Enhanced formation of cubic ice in aqueous organic acid droplets

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Abstract

The homogeneous nucleation of ice in solution droplets is known to be an important mechanism of ice particle formation in the Earth’s upper troposphere. It is known that the metastable cubic phase of ice can form when inorganic solution droplets freeze below about 200 K and that this may influence cloud properties and water vapor in the upper troposphere. However, many tropospheric aerosols contain a large and sometimes dominant proportion of oxygenated organic material in addition to inorganic substances. It is shown here that the threshold freezing temperature below which cubic ice forms and persists is shifted to considerably higher temperatures in solution droplets containing a carboxylic acid (2-hydroxypropane-1,2,3-tricarboxylic acid, citric acid, $C_6H_8O_7$). Cubic and the stable hexagonal ice are the only phases to crystallize in micrometre sized citric acid droplets and therefore always exist in contact with aqueous citric acid solution. It is argued that the extremely high viscosity of low temperature aqueous citric acid solutions plays an important role in stabilizing cubic ice. The implications of these findings for ice clouds in the Earth’s atmosphere are discussed.

Keywords: homogeneous nucleation, cubic ice, solvent mediated phase transformation, ice clouds, upper troposphere, humidity, solution viscosity, glass formation, organic acids

1. Introduction

Ice clouds play an important role in the transport and distribution of water vapor in the Earth’s atmosphere [1] and also impact our climate by scattering and absorbing radiation [2]. However, our quantitative understanding of ice cloud formation processes remains poor.

An important mechanism of upper tropospheric (UT) ice cloud formation is through the homogeneous nucleation of ice within aqueous solution droplets [3]. Laboratory measurements demonstrated that homogeneous freezing of inorganic aqueous solution droplets relevant for the UT can result in the formation of cubic ice (ice I$_c$) [4]. Ice I$_c$ is metastable and has a distinct crystal structure to the stable hexagonal phase (ice I$_h$). The equilibrium vapor pressure of ice I$_c$ was recently measured to be 11 ± 3% larger than that of ice I$_h$ [5]. Hence, the relative humidity ($RH_{Ih}$, defined as $P_{H_2O}/P_{Ih}^{eq}$, where $P_{H_2O}$ is the vapor pressure of water, while $P_{Ih}^{eq}$ is the equilibrium vapor pressure of water vapor over a flat hexagonal ice surface) within a cloud composed of ice I$_c$ will tend to 111%, rather than the 100% expected if the particles were composed of the stable hexagonal phase. Murphy [6] demonstrated that any particles which transformed to ice I$_h$ within a cloud of ice I$_c$ particles would grow at the expense of the ice I$_c$ particles in a process analogous to the Bergeron–Findeison process. This may result in a cloud composed of a lower number density, but larger particles, which may lead to enhanced sedimentation and dehydration compared with a cloud initially composed of ice I$_h$ particles.

In a recent study it was shown that the freezing temperature ($T_f$) threshold below which ice I$_c$ forms as the dominant product is strongly dependent on the solute type [7]. It was found that droplets of aqueous ($NH_4)_3H(SO_4)_2$ (ASR = 1.5, LET) freeze dominantly to cubic ice below 200 ± 1 K, whereas aqueous NH$_4$HSO$_4$ (ASR = 1.0, AHS) only freeze to ice I$_c$ below 183 ± 1 K. Given that temperatures regularly fall below 200 K in the tropical tropopause layer, but the minimum climatologically temperature is typically ∼186 K [8], it was concluded that ice I$_c$ formation in the atmosphere is strongly solute dependent.

