Ice nucleation in aqueous solutions of poly[ethylene glycol] with different molar mass

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(Received 21 January 2003; accepted 12 March 2003)

Homogeneous ice nucleation was investigated in aqueous solutions of poly[ethylene glycol] (PEG) with a molar mass between 300 and 6000 g mol\(^{-1}\). Experiments were performed with a differential scanning calorimeter using emulsified aqueous PEG solutions with concentrations of 0–44 wt %. Equilibrium phase transition temperatures are determined and discussed, in particular the simultaneous occurrence of metastable and stable eutectic temperatures. The observed homogeneous freezing temperatures of ice reveal a continuous increase in the supercooling of PEG solutions with increasing molar mass of the PEG. The freezing behavior was investigated within the framework of water-activity-based ice nucleation theory. The latter predicts that homogeneous ice nucleation in aqueous solutions is independent of the nature of the solute, but depends only on the water activity of the solution. Water activity data of various PEG solutions in the stable and supercooled range were compared. It was found that the water activity of PEG solutions decreases with decreasing temperature. This trend is stronger for the PEGs of larger molar mass, and can explain why solutions of larger PEGs supercool more readily. Our study shows that the predictions of water-activity-based ice nucleation theory are consistent with the observed freezing behavior and with the thermodynamic properties of PEG solutions. It is also in agreement with the suggestion of a thermodynamic control of ice nucleation in aqueous systems due to the existence of a liquid phase spinodal. © 2003 American Institute of Physics. [DOI: 10.1063/1.1571818]

I. INTRODUCTION

In many environments liquid water is found in a supercooled metastable state below its equilibrium melting temperature, \(T_m\), of 273.15 K.\(^1\)–\(^3\) Small amounts of pure liquid water can be cooled to about 235 K before homogeneous ice nucleation commences.\(^1\)–\(^5\) The temperature at which homogeneous ice nucleation in micrometer-sized samples of water and aqueous solutions occurs will be referred to as the freezing temperature, \(T_f\). The nucleation of ice from supercooled water and aqueous solutions plays an important role in the formation of ice clouds,\(^6\)–\(^9\) in the storage of water containing materials,\(^10,11\) and for the survival of biological cells in the cold.\(^12\)–\(^16\) In aqueous solutions the melting and freezing points are reduced when compared to pure water.\(^2,9,17\)–\(^19\) Examination of experimental data for a number of solutes has revealed a linear relationship between the freezing temperature depression (\(\Delta T_f\)) and the equilibrium melting point depression (\(\Delta T_m\)) in aqueous solutions.\(^10,18\) The investigated systems also included aqueous polymer solutions of poly[ethylene glycol] (PEG) and poly[vinyl pyrrolidine].\(^19\) The investigated polymer solutions showed a similar ice nucleation behavior, but they exhibited a much larger supercooling than solutions of salts and simple molecules. This is illustrated by the fact that the ratio \(\Delta T_f/\Delta T_m\) for solutions of the two polymers is roughly 2.5 times larger than that of nonpolymeric solutions.\(^2,10,18\) No conclusive physical interpretation has been offered of why polymer solutions supercool more readily than nonpolymeric solutions.\(^2\) In the following we will focus on the supercooling behavior of PEG solutions. PEG reserves a special place among water soluble polymers, because it is very soluble in water over a wide range of molar mass and concentrations. Its high solubility at room temperature is the result of hydrogen-bond formation between the oxygen atoms of PEG and the hydrogen atoms of water.\(^20\) In addition, PEG has a number of applications in industry. For example, it is commonly used as an excipient to increase the aqueous solubility of pharmaceutical drugs\(^21\) and is utilized for edible films in food industry.\(^22,23\)

In the present paper, the homogeneous ice nucleation temperatures and melting points of aqueous PEG solutions are investigated with a differential scanning calorimeter. The experimental results are analyzed by comparing \(\Delta T_f\) and \(\Delta T_m\) as a function of the PEG molar mass. Furthermore, the freezing behavior of PEG solutions is investigated within the framework of water-activity-based ice nucleation theory. For this purpose water activity data of various PEG solutions in the stable and metastable range are compared, and the physical implications of these data are discussed.

