Influence of Ions on the Size Dependent Morphology of Aerosol Particles

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Abstract

The study of aerosol particles composed of mixtures of organic and inorganic compounds provides insights for understanding chemistry in the atmosphere as well as information about phase transitions of systems under confinement. In the submicron size regime, we have previously found that liquid-liquid phase separation can be inhibited at sufficiently small particle diameters leading to phase separated particles at larger sizes and homogeneous particles below a threshold diameter. In this paper, we have investigated the influence of cations and anions in the inorganic compound (NH_4^+, Na^+, SO_4^{2-}, HSO_4^-, and Cl^-) on the phase separation of submicron aerosol particles. Each of five salts were studied with two different organic compounds. Surprisingly, a strong dependence on the identity of the cation is evident in the size dependence of the particle morphology and no

dependence on the anion was found. Sodium containing samples exhibit phase separation in particles below 20 nm in diameter whereas ammonium containing samples cease to undergo phase separation in particles between 45 and 65 nm in diameter. The separation relative humidity for supermicron droplets also depends on the identity of the cation in the inorganic component if the anion is the same across the salts compared. In addition, the correlation between the separation relative humidity and size dependence was investigated and displays a trend, but is not a dominant feature of the data. We explain the results in terms of hard and soft ions, where the harder cation (Na^+) leads to phase separation down to smaller sizes while the softer cation (NH_4^+) prevents phase separation and causes particles up to a larger diameter to remain homogenous. This study has implications for atmospheric chemistry in regions dominated by sea spray aerosol, which contains sodium as the primary cation, when compared to continental aerosol, where ammonium is an abundant cation. Additionally, these findings can be used to understand the influence of cations on the phase transitions of confined materials.

Introduction

Aerosol particles are ubiquitous in Earth's atmosphere and impact human health and climate. Particles can interact with radiation from the Sun in two different ways, directly when they scatter and absorb radiation, or indirectly when they act as nuclei for cloud droplets and the clouds scatter and absorb radiation. The Intergovernmental Panel on Climate Change reports a large uncertainty in the direct and indirect radiative effects of aerosol particles.[1] This uncertainty is in part due to the diversity of aerosol particle types in the atmosphere, which leads to the necessity of simplifying particle types and processes in models. Aerosol particles differ by their composition, size, shape, and internal structure. Below, we refer to the internal structure of particle

components as particle morphology. These factors also influence the water uptake and the heterogenous chemistry that the aerosol particles may undergo.[2-7]

Many particles are composed of mixtures of organic and inorganic compounds (organic/inorganic aerosol particles).[8-10] By organic compound, we mean a compound primarily composed of carbon and hydrogen, but also frequently containing oxygen, nitrogen, and/or sulfur atoms. By inorganic compound, we are typically referring to a salt. As the relative humidity (RH) that a particle is exposed to changes, the particle may change from a solid- or semisolid-like particle to a liquid-like particle and *vice versa*.[11] Additionally, as the water content of the particle is altered, it may undergo liquid-liquid phase separation (LLPS), where the particles form an inorganic core with an organic coating.[12-15] The common morphologies of these particles are homogeneous, core-shell, and partially engulfed.[16-17] LLPS has been found to occur at high RH (>90 %) in secondary organic aerosol particles in the absence of salt as well as in particles composed of organic/inorganic components at a large range of RH values (25 – 100%).[10, 12-14, 18-26] The lower limit is typically due to efflorescence, though in some cases factors like acidity inhibit both LLPS and efflorescence.[27]

The composition determines whether a particle undergoes LLPS. Different salts have different propensities to undergo phase separation depending on the salting out ability of their individual cations and anions. The salting out effect is commonly described using the Hofmeister series, however, other metrics such as Hansen solubility parameters can be used to describe LLPS.[28-29] A previous study on aerosol particles found that as the anions become more kosmotropic (water-ordering), phase separation is less likely to occur, and that the separation relative humidity (SRH) tends to track with the Hofmeister series, that is, kosmotropic salts typically have lower SRH values than chaotropic (water-disordering) salts.[24, 30] You et al. focused

on ammonium sulfate, ammonium bisulfate, sodium nitrate, and sodium chloride with a variety of organic compounds, and primarily investigated the role of the anion.[24] The salting out and SRH trends hold true when the anion originates from inorganic salts, when the anions are added via strong acids, and in systems where the anions are present from both inorganic salts and strong acids.[30] The cations used in the cited studies were H^+ for the acids or a mixture of NH_4^+ and Na^+ with different anions.[24, 30] Aerosol particle studies have focused on the role of the anion because anion effects are often stronger than cation effects.[31]