In an attempt to rationalize this strong solute dependence, Murray and Bertram [9] proposed an ice I$_c$ to ice I$_h$ solvent
mediated phase transformation within partially crystallized solution droplets. In this mechanism it was argued that cubic ice is always the phase to nucleate and initially crystallize. There is substantial experimental and theoretical evidence to support this (see [9]). As ice Ih crystallizes in solution droplets, solute ions are rejected to form an increasingly concentrated aqueous solution. If there are no kinetic limitations to ice crystal growth and the solute phase does not crystallize, ice will exist in equilibrium with this concentrated aqueous solution. Ice Ih most likely nucleates efficiently on ice Ic since there is a very good lattice match [6]. Hence, ice Ih and ice Ic most likely exist in the same solution droplet and share a common aqueous phase through which water molecules may diffuse. This may result in a mass transfer from metastable ice Ic to stable ice Ih crystals. The rate at which this phase change occurs therefore depends on the rate of diffusion of water through the aqueous solution and will become limited when diffusion becomes very slow. Under these conditions Murray and Bertram [9] proposed that ice Ih would be ‘stabilized’. Unfortunately, no measurements of transport properties existed in very concentrated and cold (NH4)2H(SO4)2 or NH4HSO4 solutions and this proposed mechanism, while physically reasonable, remained untested. In this study a system has been selected where glass transition temperatures have been measured. The glass transition is the temperature at which a liquid becomes so viscous that it transforms into an amorphous solid in which molecular diffusion is extremely slow. Hence, it will be possible to test this postulated connection between cubic ice formation and the viscosity of the aqueous solution.

In this study, the ice phase that forms in citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, HO2CCH2CO2H) has been tested as a function of solute concentration. Citric acid was chosen for these experiments for a number of reasons. First, organic material accounts for up to 70% of the mass of fine aerosol in the troposphere, and 20–70% of this is water soluble [10]. The organic fraction of atmospheric aerosol is made up of a massive range of individual compounds, but it is recognized that oxygenated compounds containing COOH, OH and C=O groups are ubiquitous [11]. An important property of these compounds is their ability to form hydrogen bonds; they therefore have the potential to significantly influence molecular diffusion and viscosity. In situ single particle mass spectrometry measurements of UT aerosol confirm that oxygenated organic material is usually present and is usually internally mixed with sulfate [12]. In some cases organic material dominates even at 15 km altitude in the tropics [12]. Citric acid contains three COOH groups, one OH group and is highly soluble despite its relatively large molecular mass (192 D). Hence, it is suggested here that citric acid is a sensible proxy for the oxygenated organic fraction of tropospheric aerosol and is indeed known to be present as a minor constituent [11].

The second reason for the choice of citric acid solutions for the present study is that their physical properties have been characterized since citric acid is a common ingredient in food, pharmaceuticals and important in some biological processes. These properties include water activity [13–17], ice melting temperatures [18, 19] and also the glass transition temperature as a function of citric acid concentration [20]. It will be suggested that the proximity of the glass transition temperature to the ice–liquid equilibrium line may provide a useful guide as to which ice phase can be expected.

2. Experimental details

A powder x-ray diffractometer equipped with a cold stage has been employed to investigate the crystallization of aqueous citric acid solution droplets. This PANalytical X’Pert instrument, in Bragg–Brentano reflection geometry, was equipped with a Cu Kα x-ray source and X'Celerator detector.

Aqueous solutions were prepared gravimetrically (0–49.2 wt%) and then mixed with an oil phase, which consisted of 10 wt% lanolin surfactant in paraffin mineral oil. The oil and surfactant were insoluble in the aqueous phase. The proportion of aqueous phase in oil phase was also recorded gravimetrically. A few milliliters of emulsion were prepared using a magnetic stirrer for 5 min; this produced droplets of volume median diameter between 5–10 μm.

There are a number of reasons for employing emulsified samples in these experiments. First, it allows the investigation of homogeneous freezing by reducing the probability of heterogeneous nucleation in any one droplet in comparison to a bulk sample. If nucleation should occur heterogeneously, crystallization will be contained within individual droplets since they are separated by oil. Second, each droplet crystallizes independently of the next, hence there is no preferred crystallographic orientation in the sample overall. Preferred orientation can significantly alter the relative intensities of the diffraction peaks and is observed in samples of ice deposited on a surface from the gas phase [5, 21]. The diffraction patterns here and in previous x-ray diffraction experiments employing emulsions exhibit no preferred orientation [4, 7, 22, 23]. Third, the solute concentration of the solution droplets is fixed, which simplifies the interpretation of the data.

There are suggestions in the literature that nucleation occurs at the surface of droplets [24], if this were the case one might expect the surfactant to influence nucleation. However, agreement of data for freezing of droplets in and out of emulsions strongly suggests the surfactant and oil phase do not interfere with the nucleation process [25]. Also, measurements of nucleation in super-micron droplets are consistent with nucleation in the volume rather than at the surface [26].