II. EXPERIMENT

A. Setup

We have used a heat flow differential scanning calorimeter (DSC) for the measurements reported below. Figure 1 shows a schematic picture of the apparatus.\(^24\) It is similar in design to the calorimeter described by Mañosa et al.,\(^25\) but contains an additional active cooling/heating unit. The main part of the calorimeter consists of two peltier elements (7) mounted on a temperature controlled copper plate (6). The
copper plate is fixed to a steel cylinder (4) connected to a copper rod (3) that is placed into a liquid nitrogen filled dewar (2). The copper plate (6) and the steel cylinder (4) are clamped to each other (11) with a thin heating foil (5; Minco, HK 5561R37.1L12A) in between. Thin layers of a heat sink compound (Dow Corning 340) were applied on both sides of the foil to maximize heat transfer between the different components. The heat output of the foil is regulated using a temperature controller (Neocera LTC-11) such that the foil counteracts the permanent heat sink of the steel cylinder. With this setup constant cooling and heating rates of 0.5–5 K min\(^{-1}\) can be achieved in the temperature range between 170 and 285 K.

The two peltier elements (Telemer Electronic, PE-065-05-15) are fixed symmetrically to the centerline onto the copper plate. One peltier element holds the reference pan and the other one the sample pan (9). A small brass plate with a layer of insulating foam (12) is used to fix the pans on the peltier elements. The bottom sides of the peltier elements are always at the same temperature since both are attached to the copper plate (6). The top side temperatures, however, can deviate from each other. When the sample absorbs (or releases) heat during a phase transition its temperature is smaller (or larger) than the one of the reference leading to a voltage difference between the two peltier elements.\(^{25}\) This difference (in the millivolt range) was measured with a digital multimeter (Keithley 2700). The temperature is continuously monitored with a platinum resistance temperature sensor (PT100, 1/3 DIN Class A, 2 × 2.3 × 0.6 mm in size) attached to the peltier element holding the reference. Another PT100 temperature sensor is fixed to the copper plate and serves as an input for the temperature controller. The main part of the calorimeter is closed with a steel cap (13) and a thermal insulation cap (14) in order to minimize heat and humidity exchange with room air.

**B. Sample preparation**

In order to investigate homogeneous ice nucleation, impurities that induce heterogeneous ice nucleation must be excluded. This is usually achieved by dispersing a sample into numerous small entities, such that only a minor fraction of these entities contain impurities.\(^{1–4}\) The most common technique applied for this purpose is the use of emulsions, in which aqueous droplets, typically a few microns in diameter, are dispersed in an inert oil with the help of an emulsifier.\(^{19}\) The emulsion samples used in this study consisted of 4 parts of a homogeneous mixture of lanolin (23 wt.%) and mineral oil (77 wt.%) and 1 part of an aqueous PEG solution made from PEG and distilled Millipore water (Resistivity ≥ 18.2 MΩ cm). Such a mixture, with a total volume of about 3 cm\(^3\), was dispersed by stirring the sample in a plastic test tube for 1 h at 7000 rpm using a commercial drilling machine and a homemade stirrer. The size of the aqueous droplets in the resulting emulsion was investigated with an optical microscope and was found to be approximately 4 ± 2 µm. About 20 ± 4 mg of such an emulsion was transferred into commercial DSC pans (50 µl, Perkin-Elmer, B016-9321) for each measurement. The reference pan was filled with the same amount of the lanolin/oil mixture. This mixture did not show any phase transitions between 170 and 285 K. Aqueous PEG solutions were prepared from commercially available PEG samples without further purification: PEG300 (Aldrich, number average molar mass \(M_n = 306 \text{ g mol}^{-1}\)), PEG1000 (Fluka, \(M_n = 823 \text{ g mol}^{-1}\)), and PEG6000 (Fluka, \(M_n = 5578 \text{ g mol}^{-1}\)).