Another factor that can influence the phase separation of organic/inorganic aerosol particles is the size of the particles. Previous research from our group has shown that phase separation exhibits a size dependence in the submicron size regime. While larger particles undergo phase separation, smaller particles (< ~30 nm in diameter) remain homogenous.[32-34] This trend is expected to be maintained even at infinitely slow drying rates.[32] Drying rate does, however, influence at which size particles transition from homogenous to phase separated.[32] The size dependent morphology can also be impacted by the mechanism of phase separation, that is, whether the particle undergoes LLPS via nucleation and growth or spinodal decomposition.[33] However, to see an influence due to nucleation mechanism, it is necessary for the sample to be in a very narrow region of the phase diagram close to the critical point. Particle morphology is important for particle properties including the fact that it can influence the ability of particles to act as cloud condensation nuclei.[35] By vitrifying aqueous particles, the size dependence in liquid particles and the separation relative humidity have been studied.[36-37] Our previous studies on LLPS in submicron aerosol particles have all used ammonium sulfate as the inorganic component of the aerosol particles.

In this paper, we will outline the influence of cations and anions on the size dependent morphology of submicron aerosol particles. The presence of a size dependent morphology with salts other than ammonium sulfate is shown for the first time with the use of ammonium bisulfate, sodium chloride, ammonium chloride and sodium sulfate. The correlation between the bulk separation relative humidity and the size dependence of the morphology is also investigated.

Experimental Methods

The particles in this study are composed of an organic and an inorganic compound. The organic compounds are 2,5-hexanediol (TCI, > 98.0%) and diethylmalonic acid (Sigma Aldrich, 98%). The inorganic compounds are ammonium sulfate (EMD Millipore,> 99.0%), ammonium bisulfate (Alfa Aesar, >99.9%), sodium chloride (EMD Millipore, > 99.0%), ammonium chloride (BDH, 99.5%) and sodium sulfate (Fisher Chemicals, 99.14%). The aerosol particles were made using 0.03 wt. % solutions with a 2:1 organic to inorganic mass ratio pumped into a constant output atomizer. The particles were then dried to < 5% RH using a diffusion dryer at a rate of ~99% RH/s. A miniMOUDI cascade impactor (TSI 135-8A) was used to collect the particles on 200 mesh copper grids with a carbon film (Electron Microscopy Sciences, Hatfield, PA). Samples were stored in a desiccator until imaging to prevent moisture from contaminating the impacted aerosol particles. The particles were then imaged using a FEI Talos C with a X-FEG source, operating at 200 kV and coupled with cryo-holder and a cryo-box to minimize radiation damage. In this study, particles analyzed were larger than 15 nm in diameter because while the TEM can clearly image smaller particles, it is difficult to use sufficient magnification to obtain the necessary resolution needed to determine internal morphology without destroying the fragile particles. The images were analyzed using ImageJ (NIH, Bethesda, MD). The particles were characterized based on their area equivalent diameters of the particles and their morphologies. In this and previous studies, we have

assumed that particles that undergo liquid-liquid phase separation (LLPS) at relative humidity (RH) values higher than efflorescence, as measured by optical microscopy, will undergo LLPS at RH values higher than efflorescence in our system.

Separation relative humidity (SRH) values measured for this paper were collected using the same equipment and methodology as outlined in Ott et al. and will only be described briefly here.[38] Particles were made by spraying a 5 wt. % solution containing a 2 to 1 organic to inorganic ratio onto a hydrophobic slide. A Nikon Ti2 inverted microscope with a 10x objective was paired with an environmental chamber. A Vaisala HMP60 humidity probe with ±3% uncertainty between 0 and 90% relative humidity (RH) and ±5% above 90% RH was used. The RH is changed at an average of 1% per minute and images were taken every 5 minutes as well as at phase transitions. The RH was changed at a rate lower than 1% per minute in the regions where phase transitions occur. Reported SRH values are an average of 30 or more particles ranging in size from 20 to 200 μm in diameter.

Results

The effects of cations and anions on the phase separation of aerosol particles are characterized below. A variety of different particle morphologies were seen for the dried particles analyzed in this study. Two examples of each type of particle morphology are shown in Figure 1 and were chosen to be representative of all of the different types of partially engulfed (Figure 1 a and b), inclusion containing (Figure 1 c and d), and homogenous particles (Figure 1 e and f) for all ten systems studied in this paper. The particles classified as homogenous when containing sodium chloride often still look cubic, which we hypothesize is due to cocrystallization with the organic compound. Sodium chloride cocrystallization has been previously observed with other organic compounds such as glucose and cellulose.[39-40] The sodium chloride containing particles

were the only types that maintained a consistently cubic structure with both phase separated and homogeneous particles. A comparison of a small phase separated particle and a small homogeneous particle is shown in Figure S1. In some cases, it can be difficult to determine which type of phase separated morphology a particle has, but since all phase separated particles are counted together for the histograms, errors in these assignments are not expected to influence the final outcome of the study. Particles are surrounded by a bright ring, called the Fresnel fringe, that is not part of the particle and is caused by under focusing the microscope to increase contrast in the particle. The fringe is outside of the particle and is typically much smaller than the outside phase of the particle. The Fresnel fringe is not expected to influence the ability of the user to determine the morphology of the particle.

