Visualizing the three-step freezing process and three-phase reaction not predicted by the (NH4)2SO4/H2O phase diagram

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ABSTRACT: According to the conventional phase diagrams, aqueous solutions freeze at the liquidus and are frozen/solid below the eutectic solidus. Herein, using differential scanning calorimetry (DSC) and optical cryo-microscopy (OC-M), we demonstrate that hypoeutectic, eutectic 40 wt% (NH4)2SO4 and hypereutectic (NH4)2SO4/H2O remain liquid well below the eutectic solidus before freezing in three steps: fast-slow-fast. The first fast freezing produces a ramified ice microstructure (IM) and freeze-concentrated solution (FCS) containing up to ~70 wt% (NH4)2SO4. As temperature decreases further, the slow freezing of FCS precedes its fast freezing, which produces a striped IM and (NH4)2SO4 microcrystals. Videos recorded upon warming of frozen (NH4)2SO4/H2O reveal a new three-phase reaction, which is the recrystallization of ice and (NH4)2SO4 microcrystals into the lamellar eutectic ice-(NH4)2SO4 superlattice. This work demonstrates limitations of the (NH4)2SO4/H2O phase diagram and proposes an effective strategy for studying other deeply supercooled solutions whose behavior is not predicted by the phase diagram.

Understanding the freezing process is important for life sciences,1-3 nanotechnology,4 different natural,6,10 biotechnological11-17 and industrial18-20 processes. Common to all these scopes is a freeze-induced phase separation (FIPS) into ice and a freeze-concentrated solution (FCS).10,12,14,21-23 IM/FCS morphology and the phase state of FCS determine the properties of frozen solutions3,25-27 and, consequently, the properties of freeze-dried lyophilized products,21-15 glaciers,8,28 sea ice,9,29 ice clouds,10 etc. Unlike bulk solutions, which freeze at the liquidus,30-33 millimeter-scaled drops can be supercooled below the eutectic solidus.34 Depending on solute molecular structure, several freezing6,10,34,35 and glass transition12,35 events occur upon cooling. The number of freezing and melting events depends on solution size.5,35 Freezing and accompanying FIPS resume upon warming of glassy FCS.12,35 These results differ from the predictions of phase diagrams and show that further study of deeply supercooled solutions is necessary.

In this work, we employ DSC for the study of deeply supercooled eutectic and hypereutectic (NH4)2SO4/H2O and OC-M for visualization of the phase transitions of deeply supercooled hypoeutectic, eutectic and hypereutectic (NH4)2SO4/H2O. Ammonium sulfate, (NH4)2SO4, has practical implications38 and plays an essential role in the atmosphere.39,40 Details of the DSC and OC-M experiments are reported elsewhere.10,12,34,37

DSC measurements: In Figure 1a, the cooling thermograms of millimeter-scaled drops contain two exothermic peaks T_{f,ice} and T_{f,FCS}. Warming thermograms contain one broad endothermic peak that begins at the eutectic temperature T_{E}=254K. In Figure 1b, magnified thermograms reveal an inclined thermogram between T_{f,ice} and T_{f,FCS}. The para-to-ferroelectric and ferro-to-paraelectric transitions at T_{C}=223.5K indicate that (NH4)2SO4 crystals form at T_{f,FCS}. Thermograms of emulsified micrometer-scaled drops contain only peaks T_{f,µm} and T_{E} (Figure 1c).

Figure 1. DSC thermograms of eutectic and hypereutectic (NH4)2SO4/H2O. a. Thermograms of millimeter-scaled drops. Peaks T_{f,ice} and T_{f,FCS} are due to ice crystallization and the fast freezing of FCS, respectively. T_{E} denotes the eutectic melting. b. The 20-fold magnification of thermograms from Figure 1a. Transition peaks are reduced to fit the figure. Arrows mark inclined thermograms of the slow freezing of FCS. T_{C} is the Curie temperature. c. Thermograms of emulsified micrometer-scaled drops. T_{f,µm} is a...
freezing temperature. Heat flow scale bar (W/g) and concentration (wt%) are indicated.

