

# Different freezing behavior of millimeter- and micrometer-scaled $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$ droplets

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## Abstract

Although the freezing of aqueous solutions is important for nature and different branches of science and freeze-applications, our understanding of the freezing process is not complete. For example, numerous measurements of micrometer-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets report one freezing event below the eutectic point. However, measurements of larger millimeter-scaled droplets reveal two freezing events: the freezing out of ice and subsequent freezing of a residual freeze-concentrated solution. To resolve this apparent contradiction we performed numerous calorimetric measurements which indicate that the freezing of a residual solution of millimeter-scaled 5–38 wt%  $(\text{NH}_4)_2\text{SO}_4$  droplets occurs mainly between  $\sim 210$  and 225 K. We also find that micrometer-scaled droplets produce one freezing event which is within or in the vicinity of the  $\sim 210$ –225 K region. This fact and the analysis of thermograms suggest that the residual solution of micrometer-scaled droplets may partly crystallize simultaneously with ice and partly transform to glass at  $T_g \approx 172$  K. Our results suggest for the first time that the size of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets may affect the number of freezing events below the eutectic point.

(Some figures in this article are in colour only in the electronic version)

In nature, water and aqueous solutions are often dispersed (e.g. in the atmosphere) or confined to small dimensions and attached to different surfaces (soils, rocks, biological tissues etc) [1]. Understanding of the freezing behavior of aqueous solutions is important for medicine, biology and cryobiology (the survival of living matter at low temperature and preservation of biological tissues) [2, 3], the atmosphere (formation of the ice phase in high-altitude clouds) [4, 5], freezing of water in soils, rocks, and seas (change of the acidity of solutions and concomitant change in the rate of chemical

reactions) [6], freeze-applications (e.g. freeze-purification of waste water) [7], etc. In this paper, although we will only deal with the  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  system, the obtained knowledge may also be applied to other aqueous inorganic and organic solutions.

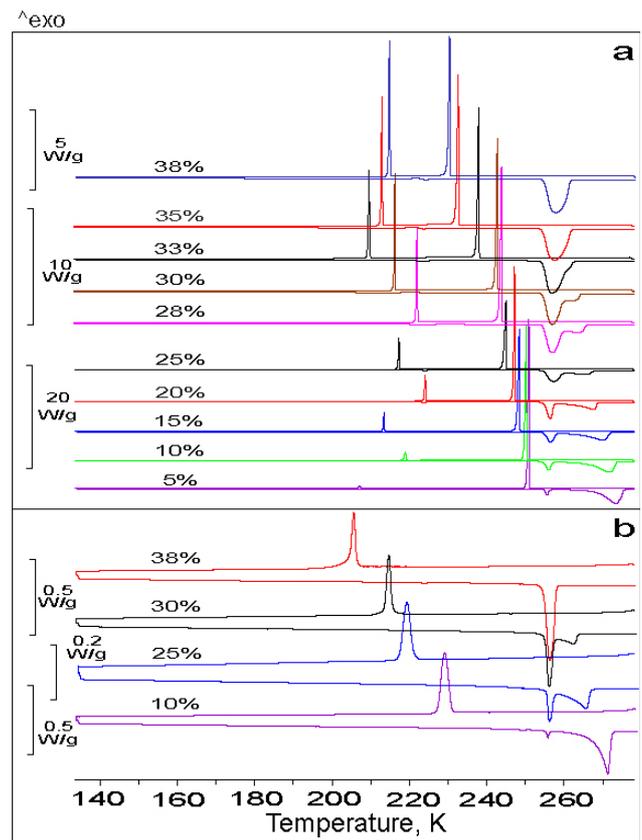
Recently, interest in the freezing behavior of micrometer-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets has grown immensely. It is thought that in the upper troposphere, ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , which is formed by the complete neutralization of  $\text{H}_2\text{SO}_4$  by  $\text{NH}_3$ , is an important component of solid and aqueous aerosol particles [8] and therefore may affect the formation of cirrus ice clouds [8, 9]. Submicrometer-

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and micrometer-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets have been intensively investigated by several scientific groups using different experimental techniques [9–16] (a comprehensive reference list and comparison of experimental results are given in [12] and [14]). The investigations were mainly focused on the determination of a homogeneous freezing temperature and did not consider the fate of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions during freezing. It was implicitly thought that if the freezing of small  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets occurs well below the eutectic point of  $T_e \approx 254.5$  K, then ice and  $(\text{NH}_4)_2\text{SO}_4$  crystallize simultaneously to form completely solid particles. Therefore, numerous studies in the past have reported only one freezing event. However, recent measurements reveal that larger millimeter-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets always freeze in two steps below  $T_e$  [17]. Firstly, pure ice freezes out at  $T_{\text{ice}}$  and then a residual freeze-concentrated solution freezes at  $T_{\text{res}} < T_{\text{ice}}$ . The different freezing behavior of millimeter- and micrometer-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets is evident and certainly needs to be explained.

