In–situ observation for RH–dependent mixing states of submicron particles containing organic surfactants and inorganic salts

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Abstract: Aerosol mixing state plays an important role in heterogeneous reactions and CCN activity. Organic surfactants could affect aerosol mixing state through bulk–surface partitioning. However, the mixing state of surfactant containing particles remains unclear due to the lack of direct measurements. Here, in–situ characterizations of mixing state for 20 kinds of submicron particles containing inorganic salts (NaCl and (NH₄)₂SO₄) and atmospheric organic surfactants (organosulfates, organosulfonates, and dicarboxylic acids) were conducted upon relative humidity (RH) cycling by Environmental Scanning Electron Microscopy (ESEM). As RH increased, surfactant shells inhibited water diffusion exposing to inorganic core, leading to notably increased inorganic deliquescence RH (88.3–99.5%) compared with pure inorganic aerosol. Meanwhile, we directly observed obvious Ostwald ripening process, that is, the growth of larger crystals at the expense of smaller ones, in 6 among 10 NaCl–surfactants systems. As a result of water inhibition by surfactant shell, Ostwald ripening in all systems occurred at RH above 90%, which were higher than reported RH range for pure NaCl measured at 27°C (75–77%). As RH decreased, 8 systems underwent liquid–liquid phase separation (LLPS) before efflorescence, showing a strong dependence on organic molecular oxygen–to–carbon ratio (O:C). Quantitatively, LLPS was always observed when O:C ≤ 0.4 and was never observed when O:C > ~0.57. Separation RH (SRH) of inorganic salt–organic surfactant mixtures generally followed the trend of (NH₄)₂SO₄ < NaCl, which is consistent with their salting out efficiencies reported in previous studies. Phase separations were observed after efflorescence for systems without LLPS. Our results provide a unique insight into the consecutive mixing processes of the inorganic–surfactant particles, which would help improve our fundamental knowledge of model development on radiative effect.
1 Introduction

Atmospheric particles are complex mixtures of multiple inorganic and organic matters (Pöschl, 2005). When relative humidity (RH) varies, particles can undergo phase transitions such as deliquescence (Peng et al., 2001), efflorescence (Takahama et al., 2007), and liquid–liquid phase separation (LLPS) (Martin, 2000), hence altering mixing state. The transition of aerosol mixing state can influence gas uptake, hygroscopicity, cloud condensation nuclei (CCN) activity, and radiative absorption (Riemer et al., 2019).

Upon hydration, previous studies suggested that different mixing state between inorganic and organic matters influence aerosol hygroscopic behaviours (e.g., deliquescence) and solar radiation (Peng et al., 2016; Li et al., 2021). For instance, Peng et al. (2016) observed deliquescence RH of internal mixed NaCl–oxalic acid at 73%, being slightly lower than that of pure NaCl (75%) because of the interactions between inorganic and organic matters. However, Li et al. (2021) found a different deliquescence process if ammonium sulfate (AS) was coated by secondary organic aerosol, the organic shell firstly dissolved at ~50% RH but water uptake of the AS core was inhibited, leading to a higher deliquescence RH of AS (~83–90%). By cryogenic transmission electron microscopy (cryo–TEM), Zhang et al. (2022) directly observed collected particles from a rural site remained LLPS (inner inorganic phase and outer organic phase) between organic matter and inorganic salts when RH raised to 75 ± 2% and 86 ± 2%, but LLPS disappeared when RH increased to 95 ± 2%. They later suggested that LLPS with higher ratio of organic coating thickness to black carbon size can drive black carbon from inorganic core to organic particle coatings, which could result in 18% radiative absorption overestimation of black carbon aerosols in climate models by assuming a core-shell particle structure.