The cooling thermograms in Figure 1 are similar to those of hypoeutectic millimeter-scaled and micrometer-scaled (NH₄)₂SO₄/H₂O drops, 34,36,41 Hypoeutectic T_f,ice, T_f,FCS and the inclined thermogram between them were related to ice crystallization, the fast freezing of FCS and slow freezing of FCS. However, in Figure 1b, the nature of T_f,ice, T_f,FCS and the inclined thermogram is unclear, because according to the (NH₄)₂SO₄/H₂O phase diagram, 42 the eutectic solution produces the eutectic ice/(NH₄)₂SO₄ mixture and hypoeutectic solutions produce (NH₄)₂SO₄ crystals and the eutectic ice/(NH₄)₂SO₄ mixture (Figure 2).

Unlike the warming thermograms in Figure 1, the warming thermograms of hypoeutectic millimeter-scaled drops contain the eutectic melting T_m and ice melting T_f,ice,43,36,41 and micrometer-scaled drops contain one 36 or two 37 eutectic melting events and ice melting.

**Figure 2.** Extended (NH₄)₂SO₄/H₂O phase diagram. AE and EB are the liquidus and solubility line of the (NH₄)₂SO₄/H₂O phase diagram. 42 Freezing T_f,ice, T_f,FCS, T_m,FCS and melting T_m, T_b, T_m,FCS data points are from this work and refs.36 and 37 (see text and SI). Blue dashed lines mark temperature regions in which T_f,ice and T_f,FCS were detected in our DSC experiments. Arrows show the change of concentration during ice crystallization. T_equil is taken from ref.43 for comparison. T_equil was measured when a levitated millimeter-scaled (NH₄)₂SO₄/H₂O drop was in equilibrium with ice on chamber walls. 43

To identify the nature of T_f,ice, T_f,FCS and the inclined thermogram in Figure 1b, we performed truncated measurements in which 25-45 wt% (NH₄)₂SO₄ drops were cooled to temperature above T_f,FCS. 34 The obtained thermograms contain an exothermic peak and prolonged endothermic peak (Figure 3a). The latter is due to the melting of ice that is in contact with a highly-concentrated FCS. 12,34,36 Supplementary Video 1 (SV1) demonstrates such prolonged ice melting.  SV1 shows that ice starts melting at ~235K << T_m=254K, indicating that the concentration of FCS is much higher than the eutectic 40 wt% (NH₄)₂SO₄ (SI). The FCS concentration is not constant, but increases with the concentration of initial solution and can reach ~70 wt% (NH₄)₂SO₄. Further, all T_m’s from Figure 3a exactly meet the equilibrium ice melting T_m, and its extrapolation below T_m (Figure 2). This indicates that in Figure 3a and, consequently, in Figure 1b, T_f,ice is due to ice crystallization. It follows from this that T_f,FCS and the inclined thermogram also have the same nature as those of hypoeutectic (NH₄)₂SO₄/H₂O. Videos presented below confirm these unexpected results.

**Figure 3.** The truncated thermograms of 25-45 wt% (NH₄)₂SO₄. a, A sharp peak T_f,ice and prolonged peak T_m are due to the crystallization and melting of ice, respectively. Crosses mark temperatures T_m,FCS at which the ice in contact with FCS starts melting (see SI). b, The 20-fold magnification of warming 25 wt% (NH₄)₂SO₄ thermogram shows how T_m,FCS is determined.

**OC-M measurements:** SV2-SV8 demonstrate freezing events T_f,ice and T_f,FCS that occur in a millimeter-scale drop and films ~10-15 microns thick. 30,42 Since SV3-SV8 are more informative than SV2, below we will consider only videos recorded from (NH₄)₂SO₄/H₂O films.

SV3-SV5 of hypoeutectic, eutectic and hypereutectic films without (NH₄)₂SO₄ crystals demonstrate separated events T_f,ice and T_f,FCS, which manifest themselves as moving T_f,ice-front and T_f,FCS-front. The T_f,FCS-front pushes unfrozen FCS to the edge of film and forms bulges, which freeze last. SV6-SV8 show that in the films with (NH₄)₂SO₄ crystals, T_f,ice-front and T_f,FCS-front propagate rapidly one after the other. This indicates that (NH₄)₂SO₄ crystals promote the fast freezing T_f,FCS. SV6-SV8 also demonstrate that (NH₄)₂SO₄ crystallizes much slower than ice.

