

Heterogeneous Nucleation onto Monoatomic Ions: Support for the Kelvin-Thomson Theory

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In this study, the process of heterogeneous nucleation is investigated by coupling a high-resolution differential mobility analyser (DMA) to an expansion-type condensation particle counter, the size-analyzing nuclei counter (SANC). More specifically, we measured the activation probabilities of monoatomic ions of both polarities by using n-butanol as condensing liquid. All seed ions were activated to grow into macroscopic sizes at saturation ratios well below the onset of homogeneous nucleation, showing for the first time that the SANC is capable of detecting sub-nanometer sized, atomic seed ions. The measured onset saturation ratios for each ion were compared

to the Kelvin-Thomson (KT) theory. Despite the fact that certain dependencies of activation behaviour on seed ion properties cannot be predicted by the KT theory, it was found that with a simple adjustment of the n-butanol molecular volume (9–15% lower compared to bulk properties) good agreement with experimental results is achievable. The corresponding density increase may result from the dipole-charge interaction. This study thus offers support for the application of the KT model for heterogeneous, ion-induced nucleation studies at the sub-nanometer level.

1. Introduction

Phase transitions from the gaseous to the liquid or solid state (nucleation) can occur in the case of supersaturated vapors. This process is of importance in understanding particle formation and growth in the ambient environment^[1] as well as in soot formation combustion systems.^[2] Nucleation can occur homogeneously without the presence of other liquid/solid compounds, or heterogeneously through the formation of vapor clusters on an already present seed molecule or particle. Homogeneous nucleation has been investigated by different experimental and theoretical means, using de Laval nozzles,^[31] two-piston expansion chambers,^[32] and with large scale molecular dynamics simulations.^[33] Nonetheless, there remain a number of issues related to nucleation that remain poorly understood, and further experimental and theoretical studies are needed to fully understand and predict gas phase to condensed phase transitions.

One such feature of nucleation in need of improved understanding is the formation of condensed droplets of a vapor onto pre-existing seeds of a different chemical composition. The presence of seed species can lower the energy barrier for the phase transition process, and thus enables condensed phase formation at lower vapor concentrations compared to the homogeneous process.^[3] Of particular interest is heterogeneous nucleation of vapor onto ions, as models of the interaction between the neutral condensing vapor and charged aerosol particles predict a significantly lower energy barrier for nucleation. Specifically, in classical models of ion-induced nucleation there is a local minimum in the free energy (as a function of condensed phase droplet size) corresponding to ion-vapor molecule complexes containing a certain number of vapor molecules (stable prenucleation clusters) followed by a maximum corresponding to larger sized complexes (critical clusters, after which growth is no longer limited by an energy barrier).^[7]

Testing the applicability of classical models in describing ion-induced nucleation requires very accurate measurements of the nucleation rate or activation probability (i.e. the probability that super-micrometer droplets will nucleate from an existing seed ion as a function of saturation ratio). Accurate measurements of activation probabilities for ions require uniform supersaturations of the condensing vapor, as well as chemically homogeneous seed ions.^[4] It is known from previous studies that heterogeneous, ion-induced nucleation is highly affected by both, the condensing vapor chemical structure and the seed ion properties, including the ion size, structure, chemical composition, and charge state.^[5,11] However, the classical ion-induced nucleation theory, also referred to as Kelvin-Thomson Theory (KT),^[6,7] only incorporates bulk vapor properties (surface tension and dielectric constant) and geometric descriptions of

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ion properties (ion size) to predict heterogeneous nucleation rates and activation probabilities. Therefore it can hardly be used to explain the dependence of the nucleation process on chemical structure or charge polarity. It is hence not surprising that several experimental studies of nucleation onto ions have yielded significant deviations from KT predictions,^[5,8–13] however, the actual origins of these deviations are often hard to identify. Difficulties in testing the accuracy of KT theory derive primarily from the way prior experiments have been performed. In most studies the nucleation process is studied experimentally by measuring the activation behavior of ions.^[5,11] Accordingly the droplets are measured only after they have passed the energy barrier and the droplets have grown into macroscopic sizes. Very often these measurements are performed in condensation particle counters (CPCs),^[14] where ions pass through a profile of different saturation ratios and temperatures in the growth zone, i.e. ions are not exposed to a uniform vapor concentration and temperature for a prescribed time, and it is difficult to uniquely link the activation probability to experimental parameters. Alternatively, ion mobility in combination with mass spectrometry has been used to examine vapor molecule adsorption onto chemically and structurally identified ions.^[9,15,16] However, such measurements are only possible under sub-saturated conditions, and hence can only serve as indirect test of models predicting nucleation rates and probabilities.