Upon dehydration, phase separation has been frequently observed in ambient particles (You et al., 2012; Ting et al., 2018; Zhang et al., 2020; Zhang et al., 2022). For example, LLPS occurred at > 90% RH for particles containing water extraction of collected atmospheric particles in Atlanta and simulations indicated that LLPS can decrease particle uptake of N₂O₅ thus increase concentrations of gas–phase NO₃ and N₂O₅ (You et al., 2012). Factors contributing to LLPS, e.g. oxidation levels (Bertram et al., 2011; Song et al., 2017; Song et al., 2019), organic fraction (Ciobanu et al., 2009; Song et al., 2012b), inorganic species (You et al., 2013), and temperature (You and Bertram, 2015; Roy et al., 2020) have been discussed for some specific inorganic–organic or organic–organic systems in literature. Song et al. (2012a) and You et al. (2013) found LLPS always occurred for O:C < ~0.5, never occurred for O:C > 0.8, and when O:C was between 0.5 and 0.8, LLPS was depended on inorganic species. Organic fraction showed controversial effects on LLPS (Bertram et al., 2011; Song et al., 2012b) since Bertram et al. (2011) found a weak effect of organic fraction on LLPS for 8 out of 11 AS–organic systems but the rest systems exhibited a quantifiable dependence of separation RH (SRH) on organic fraction. You et al. (2013) reported SRH among out of 20 organics generally followed the trend of (NH₄)₂SO₄ ≥ NH₄HSO₄ ≥ NaCl ≥ NH₄NO₃, which is consistent with their previous reported salting out efficiencies. Temperature did not strongly affect SRH between 253–290 K for AS–organics (O’Brien et al., 2015; You and Bertram, 2015) and NaCl–organics systems (Roy et al., 2020). Recently, dry rate (Altaf and
Freedman, 2017; Altaf et al., 2018) and size effect (Freedman, 2020; Ott and Freedman, 2021) on LLPS were found for submicron particles. Undergoing drying by slow rate (~ 27% per minute), phase separation of AS-pimelic acid system occurred in larger particles (75 ~ 322 nm diameter), but smaller particles (below 25~135 nm diameter) were homogeneous. In slow drying rates (0.04 to 0.08% RH per second), particles with diameter below 43 nm were homogeneous but larger particles (28 ~ 629 nm) were mainly phase-separated (Altaf and Freedman, 2017). Freedman (2020) further explained that LLPS is scarcely occurred in smaller particles as smaller particles cannot overcome the energy barrier needed to form a new phase.

Dicarboxylic acids (Ruehl and Wilson, 2014), organosulfates (Bruggemann et al., 2020; Reed et al., 2022), and organosulfonates (Bruggemann et al., 2020; Guo et al., 2020) are important organic constituents in secondary organic aerosol. Primary emission and secondary transition were major sources of dicarboxylic acids and their mass contribution of dicarboxylic acids to total particulate carbon exceeds 10% (Römpp et al., 2006; Ho et al., 2010; Hyder et al., 2012). Organosulfates and organosulfonates, as significant reservoirs of sulfur, comprise an estimated 5%-30% of the total organic aerosol mass (Tolocka and Turpin, 2012; Reed et al., 2022). Above mentioned organics contain both hydrophilic (e.g., sulpho group) and hydrophobic groups (e.g., alkyl group), showing surface activity and causing bulk–surface partitioning (Noziere, 2016; Ruehl et al., 2016), hence affecting individual aerosol morphology (Kwamena et al., 2010). However, mixing state of submicron inorganic–surfactant particles remain unclear due to the lack of direct measurements. Here, we directly observed mixing states of submicron particles containing inorganic salt and organic surfactant with varying organic volume fraction (OVF) upon humidity cycling by Environmental Scanning Electron Microscopy (ESEM). Our results could provide unique insights into the dynamic evolution of inorganic–surfactant particles under fluctuating atmospheric conditions.

