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Formation of Low-Temperature Cirrus from H_2SO_4/H_2O Aerosol Droplets

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We present experimental results obtained with a differential scanning calorimeter (DSC) that indicate the small ice particles in low-temperature cirrus clouds are not completely solid but rather coated with an unfrozen H_2SO_4/H_2O overlayer. Our results provide a new look on the formation, development, and microphysical properties of low-temperature cirrus clouds.

Low-temperature thin and subvisible cirrus (SVC) ice clouds are important climate regulators,[1] because they cover about 30% of the globe, with larger frequency of occurrence in the tropics.[2] Being globally widespread, these clouds impact climate by reflecting solar radiation,[1,3] preventing terrestrial radiation from escaping to space,[3] and supplying surfaces for the chemical destruction of ozone,[4,5] which is an important greenhouse gas. Formation and microphysical properties of the clouds are not fully understood yet. Here we show, to our best knowledge for the first time, that the small ice particles are not completely solid, as is usually believed, but rather coated with a H_2SO_4/H_2O overlayer. The overlayer can slow down the growth rate of ice particles and change cloud radiative properties[6] and the rate of ozone loss in comparison with uncoated ice.

Depending on the latitude, low-temperature cirrus clouds are observed between ~10 and 20 km in the temperature range 210−188 K, with higher and colder clouds in the tropics. The clouds originate from aqueous droplets of composition <30 wt % H_2SO_4[5] formed by H_2O condensation onto concentrated stratospheric H_2SO_4/H_2O aerosol droplets entering the upper troposphere due to tropopause folds,[7] large-scaled stratospheric waves,[8] and gravitational deposition.[9] After dilution, the largest aerosol droplets, which are 1.2−1.8 μm in diameter,[7,10] may grow up to 2 μm and larger.

Optical studies of micrometer-size droplets (~13 μm) showed that in the temperature region between 210 and 188 K only the droplets of composition 18−25 wt % H_2SO_4 produced ice.[11] These studies revealed only one freezing event, namely, the formation of ice. Our DSC measurements (described in detail previously[12]) of emulsified 5−26 wt % H_2SO_4 droplets of diameter 0.5−6 μm revealed three freezing and three melting events, as shown in Figure 1.

In Figure 1, three transition peaks indicate that three solids form/melt during the cooling/warming cycle. We determined the types of solids formed on cooling from the peak melting temperatures and relation between the surface areas of the colder double transition peaks. Because the warmer melting peak exactly matches the ice melting temperature in the equilibrium phase diagram of H_2SO_4/H_2O, the solid is ice.[12] The colder double peaks are due to eutectic freezing/melting ice/SAT (sulfuric acid tetrahydrate $H_2SO_4 \cdot 4H_2O$) and sulfuric acid octahydrate $H_2S4 \cdot 8H_2O$ (SAO), because the double melting peaks exactly match eutectic melting temperatures of ice/SAT and SAO.[13] Ice/SAT and SAO originate from a residual solution formed on cooling by expelling acid molecules from the ice lattice during nucleation and growth of ice. We determined the composition of the residual solution, which is ~38 wt % H_2SO_4, from the melting temperatures of eutectic ice/SAT and SAO.[13] These melting temperatures are very close, ~199 and 200 K, respectively.[13] Between the single and double transition peaks in Figure 1, particles are in the mixed-phased state: ice + H_2SO_4/H_2O solution (overlayer) of composition ~38 wt % H_2SO_4. The separation into the ice and the residual solution