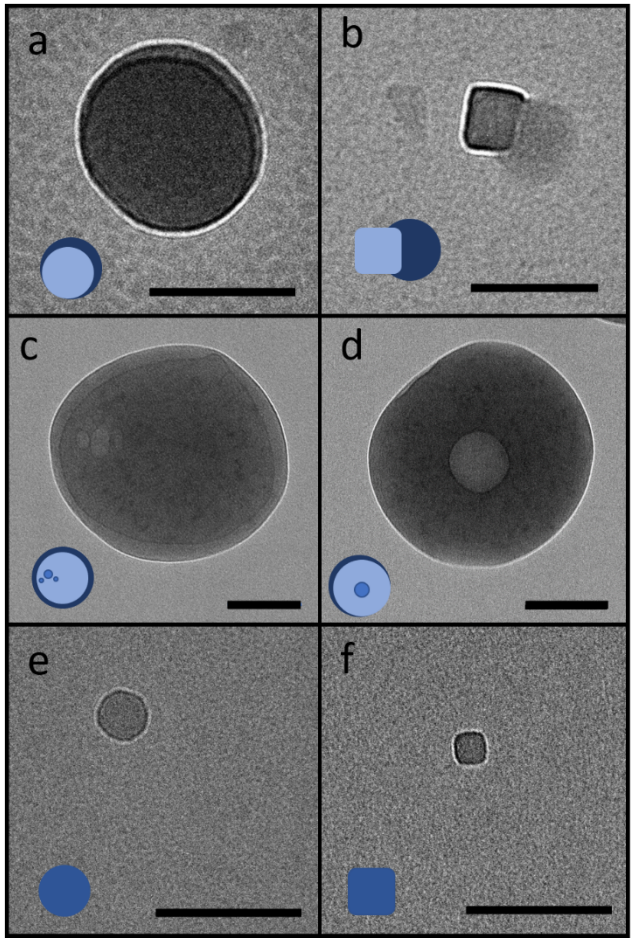

Figure 1: Sample images of particle morphologies with (a) showing a partially engulfed particle from the diethylmalonic acid and ammonium bisulfate system and (b) representing a partially engulfed particle composed of diethylmalonic acid and sodium chloride. Figure 1c shows an inclusion-containing particle composed of diethylmalonic acid and ammonium chloride and (d) shows another inclusion-containing particle from the 2,5-hexanediol and ammonium chloride system. Figure 3e shows a homogeneous particle from the diethylmalonic acid and ammonium chloride system and (f) shows a homogeneous particle composed of 2,5-hexanediol and sodium chloride. Illustrations of each particle type are included with the images. All scale bars are 100 nm.

The influence of the ammonium cation on the size dependence of LLPS is shown in Figure 2 in terms of three different anions. Figure 2 a, b, and c show the ammonium cation with 2,5-hexanediol. Figure 2a shows 2,5-hexanediol with ammonium sulfate. 380 particles were studied between 15 and 250 nm in diameter with all particles below 65 nm being homogenous, those larger than 101 nm being phase separated, and a mixture of both between these two diameters. In this

histogram, as well as all other histograms shown in this paper, it is important to note that the data for these histograms are collected with a goal of comparing where the largest homogenous particles are present and where the smallest phase separated particles are present. Because of this fact, the histograms should not be interpreted as number size distributions of the impacted particles. Only in the transition region where both morphologies are observed is the histogram indicative of the distribution of particle morphologies. Outside of that region, however, the histogram does not provide accurate information about the particle size distribution. This result is due to the focus on imaging particles in the transition region where both phase separated and homogeneous morphologies are found as opposed to equal amounts of imaging across all size ranges. Ammonium bisulfate with 2,5-hexanediol is shown in Figure 2b. With this mixture, 427 particles were studied and all those below 47 nm in diameter were homogenous, all those above 93 nm were phase separated, and between, a mixture of both morphologies are found. Figure 2c shows the ammonium chloride/2,5-hexanediol mixture where 393 particles were studied and all of those below 55 nm were homogenous, and all of those above 66 nm were phase separated with a small region between 55 and 66 nm where both morphologies were found. In this series of 2,5-hexanediol with ammonium salts, the region where phase separated particles transition to homogenous particles remains relatively constant, with the range of diameters at which the smallest phase separated particle is observed for each system ranging only by 18.3 nm from 47.0 to 65.3 nm.