2 Materials and Methods

2.1 Chemicals

NaCl and AS were purchased from Sinopharm chemical reagent (purity ≥ 99.8%) and Sigma Aldrich (purity ≥ 99 %), respectively. The studied organic substances include 10 surface active organics (five organosulfonates, three organosulfates and two dicarboxylic acids). The five organic sulfonates were sodium propane sulfonate (C₃H₇SO₃Na), sodium butane sulfonate (C₄H₉SO₃Na), sodium pentane sulfonate (C₅H₁₁SO₃Na), sodium heptane sulfonate (C₇H₁₅SO₃Na), sodium octane sulfonate (C₈H₁₇SO₃Na). The three organic sulfates were sodium methyl sulfate (CH₃SO₃Na), sodium ethyl sulfate (C₂H₅SO₃Na) and sodium octyl sulfate (C₈H₁₇SO₃Na). Two dicarboxylic acids were pimelic acid (PA) and phenylmalonic acid (PhMA). Relevant properties of used chemicals were summarized in Table 1. These organic surfactants were of various solubilities, from sparingly soluble (e.g., 0.07 mol L⁻¹ for C₅H₁₁SO₃Na) to highly soluble (e.g., 2.7 mol L⁻¹ for C₈H₁₇SO₃Na). O:C ratios were from 0.38 to 4, covering most of the molar ratios in the atmosphere (0.1~1.0) (You et al., 2013). The studied organic substances contain functional groups such as sulfonates, sulfates, carboxylic acids and aromatics, which were universally detected in atmospheric aerosol samples (Takahama et al., 2007).
Table 1  Organic surfactants and their relevant properties investigated in this study.

<table>
<thead>
<tr>
<th>Species</th>
<th>Compounds</th>
<th>Formula</th>
<th>*Solubility (mol L$^{-1}$)</th>
<th>O:C</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic sulfonate</td>
<td>Sodium propane sulfonate</td>
<td>$\text{C}_3\text{H}_7\text{SO}_3\text{Na}$</td>
<td>2.0</td>
<td>1.00</td>
<td>&gt;98%</td>
<td>Aladdin</td>
</tr>
<tr>
<td></td>
<td>Sodium butane sulfonate</td>
<td>$\text{C}_4\text{H}_9\text{SO}_3\text{Na}$</td>
<td>2.7</td>
<td>0.75</td>
<td>≥99%</td>
<td>Aladdin</td>
</tr>
<tr>
<td></td>
<td>Sodium pentane sulfonate</td>
<td>$\text{C}<em>5\text{H}</em>{11}\text{SO}_3\text{Na}$</td>
<td>2.3</td>
<td>0.60</td>
<td>98%</td>
<td>Aladdin</td>
</tr>
<tr>
<td></td>
<td>Sodium heptane sulfonate</td>
<td>$\text{C}<em>7\text{H}</em>{15}\text{SO}_3\text{Na}$</td>
<td>1.9</td>
<td>0.43</td>
<td>98%</td>
<td>Macklin</td>
</tr>
<tr>
<td></td>
<td>Sodium octane sulfonate</td>
<td>$\text{C}<em>8\text{H}</em>{17}\text{SO}_3\text{Na}$</td>
<td>0.9</td>
<td>0.38</td>
<td>≥99%</td>
<td>Macklin</td>
</tr>
<tr>
<td>Organic sulfate</td>
<td>Sodium methyl sulfate</td>
<td>CH$_3$SO$_4$Na</td>
<td>2.1</td>
<td>4.00</td>
<td>98%</td>
<td>Energy Chemical</td>
</tr>
<tr>
<td></td>
<td>Sodium ethyl sulfate</td>
<td>C$_2$H$_5$SO$_4$Na</td>
<td>0.4</td>
<td>2.00</td>
<td>98%</td>
<td>Meryer</td>
</tr>
<tr>
<td></td>
<td>Sodium octyl sulfate</td>
<td>C$<em>8$H$</em>{17}$SO$_4$Na</td>
<td>0.07</td>
<td>0.50</td>
<td>99%</td>
<td>Rhawn</td>
</tr>
<tr>
<td>Dicarboxylic acid</td>
<td>Pimelic acid (PA)</td>
<td>C$<em>7$H$</em>{12}$O$_4$</td>
<td>0.31</td>
<td>0.57</td>
<td>99%</td>
<td>Macklin</td>
</tr>
<tr>
<td></td>
<td>Phenylmalonic acid (PhMA)</td>
<td>C$<em>9$H$</em>{16}$O$_4$</td>
<td>0.7</td>
<td>0.44</td>
<td>98%</td>
<td>Aladdin</td>
</tr>
</tbody>
</table>

* https://comptox.epa.gov/ (last access: 12 March, 2023)