An ideal test of KT theory would involve (1) monodisperse ions of simple composition, (2) measurement of the activation probability in a region of uniform supersaturation, and (3) ions which neither dissolve nor change composition or structure during the heterogeneous nucleation process. Such experiments would allow to test the validity of the KT theory, and help understanding how initial formation of prenucleation clusters affects the critical cluster size and the activation energy behavior. The current study satisfies criteria (1)–(3) to a good approximation. We have utilized ion mobility spectrometry to isolate a series of monoatomic ions at atmospheric pressure for subsequent investigation of heterogeneous ion induced nucleation. Specifically, to examine heterogeneous nucleation, we adopt the approach introduced by Winkler et al.^[17] In this prior study, larger R_4N^+ ions were used for nucleation studies of n-propanol. This study showed that seed ions smaller than the critical cluster size predicted by KT theory can be activated to grow into macroscopic droplets, however, the influence of changing ion conformation/solvation may have had an influence on n-propanol condensation onto R_4N^+ ; this may complicate interpretation of the results. In employing monoatomic ions of both polarities as seeds in the current study to investigate the nucleation of n-butanol, we exclude the possibility of structural/conformational modification upon vapor attachment. Monoatomic ions can be better approximated as spherical seeds than molecular ions, and monoatomic ions are small in size in comparison to n-butanol vapor molecules.

2. Experimental Section

We examined the nucleation probability of monoatomic ions upon introduction of n-butanol into the size analyzing nuclei counter (SANC).^[21] For measurements, the ions were generated via electrospray ionization (ESI) of 10 mM solutions in methanol from KI, RbI, CsI, and THABr (tetraheptylammonium-bromide) in N_2 . Depending on the polarity applied to the electrospray source, THA^+ , K^+ , Rb^+ , Cs^+ , or I^- , and Br^- ions were formed, but ESI also generates cluster ions of a variety of charge states (e.g. $[Cs]_n[Cs+I]_z$).^[18] To isolate only the atomic ions (or THA^+ in the case of THABr ESI), a high-resolution (resolving power of ~ 50) parallel plate differential mobility analyzer (DMA, Model P5, SEADM Inc., Madrid, Spain), which acts as filter, only transmitting ions with mobilities in a narrow range,^[19] was operated with a fixed sheath flowrate of N_2 and fixed voltage to maximally transmit only the seed of interest; this was possible because no multiply charged cluster ions had similar mobilities to the monomer ions. The DMA was calibrated with tetraheptylammonium⁺ (THA^+) ions as described previously,^[20] and the chemical composition of generated ions was confirmed in a tandem system consisting of a DMA and a mass spectrometer (DMA-MS, QSTAR XL quadrupole-time-of-flight MS, MD Sciex) as described in Maisser & Hogan.^[15] The concentration of the generated ions was monitored by an electrometer to ensure stability of the ion source.

A flow of 6 l/min exited the DMA. The exiting flow was split and 3 l/min were used to measure the particle number concentration with a Faraday Cup Electrometer (FCE). The remaining 3 l/min flow was introduced to the SANC, which is an expansion chamber that exposes the ions to a uniform and well-defined vapor concentration and controlled temperature (and hence controlled supersaturation), while utilizing light scattering to infer the concentration of nuclei grown to super-micrometer droplets. The vapor used was n-butanol (which is predominantly used in commercial detection systems relying on heterogeneous nucleation)^[14] and was introduced into the system by controlled injection from a syringe pump, followed by evaporation in a custom-made heating unit. Before entering the expansion chamber the flow containing the seed ions considered was mixed with the well-defined nearly saturated vapor-air stream from the evaporation system. Vapor supersaturation was achieved by adiabatic expansion. The heterogeneously formed droplets were measured by the Constant Angle Mie Scattering (CAMS) method.^[22] With this method both the radius of the droplets and the number concentration can be determined simultaneously.