After studying 2,5-hexanediol, another organic compound was selected for comparison. The same salts were studied with diethylmalonic acid and their results shown in Figure 2 d, e, and f. 757 particles were studied for diethlymalonic acid with ammonium sulfate where the smallest phase separated particle was 51 nm in diameter and the largest homogenous particle was 83.9 nm

in diameter (Figure 2d). For the ammonium bisulfate and diethylmalonic acid mixture, shown in Figure 2e, 392 particles were studied and all those below 43 nm in diameter were homogenous while all those above 80 nm in diameter were phase separated. Additionally, in Figure 2f, the diethylmalonic acid and ammonium chloride mixture was studied and the smallest phase separated particle was found to be 46 nm in diameter and the largest homogenous particle was 71 nm in diameter for the 353 particles studied. The smallest phase separated particles for the systems consisting of the three ammonium salts with 2,5-hexanediol differ by only 8.2 nm from 43.0 to 51.2 nm, and the diameters over which both morphologies are found is small for each system. To better understand the influence of the cations as well as the anions, the same anions and organic compounds were studied with the sodium cation.

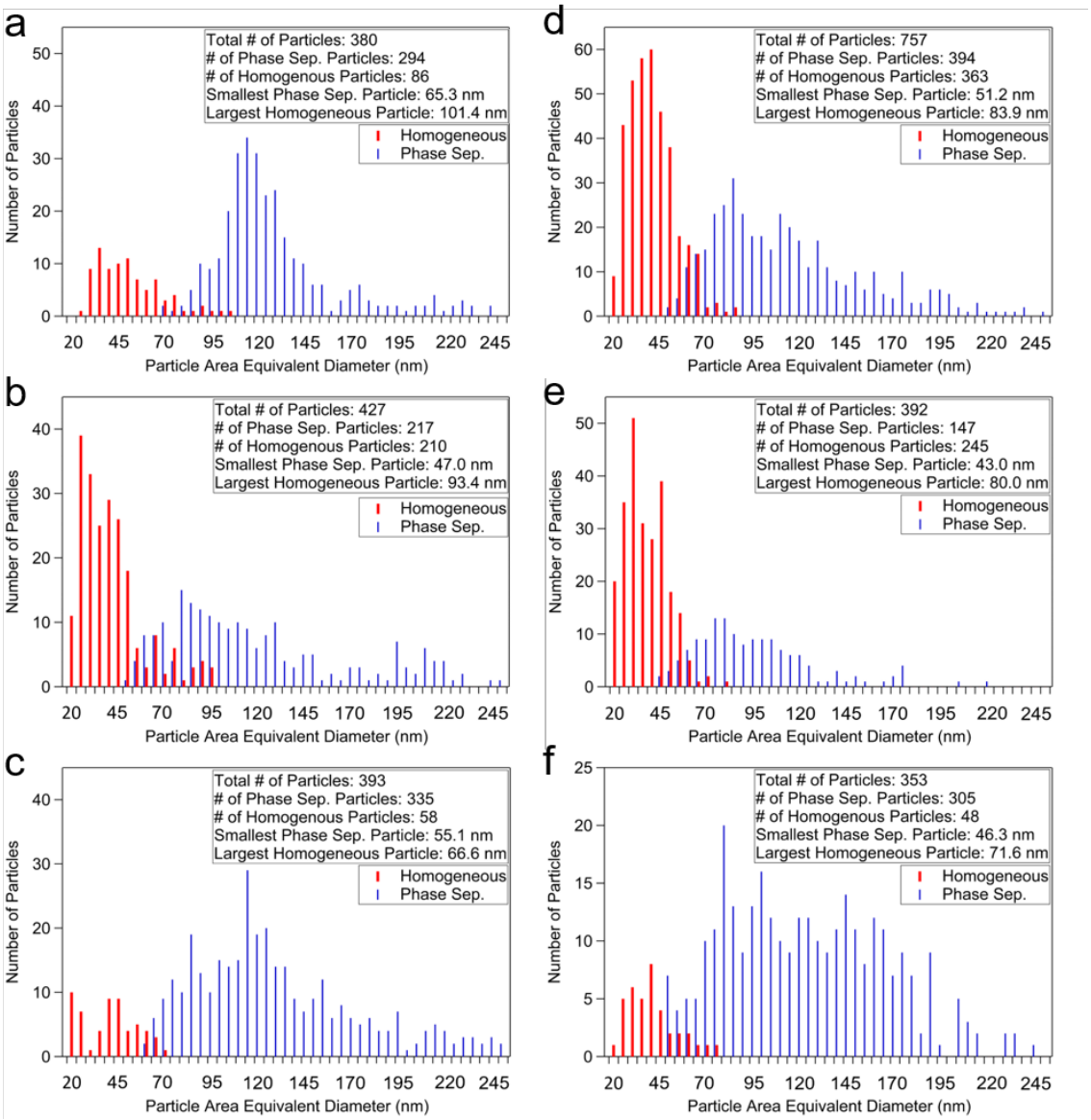

Figure 2: Histograms showing the number of particles with each morphology vs. area equivalent diameter for 2,5-hexanediol with a) ammonium sulfate, b) ammonium bisulfate, and c) ammonium chloride; and diethlymalonic acid with d) ammonium sulfate, e) ammonium bisulfate, and f) ammonium chloride. All histograms for the ammonium containing systems transition to only homogenous particles in a similar size range.

The results for salts containing a sodium cation look significantly different from those systems containing the ammonium cation and are shown in Figure 3. When 357 particles composed of 2,5-hexanediol and sodium chloride were studied, particles as small as 16 nm were found to be phase separated. While this histogram does not fully show that the particles transition from all