In this paper, we present the differential scanning calorimetry (DSC) results for the freezing behavior of millimeter-scaled and micrometer-scaled emulsified  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets of subeutectic composition ( $\lesssim 40$  wt%  $(\text{NH}_4)_2\text{SO}_4$ ). In agreement with past measurements, we find that micrometer-scaled emulsified droplets indeed produce only one freezing event. The analysis of DSC thermograms shows that in contrast to the millimeter-scaled droplets, the residual solution of emulsified droplets may partly crystallize to a mixture of ice/ $(\text{NH}_4)_2\text{SO}_4$  simultaneously with the freezing out of pure ice and partly transform to glass at the glass transition temperature of  $T_g \approx 172$  K. Our results show for the first time that the temperature of the freezing out of pure ice,  $T_{\text{ice}}$ , which is mainly determined by the size of the  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets, can govern the number of freezing events. The presented results may be useful for a better understanding of the impact of size on the freezing behavior of other aqueous droplets.

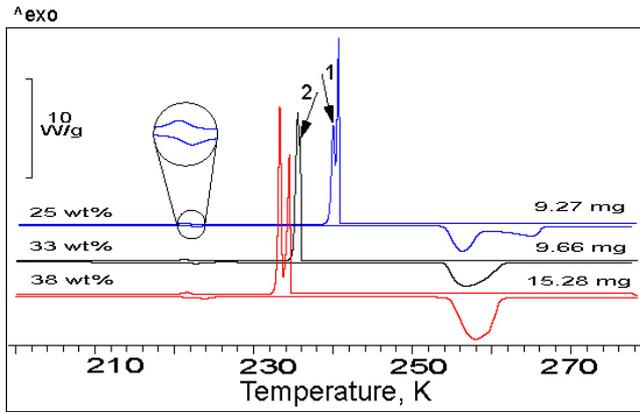
We prepared 5, 10, 15, 20, 25, 28, 30, 33, 35, and 38 wt%  $(\text{NH}_4)_2\text{SO}_4$  solutions by mixing 99.99%  $(\text{NH}_4)_2\text{SO}_4$  crystals (Sigma Aldrich) with the corresponding amount of ultrapure deionized water. Emulsions were prepared according to a well known and widely used emulsification technique described elsewhere [5, 9, 17, 18]. Briefly, the oil phase for the preparation of emulsions was prepared by mixing 80 wt% Halocarbon 0.8 oil (Halocarbon Products Corp.) and 20 wt% lanolin (Sigma Aldrich). The solution/oil mixtures of 1/10 by volume were shaken for 5–8 min with a high speed shaker (Thermolyne Maxi-Mix) at 1400–2000 rpm. The diameter of emulsified droplets was measured with an optical microscope and was found to be between  $\sim 1$  and  $20 \mu\text{m}$ . Millimeter-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets and emulsion samples were placed and then hermetically cold sealed in standard DSC aluminum (Al) crucibles of volume  $40 \mu\text{l}$ . Since in atmospheric oxygen, metallic Al very rapidly becomes covered with an oxide  $\text{Al}_2\text{O}_3$  film of thickness  $\sim 4$  nm, the  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets were in fact in contact with the  $\text{Al}_2\text{O}_3$  surface. Being placed on the Al ( $\text{Al}_2\text{O}_3$ ) surface, millimeter-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets form an approximate hemisphere with a contact angle