3. Results and Discussion

The activation probability P is measured by the SANC/CAMS method and is expressed as:

$$P = \frac{N_a}{N_t} = 1 - \exp(-Jt) \quad (1)$$

N_a is the number of activated seed ions, N_t is the total number of seed ions, J is the heterogeneous nucleation rate, and t is the time for activation. The onset saturation ratio S_{onset} for a specific seed ion is defined as the saturation ratio at $P = 0.5$. Shown previously,^[23] the activation probability about S_{onset} has the form of a cumulative Gumbel distribution:

$$P(S) = 1 - \exp\left\{-\exp\left[\ln(\ln 2) + (n^* + 1)\left(\ln\left(\frac{S}{S_{\text{onset}}}\right)\right)\right]\right\} \quad (2)$$

where n^* is the number of additional vapor molecules (onto the prenucleation cluster) required to form a critical cluster. S_{onset} and n^* can hence be determined by fitting to experimental measurements. These two fit parameters are related to the slope of the activation curve:

$$\left(\frac{dP(S)}{dS}\right)_{S=S_{\text{onset}}} = \frac{\ln 2}{2} \frac{(n^* + 1)}{S_{\text{onset}}} \quad (3)$$

Using equations (2) and (3), we are able to analyze the experimental nucleation data independent of any theoretical model by applying the nucleation theorems.^[24,25]

The heterogeneous nucleation probability (P) was measured as a function of saturation ratio at a temperature of 271.5 ± 1 K. In all experiments, the concentration of seed ions was sufficiently small to prevent substantial vapor depletion due to condensation and such that the heat of condensation did not lead to a detectable increase in temperature. During growth the temperature in the system will certainly rise, however, during the short time of nucleation conditions it is assumed to be constant. Results are plotted in Figure 1 for all monoatomic

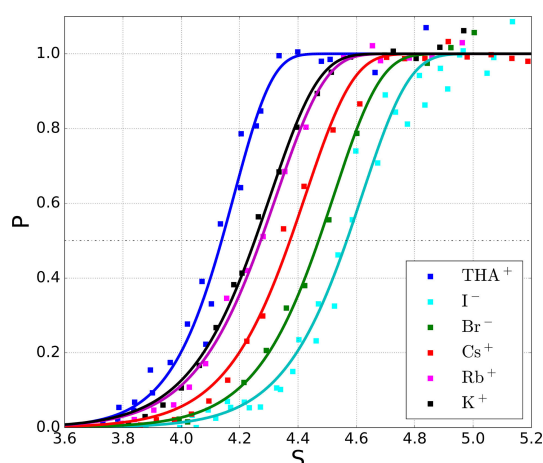


Figure 1. The experimentally measured activation curves for 5 different monoatomic ions and THA^+ ; the solid lines represent the least square fits of $P(S)$ according to equation Eq. 2. The temperature for each measurement was 271.5 K.

ions and THA^+ . Deviations of the experimental data points from the curves are primarily attributable to statistical fluctuations in the concentration of seed ions present in the expansion chamber. It should be noted that all measured S_{onset} values are significantly lower than S_{onset} determined for the homogeneous case, which for n-butanol at this temperature is between 5.5 and 6.^[29] The experimental data shows that the THA^+ ion exhibits the lowest onset saturation ratio compared to the monoatomic ions. This is in line with theoretical models predicting that larger ions require lower super-saturations to

get activated. However, Figure 1 and Table 1 also show that for the five monoatomic ions with increasing ionic radius, a higher S_{onset} is needed for the nucleation of droplets onto ions. Evident in the data is also that negatively charged ions require higher onset saturation ratios compared to positively charged ions. These findings are in line with the ion mobility measurements of Maisser & Hogan,^[15] where it was found under sub-saturated conditions that n-butanol would adsorb to smaller atomic ions to a greater extent than it would to larger ions.