phase separated to all homogenous, the one phase separated particle in the 20 nm size bin, compared to the 40 homogenous particles in the same size bin indicate that the transition from all phase separated particles to all homogenous particles would occur soon if smaller particles were studied. In this system, all particles above 49 nm in diameter were phase separated and all studied sizes smaller were a mixture. Similarly, the 2,5-hexanediol and sodium chloride particles do not show the complete transition to homogenous particles. The smallest phase separated particle is 16 nm in diameter. In this case, we once again see the rapidly falling off trend in the number of phase separated particles with the homogeneous particles in a much higher abundance. This distribution of morphologies is indicative of the final transition to only homogenous particles, but the size range studied does not allow that transition to be fully seen. All particles above 52 nm in diameter are phase separated and the sizes studied below that are a mixture of phase separated and homogenous. In the diethylmalonic acid and sodium chloride system, we see the transition from phase separated to homogenous with the smallest phase separated particle having a diameter of 22 nm in diameter and the largest homogenous particles having a diameter of 46 nm. Diethylmalonic acid and sodium chloride is the one sodium system that shows the complete transition to homogenous particles in the size range studied. With a smallest phase separated particle at 17 nm in diameter, the diethylmalonic acid and sodium sulfate system does not quite see the transition to fully homogenous particles in the particle size range studied, but is likely sitting right on the edge of that transition. This system has a mixture of particle morphologies up to 50 nm in diameter, at which point the particles become solely phase separated. All of the sodium systems transition or are estimated to transition to solely homogenous particles in the 15 to 20 nm range based on the shape of the particle distributions in this region of the histogram. This range is much lower than

seen for the ammonium particles which transitioned to solely homogeneous particles between 43 and 65 nm.