**Figure 1.** (a) Collection of DSC thermograms obtained from millimeter-scaled 5–38 wt%  $(\text{NH}_4)_2\text{SO}_4$  droplets. In the cooling thermograms (upper lines), the two sharp exothermic peaks directed upwards are due to the heat of fusion released during the freezing out of pure ice (warm peaks) and the freezing of a residual solution (cold peaks). In the warming thermograms (lower lines), the two endothermic peaks are due to the heat of fusion absorbed during the melting of the eutectic mixture of ice/ $(\text{NH}_4)_2\text{SO}_4$  and pure ice, respectively [17]. The three different scale bars, which indicate heat flow through the droplets, correspond to the three groups of thermograms. (b) DSC thermograms obtained from the emulsified micrometer-scaled droplets of concentrations of 10, 25, 30, and 38 wt%  $(\text{NH}_4)_2\text{SO}_4$ . The single exothermic peak is due to the heat of fusion released during the freezing out of pure ice and partial freezing of a residual solution (see text for details). In the warming thermogram, the endothermic melting peaks are the same as in (a). The numbers denote the concentration of droplets. The programmed scanning cooling and warming rates are  $3 \text{ K min}^{-1}$ .

of  $\sim 70^\circ$ – $90^\circ$ . The diameter and weight of millimeter-scaled droplets were  $\sim 1$ – $1.5$  mm and  $\sim 5$ – $15$  mg, respectively. The weight of emulsion samples was between 20 and 35 mg. The freezing behavior of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets was measured using a Mettler Toledo DSC 822. The DSC device was calibrated using the melting points of indium (429.75 K), water (273.15 K), and heptane (182 K) to an accuracy of better than  $\pm 0.3$ – $0.4$  K. The measurements were performed at a scanning rate of  $3 \text{ K min}^{-1}$  between 278 and 133 K. A number of repetitive measurements were performed to verify the reproducibility of the results.

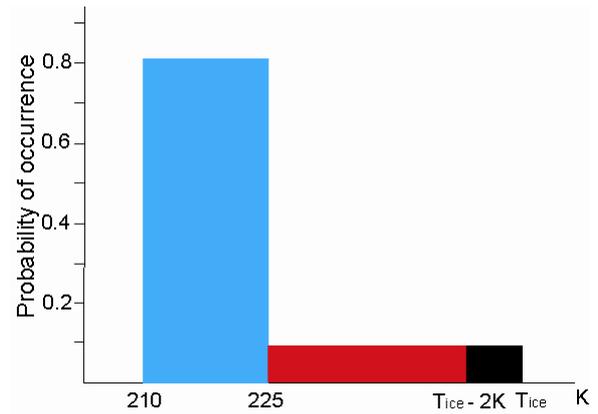
In figure 1(a), DSC thermograms obtained from the millimeter-scaled droplets of a concentration of 5–38 wt%  $(\text{NH}_4)_2\text{SO}_4$  are collected. The thermograms obtained from the



**Figure 2.** DSC thermograms obtained from 25, 33, and 38 wt%  $(\text{NH}_4)_2\text{SO}_4$  millimeter-scaled droplets. The arrows show the freezing of a residual solution (1) and the freezing out of pure ice (2), respectively. The magnified part shows paraelectric-to-ferroelectric ( $\text{P} \rightarrow \text{F}$ ) and reverse ferroelectric-to-paraelectric ( $\text{F} \rightarrow \text{P}$ ) transitions at  $\sim 223$  K [17]. The numbers denote the concentration and weight of droplets. The scanning cooling and warming rates are  $3 \text{ K min}^{-1}$ .

emulsified micrometer-scaled droplets of concentrations of 10, 25, 30, and 38 wt%  $(\text{NH}_4)_2\text{SO}_4$  are presented in figure 1(b). Comparison of figures 1(a) and (b) shows that in the cooling thermograms (upper lines) of millimeter-scaled droplets there are two freezing temperatures,  $T_{\text{ice}}$  and  $T_{\text{res}}$ , whereas in the cooling thermograms of micrometer-scaled droplets there is only one. It is seen in figure 1(a) that the millimeter-scaled droplets produce sharp freezing peaks, whereas in figure 1(b) the micrometer-scaled droplets produce broad bell-shaped freezing peaks which are due to the freezing of a large number ( $\gtrsim 10^5$ ) of size-distributed droplets. In both cases, in the warming thermograms (lower lines) there are two melting events which are produced by melting of the eutectic solid mixture of ice/ $(\text{NH}_4)_2\text{SO}_4$  (colder melting peaks at constant temperature) and pure ice, respectively [17]. It is also seen that as the concentration increases, the peak melting temperature of ice approaches the eutectic melting of ice/ $(\text{NH}_4)_2\text{SO}_4$ . At a concentration of  $\sim 38$  wt%  $(\text{NH}_4)_2\text{SO}_4$ , the two melting events overlap. While the temperatures of two melting events are similar for millimeter- and micrometer-scaled droplets of the same composition, the freezing temperatures are different, which is accounted for by the different size of the droplets.