Applying the KT theory, the total Gibbs free energy change for the formation of a cluster composed of n molecules of the condensing liquid about a seed ion is given by the equation:^[27,30]

$$\Delta G_n = -nk_B T \ln S + 4\pi\sigma(r_n^2 - r_0^2) - \frac{(qe)^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_l}\right) \left(\frac{1}{r_0} - \frac{1}{r_n}\right) \quad (4a)$$

where σ is the surface tension of the condensing liquid, q is the integer charge state of the ion, e is the unit electron charge, ϵ_0 is the permittivity of free space, ϵ_l is the dielectric constant of the condensing liquid, r_0 is the seed ion effective radius, and r_n is the effective radius of the cluster with n molecules of the condensing liquid.

Approximating condensed clusters as spheres links the radius to n via the equation:

$$r_n = \left(r_0^3 + \frac{3V_m n}{4\pi}\right)^{\frac{1}{3}} \quad (4b)$$

where V_m is the molecular volume of the condensing liquid. Substituting (4b) into (4a) and differentiating with respect to n yields:

$$\frac{d\Delta G_n}{dn} = -k_B T \ln S + 2\sigma V_m \left(r_0^3 + \frac{3V_m n}{4\pi}\right)^{-\frac{1}{3}} - \frac{(qe)^2 V_m}{32\pi^2 \epsilon_0} \left(1 - \frac{1}{\epsilon_l}\right) \left(r_0^3 + \frac{3V_m n}{4\pi}\right)^{-\frac{4}{3}} \quad (4c)$$

Setting equation (4c) to zero typically leaves two solutions for n ; the smaller corresponds to a free energy minimum and can be interpreted as the number of molecules of the prenucleation cluster (n_{pre}), while the larger corresponds to a maximum and the number of n-butanol molecules of the critical cluster (n_{crit}). It can be seen in Figure 2 that the KT curves for the monoatomic ions exhibit pronounced minima, except for THA^+ . This is qualitatively in agreement with the observations at sub-saturated conditions, where much lower vapor uptake rates were observed for THA^+ compared to the monoatomic ions.

In order to theoretically explain experimental deviations from the KT theory, modified KT (MKT) models have been introduced like Yu (2005). The MKT accounts for the change in electric potential energy of the ion due to the condensation of the dielectric film, and the associated energy change due to the interaction of the ion with the dipole moment of the

Table 1. A summary of experimentally inferred S_{onset} and n^* values, as well as KT theory bulk and fit n_{pre} , n_{crit} , and V_m . The deviation of n^* values \pm and the percent deviation in V_m from bulk expectations is also noted.

Seed Ion ^[a]	Ion Radius [Å]	S_{onset} exp.	n^* exp.	\pm exp.	n_{pre} bulk KT	n_{crit} bulk KT	n^* bulk KT	n_{pre} fit KT	n_{crit} fit KT	V_m [Å ³] fit KT	V_m Percent
K^+	1.52	4.252	25.81	[23.24, 26.27]	8.8	61.9	53.1	13.71	39.51	129.2	14.9%
Rb^+	1.66	4.272	25.70	[24.89, 26.05]	8.8	61.0	52.2	13.63	39.32	129.6	14.6%
Cs^+	1.81	4.372	26.86	[22.37, 27.80]	8.9	57.0	48.1	13.02	39.87	132.5	12.7%
Br^-	1.82	4.470	28.05	[26.48, 28.25]	9.1	53.4	44.3	12.47	40.52	135.5	10.7%
I^-	2.06	4.567	28.51	[22.07, 36.51]	9.2	50.0	40.8	12.03	40.55	137.9	9.1%
THA^+	5.85	4.138	31.92	[29.60, 32.98]	3.0	61.4	58.4	6.39	38.31	129.8	14.5%

