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Single freezing and triple melting of micrometre-scaled (NH₄)₂SO₄/H₂O droplets

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Atmospheric aerosol droplets containing NH_4^+ and SO_4^{2-} ions are precursors of cirrus ice clouds. However, the low-temperature phase transformation of such droplets is not understood yet. Here we show for the first time that micrometre-scaled $(NH_4)_2SO_4/H_2O$ droplets produce one freezing event but three melting events which are the melting of (i) pure ice, (ii) eutectic ice/$(NH_4)_2SO_4$, and (iii) eutectic ice/$(NH_4)_3H(SO_4)_2$. We also find that the melting of ice/$(NH_4)_3H(SO_4)_2$ consists of two eutectic melting events, presumably ice/letovicite-II and ice/letovicite-III.

Past measurements revealed that NH_4^+ and SO_4^{2-} ions are abundant in atmospheric aerosol particles.[1] It is thought that aqueous aerosol droplets containing ammonium sulfate, $(NH_4)_2SO_4$,[2,3] ammonium bisulfate, $(NH_4)HSO_4$,[4–6] and letovicite, $(NH_4)_3H(SO_4)_2$,[3,4] which are formed by the reaction of H_2SO_4 with NH_3, are the precursors of cirrus ice clouds. Cirrus clouds, being globally widespread, impact radiative balance of the Earth, redistribute water vapour (dominant greenhouse gas) to lower altitudes, and supply surfaces for heterogeneous reactions destructing ozone (important greenhouse gas at high altitudes). Naturally, these processes depend on the microphysics of cirrus, *i.e.*, on the size, composition, surface phase state, *etc*. For better understanding of the microphysics of cirrus, it is important to know the freezing behaviour of aqueous droplets in size and with composition representative of the atmosphere.

Freezing of $(NH_4)_2SO_4/H_2O$ has been intensively studied both in bulk and dispersed phases (see ref. 7 and 8 and citations therein). Past studies were focused mainly on the measurement of the homogeneous freezing temperature. Implicitly, it was assumed that on cooling in $(NH_4)_2SO_4/H_2O$ only a single freezing event takes place (like in other aqueous solutions). Recently we showed, using differential scanning calorimetry (DSC) results, that millimetre-scaled $(NH_4)_2SO_4/H_2O$ droplets always produce two freezing events[9]

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whereas micrometre-scaled emulsified droplets only one.[10] The first freezing event is the freezing of pure ice and the second one is the freezing of a freeze-concentrated residual solution formed by the segregation of ions from the ice lattice. The residual solution tends to freeze in a temperature region of ∼214–225 K.[10,11] The single freezing event of micrometre-scaled droplets was accounted for by the fact that the freezing out of pure ice occurs near or within the ∼214–225 K region.[10] As a result the two freezing events either overlap, forming one freezing event, or part of the residual solution does not freeze, but transforms to glass at ∼172 K. On warming after devitrification at ∼172 K the terminated freezing of the residual solution recommences to form an ice/$(NH_4)_2SO_4$ solid mixture at ∼185 K. On further warming micrometre-scaled droplets, similar to millimetre-scaled droplets, produce two melting events: the melting of the eutectic mixture of ice/$(NH_4)_2SO_4$ and of pure ice.[10] In this paper, we present additional DSC results which demonstrate that in fact micrometre-scaled emulsified $(NH_4)_2SO_4/H_2O$ droplets produce also a third melting event which consists of two eutectic points, probably of ice/letovicite-II and ice letovicite-III. Our results give a new look at the freezing behaviour of emulsified $(NH_4)_2SO_4/H_2O$ which can be useful for the physical chemistry of the freezing of small aqueous droplets and cloud physics and chemistry.

