

HETEROGENEOUS NUCLEATION OF N-BUTANOL VAPOR ON VARIOUS MONOATOMIC IONS – COMPARISON OF EXPERIMENTS WITH DIFFERENT VERSIONS OF KELVIN-THOMSON THEORY

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INTRODUCTION

The investigation of the fundamental process that enables and predicts phase change is of great interest. Both homogeneous and heterogeneous nucleation/condensation processes are applied for e.g. nanoparticle synthesis, but also are responsible for new particle formation (NPF) in the atmosphere and thus, affect our climate and human health.

With advances in aerosol instrumentation towards smaller and smaller particles an increasing attention was drawn to the investigation of the process of heterogeneous nucleation for seed particles close to the Kelvin diameter. With the introduction of the ultrafine condensation particle counter (CPC) by Stolzenburg and McMurry in 1991 particle detection down to about 3 nm became possible. For a long time the Kelvin diameter was seen as a fundamental lower detection limit for the CPCs. However, this assumption could not hold some experimental investigations. Seto et al. (1997) found that ions of about 1.5 nm could be activated in a turbulent mixing CNC (condensation nuclei counter). Gamero and de la Mora (2000) used dibutyl phthalate vapor and showed that there was no lower limit to the particle size that could be activated. The definite confirmation, that detection below the Kelvin limit is possible, was provided by observations of Winkler et al. (2008) in an expansion type CPC using monodisperse particles down to about 1 nm.

A universal theory predicting heterogeneous nucleation especially for particles smaller than the Kelvin diameter is still missing. Many seed properties that were found to have an influence on nucleation, e.g. polarity and chemical composition, are not considered in classical models such as the classical nucleation theory (CNT). The development of a theory is complicated also due to the lack of meaningful experimental measurements. Accurate experimental measurements of activation probabilities require highly homogeneous nuclei and supersaturations (Fernandez de la Mora, 2010). This still is difficult to achieve using general state-of-the-art aerosol instruments.

In this study we were able to overcome these experimental difficulties by using highly specialized aerosol instruments that can meet both of the prerequisite; firstly, a high resolution and transmission DMA for the size selection of highly monodisperse seed ions of defined chemistry and both polarities; and secondly, an expansion type CPC, exposing the seed ions to a homogeneous supersaturation. In addition to the experimental work we compared the results to existing theories by applying the classical nucleation theory (CNT) for the case of insoluble and perfectly wetting seed particles.

METHODS

Heterogeneous nucleation onto 5 different monoatomic seed ions of both polarities (K^+ , Rb^+ , Cs^+ , Br^- , I^-) was investigated at a nucleation temperature of 271.5K using the Size Analyzing Nuclei Counter (SANC) (Wagner et al. 2003). The ions were generated by electrospray ionization of 10 mM methanol solutions of potassium, rubidium and cesium iodide salt as well as tetraheptylammonium bromide (purchased from Sigma-Aldrich, St. Louis, MO, USA). The ions were classified by a planar differential mobility analyzer (DMA, Model P5, SEADM Inc., Madrid, Spain). The purity of the generated ions was confirmed by DMA – Mass Spectrometry (DMA-MS), using the same planar DMA and a QSTAR XL quadrupole-time-of-flight MS, MD Sciex).

N-butanol vapor was added to the system by controlled injection from a syringe pump, followed by quantitative evaporation in a custom-made heating unit. Thereby, a well-defined and nearly saturated binary vapor-air mixture together with size selected, monodisperse ions from the DMA were passed into the temperature controlled expansion chamber of the SANC (cf. Figure 1). Vapor supersaturation was achieved by adiabatic expansion and the number concentration of droplets nucleated on the ions was measured with the Constant Angle Mie Scattering (CAMS) method (Wagner, 1985). Therewith the radius and the number concentration of the growing droplets can be determined simultaneously.

The nucleation or activation probabilities using the SANC/CAMS method can be expressed as:

$$P = \frac{N_{activated}}{N_{total}} = 1 - \exp(-Jt).$$

Here, J is the related heterogeneous nucleation rate and t is the time for activation. We define the onset conditions as the conditions at which the nucleation probability reaches the value $P = 0.5$.

A schematic diagram showing the experimental setup is illustrated in Figure 1. By varying the injection rate of the syringe pump and the pressure drop in the expansion chamber, different nucleation conditions were analyzed, while keeping the nucleation temperature constant at $271.5 \pm 1K$.

