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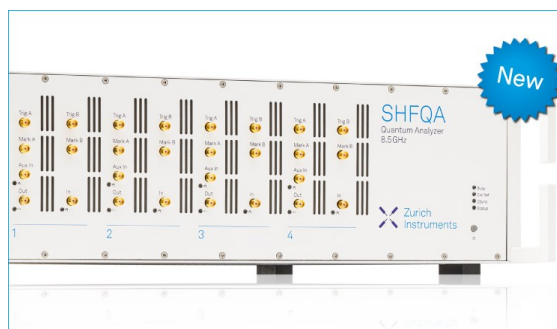**ARTICLES YOU MAY BE INTERESTED IN**

The Role of Dynamic Surface Tension in Cloud Droplet Activation

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Abstract. We present new data on the cloud droplet forming abilities of two-component particles that contain the surfactant sodium dodecyl sulfate and sodium chloride or ammonium sulfate. The experiments were designed to test specific predictions made by Köhler theory that accounts for the reduction of surface tension and the partitioning of the surfactant between the interior and the surface of the droplet. We also introduced a pre-humidification step followed by a six minute time delay to test whether dynamic surface tension may lead to kinetic limitations on the partitioning process. Our results confirm previous studies that show that surfactants do not enhance cloud droplet activation relative to what would be predicted from water activity alone. The data obtained with and without time delay were indistinguishable within measurement uncertainty, suggesting that dynamic surface tension does not need to be considered in Köhler theory.

Keywords: Cloud condensation nuclei, Köhler theory, dynamic surface tension.
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INTRODUCTION

The abundance, size, and chemical composition of cloud condensation nuclei (CCN) play a key role in the microphysical properties of warm clouds. For instance, increasing the cumulative CCN number concentration leads to higher albedo and lower autoconversion efficiency for otherwise equal clouds. The cumulative CCN concentration can be used to predict the cloud droplet number concentration for ascending air parcels and is determined by the aerosol size distribution and chemical composition. In most cases modified Köhler theory adequately predicts the supersaturation required for particles of known mass and chemical composition to serve as CCN. In this framework, particle activation as CCN is described using the molar volumes, activity coefficients, solubilities, and surface tensions of all components comprising a particle. For most inorganic compounds present in the atmospheric aerosol, e.g., various sulfate and nitrate salts, these properties are well-characterized and theoretically understood over a broad range of temperatures. However, this is not the case for organic compounds, which can contribute up to 90% of the non-refractory submicron aerosol. These compounds have a broad range of sources and their chemical composition evolves with time due to continuous exposure to oxidants in the gas and particulate phase, making their contribution to the CCN concentration more difficult to determine.

In the talk I will describe part of our ongoing effort to develop a predictive model for the CCN activity of organic compounds of known chemical structure. Such a model would enable a better understanding how a unique organic compound's indirect impact on cloud and climate systems is changed by factors such as the presence and identity of other compounds and the timescale of droplet formation. In developing such a predictive framework for organic aerosol CCN activation, the role of surface active compounds is an important consideration. In this extended abstract we describe new laboratory experiments of CCN activation using aerosols that contain fractions of strongly surface active compounds. The goal of these experiments was to test the validity of the critical supersaturations predicted by current frameworks that use Köhler and that include surfactants.

MOTIVATION

The treatment of surfactants in Köhler theory is complicated by the surfactants' propensity to concentrate at the surface of the droplet. This leads to a radial gradient of surfactant inside the nucleus. Because the bulk-to-surface ratio is small for sub-micron size droplets, migration of the surfactant to the surface weakens as this migration depletes the bulk concentration of surfactant molecules. Model systems comprising a mixture of sodium chloride (NaCl) and the strong surfactant sodium dodecyl sulfate (SDS) are used here to illustrate this effect. Theory predicts that a substantially higher supersaturation is required to activate a particle consisting of 98% SDS with 2% NaCl by volume than to activate a particle of the same size consisting of 100% SDS (cf. Figure 2 in Raatikainen and Laaksonen[1]). The addition of NaCl raises the concentration of the sodium ion, which is common to both solutes. This raises the critical supersaturation to activate the particle because the common ion alters the gradient in chemical potential and affects the radial distribution of surfactant in the drop[1]. In the absence of the surfactant ion, the addition of the hygroscopic sodium ion would lower the critical supersaturation required for cloud droplet formation.