**C. Calibration**

The calorimeter was calibrated using emulsified water and aqueous solutions of (NH\(_4\))\(_2\)SO\(_4\), KCl, NaF, NaCl, NaBr, and NaI. The samples were cooled at a rate of 3 K min\(^{-1}\) and heated at rate of 1 K min\(^{-1}\). The resulting melting temperatures, eutectic temperatures, and freezing temperatures were compared to literature values.\(^{18,26–29}\) The observed variation in the freezing temperatures is larger than the one in the melting temperatures, because homogeneous freezing is a nonequilibrium (kinetic) phase transition, which depends on the size of the investigated droplets. Our samples consisted of droplets with a size distribution that can vary slightly between different samples. In contrast, the equilibrium melting temperatures do not depend on the size of the droplets in the investigated emulsion samples. Based on our measurements, we estimate the uncertainty in the freezing and melting points reported below to be ± 1.0 K and ± 0.75 K, respectively.

**D. Typical experiments**

Figure 2 is an example of cooling and warming experiments performed with emulsion samples of aqueous PEG1000 solutions with different concentrations. The minima of the curves in Fig. 2(a) correspond to the freezing temperature of each sample. The amount of released latent heat decreases with increasing concentration, because less ice is formed at the higher concentrations. For the largest

- \(\text{Resistivity} \geq 18.2 \text{ MΩ cm}\)
- \(M_n = 306 \text{ g mol}^{-1}\)
- \(M_n = 823 \text{ g mol}^{-1}\)
- \(M_n = 5578 \text{ g mol}^{-1}\)
- \(\text{Cooled at a rate of } 3 \text{ K min}^{-1}\)
- \(\text{Heated at rate of } 1 \text{ K min}^{-1}\)
- \(\pm 1.0 \text{ K}\)
- \(\pm 0.75 \text{ K}\)
concentration (~43.3 wt. %) the released heat becomes so small that the corresponding freezing temperature is hardly discernible with the sensitivity of our apparatus. In the warming experiments shown in Fig. 2(b) two different peaks can be identified in each curve with the exception of the pure water sample. The peak at about 250 K corresponds to the eutectic temperature of the H₂O/PEG1000 system. The second peak with a variable temperature indicates the ice melting point of each sample. While the ice melting peak gets larger as the solution becomes more dilute, the eutectic peak gets larger with increasing concentrations since the composition of the samples approaches the eutectic composition of 58 wt. % (Ref. 30).

III. RESULTS AND DISCUSSION

A. Experimental results

The freezing, melting, and eutectic temperatures for emulsion samples of three different aqueous PEG solutions (PEG300, PEG1000, and PEG6000) were investigated over a concentration range of about ~44 wt. %. The results for PEG300 are shown in Fig. 3(a). The open circles indicate the measured ice melting points, $T_m$, and the open squares the ice freezing temperatures, $T_f$. At least two independent samples were investigated for each concentration and the corresponding temperatures are shown separately in Fig. 3. The individual data points are hardly discernable in most cases.
cases indicating the very good reproducibility of the measurements. We note that no eutectic phase transition was observed for the PEG300 solutions in the investigated concentration range.

Figure 3(b) depicts the results for PEG1000. In addition to the freezing and melting temperatures, a eutectic phase transition (open triangles) was found in all samples at a temperature of about 250 K. Our results for the melting temperatures and eutectic temperatures are in good agreement with literature data\textsuperscript{30} shown as solid symbols in the figure. The latter data were obtained with a commercial DSC using bulk samples. The agreement between these data and our measurements indicates the suitability of our apparatus and also shows that the emulsification process had no appreciable effect on the thermodynamic properties of the aqueous PEG solutions.

The results for the PEG6000 solutions are shown in Fig. 3(c) together with available literature data\textsuperscript{30,31} Again there is good agreement for the ice melting temperatures (open and closed circles). For the case of the eutectic phase transition our results differ from previous studies. We observed two transitions (indicated as open triangles and diamonds) at about 260 K, both of which were independent of the concentration of the PEG solution. The first one is close to the one observed in bulk samples from the literature (solid triangles\textsuperscript{30,31}), while the second one occurred at a slightly higher temperature. The two transitions are shown in more detail in Fig. 4 which depicts warming curves for two aqueous PEG6000 solutions with concentrations of 38.0 and 41.5 wt.%. The latent heat absorption due to the low temperature transition (1) is much smaller than the one corresponding to the high temperature transition (2).