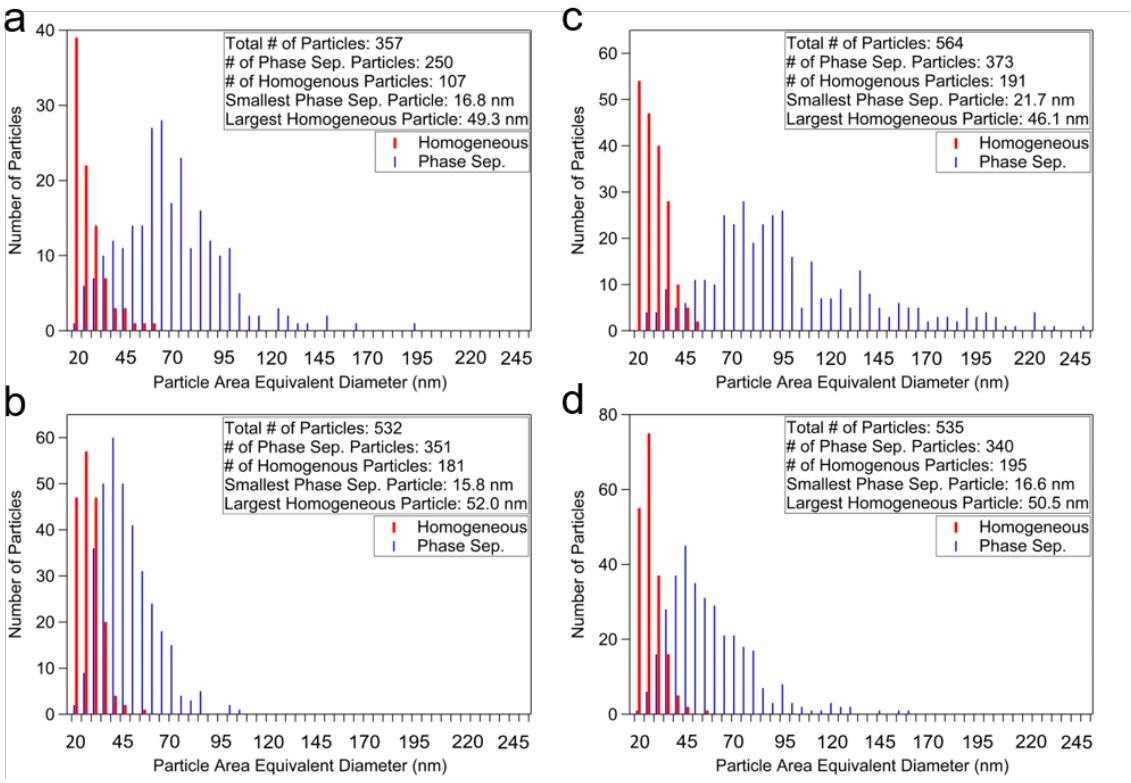

Figure 3: Histograms showing the morphology of aerosol particles as a function of area equivalent diameter for 2,5-hexanediol with a) sodium chloride and b) sodium sulfate; and diethylmalonic acid with c) sodium chloride and d) sodium sulfate. All histograms for sodium containing systems transition to homogenous particles in a similar size range that is consistently smaller than their ammonium containing counterpart.

In this study, the majority of particles that undergo phase separation exhibit a partially engulfed morphology. The one exception to this result is 2,5-hexanediol and ammonium chloride where 212 of the phase separated particles are core shell and 132 are partially engulfed. This mixture of morphologies may be due to the orientation of the particles on the substrate or due to the fast-drying rate used, which can prevent particles from reaching their thermodynamic equilibrium morphology.[41-42] This mixture of morphologies has been seen previously in aerosol

particles composed of polymer mixtures that undergo LLPS.[43] In many of the systems studied, a small number of the particles exhibited inclusions. When imaging the particles, the morphology did not change with extended beam exposure or show increased texture or changing size, which is indicative of inclusions rather than radiation damage from the electron beam in the TEM.[44] In the cases of 2,5-hexanediol and ammonium bisulfate, 2,5-hexanediol and ammonium chloride, diethylmalonic acid and ammonium bisulfate, diethylmalonic acid and ammonium chloride, and diethylmalonic acid and ammonium sulfate, less than 10 of the phase separated particles contained inclusions. 2,5-hexanediol and ammonium sulfate had 32 particles with inclusions. These inclusions typically occur in particles that are greater than 100 nm in area-equivalent diameter but do not appear to have any additional dependence on size.

Discussion

The organic compounds, 2,5-hexanediol and diethlymalonic acid, were chosen for this study because of the degree of sensitivity of their separation relative humidities (SRH) to different salts. 2,5-hexanediol SRH values are highly dependent on the identity of the salts, whereas the diethylmalonic acid SRH values are largely independent of the identity of the salts. According to the work of You et al., 2,5-hexanediol has statistically different SRH values for ammonium sulfate (88.8 ± 3.7 %RH), ammonium bisulfate (81.0 ± 3.7 %RH), and sodium chloride (72.4 ± 2.6 %RH), whereas diethylmalonic acid has statistically similar values for those same salts, 89.2 ± 3.0 %RH, 88.1 ± 2.6 %RH, and 87.4 ± 3.0 %RH respectively.[24] We measured SRH values for these organic compounds with ammonium chloride and sodium sulfate; all other values used are from You et al. (Figure 4; Table 1))[24]. To understand the effect of SRH on the size dependence of each system, the smallest phase separated particle is used as a metric in Figure 4a. The influence of the cation

is also investigated in this figure. The triangles represent systems with diethylmalonic acid while the squares represent 2,5-hexanediol systems, and the blue markers represent systems with ammonium while the red markers represent systems with sodium. The blue shapes representing ammonium species are all grouped together at the top of the figure and the red shapes representing sodium are all group together at the bottom of the figure. The influence of anions is shown in Figure 4b. Note that Figure 4b is identical to Figure 4a except for the color and shape of the markers used. Blue shapes represent sulfate, red represents bisulfate, and green represents chloride in Figure 4b. Similarly to Figure 4a, triangles represent diethylmalonic acid and squares represent 2,5-hexanediol. In contrast to Figure 4a, the anions show no specific trends with color or shape of the markers observed. Comparing these figures indicates that the cations are more important when determining the size dependence of the morphology than the anions. Additionally, we can see that the diethylmalonic acid particles, those represented by triangles in Figure 4, appear to have a slight dependence on SRH with four of the five values following the trend of a decrease in the diameter of the smallest phase separated particle with a decrease in SRH which produces an R^2 of 0.26 with a linear trendline. The 2,5-hexanediol markers do not appear to have a trend with SRH. From this result, we conclude that the SRH may have a slight impact on the size dependence of the particle morphology but that ultimately, the identity of the cation in the inorganic component is more important.