Although the common ion effect is theoretically understood, experiments using NaCl mixed with SDS or sodium fatty acid salts[2] have not provided a clear experimental manifestation of this effect. Petters and Kreidenweis in 2013[3] speculated that the gradual process of bulk-to-surface partitioning may not occur at the short timescale of CCN experiments, especially if the presence of stable micelles limits the monomer flux to the surface. We therefore performed new CCN experiments that test this hypothesis. In brief, the new experiments expose the aerosol to water saturation after size selection but prior to their entrance into the CCN instrument. In some experiments an additional 6 min delay at high relative humidity (RH) conditions was included. This delay time is ~1000 times longer than the maximum equilibration timescale for surface tension estimated for bulk SDS solutions[4], and thus should be sufficient to probe the system for kinetic limitations.

METHODS

Köhler Theory

Köhler theory predicts the critical supersaturation required to activate a particle of known size. To compare observations from experiments performed at different experimental conditions, i.e. different supersaturations and dry diameters, it is convenient to express CCN activity in terms of its apparent hygroscopicity parameter, κ_{app}. The approximate relationship between the dry particle diameter (D_d), the critical saturation ratio (S_c), and κ_{app} is given by Petters and Kreidenweis[5] and Christensen and Petters[6] as

$$\kappa_{app} = \frac{4A^3 \sigma_w^3(T)}{27T^3 D_d^3 \ln^2 S_c},\qquad(1)$$

where $A = 8.69251 \ 10^{-6}$ K m^3 J^{-1}, $\sigma_w(T)$ is the temperature-dependent surface tension of pure water, and T is temperature. If the solute lowers the surface tension, the relationship between S_c and D_d requires taking concentration gradient inside droplet into account. A relatively simple set of equations to solve this problem is given by Petters and Kreidenweis[3]. Briefly, the model uses the analytical approximation of the surfactant gradient inside the droplet derived by Raatikainen and Laaksonen[1] to predict the critical saturation ratio for a given dry diameter, accounting for both the Raoult effect of the solutes and the surface tension as a function of concentration as fitted to the semi-empirical Szyskowsk equation. The resulting S_c/D_d pair can be evaluated via Eq. 1 to find an expected κ_{app} for mixtures that contain surfactants that are internally mixed with water soluble and hygroscopic solutes.

Experimental

Chemicals used The following chemicals were used: Ammonium sulfate, 99.9% pure (Sigma Aldrich); sodium dodecyl sulfate, 99%+ (Sigma Aldrich); sodium chloride, 99+% (Acros); sulfuric acid p. a. (Fisher Scientific); ultrapure water (in house generated, 18.2 MΩ resistivity, < 5 ppm of organic content). All chemicals were used without further purification.

Particle generation Aqueous stock solutions containing a known ratio of sodium dodecyl sulfate and either ammonium sulfate or sodium chloride were prepared. Aerosols were generated via atomization with a Collison-type atomizer (TSI Inc. 3076).

CCN measurements CCN activity was measured using a Droplet Measurement Technologies (DMT) continuous-flow streamwise thermal gradient CCN instrument. The instrument was operated in two distinct modes. These are dry diameter scans (D_d-scan) or supersaturation scan (*s*-scan). During D_d-scans the CCN instrument operates at constant thermal gradient while a differential mobility analyzer (DMA) sequentially steps through dry diameters. After inversion for multiply charged particles[7] the κ_{app} value can be obtained via Eq. (1). During supersaturation scans, the dry diameter is held constant while the CCN instrument steps through different temperature gradients.

The relationship between temperature gradient and instrument supersaturation is obtained via a calibration described in Christensen and Petters[6].