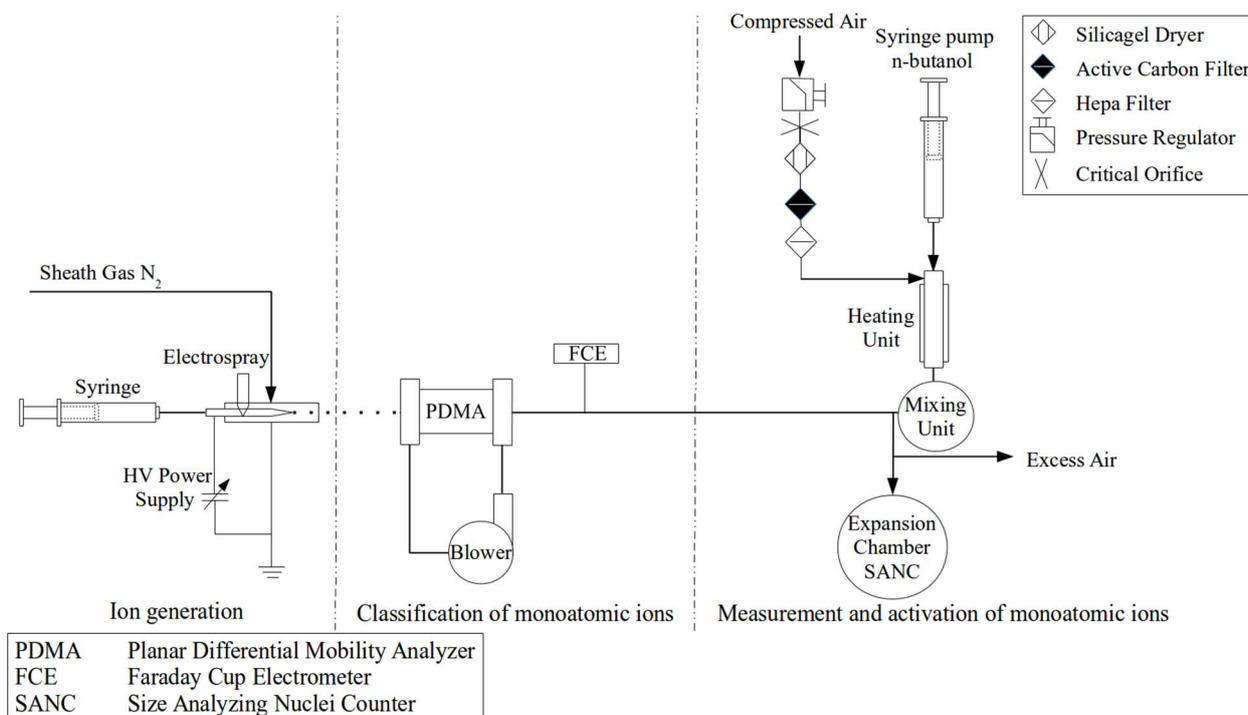


Figure 1. Schematic diagram for the experimental setup.

Experimental saturation ratios determined for n-butanol at constant nucleation temperature for ions with different polarity are shown in Figure 2. It can be seen in the experimental data that negatively charged ions require higher onset saturation ratios compared to positively charged ions. Furthermore the experimental results show that with increasing ionic radius also a higher S_0 is needed for the observed size range. This is related to the ion – dipole interaction, which scales with the inverse of the ion radius. As a consequence, it makes it harder for an already attached vapor molecule to evaporate with decreasing ion size. The nucleation probability $P(S)$ at S_0 has the form of a cumulative Gumbel distribution (Winkler et al. 2016)

$$P(S) = 1 - \exp\{-\exp[\ln(\ln 2) + (n^* + 1)(\ln S - \ln S_0)]\}.$$

By applying this form of distribution as a two-parameter fit function the parameters n^* (additional number of molecules to build a critical cluster) and S_0 can be evaluated. Thereby the onset saturation ratio and n^* can be evaluated simultaneously.