In our measurements we used emulsified $(NH_4)_2SO_4/H_2O$ and $(NH_4)_3H(SO_4)_2/H_2O$ solutions. The details of the preparation of solutions, emulsions, and DSC measurements have been reported elsewhere.[2,5,6,9–11] Shortly, solutions were prepared by mixing 99.99% $(NH_4)_2SO_4$ (Sigma Aldrich) and 99.5% $(NH_4)HSO_4$ (Fluka) with the corresponding amount of ultrapure deionized water. The emulsion oil-phase was produced by mixing 80 wt% Halocarbon 0.8 oil (Halocarbon Products Corp.) and 20 wt% lanolin-surfactant (Sigma Aldrich). Optical microscopy measurements indicate a diameter of droplets between ∼1 and 50 μm. A Mettler Toledo DSC 822 calorimeter was used for freezing/melting measurements between 278 and 133 K at a scanning rate of 3 K min⁻¹. A number of repetitive measurements were performed to verify reproducibility. The repetitive measurements were performed on several samples of the same emulsion and on samples of different emulsions of the same solution.
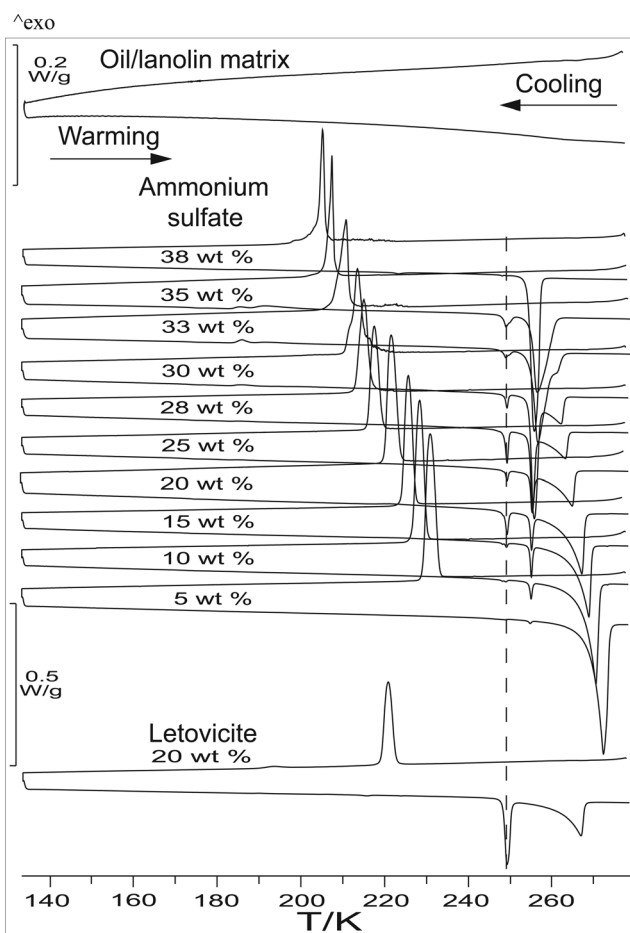
Fig. 1 presents the collection of thermograms obtained from emulsified 5–38 wt% $(NH_4)_2SO_4$ solutions. The thermogram of a pure halocarbon oil/lanolin matrix is presented to
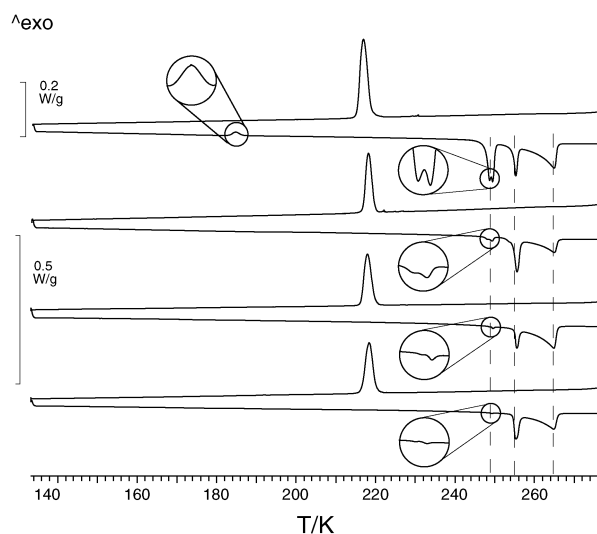
Fig. 1 DSC thermograms obtained from a pure halocarbon oil/lanolin matrix, emulsified 5–38 wt% $(NH_4)_2SO_4$ and 20 wt% $(NH_4)_3H(SO_4)_2$ solutions. The arrows show the direction of the temperature change of 3 K min^{-1}. The scaled bar denotes heat flow through samples.