About 0.1 ml of the emulsion was placed in the sample holder on the cold stage, Anton Paar TTK 450, which was initially at room temperature. The temperature of the droplets was then ramped down at an average rate of 5 K min⁻¹ to 173 K. As the droplets were cooled the ramp was paused for ~30 s every 5 K (or 10 K in a few cases), in order to measure the diffraction pattern at the position of the ice peak at 2θ = 40°. Hence, the temperatures over which the droplets froze could be determined by the growth of this peak out of the amorphous background. Once at low temperature the full diffraction pattern was measured between 2θ = 20° and 50°, which covers all major peaks in both cubic and hexagonal
Figure 1. Examples of diffraction patterns of aqueous citric acid solution droplets which were cooled to 173 K at a rate of 5 K min$^{-1}$ from room temperature. The peaks exclusive to hexagonal ice are labeled ‘h’, while those common to cubic and hexagonal ice are labeled ‘h + c’. Regions of the diffraction patterns containing Bragg peaks from the cell construction materials have been removed.

Figure 2. The intensity ratio $I_{33}/I_{40}$ as a function of droplet homogeneous freezing temperature. Data from the present study is shown for citric acid, filled circles, pure water (triangles) and NH$_4$HSO$_4$ (open squares). This data is compared with parameterizations for NH$_4$HSO$_4$ (AHS) and (NH$_4$)$_3$H(SO$_4$)$_2$ (LET) reported in [7] for droplets with 5–10 μm diameter [7]. A ratio of $I_{33}/I_{40} = 0.53 \pm 0.03$ indicates ice Ih formed and a ratio of zero indicates ice Ic with some stacking faults formed.

ice. Phase changes on warming were measured in much the same way as was done for freezing. An average ramp of 1 ± 0.1 K min$^{-1}$ and 1 K intervals were used to determine ice melting temperatures.

3. Results

Typical diffraction patterns of the frozen aqueous citric acid solution droplets are illustrated in figure 1. Pattern a is of 20.6 wt% citric acid droplets which froze at 224 ± 6 K and shows that a significant amount of the stable ice Ih formed. Whereas, pattern b is of 32.4 wt% droplets which froze at 219 ± 6 K and several peaks associated with hexagonal symmetry are absent—indicating no bulk ice Ih formed and that the dominant product was ice Ic. As with diffraction patterns of ice Ih in the literature, the distorted peak at 23$^\circ$ and the raised portion of the pattern between ∼22$^\circ$ and 26$^\circ$ is evidence of stacking faults [22, 27, 28]. Note that in both of these patterns there are no peaks associated a crystalline solute phase indicating that the aqueous citric acid solution remained non-crystalline.

Diffraction patterns, such as those shown in figure 1, were recorded for citric acid solution droplets with concentrations ranging from 0 to 49.2 wt%. More concentrated solution droplets tended not to crystallize on cooling indicating that crystallization did not occur. The inhibition of crystallization will be addressed in a separate manuscript. As a measure of the ice phase, we determined the intensity ratio $I_{33}/I_{40}$, where $I_{33}$ is the intensity of the ice Ih peak at 33$^\circ$ and $I_{40}$ is that of the peak common to ice Ic and ice Ih at 40$^\circ$, from each diffraction pattern. Peak intensities were determined by fitting Gaussian profiles to the respective peaks as was done previously [7].

The intensity ratio, $I_{33}/I_{40}$, is plotted as a function of $T_f$ (the ice freezing temperature) in figure 2. A ratio of $I_{33}/I_{40} = 0.53 \pm 0.03$ indicates pure ice Ih formed (see the auxiliary material in [7]), while a ratio of zero indicates ice Ic with stacking faults formed. Inspection of figure 2 reveals citric acid solution droplets froze dominantly to ice Ic at and below the threshold freezing temperature ($T'_f$) of 219 ± 6 K. This is in contrast to literature data (also plotted in figure 2) for NH$_4$HSO$_4$ (AHS) (measurements with AHS using the current set-up are in agreement with literature data) and (NH$_4$)$_3$H(SO$_4$)$_2$ (LET) solution droplets [7] where cubic ice forms only at considerably lower freezing temperatures. The implications of this result for the atmosphere are discussed later.