2.2 Aerosol generation and collection

The process of aerosol generation and collection was detailedly described by Xiong et al. (2022). In brief, particles were nebulized from solutions of organic and inorganic matters (~5 g L$^{-1}$) mixed with deionized water (Millipore, resistivity = 18.2 MΩ). After drying (RH < 15%) by a silica-gel diffusion dryer, particles were deposited with an eight stage non−viable particle sizing sampler (Models BGI20800 Series, BGI Incorporation) onto 400 mesh copper grids coated with carbon films (Zhongjingkeyi Films Technology Co. Ltd.). Copper grids were mounted on the 7th stage, selecting particles with aerodynamic size of 0.7–1 μm. Collected samples were stored under dry condition (RH < 10%) and were immediately characterized within 24 hours to avoid possible sample aging.
2.3 Mixing state observation

Mixing state was observed by Environmental Scanning Electron Microscopy (ESEM, Thermo Quattro S) with a temperature–controlled stage. The RH in chamber was controlled by adjusting the temperature (± 0.1 °C) at a predefined pressure (610 Pa). Temperature varied between 0.1 to ~ 25 °C, which has negligible influence on the LLPS of AS–organic (O’brien et al., 2015; You and Bertram, 2015) and NaCl–organic systems (Roy et al., 2020). In each experiment, the RH raised from low (~ 30%) to high condition (~100%) at the change rate of 2–3% RH min⁻¹. High RH lasted for at least 5 minutes for equilibrium, promising complete dissolution (O’Brien et al., 2015). Then, RH decreased to dry condition at similar change rate. Cloud parcel modelling suggests that atmospheric RH fluctuations typically occur from 0 to 3.6% min⁻¹ (Pöhlker et al., 2014).

Therefore, we assume that the water uptake in our experiments approximates atmospheric conditions (Shiraiwa et al., 2013). Images of mixing states during the whole RH period were acquired at an electron acceleration voltage of 30 kV. The images were recorded with line scanning rates of 3–5 µs to minimize the possible beam damage (O’Brien et al., 2015). Each image contained at least 5 particles.

3 Results and Discussion

3.1 Mixing states upon hydration

Deliquescence RH (DRH) and Efflorescence RH (ERH) of pure NaCl (Fig. 1a–d and Fig. S1a–b) and AS particles (Fig. 2a–d and Fig. S1c–d) were firstly tested via the experimental setup. DRH of NaCl and AS were observed at 80.9 ± 0.1% (literature: 77 ± 1% (Pöhlker et al., 2014)) and 82.1± 0.6% (literature: 82.0% (Onasch et al., 1999)). ERH of NaCl and AS were 48.3 ± 0.4% (literature: 48 ± 2% (Zeng et al., 2014)) and 30.7 ± 0.9% (literature: 31 ± 1% (Cheng and Kuwata, 2023)).

Generally, the experimental DRH and ERH values correspond well with those in literature, confirming the reliability of the experimental setup. DRH of NaCl showed slight deviation by about nearly 4%, which could be explained by kinetic effects when the system had not reached full equilibrium (Pöhlker et al., 2014). Before deliquescence, the substrate-supported NaCl and AS particles both showed substantial water uptake, forming an aqueous halo around a solid core. Similar observational results of NaCl and AS have been reported, and could be explained by interactions at the sample/substrate interface, which plays an important role in such gradual phase transition as additional energy term (Wise et al., 2008; Pöhlker et al., 2014).