Images 4a and 4b show that (NH₄)₂SO₄ crystals are yellow in a transmitted light mode and dark green in reflected light mode (arrows 1 and 2). The frozen FCS bulges and channels (arrows 3 and 4) have the same color, indicating that they contain crystalline (NH₄)₂SO₄. Image 4c shows the IM/FCS morphology of completely frozen solution. The frozen FCS looks like a population of isolated channels and pockets. In fact, they are interconnected because T_f,FCS-front is always even and propagates evenly (image 4d and SV3-SV8). The different brightness of images 4d-4f is due to the non-uniform IM/FCS morphology. Dark strips are rich with ice. Image 4g shows that ice nucleation is a pointwise event.

In SV9, the moving T_f,ice-front forms FCS bulges. Unlike the FCS bulges formed by T_f,FCS-front (SV3-SV5), which freeze immediately after formation, these bulges remain liquid. As temperature decreases further, they grow due to the slow freezing of FCS, which is due to the diffusion of H₂O from the FCS to IM. Since the specific volume of ice is larger than that of water, the growing IM squeezes FCS channels (image 4c) and this leads to the growth of FCS bulges.
a

mograms show that the shape of peaks T_melting peak stretched. Answers are given below.

demonstrate that the propagation speed of T_melting peak (Figure 1a) forms somehow, because warming thermograms contain the eutectic superlattice should melt as a pure element at T_E.

three questions arise: how does FCS freeze, how does the eutectic superlattice specified by a precise molecular percentage ratio between H_2O and (NH_4)_2SO_4. Nonetheless, it forms somehow, because warming thermograms contain the eutectic melting peak (Figure 1a and Figure 1a in ref.36). However, it is stretched over a temperature region, whereas the eutectic superlattice should melt as a pure element at T_E. Hence, three questions arise: how does FCS freeze, how does the eutectic ice-(NH_4)_2SO_4 superlattice form, and why is the eutectic melting peak stretched? Answers are given below.

The fast freezing of FCS. Cooling 5-48 wt% (NH_4)_2SO_4 thermograms show that the shape of peaks T_{f,ice} and T_{f,FCS} is identical (Figure 1a and Figure 1a in ref.36). SV7, SV8 and SV10 demonstrate that the propagation speed of T_{f,ice}-front and T_{f,FCS}-front is the same. These observations suggest that ice crystallization plays a major role at T_{f,FCS}. The absence of an incline thermogram below T_{f,FCS} (Figure 1b and Figure 6 in ref.41) indicates that all the water in FCS transforms to ice. The accompanying rapid increase of concentration to 100 wt% (NH_4)_2SO_4 leads to a high nucleation rate. Since (NH_4)_2SO_4 crystallizes slowly (SV6-SV8), the high nucleation rate produces numerous (NH_4)_2SO_4 microcrystals. Indeed, these microcrystals are visible after the eutectic melting in the FCS bulges of hypoeutectic films (SV11-SV13). In eutectic and hypereutectic films, (NH_4)_2SO_4 microcrystals survive even above 273K (SV14, SV15). Note, frozen FCS is striped and consists of the irregular layers of ice and (NH_4)_2SO_4 microcrystals (images 5a and 5b).

Figure 4. Images of frozen (NH_4)_2SO_4/H_2O films. a, d, e, and f are taken in a transmitted light mode and images b, c and g in reflected light mode. a, b. Images are taken from the same region. Arrows 1-4 mark long and small (NH_4)_2SO_4 crystals, a FCS bulge and FCS channel, respectively. Dark/bright spots are ice crystals formed by vapor deposition on a cover glass. c, IM/FCS morphology under a high magnification. d. A snapshot of two T_{f,ice}-fronts and one T_{f,FCS}-front taken from SV5. e, f. Frozen FCS bulges and non-uniform IM/FCS morphology. g. The spot of ice nucleation. Concentration, scale and temperature are indicated.