demonstrate that the matrix does not introduce artifacts in the thermograms of emulsified solutions. The peaks directed upwards are due to the enthalpy of fusion released during freezing. The endothermic peaks directed downwards are a result of the enthalpy of fusion absorbed during melting. In the warming thermograms clearly three distinct melting events are seen. The warmest melting event is due to the melting of pure ice.[9–11] The peak temperature of the melting of pure ice decreases with increasing concentration in accordance with the phase diagram of $(NH_4)_2SO_4/H_2O$.[3] The middle melting event is due to the eutectic melting of ice/$(NH_4)_2SO_4$.[9] The fact that the third melting peak remains constantly at ~ 249 K in spite of different concentrations suggests it to be the eutectic melting of ice/new-solid. Calorimetric measurements indicate the onset of eutectic melting of bulk ice/$(NH_4)_3H(SO_4)_2$ to take place at ~ 248 K.[3] Similarly, X-ray diffraction measurements of emulsified $(NH_4)_3H(SO_4)_2/H_2O$ show an onset of the eutectic melting at ~ 247 K.[6] Our DSC measurements of emulsified $(NH_4)_3H(SO_4)_2/H_2O$ droplets of different concentrations give the eutectic melting of ice/$(NH_4)_3H(SO_4)_2$ of ~ 248 K. In Fig. 1, the thermogram of 20 wt% $(NH_4)_3H(SO_4)_2$ droplets is shown for comparison. It is seen that the third melting event of $(NH_4)_2SO_4/H_2O$ droplets coincides with the eutectic melting

of ice/$(NH_4)_3H(SO_4)_2$. Thus we assign the third melting event to the eutectic melting of ice/letovicite. It should be emphasized that the formation of letovicite by freezing $(NH_4)_2SO_4/H_2O$ droplets was neither predicted theoretically by the thermodynamic E-AIM model[12] nor detected in past experiments. However, the formation of letovicite in the more acidic NH_4HSO_4/H_2O system was theoretically predicted by the E-AIM model[12] and observed during the cooling of bulk (3–70 μL) samples[5,13] and emulsified NH_4HSO_4/H_2O droplets.[6]

In Fig. 2, the thermograms obtained from four different emulsified 25 wt% $(NH_4)_2SO_4$ droplets are presented. Magnification reveals the presence of crystallization on warming at ~ 185 K and the peak at ~ 249 K to be a double peak. Similar double peaks (in rare occasions, a broad single peak) are observed in the thermograms obtained from droplets of other concentrations. This indicates that in fact two solids melt in the course of ice/letovicite eutectic melting. According to the literature, bulk letovicite exists in six polymorphic crystalline phases called letovicite-I to letovicite-VI.[14,15] In the temperature region of our measurements, between 278 and 133 K, letovicite can exist as letovicite-II and letovicite-III, and the transition temperature between these two phases is reported at 263 K. Since $(NH_4)_2SO_4/H_2O$ droplets freeze at a temperature much below 263 K (Fig. 1) and the eutectic melting of ice/$(NH_4)_3H(SO_4)_2$ is also below 263 K, one peak can be due to the eutectic melting of ice/letovicite-III. Although bulk letovicite-II is thermodynamically unstable below 263 K, we assume that in micrometre-scaled droplets letovicite-II can be formed and exist also below 263 K. The assumption is justified by the following: (i) in finely dispersed and geometrically constrained aqueous systems, metastable crystalline phases can nucleate and exist even in thermodynamically unfavorable temperature regions. For example, in porous media, metastable cubic ice can be formed above 210 K and exists up to 273 K in spite of a transition temperature from bulk cubic-to-hexagonal ice of ~ 210 K.[16–19] (ii) It has been reported that in emulsified $(NH_4)_3H(SO_4)_2/H_2O$ droplets, letovicite-II is formed instead