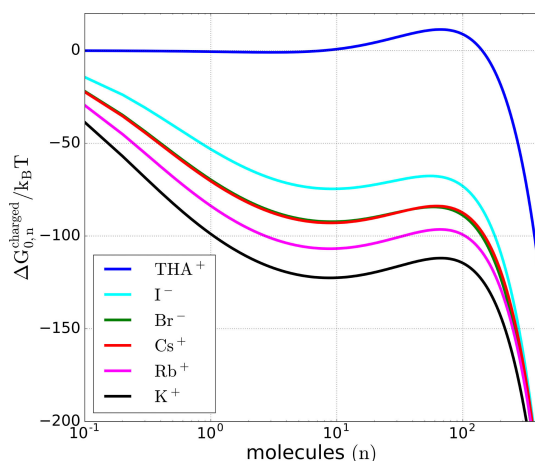


Figure 2. The formation free energies for ion-induced nucleation of n-butanol on different monoatomic ions and THA^+ , according to KT theory.

condensing molecules.^[27] Thereby the total free energy change to form a charged n-mer from the core ion of radius r_0 is given by:

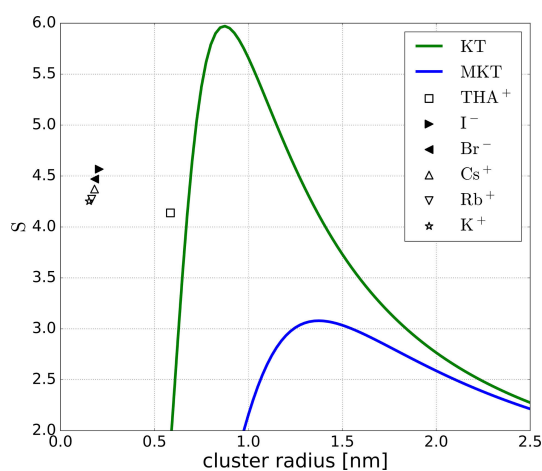


Figure 3. Saturation ratio as a function of cluster radius for KT and MKT theory. The black symbols are the measured onset saturation ratios for the corresponding monoatomic ions depending on their ionic radius.

$$\begin{aligned} \frac{d\Delta G_n}{dn} = & -k_B T \ln S + 2\sigma V_m \left(r_0^3 + \frac{3V_m n}{4\pi} \right)^{-\frac{1}{3}} \\ & - \frac{(qe)^2 V_m}{32\pi^2 \epsilon_0} \left(1 - \frac{1}{\epsilon_l} \right) \left(r_0^3 + \frac{3V_m n}{4\pi} \right)^{-\frac{4}{3}} - \sum_{n=1}^n \frac{1}{2} \alpha E_{n-1}^2 \\ & + k_B T \ln \left\{ \exp \left(\frac{\mu_0 E_{n-1}}{k_B T} \right) - \exp \left(-\frac{\mu_0 E_{n-1}}{k_B T} \right) \right\} / \left(2 \frac{\mu_0 E_{n-1}}{k_B T} \right) \end{aligned} \quad (4d)$$

where E_{n-1} is the electric field strength at $r = r_{n-1} + r_1$ from the center of the core ion:

$$E_{n-1} = \frac{qe}{4\pi\epsilon_0(r_{n-1} + r_1)^2} \quad (4e)$$

and r_1 is the radius of a n-butanol molecule. μ_0 is the permanent dipole moment of the clustering molecule and α is the polarizability of the clustering species.

For comparison, in Figure 3 the measured onset saturation ratios are plotted as a function of the ionic radii, depicted as black symbols and the calculated saturation ratio for KT and MKT theory (equations 4c and 4d, respectively, the left-sides set equal to zero) depending on the cluster radius.

The comparison between experimental data and MKT shows that the onset saturation ratios required for the activation of the considered ions are clearly underestimated by the MKT theory. The reduction of the potential barrier, which is due to the polarizability and the dipole moment of n-butanol molecules, leads to a substantially lower saturation ratio needed for the activation – this is not in line to our observations. Therefore, for further data analysis the Kelvin-Thomson theory according to (4c) was applied.

