n-mer formation is associated with the change in the Gibbs free energy [8,19],

$$\Delta G = \Delta\mu n + \sigma A + \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left[\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right]\left[\frac{1}{r} - \frac{1}{r_0}\right], \quad (2)$$

where μ is the chemical potential, q is the number of elementary charges in the particle, e_0 is the elementary charge, ε_r is the relative permittivity of the embryo, ε_g is the relative permittivity of gas mixture, ε_0 is the vacuum permittivity, σ is the surface tension, A is the particle surface area, r is the particle radius, r_0 is the radius of the core ion, and n is the number of molecules in the cluster.

The classical IIN theory is derived assuming the flat vapor concentration profile in the vicinity of the growing particle or cluster that leads to the following equation for the difference in the chemical potentials of the gaseous and the condensed phases $\Delta\mu = \mu_L - \mu_g = \mu_L - \mu_{g\infty} = -k_B T \ln S$. Here S is the supersaturation ratio, and subscripts g, ∞, and L refer to the gas phase, ambient vapor, and condensed phase, respectively. However, in the polar vapors the condensing monomers are involved in the interaction with the electrical field of the charged embryo that increases their concentration in the vicinity of the charge particle or cluster and raises the vapor pressure over the particle or cluster surface (p_s) [12,20]:

$$\ln\left(\frac{p_s}{p_\infty}\right) = \frac{\alpha(qe_0)^2\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)^2}{32\pi^2\varepsilon_0^2 r^4 k_B T} + \ln\left\{\frac{\sinh\left[\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{qe_0 l}{4\pi\varepsilon_0 k_B T r^2}\right]}{\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{qe_0 l}{4\pi\varepsilon_0 k_B T r^2}}\right\} = C_d(l, r, T), \tag{3}$$

where l is the dipole moment of condensing monomers and α is the polarizability. In order to obtain the size of the equilibrium cluster ion and critical embryo, one performs the search for the extreme points of function ΔG that lead to the following formula [12]:

$$\ln S = S_\sigma(r) + S_T(r) + S_d(r), \tag{4}$$

where r is the radius of either equilibrium or critical cluster. Terms $S_T(r) = \frac{-M}{k_B T\rho}\left(\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right)\frac{(qe_0)^2}{32\pi^2\varepsilon_0 r^4}$ and $S_\sigma(r) = \frac{M}{k_B T\rho}\frac{2\sigma}{r}$ relate to the Thomson and Kelvin effects, respectively, and $S_d(r) = -C_d(r)$ is the correction due to dipole-charge interaction. Here M is the mass of the vapor molecule and ρ is the bulk density of condensed phase. Equation (4) is a generalized form of the classical Kelvin-Thomson equation [18] corrected by the effect of vapor polarity. Now we complete the derivation by combining the basic equations [(1)–(3)] to obtain

$$J = N\left\{\sum_{i=n_0}^{i_{\max}}\left[\mathrm{EF}_i\beta_i^{(c)}\exp\left(\frac{-(\Delta G_i - \Delta G_{n_0})}{k_B T}\right)\right]^{-1}\right\}^{-1}, \tag{5}$$

where $\Delta G_i = \Delta G_S + \Delta G_\sigma + \Delta G_T + \Delta G_d$, $\Delta G_S = -k_B T \ln S i$, $\Delta G_\sigma = \sigma A(i)$, $\Delta G_d = -k_B T C_d i$, with $\Delta G_T = \frac{q^2 e_0^2}{8\pi\varepsilon_0}\left[\frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_r}\right]\left[\frac{1}{r(i)} - \frac{1}{r_0}\right]$. ΔG_S, ΔG_σ, ΔG_T, and ΔG_d relate to the vapor activity in the gas phase, surface tension, Thomson effect, and dipole-charge interaction, respectively. According to the classical scenario ([16], pp. 553–555), we simplify (5) by replacing the summation with an integral and expanding ΔG_i in a Taylor series around its minimum and get, after some algebra, the expression for the nucleation rate in the close analytical form

$$J = \mathrm{EF}_{n^*} N \beta_{n^*}^{(c)} \exp\left(\frac{-(\Delta G_{n^*} - \Delta G_{n_0})}{k_B T}\right). \tag{6}$$

As may be seen from Eqs. (5) and (6), the dipole-charge interaction modifies the ion-induced nucleation rates through both the enhancement of the condensation ($\beta_{n^*}^{(c)}$) and the reduction of the evaporation (exponent). While the classical IIN theory includes the Thomson effect related to the properties of the condensed phase only, the new theory suggests that both the Thomson effect and the dipole-charge interaction in the gas phase have to be accounted for simultaneously.