Unlike the fast freezing T_{f,ice} and the slow freezing of FCS, the physics of fast freezing T_{f,FCS} is unclear. The FCS concentration is much larger than the eutectic concentration (SI) and, therefore, the fast freezing T_{f,FCS} cannot produce the eutectic ice-(NH_4)_2SO_4 superlattice specified by a precise molecular percentage ratio between H_2O and (NH_4)_2SO_4. Nonetheless, it forms somehow, because warming thermograms contain the eutectic melting peak (Figure 1a and Figure 1a in ref.36). However, it is stretched over a temperature region, whereas the eutectic superlattice should melt as a pure element at T_E. Hence, three questions arise: how does FCS freeze, how does the eutectic ice-(NH_4)_2SO_4 superlattice form, and why is the eutectic melting peak stretched? Answers are given below.

The formation of eutectic ice-(NH_4)_2SO_4 superlattice. All frozen 10-48 wt% (NH_4)_2SO_4 films/samples darken as temperature increases (SV11-SV15, images 5c, 5d). At T_E, the dark structure abruptly collapses, indicating that it is the eutectic ice-(NH_4)_2SO_4 superlattice. To our best knowledge, its structure is unknown. For alloys, four eutectic superlattice structures were identified: lamellar, rod-like, globular and acicular. Most likely, the striped structure of frozen FCS contain tiny regions of the lamellar eutectic ice-(NH_4)_2SO_4 superlattice consisting of the alternative molecular layers of ice and (NH_4)_2SO_4. Upon warming, molecular diffusion increases, and the eutectic regions grow owing to the recrystallization of ice and (NH_4)_2SO_4 microcrystals. The large number and different orientation of the growing eutectic regions increase the sample optical density and this explains the darkening process. The recrystallization of the metastable ice/(NH_4)_2SO_4 structure into the lamellar eutectic ice-(NH_4)_2SO_4 superlattice is a new three-phase reaction.
SV10 and image 5e demonstrate that the fast freezing $T_{\text{FCS}}$ begins spatially on/around (NH$_4$)$_2$SO$_4$ crystals after the $T_{\text{ice}}$ front has passed them. It is obvious that the crystals do not induce pointwise ice nucleation (image 4g), but spatial nucleation of the lamellar eutectic ice-(NH$_4$)$_2$SO$_4$ superlattice. Since ice crystallizes much faster than (NH$_4$)$_2$SO$_4$, this leads to the formation of metastable striped ice/(NH$_4$)$_2$SO$_4$ structure discussed above. In the samples without (NH$_4$)$_2$SO$_4$ crystals, the fast freezing $T_{\text{FCS}}$ begins on crystals formed/nucleated within the highly-super saturated FCS, often at the edge of samples where the concentration is larger due to water evaporation (images 5f and 5g).

**Stretched eutectic melting.** In frozen hypoeutectic samples, not all ice participates in the eutectic superlattice crystallization. In frozen eutectic and hypereutectic samples, due to the non-uniform IM/FCS morphology, there are regions in which part of the ice also does not enter the eutectic superlattice. Above $T_{\text{a}}$, the formed eutectic solution accelerates the melting of the remaining ice that makes the eutectic melting peak stretched (Figure 1a).

Finally, the degree of supercooling of micrometer-scaled (NH$_4$)$_2$SO$_4$/H$_2$O drops is so large that $T_{\text{a}}$ occurs near to, within or below the temperature region where $T_{\text{FCS}}$ occurs (Figure 2). In this case the three freezing steps merge (Figure 1e), indicating that the freezing process of (NH$_4$)$_2$SO$_4$/H$_2$O is size-dependent. In summary, the presented DSC results and OCM videos explain the nature of the three-step freezing and three-phase reaction of deeply supercooled (NH$_4$)$_2$SO$_4$/H$_2$O. These results extend the (NH$_4$)$_2$SO$_4$/H$_2$O phase diagram and provide a new insight into the physical chemistry of other deeply supercooled solutions, whose behavior is not predicted by the phase diagram. The proposed approach to estimate the FCS concentration (SI) makes it possible to use (NH$_4$)$_2$SO$_4$/H$_2$O as a model for the theoretical simulation of FIPS, which is currently in its infancy. This work further demonstrates that instead of considering only ice nucleation, it is necessary to consider the entire freezing process (ice nucleation, FIPS, ice/FCS morphology) when studying and modeling the formation, development and properties of ice clouds.