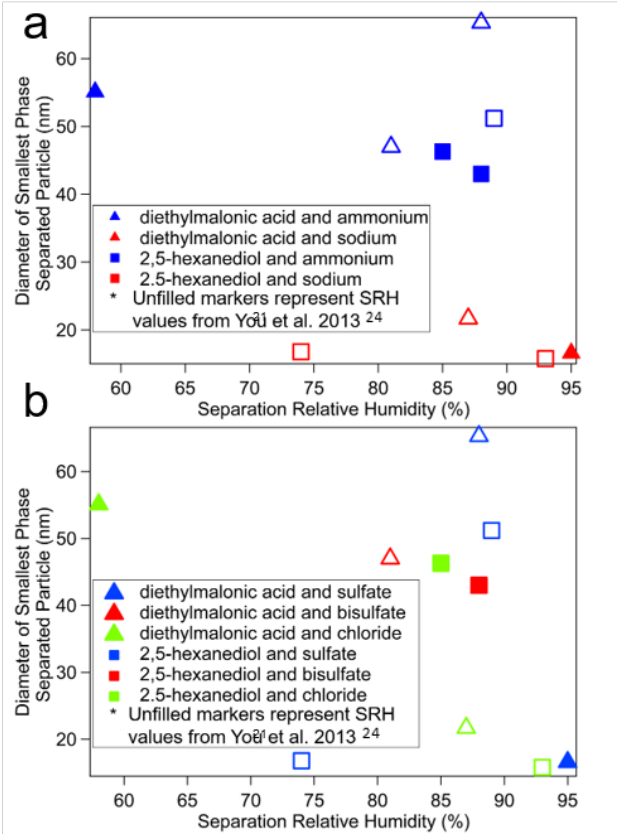

Figure 4: The smallest phase separated particle for each system vs. SRH with markers color coded according to a) the cation present in solution and b) the anion present in solution. The SRH values for ammonium sulfate, ammonium bisulfate, and sodium chloride are from You et al. 2013.[24] A trend is observed with the identity of the cation in a, but no distinctive trend is found in b.

Table 1: Comparing the SRH values for different ion combinations using data from You et al. 2013 combined with new data.

		Na^+ SRH	NH_4^+ SRH
Diethylmalonic acid	SO_4^{2-}	95 ± 0.4	89 ± 3*
Diethylmalonic acid	Cl^-	87 ± 3*	85 ± 1
2,5-hexanediol	SO_4^{2-}	93 ± 1	88 ± 3*
2,5-hexanediol	Cl^-	74 ± 4*	58 ± 2

* Values come from You et al. 2013.[24]

In a previous study, the influence of kinetics and thermodynamics on the size dependent morphology were studied.[32] The diameters of the largest homogeneous particle and the smallest phase separated particle depend on the drying rate. As the drying rate slows, the diameters of the largest homogeneous and smallest phase separated particles decrease.[32] At the slowest drying rates, the size dependence persists, indicating an underlying thermodynamic origin of this phenomenon. Because fast drying rates are used in this study, the largest homogeneous particle and the smallest phase separated particle of each system are larger than they would be with a slower drying rate.

The impact of the solubility of the inorganic component was also considered. In Table 2, the CRC values for solubility are listed. The ammonium values are all higher than the sodium values, however if solubility were the reason for this trend, we would not have expected the ammonium chloride size dependence to more closely align with the sodium salts. Based on this, we conclude that solubility is not the primary controlling factor in the ability of small particles to undergo LLPS. Another factor that was investigated was the surface tension of the solutions. 8 mM salt solutions with 5 mM diethylmalonic acid were studied and values for ammonium sulfate,

ammonium chloride, sodium sulfate, and sodium chloride did not show any significant differences (Table S1).

Table 2: CRC solubility values for the salts used in this study

	Solubility in g/100 g H_2O	Smallest Phase Separated Particle Diameter (nm)	
		Diethylmalonic Acid	2,5-Hexanediol
Ammonium chloride	39.5[a]	46	55
Ammonium bisulfate	100[a]	43	47
Ammonium sulfate	76.4[a]	51	65
Sodium chloride	36.0[a]	22	17
Sodium sulfate	28.1[a]	17	16

[a] CRC Handbook of Chemistry and Physics,[45]