In all experiments particle size classification inside the DMA occurred at RH less than 10%. In typical CCN experiments the dry particle stream is then passed to a condensation particle counter to obtain total number concentration and the CCN instrument to get CCN number concentration. In the CCN instrument, only the sheath flow is humidified (cf. Figure 1 in Christensen and Petters[6]). The dry sample flow enters the instrument and the sample flow reaches supersaturation within a few seconds[8]. To conduct the humidified experiments, the sample flow of 1.5 L min^{-1} was routed through a Nafion tube (PermaPure, MH-series, 0.110 in. outer diameter, 12 in. long). Liquid water held at room temperature permeates the membrane setting to dew point temperature of the sample flow close to the temperature of the room. The resulting RH was measured to exceed 90%. For experiments that included a delay volume, the humidified sample stream was routed through a 9 L sealed Pyrex bottle. The system resembles a mixed flow reactor and results in an average residence time inside the bottle of 6 min. A small amount of ultrapure water was added to the bottle to ensure that the particles experienced conditions very close to water saturation.

RESULTS

Results from the CCN experiments are summarized in Figure 1. D_d-scans for pure SDS were performed in early 2012 and were obtained using the method described in Christensen and Petters[6]. The vertical bar indicates the variability from 8 scans performed at a streamwise gradient of 6°C. Results from s-scans with different dry diameters, pre-humidification, and time delay settings are also shown. Each point represents the κ_{app} inferred from a single s-scan. Experiments were performed in January 2013 over a consecutive period of ~2 weeks. On any particular day, experiments were performed by performing an s-scan followed by swapping out the stock solution. We adopted this procedure to capture variability between scans and to identify potential sources of variability stemming from our overall experimental procedures.

Superimposed on the results in Figure 1 are the predictions from theory. The solid line and grey shaded area in Figure 1a shows the predicted κ_{app} for the SDS/NaCl system that is identical to the calculations shown in Figure 2 by Petters and Kreidenweis[3], although the considered dry diameter range was narrowed to 60 nm < D_d < 80 nm. For the SDS/$(NH_4)_2SO_4$ system κ_{app} was computed using Eqs. (5) – (7) in Petters and Kreidenweis[3], which assume that there are is no common counter ion. The dashed lines show the predicted κ_{app} from a linear mixing rule that incorporates the κ_{app} of each of the pure components according to their volume fractions in the dry particle[5]. The pure component values used were $\kappa_{SDS} = 0.134$[9], $\kappa_{NaCl} = 1.28$, and $\kappa_{(NH4)2SO4} = 0.6$[5].

The data shown in Figure 1 demonstrate the following:

1. For pure SDS aerosol our observed κ_{app} ranged from 0.1 to 0.18. This is consistent with previous measurements by Rood and Williams[10] and Sorjamaa et al.[11] whose data can be summarized as $\kappa_{app} = 0.18 \pm 0.018$ and κ_{app} 0.15 ± 0.014, respectively.

2. The average κ_{app}, where the term average is denotes the midpoint of the observed range, is virtually indistinguishable from $\kappa_{SDS} = 0.134$ that one would expect if SDS activated according to its water activity and the surface tension of pure water.

3. The addition of either NaCl or $(NH_4)_2SO_4$ to the stock SDS solution did not increase κ_{app} for SDS volume fractions > 0.9.

4. Changing particle dry diameter, introducing pre-humidification, or adding a 6 min time delay between humidification and CCN activation did not lead to systematic changes in the reported κ_{app}.
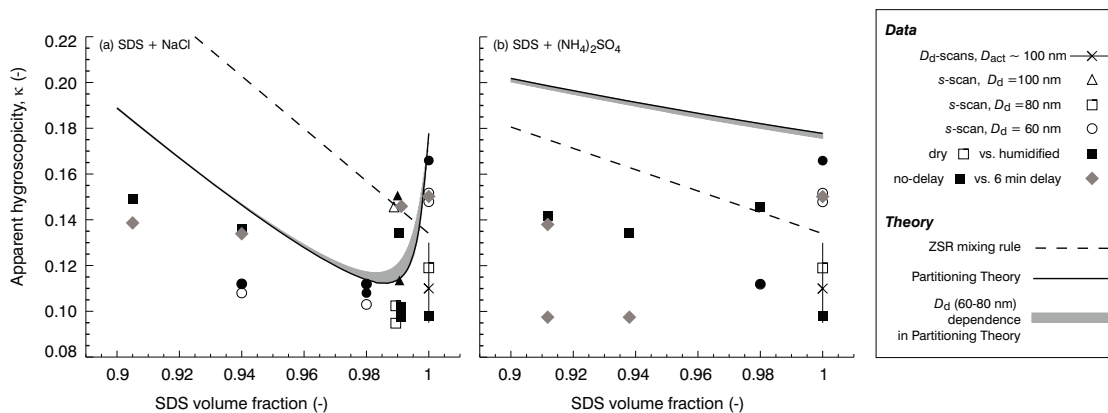