**ASSOCIATED CONTENT**

**Supporting Information.**

Supplementary Information and Supplementary Videos (15) are available in the online version of the paper.

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**REFERENCES**

1. Dos Santos-Neto, P.C.; Cuadro, F.; Barrera, N.; Crispo, M.; Menccha, A. Embryo survival and birth rate after minimum volume vitrification or slow freezing of in vivo and in vitro produced ovine embryos. Cryobiology, 2017, 78, 8–14, DOI: 10.1016/j.cryobiol.2017.08.002
2. Pearce, R. S. Plant freezing and damage. Ann. Bot. 2001, 87, 417–424, DOI:10.1006/anbo.2000.1352
3. Boldt, J. Current results with slow freezing and vitrification of the human oocyte. Reprod Biomed Online, 2011, 23 (3), 314–322, DOI: 10.1016/j.rbmo.2010.11.019
4. Muto, T.; Harada, M.; Fukushima, G.; Okada, T. Ice Confinement-Induced Solubilization and Aggregation of Cya nophospholipid Revealed by Fluorescence Spectroscopy and Lifetime Measurements. J. Phys. Chem. B 2020, 124 (18), 3734–3742, DOI: 10.1021/acs.jpcb.0c01451
5. Fujino, S.; Inagawa, A.; Harada, M.; Okada, T. Size-Tunable Micro-/Nanofluidic Channels Fabricated by Freezing Aqueous Sucrose. ACS Omega 2019, 4 (8), 13570–13576, DOI: 10.1021/acsomega.9b01966
6. Moll, C.J.; Meister, K.; Versluys, J.; Bakker, H.J. Freezing of Aqueous Carboxylic Acid Solutions on Ice. J. Phys. Chem. B 2020, 124 (25) 5201–5208, DOI: 10.1021/acs.jpcb.9b10462
7. Rempel, A.W. Hydromechanical Processes in Freezing Soils. Vadose Zone Journal 2012, 11 (4): vzj2012.0045, DOI: 10.2136/vzj2012.0045
8. Barnes, P. R. F.; Wolff, E. W. Distribution of soluble impurities in cold glacial ice. J. Glaciol. 2004, 50, 311–324, DOI: 10.3189/1727556047647829918
9. Thomas, D. N.; Kattner, G.; Engbrodt, R.; Giannelli, V. Dissolved organic matter in Antarctic sea ice. Ann. Glaciol. 2001, 33, 297–303, DOI: 10.3189/172755601781818338
10. Bogdan, A. Ice clouds: Atmospheric ice nucleation concept versus the physical chemistry of freezing atmospheric drops J. Phys. Chem. A 2018, 122 (39), 3109–3116, DOI: 10.1021/acs.jpca.8b07926
11. Kawasaki, H.; Toshinori Shimanouchi, T.; Kimura. Y. Recent development of optimization of lyophilization process. Journal of ChemTech 2019, Article ID 9502886, 14 pages, DOI: 10.1155/2019/9502886
12. Bogdan, A., Molina, M. J.; Tehlu, H.; Bertel, E.; Bogdan, N. & Loerting, T. Visualization of freezing process in situ upon cooling and warming of aqueous solutions. Sci. Rep. 2014, 4, 7414, DOI: 10.1038/srep07414
13. Tang, X. C.; Pikal, M. J. Design of freeze-drying processes for pharmaceuticals: Practical advice. Pharm. Res. 2004, 21, 191–200, DOI: 10.1023/B:PHAM.0000016234.73023.75
14. Levine, H. Amorphous food and pharmaceutical systems; RSC Publishing: Cambridge, U.K., 2002.
15. Petzold, G.; Aguilera, J. M. Ice morphology: Fundamentals and technological applications in foods. Food Biophysics 2009, 4, 378–396, DOI: 10.1007/s11483-009-9136-5