The influence of the softness/hardness of the cations was explored. Sodium is a hard cation while ammonium trends in a softer direction. Softness/hardness can also be understood as the apparent dynamic hydration of the ions. Collins studied the influence of both free ions and of charged headgroups of proteins and concluded that the apparent dynamic hydration numbers need to match in order to interact in solution.[46-48] Mehringer et al. performed further experimental and theoretical studies on the influence of charged headgroups, investigating the role of the carbon chain length.[49] Mehringer showed that by changing the carbon chain length attached to the charged headgroup, the affinity of the headgroup for binding to soft or hard ions can change.[49] Based on the short carbon chain length of the diethylmalonic acid used in this study and the work of Mehringer, we anticipate that the carboxylate group interacts more strongly with the ammonium ion than with the sodium ion. A similar argument can also be made for the alcohol groups on 2,5-hexanediol. We hypothesize that softer cations interact more strongly with the organic functional groups and thus impede the phase separation process. The hardness/softness of the headgroups is likely impacted by their charge, with neutral species likely being harder than cations (and anions

likely being softer), however we expect, based on our results, that the difference between different cations (NH_4^+, Na^+) is larger than charged vs uncharged organic species. We predict that the carboxylate group exists in both its protonated and its unprotonated state with the different salts, depending on the pH of the solution and the pKa of the organic compound. Ion-ion interactions can occur if the organic compound is charged. Ion-dipole interactions between the headgroups and the salts can also occur in both the charged and uncharged state. The salt-organic interactions may be ion-ion interactions as well as ion-dipole interactions because a mix of charged and neutral headgroups are expected for the systems in this study, depending on the pH of the solution. Based on this hypothesis, we predict that the separation relative humidity is lower for softer cations and higher for harder cations. Additionally, due to the ability of soft cations to impede phase separation, we predict that aerosol particles containing a soft cation transition from phase separated to homogenous at a larger size than those with a hard cation. The trends we see for both the bulk SRH and for the size dependence match our hypothesis. Table 1 shows the bulk SRH values for these systems. Note that the anions dominate the trend in SRH, as shown in You et al., but when species with the same anion are compared, the trend in SRH supports the hypothesis that softer cations lead to lower values.[24] In an attempt to further confirm this trend for the size dependence of particle morphology, we worked with methylammonium chloride and trimethylammonium chloride but neither showed phase separation with either diethylmalonic acid or 2,5-hexanediol. This result is consistent with increasing softness of the inorganic cation causing such a decrease in the SRH that it falls below the efflorescence relative humidity and is therefore not observed. Additionally, silver sulfate was tested but it did not appear to undergo liquid-liquid phase separation. Potassium sulfate with diethylmalonic acid was briefly studied and its results are comparable with those of sodium sulfate (Fig. S2). While modeling studies exist on the interactions

of ions with the aqueous air interface and with protein interfaces, additional studies which look at confined and phase separated interfaces are needed to better understand this role of ions in the phase separation process.[50-51]

Conclusions and Atmospheric Implications

In this paper, we investigated the influence of different salts on the size dependent morphology of submicron aerosol particles. We studied salts composed of two different cations and three different anions. Aerosol particles that contain the ammonium cation undergo their transition to all homogenous particles at a larger size than those that contain sodium as the cation. We hypothesize that the hardness or softness of the cation influences interactions with the organic compound and impacts when phase separation occurs. This effect is seen in both the size dependent morphology of submicron aerosol particles as well as in the separation relative humidity of supermicron aerosol particles.

These results have implications in atmospheric chemistry where ammonium and sodium are abundant.[52-55] Sea spray aerosol particles that can undergo phase separation due to their composition are more likely to be phase separated at most sizes due to the presence of sodium as the dominant cation. Additionally, in continental aerosol where ammonium is more abundant, the size dependent phenomenon will cause a larger number of particles to be homogenous. Most atmospheric chemistry LLPS studies have focused on the influence of anions and assumed the impact of the cation is minimal. This study shows that it is important to consider both cations and anions, where the cations are the controlling factor in determining particle morphology in submicron aerosol particles. This study also has implications for our understanding of the

properties of cations and anions and their interactions with organic molecules in confinement. Future studies should include additional size dependence studies with common divalent cations as well as modeling studies to investigate the role of cations and anions at interfaces and during the nucleation process.

ASSOCIATED CONTENT

Supporting Information: A comparison of homogeneous and phase separated particles < 30 nm in diameter, information on surface tension of diethylmalonic acid with the salts studied, and size dependence of the diethylmalonic and potassium sulfate system.

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Notes
The authors declare no competing interest.

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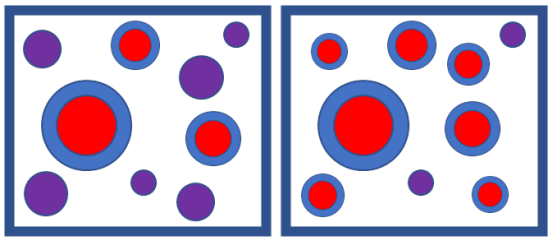

NH_4^+ containing particles

Na^+ containing particles