Fig. 2 DSC thermograms obtained from four different emulsions of 25 wt% $(NH_4)_2SO_4$ solution. The spherical parts are the magnification of a melting peak at ~ 249 K and the crystallization peak at ~ 185 K.

of stable letovicite-III below 263 K.[6] Thus the third peak at ~249 K could be due to the eutectic melting of ice/letovicite-II and ice/letovicite-III.

Fig. 2 demonstrates that the area under the melting peaks at ~249 K strongly varies from sample to sample and can reach a very small value as in the bottom thermogram. A similar variation of the peak area at ~249 K is also observed in the thermograms obtained from the droplets of other concentrations. In the DSC method, the peak area of transition peaks is proportional to the amount of the enthalpy of fusion released/absorbed during the first order phase transition. Since the enthalpy of fusion is an extensive thermodynamic property, a smaller peak area indicates a lower fraction of eutectic ice/letovicite.

In Fig. 2, one may assume that the area of the peak at ~249 K, which is proportional to the amount of melted letovicite, is larger if there is a large crystallization peak at ~185 K i.e., letovicite may be formed at ~185 K. However, analysis of the large number (~150) of thermograms obtained from the emulsified droplets of different concentrations does not show strict correlation between the areas of the peaks at ~185 K and ~249 K. The melting peak at 249 K appears even when the peak at 185 K is very small. We suggested that the peak at ~185 K can be produced by the simultaneous crystallization of $(NH_4)_2SO_4$ and ice in the smallest droplets in which the residual solution does not freeze at all but transforms to glass.[11] Sometimes the crystallization of $(NH_4)_2SO_4$ and ice occurred separately producing two peaks.[11] In Fig. 1, the two crystallization peaks formed upon warming are seen in the thermogram of 35 wt% $(NH_4)_2SO_4$. We assume that letovicite can be formed upon cooling in the larger droplets and on warming in the smallest droplets.

Fig. 1 shows that the peak area at ~249 K varies with concentration. It is larger for 28–35 wt% $(NH_4)_2SO_4$ droplets and smallest for 5 wt% and 38 wt% $(NH_4)_2SO_4$ droplets. The small peak area of 5 wt% $(NH_4)_2SO_4$ droplets is accounted for by the small total amount of NH_4^+ and SO_4^{2-} ions. However, it is unclear why the small amount of letovicite is formed in the droplets of 38 wt% $(NH_4)_2SO_4$ (Fig. 1). It is also not clear how the different amount of letovicite is formed in the droplets of the same concentration (Fig. 2). One reason could be that crystallization upon cooling and warming is a stochastic process which could result in the crystallization of the different amounts of letovicite in the droplets of different sizes.

In conclusion, we find triple melting of micrometre-sized ammonium sulfate droplets. We attribute the melting events to eutectic melting of ice/letovicite, eutectic melting of ice/ammonium sulfate and melting of pure ice. In fact, the eutectic melting of ice/letovicite shows a double peak nature and may be composed of two eutectic melting events, ice/letovicite-II and ice/letovicite-III. So, the behaviour of frozen ammonium sulfate droplets upon warming might even involve a fourth melting event. It remains unclear, why letovicite is formed during the cooling/warming of small emulsified $(NH_4)_2SO_4/H_2O$ droplets but not during the cooling of millimetre-scaled droplets placed on substrates.[9–11] These two types of droplets differ both in size and chemical surrounding. The former are completely embedded into a surfactant–oil matrix, whereas the latter are placed on Al or Au substrates[11] and surrounded by air. Whether the small size of droplets and/or surfactant–oil matrix environment render solutions more acidic and, therefore, more friendly for the formation of letovicite remains to be explored.

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