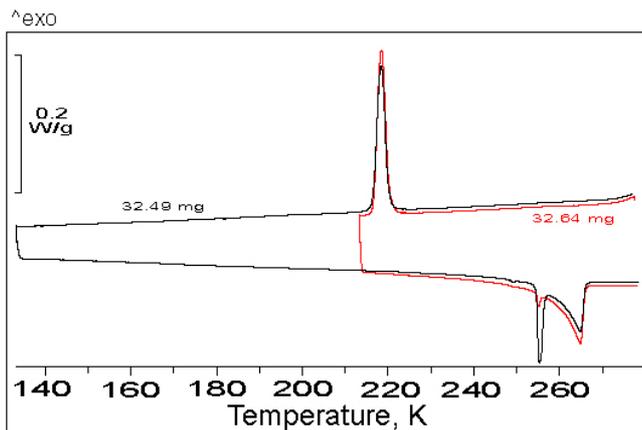
In figure 1(a), as expected, the temperature of the freezing out of ice,  $T_{\text{ice}}$ , decreases as the concentration of droplets increases. In contrast, independently of the concentration of droplets,  $T_{\text{res}}$  tends to fall into a temperature region of  $\sim 210$ – $225$  K. It should be noticed that in figure 1(a), only those thermograms are presented in which the two freezing events of  $T_{\text{ice}}$  and  $T_{\text{res}}$  are separated by a large temperature interval. The difference between  $T_{\text{ice}}$  and  $T_{\text{res}}$  can also be small (less than  $\sim 2$  K), as shown in figure 2 in which the thermograms of 25, 33, and 38 wt%  $(\text{NH}_4)_2\text{SO}_4$  are presented as an example. To estimate the frequency of the occurrence of  $T_{\text{res}}$  in the  $\sim 210$ – $225$  K region we performed more than 60 measurements of 25 wt%  $(\text{NH}_4)_2\text{SO}_4$  droplets. The residual solution freezes in  $\sim 80\%$  of all cases in the 210–225 K region,



**Figure 3.** Statistics for the freezing temperatures of the second freezing event related to the freezing of the residual solution ( $T_{\text{res}}$ ). The initial droplets are composed of 25 wt%  $(\text{NH}_4)_2\text{SO}_4$  and show the first freezing event at  $T_{\text{ice}}$ . Note that the residual solution possesses the eutectic concentration of  $\sim 40$  wt%  $(\text{NH}_4)_2\text{SO}_4$  that is larger than the overall concentration of droplets. Columns represent the probability of the occurrence of  $T_{\text{res}}$  in different temperature regions. Blue (left) column:  $\sim 210$ – $225$  K. Black (right) column: in the narrow temperature interval 2 K below  $T_{\text{ice}}$ . Red (middle) column: in between these two temperature regions. In total, more than 60 thermograms form the basis for this analysis.

in  $\sim 10\%$  of all cases within 2 K of the first freezing event (i.e. between  $T_{\text{ice}}$  and  $T_{\text{ice}} - 2$  K) and in the remaining  $\sim 10\%$  of all cases in between these two temperature regions. The probability of the occurrence of  $T_{\text{res}}$  in different temperature regions is schematically shown in figure 3. It should be noticed that the  $T_{\text{res}}$ s of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets placed on hydrophobic halocarbon grease substrate [17] also tend to fall into the  $\sim 210$ – $225$  K region. The fact that the freezing of the residual  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  solution tends to occur in a narrow temperature region is not unique. A residual solution formed after the freezing out of pure ice in micrometer-scaled emulsified  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  droplets also freezes in a narrow temperature region (see figure 1 in [19]).