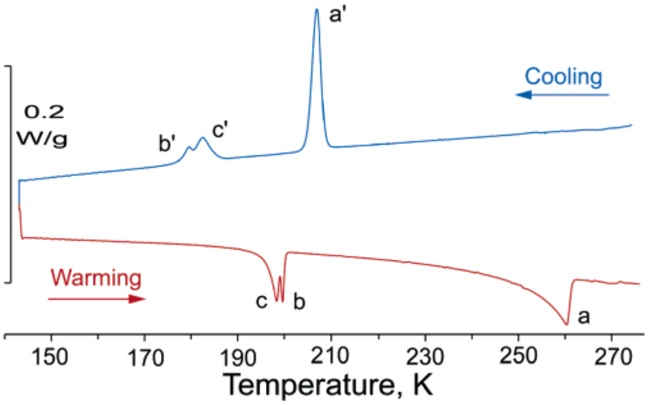

Figure 1. Calorimetric curves obtained from emulsified 20 wt % H_2SO_4 droplets at scanning rate 3 K/min. Exothermal peaks are formed when the heat of fusion evolves during the freezing of ice (peak a′) and SAO (peak b′) and the formation of a solid mixture ice/SAT (peak c′) (see text)). Endothermic peaks are formed when heat is consumed during the melting of ice, SAO, and ice/SAT (peaks a, b, and c, respectively). The scale bar indicates the heat flow.

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(i.e., the formation of the overlayer) occurs only in the freezing droplets of concentrations smaller than about 26 wt % H_2SO_4.[12] In the concentration range between ~26 and 31 wt % H_2SO_4, the freezing events overlap, producing one freezing peak. At concentrations larger than ~31 wt % H_2SO_4, only glass transition takes place (see inset in Figure 1 of ref 12).

That the residual solution envelops the formed ice crystal (or polycrystal) rather than fulfills some kind of a "fractal ice nanostructure" formed after the freezing of diluted droplets, has been inferred from the following reasons: (i) the fractal ice nanostructure possesses much larger surface free energy in comparison with that of mono- or polycrystalline ice. Therefore formation of the fractal ice nanostructure is less probable than the formation of mono- or polycrystalline ice. (ii) Our DSC measurements showed that the form (shape) of the ice melting curves obtained during the warming of frozen bulk solution drops and emulsified solutions were identical. This fact indicates that the ice formed within the micrometer-scaled drops should be mono- or polycrystalline. (iii) Koop et al. photographed the residual solution overlayer existing around the ice particles formed within micrometer-scaled solution drops (see Figure 5b in ref 11).

The freezing temperature of ice decreases with increasing concentration and reaches about 186 K at ~26 wt % H_2SO_4.[11,12] The residual solution freezes always below ~185 K,[12] which is the lowest tropopause temperature. This fact and similarity in size and composition of the laboratory and atmospheric droplets suggest that cirrus ice particles can be coated with a H_2SO_4/H_2O overlayer. Using the size of the drops and densities of corresponding H_2SO_4/H_2O solutions and ice, we calculated the overlayer thickness of initial composition of 38 wt % H_2SO_4. The calculations indicate that freezing droplets of a diameter between 0.2 and 2 μm and composition of 10−25 wt % H_2SO_4 produce an overlayer with a thickness between 10 and 240 nm.

In the atmosphere, to maintain equilibrium, H_2O will condense onto the overlayer, dilute it, and diffuse to the ice core. This diffusion-controlled ice growth rate will be smaller than that controlled by H_2O deposition onto the uncoated ice. As the ice core grows, the overlayer will thin because its volume is limited by the H_2SO_4 content. According to observations, SVC ice particles are quasi-spherical with diameters of 10−12 μm.[10] Being originated from the droplets of diameter $\geq$1.8 μm and composition $\geq$20 wt % H_2SO_4, they would possess an aged overlayer of composition of 25 wt % H_2SO_4 (diluted due to H_2O condensation) of thickness $\geq$6 nm. The existence of an H_2SO_4/H_2O overlayer was suggested to explain corona-producing low-temperature cirrus clouds.[14]

Our radiative transfer calculations showed that the overlayer slightly enhances reflection of solar radiation and reduces terrestrial radiation escaping to space in comparison with uncoated ice particles.[6] It is known that the rate of ozone loss proceeds faster in the liquid than in the solid state.[15] Because the reacto-diffusive length (the effective liquid depth over which reaction occurs) of $ClONO_2$ with H_2SO_4/H_2O aerosol droplets is ~40 nm,[16] it is clear that the overlayer will enhance the rate of ozone loss in comparison with pure ice particles. An overlayer can also increase HCl uptake that, in turn, will increase the rate of ozone loss, because the reacto-diffusive length for the aerosol droplets doped with HCl is only ~10 nm.[16]

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References and Notes

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