We believe that these observations can be attributed to the fact that PEG molecules crystallize in different modifications.\textsuperscript{32–38} These crystal modifications contain PEG molecules either fully extended or folded a small number of times, $n$. The stable crystal form is the one with fully extended ($n=0$) PEG molecules.\textsuperscript{34} Crystals containing PEG chains folded $n$ times are metastable with respect to the ones with chains folded $n-1$ number of times.\textsuperscript{34} The melting points of the different crystalline forms vary with the degree of metastability. The fully extended chain crystal ($n=0$, stable) is always observed to have the highest melting temperature, which decreases with increasing $n$, i.e., increasing metastability.\textsuperscript{32–34,36–38} Folded chain crystals have been grown both from the melt and from solution.\textsuperscript{33} Which modification crystallizes depends on the conditions during crystallization.\textsuperscript{36} Usually two, and sometimes even more modifications crystallize simultaneously in a sample. Therefore, such samples exhibit multiple melting points which, in the case of PEG, are only a couple of Kelvins apart.\textsuperscript{32–34,36} However, the observation of the different melting points in DSC experiments depends crucially on the heating rate. At lower heating rates the different melting points are more easily observed, because the thermal lag of the sample is reduced and more time is allowed for recrystallization of the sample into a more stable form upon warming.\textsuperscript{32–34}

This might explain why multiple eutectic temperatures in aqueous PEG solutions have not been observed in previous studies shown in Fig. 3, because in these studies larger samples and greater heating rates have been used than in the present work. We believe that the two transitions shown in Figs. 3(c) and 4 are the eutectic temperatures of ice with, respectively, metastable (1) and stable (2) PEG crystals. Similar observations\textsuperscript{39} of metastable and stable eutectic temperatures have also been made in the binary system glutaric acid/PEG. Chain folding preferentially occurs in larger PEG polymers and has been observed for PEG molecules with a molar mass larger than about 4000–5000 g mol\textsuperscript{-1} only.\textsuperscript{33,34} This explains why we did not observe multiple eutectic peaks in the PEG1000 solutions shown in Fig. 3(b).

We conclude from this section that the equilibrium phase diagram and all observed equilibrium transitions of the investigated PEG solutions are well understood. In the following we will focus on the observed kinetic (nonequilibrium) phase transitions, i.e., homogeneous ice nucleation in PEG solutions.

A common way to compare the freezing temperatures of different aqueous solutions\textsuperscript{2,10,17,18} is depicted in Fig. 5. The depression of the freezing temperature, $\Delta T_f = T_f(H_2O) - T_f(Sol)$, is shown as a function of the equilibrium melting point depression, $\Delta T_m = T_m(H_2O) - T_m(Sol)$. Here, $T_m(H_2O) = 273.15$ K and $T_f(H_2O) = 235$ K are the melting and the freezing temperatures of pure water adopted from the literature.\textsuperscript{1–4} $T_m(Sol)$ and $T_f(Sol)$ are, respectively, the experimentally determined melting and freezing temperatures of an aqueous solution. Figure 5 contains data of the various PEG solutions from Fig. 3 together with literature data\textsuperscript{13,19} for ethylene glycol (EG), PEG4000, and PEG9000. Figure 5 reveals that $\Delta T_f$ is basically a linear function of $\Delta T_m$ for each solute. The slope of the different data sets can be described using the parameter $\lambda = \Delta T_f/\Delta T_m$. Previous studies\textsuperscript{2,10,17} have found that a typical value for $\lambda$ in aqueous solutions of salts and simple molecules is about 2. This is indicated by the shaded region which contains data from 20 different solutes of such type.\textsuperscript{5} In contrast, polymers exhibit a value of $\lambda \approx 5$ (open circles\textsuperscript{13,19} in Fig. 5). This difference