With these results we calculated the total Gibbs free energy change to form a charged n-mer from the core ion of ionic radius r_0 (Shannon, 1976) for the classic Kelvin-Thomson (CKT) and modified Kelvin-Thomson (MKT) equation. In contrast to CKT, the MKT equation also 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 ions with the dipole moment of the condensing molecules (F. Yu, 2005). The corresponding ion-induced formation free energies have a minimum followed by a maximum, corresponding to a pre-nucleation cluster and critical cluster (P.M. Winkler et al. 2012). Thereby we can derive the number of n-butanol molecules in both clusters. To get the radius of the ion together with the condensed butanol molecules, we treated all ions and butanol molecules as a sphere. As a result, the measured onset saturation ratio vs. pre-nucleation and critical cluster radius can be compared to CKT and MKT.

Furthermore, previously conducted measurements for saturation ratios below 1 of the same monoatomic ions with n-butanol and the use of a vapor uptake model (V.K. Rawat et al. 2015) enable us to extrapolate the inverse mobility of the pre-nucleation cluster at a saturation ratio close to one. With these measurements and by using the approximation found by (J.M. Mäkelä et al. 1996) we were able to calculate the mobility equivalent diameter for the pre-nucleation cluster. Furthermore, by using the fit parameter n^* of the Gumbel distribution or the calculated number of molecules in the critical cluster from the total Gibbs free energy we were able to calculate the geometric diameter of the critical cluster.

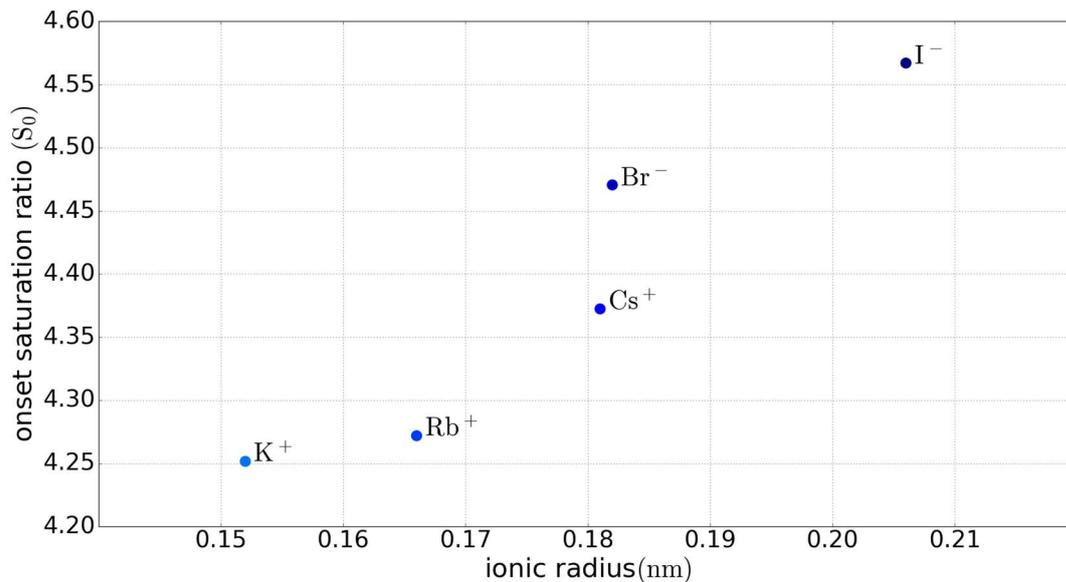


Figure 2. Experimental measurements of the onset saturation ratio vs. ionic radius for the observed ions.

CONCLUSION

We examined the nucleation probability of monoatomic ions upon introduction of n-butanol into the SANC. Thereby we could measure the onset saturation ratio and the additional number of n-butanol molecules to build a critical cluster by applying the Gumbel distribution. With these results and the assumption that the seed ions are spherical and perfectly wettable we were able to calculate the size of the pre-nucleation and critical cluster for different monoatomic ions of both polarities. Furthermore, by applying the vapor uptake model (V.K. Rawat et al. 2015) we were able to calculate the mobility equivalent diameter of the ions at partial pressures of n-butanol below saturation. The results agree well with predictions applying the classic Kelvin-Thomson model.

In summary, we were able to quantitatively characterize the heterogeneous nucleation process for the pre-nucleation and critical nanoclusters using monoatomic singly charged ions of both polarities as seeds. The observed behavior agrees well with predictions from the classical Kelvin-Thomson model.

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