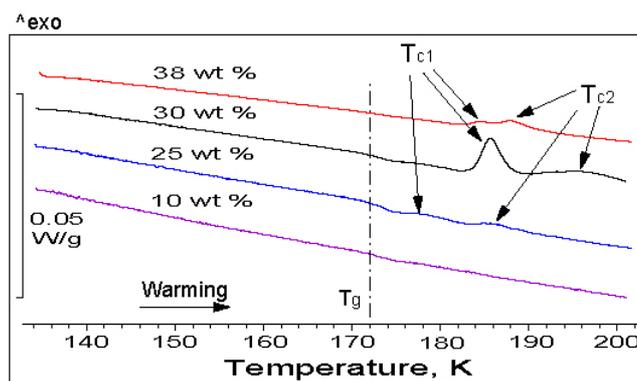
We also performed additional measurements on droplets of other concentrations, though not so extensive as for 25 wt%  $(\text{NH}_4)_2\text{SO}_4$  droplets. The measurements showed that the  $T_{\text{res}}$ s of the droplets of concentration larger than 20 wt%  $(\text{NH}_4)_2\text{SO}_4$  more often fall into the small temperature region within 2 K below  $T_{\text{ice}}$  than the  $T_{\text{res}}$  of less concentrated ones. The reason for such tendency can be found in figure 1(a). Seeing that  $T_{\text{ice}}$  gradually decreases with increasing concentration and  $T_{\text{res}}$  tends to occupy the constant region of  $\sim 210$ – $225$  K, the difference of  $T_{\text{ice}} - T_{\text{res}}$  decreases with increasing concentration. The less concentrated droplets produce the larger difference of  $T_{\text{ice}} - T_{\text{res}}$  because, as is seen in figure 1(a), their  $T_{\text{ice}}$  is warmer and  $T_{\text{res}}$  is similar. The largest difference of  $T_{\text{ice}} - T_{\text{res}} \approx 45$  K is produced by the most diluted droplet of 5 wt%  $(\text{NH}_4)_2\text{SO}_4$ . Here it should be noticed that for all concentrations, we never obtained any thermogram in which the two freezing events completely overlapped. At sufficiently large magnification apparently overlapping freezing peaks are clearly recognized as two individual freezing peaks (not shown), i.e.  $T_{\text{ice}} - T_{\text{res}} > 0$  K.



**Figure 4.** The complete (black) and truncated (red) DSC thermograms obtained from micrometer-scaled emulsified 25 wt%  $(\text{NH}_4)_2\text{SO}_4$  droplets of approximately similar weight. In the truncated measurement, the weight of the emulsion sample is 32.64 mg and that in the complete measurement 32.49 mg. The scanning cooling and warming rates are  $3 \text{ K min}^{-1}$ .

The large frequency of the occurrence of  $T_{\text{res}}$  in the temperature region of  $\sim 210\text{--}225 \text{ K}$  may be accounted for by the approximately similar concentration of a residual solution. Assuming that all  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions are expelled from the ice lattice during the first freezing event, the concentration of the residual solution [17] may be determined by using the onset of the temperature of the cold melting event and the equilibrium phase diagram of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$ . Figure 1 shows that in all thermograms the onset of the cold melting event is  $\sim 254.5 \text{ K}$ . According to the phase diagram of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  this temperature is the onset of eutectic melting. Therefore this fact indicates that the concentration of the residual solution is the eutectic concentration of  $\sim 40 \text{ wt\%}$   $(\text{NH}_4)_2\text{SO}_4$  [17]. The scattering of  $T_{\text{res}}$  within the  $\sim 210\text{--}225 \text{ K}$  region and the rare appearance of  $T_{\text{res}}$  above it is not clear. It could be brought about by some specific nuclei capable of triggering the heterogeneous freezing of the residual  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  solution at a warmer temperature. Further measurements are needed to find out whether the residual solution can freeze heterogeneously or not.

The number of melting events in warming thermograms informs us about how many solids are formed on cooling. In figure 1(a), the millimeter-scaled droplets produce two sharp freezing peaks and two broad melting peaks. In figure 1(b), looking at the symmetrical broad bell-shaped freezing peaks, one may assume that in emulsified micrometer-scaled droplets, pure ice and the eutectic mixture of ice/ $(\text{NH}_4)_2\text{SO}_4$  crystallize simultaneously, i.e. the two freezing events may overlap. To verify the assumption we performed truncated measurements in which the cooling of emulsion samples is terminated immediately at the end of freezing. Figure 4 is presented to demonstrate an example of the comparison of the truncated and complete thermograms obtained from the two emulsified 25 wt%  $(\text{NH}_4)_2\text{SO}_4$  solution samples of similar weight. It is seen that the shape and area of the freezing peaks and the area of melting peaks of pure ice are almost identical. However, in the truncated thermogram, the area of the eutectic melting peak



**Figure 5.** Ten-fold magnification of the low-temperature parts of the warming thermograms presented in figure 1(b). The dash-dot line denotes the subtle glass transition,  $T_g$ . The arrows show two crystallization events at  $T_{c1}$  and  $T_{c2}$ . The horizontal arrow shows the direction of temperature change of  $3 \text{ K min}^{-1}$ .