Figure 1c and Fig. 2e illustrate the two separated phases with dark core (blue arrow) and bright shell (green arrow) of dry deposited NaCl–C₂H₅SO₄Na and AS–C₂H₅SO₄Na particles. The dark cores are indicated to be inorganics, because darker regions are characteristic of areas with higher atomic number elements (e.g., Cl) and/or a thicker sample region (Laskin et al., 2006; O’Brien et al., 2015). Phase separations with core–shell structure were observed for all studied inorganic–surfactant systems. This may be attributed to the size range of particles we investigated (0.7–1 µm), since inorganic–surfactants particles with such size range might overcome the energy barrier needed to form a new phase (Altaf and Freedman, 2017; Altaf et al., 2018; Freedman, 2020; Ott and Freedman, 2021).
When RH increased from dry, as organic phase slowly absorbed water, NaCl and AS cores were not fully dissolved at RH of 90.1% and 91.7% (Fig. 1g and Fig. 2g), respectively, being notably higher than their DRH. The phenomenon was found for all NaCl–surfactant and AS–surfactant systems and the DRH of the inorganic salts were ranged in 88.3–99.5% (Fig. 1i and Fig. 2i). Laskina et al. (2015) measured the DRH of pure AS and NaCl at submicrometer (100 nm) and supermicrometer (3–10 μm) size ranges by hygroscopic tandem differential mobility analyzers (HTDMA) and MicroRaman Spectroscopy, respectively, and the deviations between them were both within 3%, indicating that DRH of pure AS and NaCl showed weak size dependence (> 100 nm). In addition, (Cheng and Kuwata, 2023) used low-temperature hygroscopicity tandem differential mobility analyzer (Low−T HTDMA) and observed consistent DRH of NaCl and AS within experimental error under temperature ranged in −10 °C to 22.5 °C, suggesting that the DRH of NaCl and AS experience a neglect temperature dependence. According to the above-mentioned studies, DRH of pure AS and NaCl showed weak size dependence (> 100 nm) and temperature dependence in our experiment, and we therefore concluded that surfactant shell inhibits water diffusion exposing to inorganic cores, resulting in delays of deliquescence of inorganic cores. The inhibition of surfactant shell could be triggered by increased viscosity with raised RH, since reported studies have reported that organic shells can transform form solid to semisolid with high viscosity at wet condition (Zhang et al., 2018). In a RH-constrained lab study at constant room temperature, Li et al. (2021) also observed organic coating of secondary organic aerosol (oxidizing α-pinene) started to deliquesce first, but the phase changes of AS cores from solid to liquid took place at 83–90% RH, lower than those in the current study. This was possibly caused by the water diffusion coefficient through organic phase, which could be affected by organic species and environment parameters such as temperature. Given by Nguyen et al. (2017), the diffusion coefficient of a water molecule through an organic shell could be decreased by lower temperature. In the current study, higher RH in the ESEM chamber was achieved by decreasing temperature, thus might decrease diffusion coefficient of water in organic surfactant and lead to higher DRH than those in Li et al. (2021). Previous study and the current work indicated the phenomenon (water inhabitation by organic coating) to be a common and important procedure in affecting ambient aerosol hygroscopicity, because inorganic–organic core–shell structures were ubiquitous observed in field (Li et al., 2016; Unga et al., 2018; Xu et al., 2020; Li et al., 2021; Wang et al., 2021; Zhang et al., 2022). Though the water inhabitation of organic shell in the current study was observed at temperature much lower than room temperature, it is meaningful and may affect aerosol properties in some special area such as polar regions (Lambert et al., 2013; Kirpes et al., 2022; Zavacka et al., 2022) or winter time period (Xu et al., 2021; Zhang et al., 2021) where are characteristic with low-temperature environment.

As previous study believed that deliquescence on hydration for inorganics independent of circumstances, Fig. 3 illustrates an unexpected phase transition of NaCl cores coated with C\textsubscript{2}H\textsubscript{5}SO\textsubscript{4}Na (70% OVF). As shown in Fig. 3a, a droplet with several NaCl cores was observed at 97.0% RH since discussed above that organic shell inhibits water diffusion. NaCl cores in droplet were a bigger one (marked by white square) and the rest were smaller. When RH gradually raised (Fig. 3b–c), as smaller NaCl cores serially deliquesced and dissolved, the size of the bigger NaCl core surprisingly increased, indicating a simultaneous NaCl recrystallization at the expense of smaller ones (i.e., Ostwald ripening) (Boistelle and Astier, 1988). After other small
particles totally dissolve, the bigger NaCl core deliquesced and fully dissolved at 99.5% RH (Fig. 3d). A previous study reported “efflorescence upon hydration” for 1:1 mixed NaCl-gluconic acid and AS-gluconic acid by optical tweezer (Zhu et al., 2022). Based on IR spectrum, they found the coexistence of partial efflorescence mixed state, ultraviscous state and liquid state during “efflorescence upon hydration” period, indicating an unstable crystal and concentrated liquid state of NaCl. In this circumstance, Ostwald ripening can take place. Ostwald ripening was triggered by the decrease of total system free energy, since dissolved small and effloresced big crystals reduce the total system free energy (Voorhees, 1985). We directly and observed obvious Ostwald ripening processes in 6 among 10 NaCl–surfactants systems. As a results of water inhibition by surfactant shell discussed above, Ostwald ripening here all occurred at RH above 90%, which were notably higher than reported 75%–77% for pure NaCl measured by X-ray microspectroscopy at 27°C (Põhlker et al., 2014).