FIGURE 1. Apparent hygroscopicity for internal mixtures of sodium dodecyl sulfate with sodium chloride (a) and ammonium sulfate (b) obtained from a variety of different methods. Symbols, colors, and lines are provided in the legend and methods are explained in the text.

DISCUSSION AND CONCLUSIONS

The clearest conclusion that can be drawn from our experiments is that kinetic limitations appear not to play a role in surfactant partitioning. Results remain indistinguishable within the variability of the measurements even after a 1000-fold increase in residence time over the maximum timescale observed in bulk solutions. A perhaps surprising observation is the lack of sensitivity of κ_{app} to the addition of hygroscopic material. For the SDS/NaCl system this is expected and thus broadly consistent with the prediction made by partitioning theory. Nevertheless, the data do not seem to quite follow the anticipated hockey stick curve traced by partitioning theory for NaCl fractions below 2% (Fig. 1a). There are multiple possibilities why this may be the case. First, the random variability between repeats is relatively high and thus the data should agree more closely with the theory if a larger number of observations were averaged and graphed. Second, the actual composition of the generated aerosol is unknown – the particle composition may not be representative of the bulk solution fractions. This effect has been observed for electrospray aerosol generation[12] and we cannot exclude that this occurred also with the Collison-type atomizer[13] used in this study. Similarly, differential shape effects for the pure SDS and mixed SDS/NaCl particles may potentially bias the mass selected by the atomizer, and thus lead to κ_{app} different from what is expected from theory. Third, solute-solute

interactions are not accounted for in the partitioning model. If present, deviations from theory would be expected since the water activity term would be modeled incorrectly. Finally, the minimum κ_{app} in the partitioning theory curve occurs at a 1% NaCl volume fraction. The addition of similarly small quantities of contaminants has been shown to affect the measurement of sparingly soluble compounds[14,15]. Although the purchased SDS is rated 99%+ in purity, the presence of other anions that may form water soluble sodium salts (e.g. Cl^- or OH^-) is quite likely. If other anions are present, truly pure SDS particles cannot be generated from atomizing stock solutions and the resulting pure SDS measurements could have a low bias. We conjecture that the presence of trace amounts of excess sodium salts could also explain the lower κ_{app} relative to partitioning theory that are observed for the SDS/$(NH_4)_2SO_4$ system.

The objective of our experiments was to experimentally verify or falsify the predicted curve traced by partitioning theory. If this shape could be demonstrated we would regard this as strong proof that surface-bulk partitioning indeed takes place in activating droplets. Similarly, a control experiment akin to the SDS/$(NH_4)_2SO_4$ system should not exhibit a minimum in κ_{app} at high volume fractions due to the absence of common counter ions. We conclude from our data that our proposed strong proof cannot be advanced with current state-of-the-science setups using the SDS/NaCl and SDS/$(NH_4)_2SO_4$ systems. Concurrent measurement of water activity and/or composition of the generated particles and higher precision CCN data are needed. Nevertheless, our results are fully consistent with previous studies that show κ_{app} values lower than those predicted by the ZSR rule over the full range of SDS volume fractions (cf. Figure 2 in Petters and Kreidenweis[3]). The combined sets of data provide unambiguous evidence that the presence of SDS at any concentration does not enhance the CCN activity beyond what is expected from water activity alone. Partitioning theory seems to provide a reasonable prediction of critical supersaturation for strong surfactants.

ACKNOWLEDGMENTS

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