Intensity ratios for pure water are also shown in figure 2 and show that these droplets froze to a mixture of ice Ic and ice Ih. These results are in agreement with previous results [22].

4. Discussion

The results of this and previous studies [4, 7] show that there is a strong solute dependence of the ice phase that forms and persists when aqueous solution droplets freeze homogeneously. In the introduction we described a solvent mediated phase transformation which was recently proposed as an explanation for the solute dependence of ice phase in the AHS and LET systems [9]. In this mechanism ice is thought to nucleate and crystallize in the metastable cubic
phase and then transform to the stable hexagonal phase via mass transfer through the aqueous solution. Hence, diffusion of water in the aqueous solution will control the rate at which this solvent mediated transition occurs. It is suggested here that the proximity of the ice–liquid equilibrium curve to the glass transition may provide an indication of the freezing temperature below which cubic ice will be the dominant product. In order to test this hypothesis the ice–liquid equilibrium line, the ice homogeneous freezing temperatures and the glass transition temperature (\(T_g\)) are plotted as a function of aqueous citric acid concentration in figure 3.

Before this discussion continues the determination of the various curves in figure 3 must first be addressed. Ice melting temperatures, which are by definition at the ice \(T_f\)–liquid equilibrium line, down to 261 K are recorded in the literature [18, 19] and this has been extended to 251 K in the present study. However, in order to assess if the solvent mediated phase transformation is influenced by the viscosity of the solution the ice–liquid curve must be extended to lower temperatures. The ice–liquid curve can be described in terms of solution water activity \(a_w\); similar assumptions have been made and justified in the past [30]. The resulting ice \(T_f\)–liquid equilibrium line is plotted in figure 3.

Also plotted in figure 3 is the ice \(T_f\)–liquid equilibrium curve. Since ice \(T_f\) has a larger chemical potential than ice \(T_i\), it will come to equilibrium with a solute that is slightly less concentrated. This line was determined by taking the difference in enthalpy of sublimation between ice \(T_f\) and ice \(T_i\) determined by Shilling et al [5] at 180–190 K (155 J mol\(^{-1}\)). It was assumed that the difference in entropy between ice \(T_i\) and ice \(T_f\) is negligible. Hence, the chemical potential of ice in Koop et al’s equations (1) and (2) was increased by 155 J mol\(^{-1}\); the resulting line is shown in figure 3.

Since the rate at which the proposed solute mediated phase change proceeds depends critically on molecular diffusion of water in aqueous citric acid solution, it is useful to consider the transport properties of these solutions. As an aqueous solution is cooled its viscosity will increase and molecular diffusion will decrease accordingly. The temperature at which the viscosity increases to such an extent that the liquid transforms into an amorphous (non-crystalline) solid is known as the glass transition temperature (\(T_g\)). The amorphous material below \(T_g\) is termed a glass or a glassy solid. Maltini \textit{et al} [20] recorded \(T_g\) for citric acid solutions and their results are plotted in figure 3 along with their parameterization.

The viscosity of a solution at the glass transition is on the order of 10\(^{14}\) cP [31], which is an extremely high viscosity; the viscosity of pure water at 298 K is 0.89 cP [32]. Molecular diffusion and crystal growth are kinetically inhibited below \(T_g\). It is also well known that molecular diffusion and crystal growth are extremely slow in liquids which are as much as a few tens of Kelvin above their respective \(T_g\) (e.g. [33]).

The viscosity above \(T_g\) in aqueous solutions is known to increase extremely rapidly with decreasing temperature [31]. This super-Arrhenius dependence of viscosity (\(\eta\)) on temperature can be described by the WLF (Williams–Landel–Ferry [34]) equation:

\[
\log \eta_T = \log \eta_{T_g} - \frac{17.44(T - T_g)}{51.6 + (T - T_g)}
\]

(1)

where \(\eta_T\) is the viscosity (in units of cP) at temperature \(T\), \(\eta_{T_g}\) is the viscosity at \(T_g\) and the numerical values were determined by fitting to experimental data. The relationship of molecular diffusion and viscosity can be approximated by the Stokes–Einstein equation [34]:

\[
D_i = \frac{kT}{6\pi \eta_T r_i}
\]

(2)

where \(D_i\) is the molecular diffusion coefficient of species \(i\), \(k\) is the Boltzmann constant and \(r_i\) is the hydrodynamic radius of \(i\). This relationship should be considered an approximation, since the relationship between diffusion and viscosity becomes complex at temperatures close to the glass transition [34].