![Figure 1](https://doi.org/10.5194/egusphere-2023-849)

**Figure 1.** ESEM images of (a–d) pure NaCl and (e–h) NaCl–C$_2$H$_5$SO$_4$Na (70% OVF) with different RH. Blue and green arrows indicate the inorganic phase and organic phase, respectively. DRH values of inorganic core for NaCl–surfactants systems (i). Grey area represents DRH range of NaCl obtained from Peng et al. (2022) Red line indicates the measured DRH of pure NaCl (80.9 ± 0.1%). Scale bars were 1 μm.
Figure 2. ESEM images of (a–d) pure AS and (e–h) AS–C₅H₇SO₄Na (50% OVF) with different RH. Blue and green arrows indicate the inorganic phase and organic phase, respectively. (i) DRH values of inorganic core for AS–surfactant systems. Grey area represents DRH range of AS obtained from Peng et al. (2022) Red line indicates the measured DRH of pure AS (82.1± 0.6%). Scale bars were 1 μm.
Figure 3. ESEM images of Ostwald ripening for NaCl−C$_8$H$_{17}$SO$_4$Na (50% OVF) particle. White square indicates the biggest NaCl core (assumed square) in droplet. The biggest NaCl grew larger (recrystallization) while the small NaCl cores dissolved.
3.2 Mixing states upon dehydration

LLPS

In Fig. 4a, AS–C₈H₁₇SO₄Na (50% OVF) was homogeneous under RH of 99.5%. When RH decreased to 98.2%, the particles showed two separated liquid phases (i.e., LLPS) with a dark inner phase and a light outer phase (Fig. 4b), which were highlighted by the blue and green arrows. In addition, the AS–C₈H₁₇SO₄Na remained LLPS when RH continued to decline until efflorescence of inner inorganic phase occurred (Fig. 4c). In our study, 8 among 20 chemical systems underwent LLPS, including 4 AS–organic systems and 4 NaCl–organic systems. Fig. 5 illustrates the relationship between LLPS occurrence and molar ratios (O:C and H:C) of the surface–active organics, as well as reported results of other binary inorganic–organic systems in You et al. (2013) and O’Brien et al. (2015). Firstly, no trend was observed between LLPS occurrence and H:C of the organics. This was consistent with results in previous studies (Bertram et al., 2011; Song et al., 2012a; You et al., 2013). An apparent trend was found between O:C ratio and LLPS occurrence for different systems, that is, LLPS of inorganic–organic particles were more likely to occur when O:C ratio was low. Quantitatively, LLPS was always observed for O:C < 0.4 and never observed for O:C ≥ −0.57 (grey area) was found for NaCl–surfactants and AS–surfactants systems. You et al. (2013) reported that LLPS always occurred for O:C < 0.5 and was never observed for O:C ≥ 0.8 for NaCl–organics and AS–organics with organic-to-inorganic mass ratio of 2 ± 0.1, which was different from our results. This could be attributed to the different chemical systems.

In order to analyze the effect of inorganic salts in LLPS, we compared SRH of systems which contained same organic matters but different inorganic salts. Results showed that SRH of AS–C₈H₁₇SO₄Na (70% OVF), AS–C₈H₁₇SO₄Na (90% OVF), AS–PhMA (90% OVF) and AS–PA (90% OVF) were 98.7 ± 0.5%, 81.3 ± 1.2%, 97.9 ± 1.0% and 98.5 ± 0.8%, and were all notably higher than SRH of corresponding NaCl–containing systems (92.5 ± 3.9%, 56.4 ± 1.2%, 85.6 ± 3.6% and 66.7 ± 0.8%), respectively. This was attributed to different salting out efficiency of inorganic salts, since You et al. (2013) found the SRH of inorganic–organic mixtures followed the trend of (NH₄)₂SO₄ ≥ NH₄HSO₄ ≥ NaCl ≥ NH₄NO₃, which were generally consistent with their salting out efficiency.