It can be also seen in Figure 3 that the Kelvin-Thomson theory (green curve) is not capable of predicting the measured values (black symbols), when the onset saturation ratio is plotted versus the ionic radii. To better compare the predictions of the KT model for the prenucleation and critical cluster size to the experimentally determined values of n^* (about S_{onset}), in equation (4c) we set $S = S_{onset}$, equate r_0 with in Table 1 noted ionic radii for each seed ion, and utilize the bulk properties of n-butanol for σ and ϵ_l . Bulk considerations yield a n-butanol molecular volume of $V_m = 151.75 \text{ \AA}^3$. Using this value as shown in Table 1 the values for n^* predicted by the KT model do significantly deviate from the experimental values. However, bulk consideration for V_m , the monomer volume may not be

appropriate for considerations of the prenucleation cluster size regime. Therefore we also opted to fit V_m (approximated to be constant with changing n) to measurements, by forcing difference in equation (4c) solutions to be equivalent the experimental value of n^* , i.e. such that $n^* = n_{crit} - n_{pre}$ is satisfied. As displayed in Table 1 and Figure 4, inferred molecular volumes

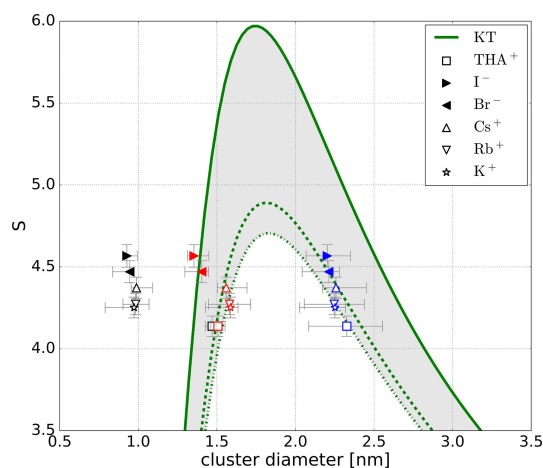


Figure 4. Saturation ratio as a function of cluster diameter for KT theory at 271.5 K, for (solid line) bulk, (dot-dashed line) lowest bulk n-butanol molecular volume and (dashed line) mean bulk n-butanol molecular volume. The black symbols are the measured onset saturation ratios for the corresponding monoatomic ions and THA^+ depending on their mobility equivalent diameter (dry ions, d_p). The red symbols are the resulting mobility diameters for sub-saturated conditions (prenucleation clusters, d_v).^[15] The blue symbols show the size of the critical cluster for the different ion species depending on the mobility equivalent diameter for a sub-saturated environment and the number of molecules n^* acquired by the SANC measurements (critical clusters, $d_k(d_v, n^*)$).

are only 9–15% smaller than the bulk volume, with the degree of disagreement higher for ions with higher measured S_{onset} . We find that in the KT model, the values of n_{pre} and n_{crit} are extremely sensitive to V_m . With this in mind, the observed level of disagreement between the inferred n-butanol molecular volume and the anticipated value is sufficiently small to suggest that although measurements displayed features which are not anticipated based on the KT model (i.e. smaller ionic radii atomic ions have smaller S_{onset}), in large part, this model correctly describes the heterogeneous nucleation process for vapor molecules onto ions, in the absence strong solvation influence or dissolution.

Also displayed in Table 1 are the resulting fit values of n_{pre} and n_{crit} as well as the values calculated applying the KT theory using the bulk value of V_m . For the atomic ions, the fit values of n_{pre} fall within the narrow range of 12–14, while n_{crit} lies in the 39–41 range.

The fit n_{pre} and n_{crit} values falling within similar ranges for all atomic ions suggests that beyond leading to small changes in the molecular volume of sorbed molecules (which suggests that clusters simply adopt slightly different structures based upon the core ion present), the influence of ion size on ion-induced nucleation is well-captured by KT theory. The fit estimates for n_{pre} are also in line with ion mobility-mass

spectrometry measurements^[15] of n-butanol uptake under sub-saturated conditions; in these experiments the observed level of uptake was less than the estimate of n_{pre} made here under supersaturated conditions.