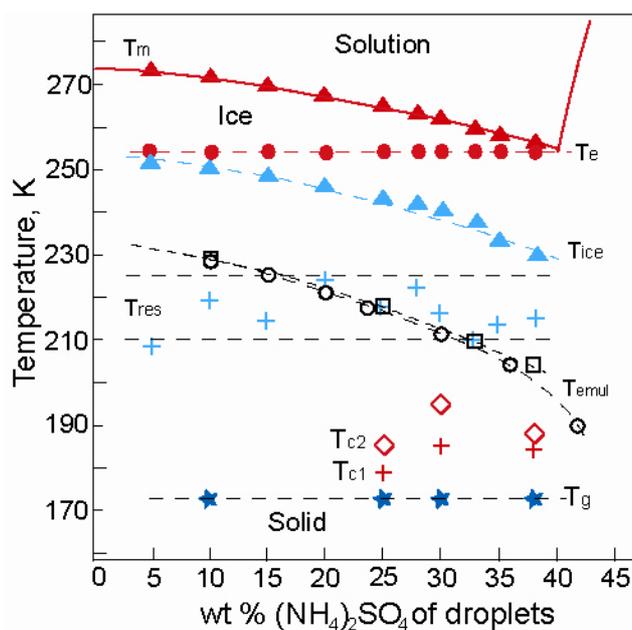
is dramatically reduced in comparison with that in the complete thermogram. In the DSC method, the area of transition peaks is proportional to the enthalpy of fusion released/absorbed during first order phase transitions. Since the change of enthalpy is proportional to the amount of material undergoing the phase transitions, the reduction of the peak area in the truncated thermogram indicates that a smaller amount of eutectic ice/ $(\text{NH}_4)_2\text{SO}_4$  is formed in the truncated measurement than in the complete measurement. Assuming that in both measurements the amount of eutectic ice/ $(\text{NH}_4)_2\text{SO}_4$  formed simultaneously with pure ice is approximately equal, this suggests that in the complete measurement, another freezing event should exist during which an additional amount of eutectic ice/ $(\text{NH}_4)_2\text{SO}_4$  is formed. However, the magnification of the cooling thermogram shows no indication of other freezing events down to  $133 \text{ K}$  but only of a subtle glass transition at  $T_g \approx 172 \text{ K}$  (not shown). The glass transition is shown in magnified warming thermograms in figure 5.

It is a well known experimental fact that crystallization (freezing) can occur not solely on cooling but also on warming after the devitrification of glass, i.e. after the transition from glass to highly viscous liquid (HVL) [19–22]. In figure 5, a ten-fold magnification of the low-temperature parts of the warming thermograms presented in figure 1(b) demonstrates the case. One can see a subtle transition from glass to HVL at  $T_g \approx 172 \text{ K}$  and two crystallization events,  $T_{c1}$  and  $T_{c2}$ . Earlier we reported that two crystallization events were observed during the warming of the residual solution of emulsified  $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  droplets [23]. The crystallization events were assigned to the separate crystallization of pure ice and  $\alpha\text{-NAT}$  (nitric acid trihydrate,  $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ ). In our case, the two crystallization events may be due to the crystallization of pure ice and  $(\text{NH}_4)_2\text{SO}_4$  crystallites. The almost invisible crystallization peaks in the thermogram of the 10 wt%  $(\text{NH}_4)_2\text{SO}_4$  droplet is accounted for by the small volume of corresponding residual solution. From the discussion of figures 4 and 5 we can suggest that some part of the ice/ $(\text{NH}_4)_2\text{SO}_4$  mixture is formed simultaneously with pure ice on cooling and some part during the crystallization on

warming after the devitrification of glassy residual solution. Since the expulsion of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  ions from the ice lattice is governed by dynamics rather than thermodynamics [17], the amount of pure ice and  $(\text{NH}_4)_2\text{SO}_4$  crystallized at  $T_{c1}$  and  $T_{c2}$ , and consequently the amount of ice/ $(\text{NH}_4)_2\text{SO}_4$  mixture crystallized simultaneously with pure ice on cooling varies from sample to sample, as is seen in figure 5. It should be noticed that a hypothesis of partial crystallization of solute had been proposed for the case of emulsified solutions of letovicite,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ , and ammonium bisulfate,  $(\text{NH}_4)\text{HSO}_4$  [24]. It had been reported that on cooling in large emulsified  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2/\text{H}_2\text{O}$  and  $(\text{NH}_4)\text{HSO}_4/\text{H}_2\text{O}$  droplets, ice and solute crystallized simultaneously, whereas in small droplets a residual solution that formed was suggested to transform to a glassy state on further cooling. If we assume that in our emulsified droplets, which are distributed in size between  $\sim 1$  and  $20 \mu\text{m}$ , the freezing out of pure ice and the freezing of the residual solution behave similarly, then it remains unclear why in some droplets the residual solution freezes simultaneously with the freezing out of ice and does not freeze on others. We assumed above that the residual solution may freeze heterogeneously if suitable nuclei are present. If the halocarbon oil/lanolin mixture around emulsified droplets contains some contaminants, which could trigger the freezing of the residual solution, then this could explain it. Further measurements are needed to verify the assumption.