16. Flores-Ramirez, A.J.; Garcia-Coronado, P.; Grajales-Lagunes, A.; Garcia, R.G.; Archila, M.A.; Cabrera, M.A.R. Freeze-Concentrated Phase and State Transition Temperatures of Mixtures of Low and High Molecular Weight Cryoprotectants. Advances in Polymer Technology, 2019, Article ID 5341242, 1–11, DOI: 10.1155/2019/5341242
17. Basile, P.; Dadali, T.; Jacobson, J.; Hasslund, S.; Ulrich-Vinther, M.; Soballe, K.; Nishio, Y.; Drissi, M.H.; Langstein, H.N.; Mitten, D.J.; O’Keefe, R.J.; Schwarz, E.M.; Awad H.A. Freeze-dried tendon allografts as tissue engineering scaffolds for Gdf5 gene delivery. Mol. Ther. 2008, 16 (3), 466–473, DOI: 10.1038/sj.mt.6300395
18. John, M.; Suominen, M.; Sromunen, O-V.; Hasan, M.; Kurvinen, E.; Kujala, P.; Mikkola, A.; Louhi-Kultanen, M. Parity and mechanical
strength of naturally frozen ice in wastewater basins. Water Research 2018, 145 (15) 418-428. DOI: 10.1016/j.watres.2018.08.063
19. Rich, A.; Mandri, Y.; Bendaud, N.; Mangin, D.; Abderafi, S.; Bébon, C.; Semilani, N.; Klein, J.; Bounahmidi, T.; Bouhaouss, A.; Veesler, S. Freezing desalination of sea water in a static layer crystallizer. Desalin. Water Treat. 2010, 13 (1-3), 120–127. DOI: 10.5004/dwt.2010.983
20. Randall, D.G.; Zinn, C.; Lewis, A. E. Treatment of textile wastewaters using eutectic freeze crystallization. Water Sci. Technol. 2014, 70 (4), 736-741. DOI: 10.2166/wst.2014.289
21. Dong, J.; Hubel, A.; Bischof, J. C.; Aksan, A. Freezing-induced phase separation and spatial microheterogeneity in protein solutions. J. Phys. Chem. B. 2009, 113 (30), 10081–10087. DOI: 10.1021/jp090710d
22. Roessl, U.; Leitgeb, S.; Nidetzky, B. Protein freeze concentration and micro-segregation analyzed in a temperature-controlled freeze container. Biotechnol Rep (Amst). 2015, Mar 26;6, 108-111. DOI: 10.1016/j.btre.2015.03.004
23. Cheng, J.; Soetjipto, C.; Hoffmann, M. R.; Colussi, A. J. Confocal fluorescence microscopy of the morphology and composition of interstitial fluids in freezing electrolyte solutions. J. Phys. Chem. Lett. 2009, 1 (1), 374-378. DOI: 10.1021/jl9000888
24. Petrenko, V. F.; Whitworth, R. W. Physics of ice; Oxford University Press, Oxford, 2006.
25. Kitada, K.; Suda, Y.; Takenaka, N. Acceleration and Reaction Mechanism of the Nitrosation Reaction of Dimethylamine with Ni-Mo clusters in Interstitial Fluids in Freezing Electrolyte Solutions. J. Phys. Chem. A 2007, 111 (36), 8780–8786. DOI: 10.1021/jp0738356
26. Takenaka, N.; Bandow, H. Chemical kinetics of reactions in the unfrozen solution of ice. J. Phys. Chem. A 2007, 111 (36), 8780–8786. DOI: 10.1021/jp0738356
27. Inagawa, A.; Ishikawa, T.; Kusunoki, T.; Ishizaka, S.; Harada, M.; Otsuka, T.; Okada, T. Viscosity of Freeze-Concentrated Solution Confined in Micro/Nanospace Surrounded by Ice. J. Phys. Chem. C 2017, 121 (22), 12321-12328. DOI: 10.1021/acs.jpcc.7b03792
28. Rohatgi, P.K.; Adams, C.M.Jr. Ice-brine dendritic aggregation formed on freezing of aqueous solutions. J. Glaciol. 1967, 6 (47), 663–679. DOI: 10.3189/00221436790019936