The measured SRH values as a function of OVF are plotted in Fig. 6. AS–C₈H₁₇SO₄Na showed SRH of 98.7 ± 0.5% when OVF was 70%, higher than those of 50% OVF (82.1 ± 1.6%) and 90% OVF (80.0 ± 0.9%). However, the phenomenon was totally different from that of AS–C₈H₁₇SO₄Na, which showed lower SRH with 70% OVF (62.2 ± 2.6%) than those of 50% OVF (69.6 ± 1.0%) and 90% OVF (81.3 ± 1.2%). Therefore, the above results indicated controversial effect of OVF on SRH (Bertram et al., 2011; Song et al., 2012b).
Figure 4. ESEM images of (a) homogeneous AS–C₈H₁₇SO₄Na particles (50% OVF) underwent (b) LLPS and (c) efflorescence.
Figure 5. Van Krevelen Diagram for the mixed inorganic–organic particles in the current study (marked as circles): (a) NaCl containing systems and (b) AS containing systems. Solid symbols indicate that LLPS was observed for particles with at least one OVF, while hollow symbols indicate that LLPS was not observed for particles with all tested OVFs. Stars indicate data obtained from You et al. (2013) and O’Brien et al. (2015). PEG represents polyethylene glycol.
Figure 6. Summary of SRH results as a function of OVF for inorganic-surfactant particles.
Solid phase separation

For mixed systems without undergoing LLPS, we found they were separated with distinct solid phase after obvious efflorescence of inorganic salts (e.g., AS−C$_2$H$_5$SO$_4$Na and NaCl−C$_2$H$_5$SO$_4$Na mixture shown in Fig. S2). In Fig. 7a, ERH of NaCl−surfactant particles with 50%, 70% and 90% OVF were ranged in 47.0−61.8%, which was higher than the measured ERH (48.3 ± 0.4%) and reported ERH range of pure NaCl (41−51%) (Peng et al., 2022). As for AS−surfactant systems (Fig. 7b), efflorescence was observed for 27 among 30 aerosol samples. We did not observe distinct occurrence of efflorescence for the rest 3 samples, and 2 samples among 3 were with 90% OVF, which could be explained by the possible loss of AS when it was persistently exposed to electronic beam (Posfai et al., 2013; O'brien et al., 2015), especially for particles in which inorganic fractions were small (i.e., high OVF). ERH values of AS−surfactants particles with 50%, 70%, and 90% OVF ranged in 31.2−46.6%, showing a close result to the reported ERH of pure AS (30−48%) (Peng et al., 2022), but higher than the measured ERH (30.7 ± 0.9%). The higher efflorescence RH of inorganic−surfactant systems could be explained by the substrate-particle interactions. Ghorai et al. (2014) found an acid displacement reaction in glutaric acid−NaCl systems, which was driven by gaseous HCl liberation and causing chloride depletion. Such interactions of chloride depletion may facilitate efflorescence transitions, resulting in efflorescence at ~ 68% RH and ~ 60% RH, respectively, for internally mixed NaCl−glutaric acid particles with molar ratios of 1:3 and 1:1. Higher ERH could also be attributed to heterogeneous nucleation initiated by chemical purities (Choi and Chan, 2002). Choi and Chan (2002) observed 54.4% ERH for a 1:1 mixed NaCl−glutaric acid, and they explained that insoluble additives crystallized and formed nuclei for the heterogeneous efflorescence of inorganic salts, leading to their higher ERH values.
Figure 7. Measurements of efflorescence relative humidity (ERH) of (a) NaCl–surfactant and (b) AS–surfactant particles. The grey areas in (a) and (b) indicate the efflorescence RH range of NaCl (41–51%) and AS (30–48%) obtained from Peng et al. (2022). Red lines in (a) and (b) represent the measured average ERH of pure NaCl (48.3 ± 0.4%) and AS (30.7 ± 0.9%).

