

Surface propensities of atmospherically relevant organic and inorganic ions investigated by spray ionization mass spectrometry

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Atmospheric water droplets such as aqueous aerosols and cloud/fog droplets play central roles both in global climate change and air pollution. They consist of not only water but also a variety of compounds including a variety of organic and inorganic ions. Some ions preferentially accumulate at the air-water interface (AWI) of droplets, while the others would keep staying in the bulk phase. Such surface propensities (SPs) of ions contribute to the ability of cloud condensation nuclei (CCN) formation, resulting in the change of radiative forcing effects.

However, the origin and mechanism of SPs are still not known well. Here, we experimentally investigated SPs at extremely low concentrations using spray ionization mass spectrometry (SIMS). We successfully disentangled the effects of hydrophobic alkyl-chain and charged head-group of ions.

In our experiments, we measured relative number densities of ions at the AWI by using SIMS [1]. First, we measured the negative ion mass spectra obtained from $R_N\text{CO}_2\text{Na}$ ($N=1\sim9$) mixture in water solutions at various solute concentrations. Signal intensities of carboxylate ions generally increased with carbon number N . The tendency was the same between 10 nM and 1 μM . This was also consistent with the previous work that measured between 1 μM and 1 mM [1]. Thus, the general tendency of SP of carboxylate vs. N (≤ 9) is found to be the same at the wide range of concentration.

Next, we measured the negative ion mass spectra obtained from aqueous $R_N\text{CO}_2\text{Na}$ ($N=1\sim9, 11$) and $R_M\text{SO}_3\text{Na}$ ($M=1\sim9, 11$) mixture solutions. The observed signal intensities of carboxylate ions were generally lower than those of sulfonate ions if the alkyl chain lengths were the same. This result implies that charged head group influences the SP of ions more than alkyl-chain part does.

Finally, we measured the negative ion mass spectra obtained from several inorganic ions (SCN^- , NO_3^- , Br^- , BF_4^- , ClO_4^- , I^-) with nonanoate and methanesulfonate mixture solutions. This measurement was carried out in order to compare the effects of alkyl chain and charged head-group on the SPs. The observed SPs of inorganic ions generally increased with the ion radius. Then, we plotted the relative SPs obtained from the above solution as a function of ion volumes. The slopes obtained from inorganic and organic ions were 8.1 and 70.5, respectively. This analysis would provide the relative contribution of hydrophobic alkyl-chain vs. charged head-group of ions. These data will be useful to predict SPs of atmospherically relevant inorganic and organic ions found in ambient marine aerosol and cloud droplets.

References:

[1] Enami et al., *J. Phys. Chem. A* **2016**, *120*, 9224–9234

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