The relative importance of dipole-charge interaction term $S_d(r)$ and Thomson term $S_T(r)$ can be seen from the values of the ratio $\phi(r) = S_d(r)/S_T(r)$. Figure 1 shows the values of $\phi(r)$ for eight different species. The species shown are chosen in such a way as to represent a wide spectrum of materials including key nucleation precursors and common chemically active or/and hazardous materials. At $r > 1$ nm, which is the typical size of the critical clusters at given conditions, the effect of the dipole-charge interaction is much stronger than that of the Thomson effect in all the cases studied here. The dipole-charge interaction reduces the size of the critical embryo and lowers the potential barrier of the cluster formation. This suggests that the dipole-charge interaction neglected in the IIN theory might be a reason for the disagreement [13,14] between the IIN and the experimental data.

In order to quantify the effect of the dipole-charge interaction on the nucleation rates, the calculations of the reduced critical supersaturation and comparison of the results obtained with the experimental data [14] have been performed. In [14] the critical supersaturation S_{cr} (defined as the supersaturation at which a steady nucleation rate is of 1–3 drops $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$) of both homogeneous nucleation and ion-induced nucleation, by the radon

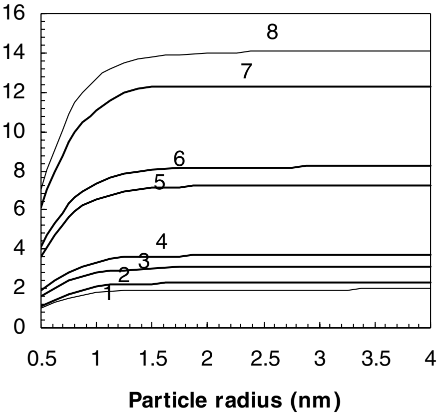

FIG. 1. $\phi(r) = S_d(r)/S_T(r)$ for *n*-butanol (1), isopropanol (2), ethanol (3), ammonia (4), acetone (5), sulfuric acid (6), water (7), and hydrogen cyanide (8) at the ambient temperature of $T = 298.15$ K.

decay of ethanol, methanol, 1-propanol, and 1-butanol as a function of the temperature, has been measured. In order to study the effect of ions on the critical supersaturations, we plotted the ratio of the critical supersaturations for ion-induced $S_{cr(ion)}$ and homogeneous $S_{cr(h)}$ nucleation denoted as reduced critical supersaturation (reduced $S_{cr} = S_{cr(ion)}/S_{cr(h)}$) versus ambient temperature. Figure 2 compares the values of reduced critical supersaturation predicted by the classical IIN theory [Eqs. (4)–(6), dipole-charge interaction neglected ($\Delta S_d = 0$, $\Delta G_d = 0$)] and the present theory (same equations, all the terms included).

As seen from Fig. 2, the classical IIN theory contracts with the experimental data. Moreover, it predicts the increase in the critical saturation ratio in all the cases studied. This is not surprising because the difference in the preexponential factors of the homogeneous and IIN nucleation theories, which is defined as the ratio of the monomer and ion number concentrations, is very high ($\sim 10^{10}$–10^{12}), and the reduction of the negative Gibbs free energy in the exponent due to the Thomson effect is not big enough to cover this difference. On the other hand, the new theory, accounting for the dipole-charge interaction, predicts the effect of ions on the nucleation rates accurately. The model predictions of the absolute values of the critical supersaturation ratio ($S_{cr(ion)}$, not shown) are also consistent with the experimental data. The temperature dependence of the absolute values of $S_{cr(ion)}$ predicted with the new theory (not shown) for 1-butanol and 1-propanol are in very good agreement with the experimental data, whereas those for methanol and ethanol differ by ~(10–25)%. This difference is likely due to the uncertainties in the surface tension data. Since no data for methanol and one point for ethanol are available in the literature for the temperatures below 290 K, we had to use the extrapolated temperature dependence of the surface tension. The contribution of the kinetic correction is small in all the cases studied here; however, it may be essential when the size of the critical embryo is below ~1 nm. The calculations show that the dependence of the nucleation rates in the polar vapors on the ion features is due to the dipole-charge interaction. This also agrees with the findings of [13,21], which demonstrated that the ionization reduces the critical supersaturation for polar dibutilphtalate [13], while the nucleation of nonpolar hexane and n-nonane is not affected by ions [21].