Looking at the areas of the eutectic melting peak in figure 4 and the crystallization peaks at  $T_{c1}$  and  $T_{c2}$  in figure 5, one may point out that more eutectic ice/ $(\text{NH}_4)_2\text{SO}_4$  material melts than is produced both on cooling and subsequent warming (note the different scale bars in figures 4 and 5). This apparent disagreement can be accounted for by the quantitative analysis of the amount of ice,  $(\text{NH}_4)_2\text{SO}_4$ , and ice/ $(\text{NH}_4)_2\text{SO}_4$  formed/melted during cooling/warming. However, one cannot perform such an analysis because of the difficulty of integrating and interpreting the area of the corresponding transition peaks and the absence of thermodynamic data at low temperatures. We account for the peak-area-disagreement as follows.

- (i) In eutectic ice/ $(\text{NH}_4)_2\text{SO}_4$  mixture,  $\sim 60\%$  of the weight is ice because the eutectic concentration is  $\sim 40 \text{ wt}\%$   $(\text{NH}_4)_2\text{SO}_4$ . The above-mentioned peak area difference can be brought about by the strong temperature dependence of the enthalpy of the freezing (fusion) of ice,  $\Delta H_{\text{ice}}$  [4, 25–28]. The temperature dependence of  $\Delta H_{\text{ice}}$  is due to the fact that the average number of hydrogen bonds per water molecule increases with decreasing temperature. In the past, the  $\Delta H_{\text{ice}}$  was calculated using the heat capacity of emulsified water droplets measured only to 236 K [27, 28]. Using different thermodynamic approximations,  $\Delta H_{\text{ice}}$  was extrapolated to 150 K [26]. In our case the crystallization of ice on warming occurs between  $\sim 178$  and 186 K. At these temperatures the extrapolation gives  $\Delta H_{\text{ice}} \approx 1350 \text{ J mol}^{-1}$ , which is  $\sim 1/4$  of the value at the  $T_e$ . Thus the peak area difference can be brought about by the temperature dependence of  $\Delta H_{\text{ice}}$ .
- (ii) There is no experimental or theoretical evidence that the enthalpy of crystallization of  $(\text{NH}_4)_2\text{SO}_4$  can be temperature dependent. Therefore we do not consider



**Figure 6.** The transition temperatures of millimeter- and micrometer-scaled  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets are superimposed on the equilibrium phase diagram of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  [30] (solid red line). The filled red and blue triangles are the peak melting,  $T_m$ , and freezing  $T_{\text{ice}}$  temperatures, respectively, of pure ice. The red circles are the onset of eutectic melting of ice/ $(\text{NH}_4)_2\text{SO}_4$ ,  $T_e \approx 254.5 \text{ K}$ . The blue crosses are the peak freezing temperatures of a residual solution,  $T_{\text{res}}$ . The transition temperatures of  $T_m$ ,  $T_{\text{ice}}$ ,  $T_e$ , and  $T_{\text{res}}$ , are taken from figure 1(a). The black squares and circles are the freezing temperatures of emulsified  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets,  $T_{\text{emul}}$ , taken from figure 1(b) and [9], respectively. The red rhombus and crosses are the two crystallization-on-warming events,  $T_{c1}$  and  $T_{c2}$ , and the blue stars are the glass transition temperature,  $T_g$ , taken from figure 5. The horizontal dashed lines show the temperature region of  $\sim 210$ – $225 \text{ K}$  (see text for details). Note that only  $T_m$ ,  $T_{\text{ice}}$ , and  $T_{\text{emul}}$  correspond to the overall concentration of droplets (see text for details).

this situation. However, we may assume that the crystallization on warming of  $(\text{NH}_4)_2\text{SO}_4$  is a sluggish process which could stem from the large viscosity of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  [29]. The crystallization of  $(\text{NH}_4)_2\text{SO}_4$  may spread over a large temperature region not seen as a distinct transition peak.