The results for KT theory calculations using (i). the bulk n-butanol molecular volume V_m , (ii). the lowest bulk V_m value determined from the fit and (iii). the mean bulk V_m value for all ions investigated are shown in Figure 4 as solid, dot-dashed and dashed lines, respectively. The data points also displayed in Figure 4 show the values for the dry ions d_p (no uptake, black symbols), the prenucleation clusters d_v (red symbols), and the critical cluster sizes $d_k(d_v, n^*)$ (blue symbols) for all seed ions.

The diameters of the dry ions and error bars were taken from Table 1 of the publication by Maißer and Hogan.^[15] The error bars refer to the values determined according to Larriba and Hogan^[28] for elastic hard sphere scattering (EHSS) and dynamic hard sphere scattering (DHSS).

The prenucleation cluster sizes in Figure 4 are estimated by fitting a vapor uptake curve (simple logarithmic fit function) to the experimental data points for vapor uptake at sub-saturated conditions taken from Maißer and Hogan.^[15] The value for the electrical mobility diameter predicted at a saturation ratio of $S=1$ was assumed to be the prenucleation cluster size.

The critical cluster sizes are calculated applying the experimentally determined n^* under the assumption of perfectly wettable surface and volumetric growth.

The calculations of the formation free energies using the KT model and bulk vapor properties (Table 1), suggest a lower molecular uptake under prenucleation conditions and an increased n^* compared to the lowered V_m determined by fitting n_{pre} and n_{crit} to the experimental data of n^* . Thereby the resulting cluster diameters decreased for prenucleation and increased for critical clusters. However, by applying the decreased monomer volume V_m to KT theory, a reduced saturation ratio for heterogeneous nucleation of n-butanol was found.

The error bars in the x-direction for the prenucleation clusters are related to the uncertainty of the fit curve to the experimental data points for the sub-saturated measurements^[15] which was found to be roughly 3% for all measurements. The uncertainty of the critical cluster sizes are calculated applying the Gaussian error propagation taking into account the uncertainties of the prenucleation cluster size and the uncertainty of n^* determined by the Gumble fit.

The error bars in the y-direction are the uncertainty of the SANC and are 3% for all data points.

Figure 4 results confirm that by reducing the monomer molecular volume, KT theory can explain ion induced nucleation for most of the considered seeds. Only the negative species show a shift to smaller prenucleation cluster sizes but the critical cluster sizes again agree with the corrected KT theory. According to Maißer and Hogan^[15] n-butanol binds more strongly to cations than to anions under sub-saturated conditions, which explains the smaller prenucleation cluster for I^- and Br^- . Thereby the resulting smaller cluster diameter leads to an increased onset saturation ratio for negatively charged monoatomic ions.

Conclusions

This work shows clearly that the presence of monoatomic ions significantly lowers the energy barrier that needs to be overcome (compared to the homogeneous case) in order to form macroscopic droplets. These successful experiments also show that the SANC can be used to detect sub-nm atomic ions. The monoatomic ions act as nucleation seeds and their S_{onset} are significantly lower compared to homogeneous nucleation. In total, we find that high-resolution ion mobility selection followed by exposure to controlled n-butanol supersaturation and controlled temperature provides quantitative information on the heterogeneous nucleation probability for n-butanol onto atomic cations and anions. This serves as a sensitive test of KT theory. There are clear features to experimental results not captured by KT theory predictions, such as an inverse correlation between seed ion size and onset saturation ratio, however, with a simple adjustment of the n-butanol molecular volume (a reduction by 9–15%), KT theory leads to anticipated prenucleation cluster sizes and critical cluster sizes which differ by an amount in near exact agreement with experiments. The volumetric decrease of the polar n-butanol molecules and the ensuing increased molecular density may be a result of the dipole-charge interaction especially under sub-saturated conditions. We hence find support for the application of KT theory in describing the free energy change from the prenucleation cluster to the critical cluster in ion induced nucleation. At the same time, we caution that in the experiments performed here, the seed ions were selected to be a model system to test KT theory capability; heterogeneous nucleation onto ions which can dissolve, change structure, or are even deformed slightly to different conformation spaces when dry and when solvated may require a more detailed model for rate prediction.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: atomic ions · heterogeneous nucleation · ion-induced nucleation · Kelvin-Thomson Theory · n-butanol

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