29. Golden, K. M. Brine percolation and the transport properties of sea ice. Ann. Glaciol. 2001, 33, 28–36. DOI:10.3189/172756401781818329
30. Purdon, F. F.; Slater, V. W. Aqueous solution and the phase diagram; London: Edward Arnold & Co., 1946.
31. http://www.chemguide.co.uk/physical/phaseeqia/saltsoln.html (accessed 2021-9-22).
32. https://academic.uprm.edu/pcaceres/Courses/EngEng/MSE7-2.pdf (accessed 2021-9-22).
33. http://csugeo.csm.jmu.edu/geolab/Fichler/IgnRx/BinryEu.html (accessed 2021-9-22).
34. Bogdan, A. Double freezing of (NH₄)₂SO₄/H₂O droplets below the eutectic point and the crystallization of (NH₄)₂SO₄ to the ferroelectric phase. J. Phys. Chem. A 2010, 114 (37), 10135–10139. DOI: 10.1021/jp105699s
35. Bogdan, A.; Molina, M. J.; Tenhu, H.; Loerting, T. Multiple glass transitions and freezing events of aqueous citric acid. J. Phys. Chem. A 2015, 119 (19), 4515–4523. DOI: 10.1021/jp510331h
36. Bogdan, A.; Molina, M. J.; Tenhu, H.; Mayer, E.; Bertel, E.; Loerting, T. Different freezing behavior of millimeter- and micrometer-sized (NH₄)₂SO₄/H₂O droplets. J. Phys: Condens. Matter 2011, 23, 035103 (6pp). DOI: 10.1088/0953-8984/23/03/035103
37. Bogdan, A.; Molina, M.J.; Tenhu, H.; Loerting, T. Single freezing and triple melting of micrometre-scaled (NH₄)₂SO₄/H₂O droplets. Phys. Chem. Chem. Phys. 2011, 13 (44), 19704–19706. DOI: 10.1039/c1cp21770d
38. Duong-Ly, K.C.; Gabelli, S.B. Salting out of proteins using ammonium sulfate precipitation. Methods Enzymol. 2014, 541, 85-94. DOI: 10.1016/B978-0-12-420119-4.00007-0
39. Zuberi, B.; Bertram, A.K.; Koop, T.; Molina, L. T.; Molina, M. J. Heterogeneous freezing of aqueous particles induced by crystallized (NH₄)₂SO₄, ice, and leucovitice. J. Phys. Chem. A 2001, 105 (26), 6458–6464. DOI: 10.1021/jp010094e
40. Abbatt, J. P. D., Benz, S., Cziczo, D. J., Kanji, Z., Lohman, U. & Mohler, O. Solid ammonium sulfate aerosols as ice nuclei: A pathway for cirrus cloud formation. Science 2006, 313, 1770–1773, DOI: 10.1126/science.1129726
41. Bogdan, A.; Loerting, T. Impact of substrate, aging, and size on the two freezing events of (NH₄)₂SO₄/H₂O droplets. J. Phys. Chem. C 2011, 115 (21), 10682–10693. DOI: 10.1021/jp2007396
42. Beyer, K. D.; Bothe, J. R.; Burmann, N. Experimental determination of the HSO₄⁻/NH₄⁺/SO₄²⁻/H₂O phase diagram. J. Phys. Chem. A 2007, 111 (3), 479–494. DOI: 10.1021/jp0645465
43. Xu, J.; Imre, D.; McGraw, R.; Tang, I. Ammonium sulfate: Equilibrium and metastability phase diagrams from 40 to 50 °C. J. Phys. Chem. B 1998, 102 (38), 7462-7469. DOI:10.1021/JP981929X
44. Smith, W. F.; Hashemi, J. Foundations of materials science and engineering (4th ed.). McGraw-Hill, 2006.
45. http://www.engineeringarchives.com/les_matsci_threephase.png (accessed 2021-9-22).

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The three-step freezing and eutectic melting of 40 wt% (NiH₄)₂SO₄

Ice + liquid FCS

Ice + frozen FCS

Solution

Slow freezing

1st fast freezing

2nd fast freezing

Eutectic melting

Cooling

Warning

Temperature, K