In figure 6, the peak transition temperatures of figures 1 and 5 are collected and displayed graphically in the phase diagram of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  [30]. Also displayed are the peak freezing temperatures of micrometer-scaled emulsified  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets taken from [9] (black circles). It is seen that our data obtained from the emulsified droplets and those of [9] almost coincide. The freezing temperatures of emulsified droplets,  $T_{\text{emul}}$ , can be considered as true homogeneous freezing temperatures of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  droplets because they are in very good agreement with the other measurements in which concentration was known to a high accuracy [9, 12, 14, 16]. The  $T_{\text{ice}}$ s of millimeter-scaled droplets are much warmer than the  $T_{\text{emul}}$ , a fact that is mainly explained by the large difference in the size of droplets. Here it should be noticed that the measured individual  $T_{\text{ice}}$ s do not

always monotonically decrease with concentration. Individual  $T_{ice}$ s are scattered by approximately  $\pm 5$  K around the  $T_{ice}$ -line in figure 6. The  $T_{ice}$ s are heterogeneous freezing temperatures and are therefore necessarily governed by the ice nucleation efficiency of the Al ( $Al_2O_3$ ) substrate and impurities. Since 99.99% of  $(NH_4)_2SO_4$  crystals and ultrapure water, which are used for the preparation of solutions, can be considered as pure substances, we may assume that  $(NH_4)_2SO_4/H_2O$  droplets contain few impurities capable of ice nucleation. The main contribution to the scattering of individual  $T_{ice}$ s is brought about by Al ( $Al_2O_3$ ) substrate. In figure 6, only the freezing and melting temperatures of  $T_{ice}$ ,  $T_{emul}$ , and  $T_m$  correspond to the overall concentration of droplets. The other transition temperatures belong to the residual solution, the concentration of which is larger than the overall concentration of mother droplets.

Figure 6 demonstrates an interesting aspect, namely, that the majority of  $T_{emul}$ s are within or in the vicinity of the  $\sim 210$ – $225$  K region, i.e. the freezing out of pure ice in micrometer-scaled droplets begins in or below the temperature region where a residual solution is unstable with respect to crystallization. This fact may serve as confirmation of the above-discussed partial freezing of a residual solution together with the freezing out of pure ice. The physical reason can be that in the  $\sim 210$ – $225$  K region, the mobility of  $NH_4^+$  and  $SO_4^{2-}$  ions is not large enough for them to be expelled completely from the ice lattice because of significant viscosity [29]. Therefore the freezing out of pure ice and the freezing of a just-forming residual solution may partly proceed simultaneously. The expelled portion of ions forms a residual solution which transforms to glass at  $T_g \approx 172$  K (see above).

In conclusion, we have presented DSC results obtained from millimeter-scaled and micrometer-scaled emulsified  $(NH_4)_2SO_4/H_2O$  droplets of subeutectic composition with the aim of accounting for the difference in their freezing behavior: the large droplets always reveal two freezing events whereas the micrometer-scaled droplets reveal only one. The two freezing events are the freezing out of pure ice and the freezing of a residual freeze-concentrated solution which is formed by the expulsion of  $NH_4^+$  and  $SO_4^{2-}$  from the ice lattice during the freezing out of pure ice. Our results confirm the past measurements in the sense that micrometer-scaled  $(NH_4)_2SO_4/H_2O$  droplets produce only one freezing event [9–16]. We find that in the case of micrometer-scaled droplets the residual solution, which starts to form during the freezing out of pure ice, may partly freeze to a eutectic ice/ $(NH_4)_2SO_4$  mixture simultaneously with the freezing out of pure ice and partly transform to glass at  $T_g \approx 172$  K. On warming, after the devitrification of glass at the  $T_g$ , the remaining residual solution continues to crystallize to eutectic ice/ $(NH_4)_2SO_4$ . Our results for the first time account for why the second freezing event had not been observed during the cooling of micrometer-scaled  $(NH_4)_2SO_4/H_2O$  droplets. Although our results suggest that the size of droplets, which mainly determines the freezing temperature of  $T_{ice}$ , affects the number of freezing events of  $(NH_4)_2SO_4/H_2O$  droplets, the role of oil/lanolin environment in the freezing of emulsified droplets remains unclear. Further measurements are needed to

elucidate the matter. To have a clear picture of how the size and environment of an aqueous solution affects freezing behavior can be useful for cloud physics and different fields of science and freeze-applications.

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