Molecular Dynamics Simulation of Surface Tension of NaCl Aqueous Solution at 298.15K: from Diluted to Highly Supersaturated Concentrations

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Sodium chloride (NaCl) is one of the key components of atmospheric aerosol particles. Concentration-depend surface tension of aqueous NaCl solution is essential to determine the equilibrium between droplet NaCl solution and water vapor, which is important in regards to aerosol-cloud interaction and aerosol climate effects. Although supersaturated NaCl droplets can be widely found under atmospheric conditions, the experimental determined concentration dependency of surface tension is limited up to the saturated concentration range due to technical difficulties, i.e. heterogeneous nucleation since nearly all surface tension measurement techniques requires contact of the sensor and solution surface. In this study, the surface tension of NaCl aqueous solution with solute mass fraction from 0 to 1 was calculated using molecular dynamics (MD) simulation. The surface tension increases monotonically and near linearly when mass fraction of NaCl (xNaCl) is lower than ∼0.265 (saturation point), which follows theoretical predictions (e.g., E-AIM, SP parameterization, and PK parameterization). Once entering into the supersaturated concentration range, the calculated surface tension starts to deviate from the near-linear extrapolation and adopts a slightly higher increasing rate until xNaCl of ∼0.35. We found that these two increasing phases (xNaCl ∼0.35) is mainly driven by the increase of excessive surface enthalpy when the solution becomes concentrated. After that, the surface tension remains almost unchanged until xNaCl of ∼0.52. This phenomenon is supported by the results from experiment based Differential Koehler Analyses. The stable surface tension in this concentration range is attributed to a simultaneous change of surface excess enthalpy and entropy at similar degree. When the NaCl solution is getting more concentrated than xNaCl of ∼0.52, the simulated surface tension regains an even faster growing momentum and shows the tendency of ultimately approaching the surface tension of molten NaCl at 298.15 K (∼148.4 mN/m by MD simulation). Energetic analyses imply that this fast increase is primarily still an excessive surface enthalpy-driven process, although concurrent fluctuation of excessive surface entropy is also expected but in a much smaller scale. Our results unfold the global landscape of concentration dependence of aqueous NaCl solution and its driven forces: a water surface tension dominated regime (xNaCl from 0 to ∼0.35), a transition regime (xNaCl from ∼0.35 to ∼0.52) and a molten NaCl surface tension dominated regime (xNaCl beyond ∼0.52).