The root mean square distance which molecules of species \(i\) diffuse in a time \((t)\) can be expressed as

\[
x_i = (6D_i t)^{0.5}
\]

(3)
mediated phase transformation. In case A, ice nucleated rate; hence, the horizontal arrow. Each of these cases will crystal growth is assumed to be rapid in comparison to cooling droplets varies as ice crystallizes within them. For simplicity how the composition of the liquid portion of the solution diffraction patterns of these droplets showed that they froze to within highly viscous or glassy aqueous solution. Indeed, the droplets cubic ice would form, and persist, which is embedded suggested here that on cooling 49.2 wt% citric acid solution over the glass transition which would result in internally mixed (iii) A further transformation would also be blocked and cubic ice stabilized in the highly viscous solution). (ii) The solvent mediated phase transformation would be limited since the diffusion distances rapidly become extremely short and crystallization would be incomplete (the extremity of crystallites and solution ‘pockets’), then the solute mediated phase change will be rapid. Whereas, if $x_{\text{H}_2\text{O}} \ll \sigma$, then the solute mediated phase change will not occur and metastable ice Ic will be kinetically stabilized.

The arrows marked A, B and C in figure 3 illustrate how the composition of the liquid portion of the solution droplets varies as ice crystallizes within them. For simplicity crystal growth is assumed to be rapid in comparison to cooling rate; hence, the horizontal arrow. Each of these cases will be discussed in turn with reference to the proposed solvent mediated phase transformation. In case A, ice nucleated and crystallized in 49.2 wt% citric acid solution droplets at 199 ± 6 K. As ice crystallized in these droplets and the solution became increasingly concentrated molecular diffusion decreased precipitously. Hence, one would predict from inspection of this trajectory that: (i) ice crystal growth would become limited since the diffusion distances rapidly become extremely short and crystallization would be incomplete (the solution concentration would most likely not even reach the glass transition line since ice crystal growth would be limited in the highly viscous solution). (ii) The solvent mediated phase transformation would also be blocked and cubic ice stabilized as the solution became extremely viscous. (iii) A further decrease in temperature may take the highly viscous solution over the glass transition which would result in internally mixed droplets containing cubic ice and glassy solution. Hence, it is suggested here that on cooling 49.2 wt% citric acid solution droplets cubic ice would form, and persist, which is embedded within highly viscous or glassy aqueous solution. Indeed, the diffraction patterns of these droplets showed that they froze to ice Ic, which is consistent with the proposed solvent mediated phase transformation and the predicted diffusion coefficients. Also, additional ice crystallized at 209 ± 6 K on warming 49.2 wt% droplets at 5 K min\(^{-1}\), indicating ice crystal growth was indeed limited at lower temperatures. The inhibition of ice crystallization will be addressed in detail in a separate manuscript [41].

Let us now consider trajectory B, where ice nucleated in 38 wt% droplets at 216 ± 4 K. As in case A, the diffusion distance drops precipitously as ice forms in these droplets and the solution becomes more concentrated. However, given sufficient time the growth of cubic ice would be limited by the ice Ic–liquid equilibrium line rather than glass formation as in case A. However, as the solution composition approaches this equilibrium it would become extremely viscous and would most likely never reach the equilibrium state where $x_{\text{H}_2\text{O}}$ would be on the order of 1 nm. Hence, it is predicted on the basis of this analysis that the solvent mediated phase transformation would be blocked in these droplets and cubic ice would result as the dominant product. This is indeed consistent with the experimental data where cubic ice was found to form as the dominant phase in 38 wt% droplets.