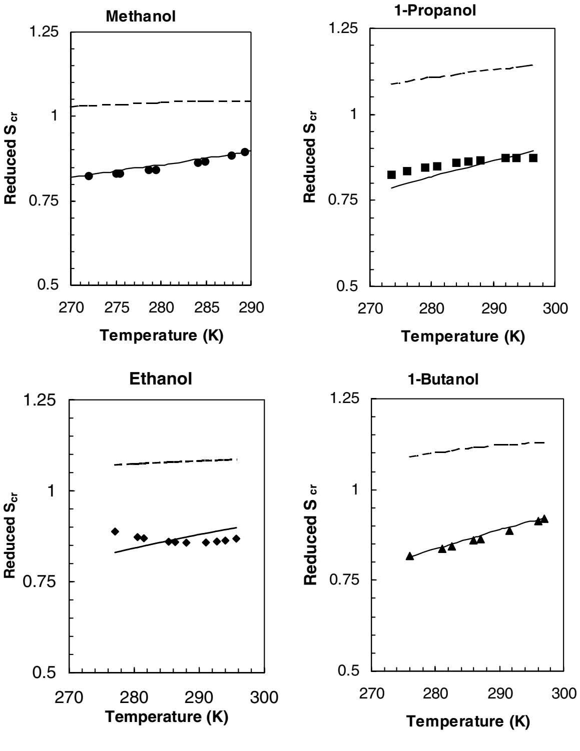

FIG. 2. Reduced critical supersaturation for ion-induced nucleation corresponding to the particle production rate of $2\ \mathrm{cm}^{-3}\ \mathrm{s}^{-1}$ given by the classical IIN (dashed lines) and the present study (solid lines). Filled symbols refer to the reduced critical supersaturation obtained from the experimental data [14].

This Letter demonstrates the influence of the dipole-charge interaction on the ion-induced nucleation. We suggest that the inconsistencies of the classical IIN theory with observations arise from the neglecting of the dipole-charge interaction and propose a new model of the nucleation rates accounting for this effect. The new model is a generalization of the classical theory of the ion-induced nucleation extended to the nucleation in polar vapors. This theory explains a different behavior of polar and nonpolar substances when nucleating and agrees with the experimental data of He and Hopke [14]. Calculations show that in the case of polar gases the effect due to the dipole-charge interaction may be much bigger than the Thomson effect, and thus the influence of the charge-related effects on the thermodynamics of the particle formation and nucleation kinetics may be much stronger than it was assumed earlier. Interaction between the charged cluster and polar vapor molecules reduces the potential barrier of the critical embryo formation that decreases the critical saturation and, consequently, polar gases, which are often active chemically, hazardous or toxic, and have a great advantage over the neutral ones when nucleating. This means that the dipole moment of the monomers in the nucleating vapors is a new parameter controlling the ion-induced nucleation.

Although the present theory is not focused on the sign effect, it possesses some potential for explaining the sign preference because both the enhancement factor EF and correction to the chemical potential of the condensable vapor strongly depend on the stretch of electrical field and the mean cluster density, which may be different for positive and negative molecular ions due to the different cluster geometry and charge distribution.

The new theory may be applied to the microphysics of the aerosol formation, air quality research, inhalation toxicology, chemical technology, environmental control in the nuclear material processing, and physicochemical processes in the dusty plasma.

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