3.3 Atmospheric implication

Inorganic salts with organic coating are ubiquitous in natural (e.g., marine aerosol) and anthropogenic aerosols (Yu et al., 2019; Li et al., 2021). Based on the direct observation of mixing state for inorganic–surfactants submicron particles, we confirmed an apparent water diffusion hindrance by organic surfactant shell upon hydration, which could notably raise inorganic deliquescence RH to nearly saturated condition. This indicates that the hygroscopicity of aerosol would be reduced in the presence of organic surfactant shell, which might decrease aerosol water content and inhibit aqueous reactions (e.g., aqueous sulfate production).

During dehydration, inorganic–surfactant particles were phase-separated before and after efflorescence. Surfactants with lower O:C ratio were more likely to undergo LLPS than those with higher O:C. Compared with homogeneous particles, phase-separated particles could decrease trace gas uptake (You et al., 2012), resulting in reduction of the formation of secondary organic aerosols (SOAs) (Zhang et al., 2018). In addition, organic phase was enriched in “outer shell”, which can
potentially alter aerosol water activity and lower aerosol surface tension, hence affecting air-liquid interfacial chemistry as well as aerosol–cloud interactions (Ruehl et al., 2016; Ovadnevaite et al., 2017).

We should note that in the atmosphere most particles are smaller (e.g., 0.1 to 0.3 μm) than sample particles and the chemical characteristics of ambient aerosol are not as simple as binary chemical systems in the current study. Therefore, the water kinetic inhibition should be further investigated for smaller particles containing more complex systems in the future. In all, information of mixing states of inorganic–surfactants particles should be incorporated into the atmospheric modeling for heterogeneous chemistry, particle hygroscopicity and growth, to improve predictions on indirect effects of aerosol–climate interactions.

4 Conclusions

Atmospheric surfactants have potential to distribute to surface, altering mixing state hence influencing aerosol hygroscopicity and CCN activity. But currently direct observation of RH–depended mixing state of aerosol containing atmospheric surfactants is scarce. In this study, dynamic mixing state and phase transitions of 20 types of submicron particles containing inorganic and surface–active organic constituents were directly investigated upon relative humidity (RH) cycling by Environmental Scanning Electron Microscopy (ESEM).

Inorganic–organic core-shell morphology was found for dry deposited mixed inorganic-surfactant particles. During hydration, organic shell inhibited water diffusion exposing to inorganic cores, resulting in higher deliquescence RH (88.3–99.5%) of inner inorganic phase compared with pure inorganic aerosol. This was because higher RH may facilitate phase transition of organic shell from solid to semisolid, raising organic viscosity thus decreasing water diffusion exposing to inorganic core. Meanwhile, we directly observed obvious Ostwald ripening of NaCl in single particle, that is, the growth of larger NaCl crystal at the expense of smaller ones, in 6 among 10 NaCl–surfactants systems. As a result of water inhibition by surfactant shell, Ostwald ripening in all systems occurred at RH above 90%, which were higher than reported RH range of pure NaCl measured at 27°C (75–77%).

During dehydration, 8 among 20 chemical systems underwent LLPS, including 4 AS–organic systems and 4 NaCl–organic systems. LLPS was always observed when O:C ≤ 0.4 and never been observed when O:C > ~0.57. SRH values of AS–surfactant particles were generally higher than SRH of corresponding NaCl–surfactant systems, which was consistent with reported salting out efficiency of inorganic salts. OVF showed a controversial effect on SRH of inorganic salt–surfactant systems. Additionally, inorganic salts–surfactant systems without LLPS underwent solid phase separation after efflorescence and also showed distinct separated phases. Our results provide a comprehensive and unique insights into the dynamic evolution of inorganic–surfactant particles under fluctuating atmospheric conditions, which could help improve our fundamental knowledge and decrease uncertainty of model estimation on global radiative effect.

Data availability. The data used in this paper can be obtained from the corresponding author upon request.
Author contributions. CX and BK did the experiments, analyzed data. CX plotted the figures and wrote the original draft. FZ and XP contributed to discussion and reviewed the manuscript. BK and ZX reviewed the manuscript and contributed to the fund acquisition. ZW administrated the project, conceptualized the study, reviewed the manuscript and contributed to fund acquisition.

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Reference


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