Finally, in the case of trajectory C, where ice nucleated in 10.8 wt% solution droplets at 229 ± 6 K, the experiments showed that a mixture of cubic and hexagonal ice formed. This suggests that the solvent mediated phase transformation was partially active. The estimated diffusion distance at the ice Ic–liquid equilibrium line is on the order of 0.1 μm. This is much smaller than the dimensions of the droplets (volume median diameter of 5–10 μm). However, the dimensions of the individual crystallites and regions of aqueous solution separating the crystallites are likely to be much smaller than the dimensions of the droplets. It is well known that the nucleation of ice in supersaturated solutions leads to dendritic growth of ice crystallites much smaller than the dimensions of the droplets themselves [35]. Photographs of ammonium sulfate crystallites that formed in micron sized aqueous droplets suggest that the crystallite sizes were approximately ≤1 μm [36], which indicates that the pockets of concentrated solution from which the ammonium sulfate crystallized were most likely of a similar size. Hence, the diffusion distance of 0.1 μm is most likely approaching the dimensions of the solution regions and some diffusion of water from cubic to hexagonal ice crystallites would therefore be expected, which is consistent with the diffraction data.

Let us now briefly consider the previous cubic ice results in LET and AHS droplets which are also shown in figure 2. Zobrist et al [37] have very recently demonstrated that $T_g$ for a number of aqueous inorganic solutions are much lower than for a number of atmospherically relevant organic acid and polyol solutions. The formation of cubic ice only at much lower freezing temperatures in LET and AHS solution droplets is consistent with the findings of Zobrist et al [37].

5. Summary and atmospheric implications

The phase of ice that forms in atmospherically relevant solution droplets has a very strong dependence on the solute type. Previously, it was shown that ice Ic forms and persists when aqueous NH₄HSO₄ droplets freeze homogeneously below 183 ± 1 K; whereas it forms in (NH₄)₂SO₄ below 200 ± 1 K. In citric acid solution droplets, citric acid is used a proxy for atmospheric oxygenated organic material, ice Ic forms and persists below 219 ± 6 K. Given the ubiquity of oxygenated organic material with similar functionality to citric acid, cubic ice may be stabilized in solution droplets under a much wider temperature range than previously thought.

The diffraction experiments presented here suggest that the solvent mediated phase transformation is blocked below 219 ± 6 K ($T_g'$) for a cooling rate of 5 K min\(^{-1}\). In the atmosphere, typical cooling rates range from 0.0007 to 0.7 K min\(^{-1}\) [38], hence the solvent mediated phase transformation would be active for a longer period of time. The freezing temperature threshold below which ice Ic forms in the atmosphere may therefore be lower than 219 K. The
point where the glass transition temperature crosses the ice \( T_{g} \)-liquid equilibrium line defines the temperature \( T_{g}^{*} \) below which ice crystallization will most likely be incomplete and the solvent mediated phase transformation will not be active even at much slower cooling rates (see figure 3). Hence, cubic ice embedded within a highly viscous (or glassy) solution will from below this threshold, even at the slowest atmospheric cooling rates (this assumes that \( T_{g} \) is cooling rate independent; Maltini et al found no difference in \( T_{g} \) when cooling at 10 or 100 K min\(^{-1}\)). According to the estimated position of the ice \( T_{g} \)-liquid line and the \( T_{g}^{*} \) line in figure 3, this threshold will be at \( \sim 208 \) K; a temperature relevant for large parts of the Earth’s upper troposphere.

A factor that should be considered when interpreting these results is the difference between the laboratory and atmospheric trajectories through the state diagram (figure 3). In our experiments concentration is fixed and temperature reduced, while in the atmosphere concentration decreases as temperature decreases and \( RH_{\text{th}} \) increases. This is important because inspection of figure 3 reveals that a droplet may start off in a highly viscous state and not take up water efficiently. It may therefore never become sufficiently dilute to freeze. Further experiments are therefore required to measure the water uptake into viscous oxygenated organic containing droplets under pertinent conditions.

Nevertheless, the results presented here provide a valuable insight to the mechanism of crystallization within atmospherically relevant aqueous solution droplets. Furthermore, if the stabilization of ice \( I_{h} \) within solution droplets leads to the formation of clouds composed of ice \( I_{h} \), \( RH_{\text{th}} \) within ice clouds larger than 100% might be expected [4, 6]. This might provide an explanation for observations of large \( RH_{\text{th}} \) within ice clouds [39, 40].

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