![FIG. 4. Warming curves for two aqueous PEG6000 solutions with concentrations of 38.0 and 41.5 wt.%. (1) metastable eutectic; (2) stable eutectic. The ice melting points of the two solutions are also indicated.](image)
between aqueous solutions of salts and simple molecules and of polymers has not been explained. The PEG data of this study in Fig. 5 indicate a gradual increase of \( \lambda \) with increasing molar mass from \( \lambda = 2.1 \) for EG, \( \lambda = 3.6 \) for PEG300, \( \lambda = 4.5 \) for PEG1000, up to \( \lambda = 5.1 \) for PEG4000, PEG6000, and PEG9000. Differences between data points of PEG4000, PEG6000, and PEG9000 are negligible. While Fig. 5 clearly reveals that \( \lambda \) depends on the molar mass of PEG, it does not provide an answer to what might be the physical cause of this behavior. In the following section we will try to elucidate the matter by investigating the thermodynamics of aqueous EG and PEG solutions.

### B. Water activity of aqueous PEG solutions

One approach to describe the kinetic ice nucleation process in aqueous solutions has been classical nucleation theory (see, e.g., Ref. 2). However, a rigorous comprehensive test of classical nucleation theory including many different solutes has not been performed due to a lack of data on crucial properties such as ice/solution interfacial energies and diffusion activation energies in strongly supercooled aqueous solutions. Recently, the first successful molecular dynamics simulations of the ice nucleation process in supercooled water has been presented.\(^{40}\) One result of that study was that the critical nucleus did not have the bulk properties of hexagonal ice.\(^{41}\) This puts into question the capillarity approximation inherent to classical nucleation theory, which assumes the critical cluster to have the bulk properties of the nucleating phase.

An alternative approach to describe ice nucleation in aqueous systems has been suggested by Rasmussen.\(^{17,18,42}\) In this approach ice nucleation occurs because the liquid phase approaches a physical or chemical spinodal, at which point the liquid reaches its limit of metastability and becomes unstable.\(^{43}\) As the liquid phase approaches the spinodal, order and/or concentration fluctuations in the liquid become larger allowing the local demixing of the liquid parent phase into two daughter phases. This triggers the formation of an ice nucleus that is in local equilibrium with one of the daughter phases. After the fluctuation is over the nucleus can grow if it is supersaturated within the liquid parent phase. Since the location of the spinodal is determined by external thermodynamic properties, the approach of Rasmussen\(^{17,18,42}\) suggests that the kinetic ice nucleation process can be described entirely through thermodynamic parameters.

More recently, Koop et al.\(^{9}\) developed a thermodynamic model for homogeneous ice nucleation from aqueous solutions. In that study the liquid phase water activity, \( a_w \), was identified to be a suitable thermodynamic parameter to describe ice nucleation in aqueous solutions, in agreement with the suggestion by Rasmussen.\(^{17,42}\) The authors concluded that homogeneous ice nucleation in aqueous solutions depends only on the water activity of a particular solution, but not on the nature of the solute. (The water activity of a solution is equal to the ratio between the water vapor pressures of the solution and of pure water under the same conditions.)

We have collected water activities of aqueous EG and PEG solutions as a function of temperature and solute concentration. Such data are available only at temperatures above \( T_m \) of the respective aqueous solutions, but not for metastable solutions in the supercooled range.

Data at higher temperatures between 308–338 K obtained from vapor pressure osmometry were taken from Eliassi et al.\(^{44}\) In addition, ice melting temperatures of EG and PEG solutions have been used to derive water activities. The values for \( a_w \) at the melting point (solid symbols along the dashed line in Fig. 6) were calculated from the measured melting points shown in Fig. 3 and from the literature\(^{19}\) using the procedure described in Refs. 45 and 46. Finally, water-activity-based ice nucleation theory was applied to predict water activities of supercooled aqueous EG and PEG solutions at their respective freezing temperature.\(^{9,47}\) The results of this analysis are depicted in Fig. 6 for solutions of EG, PEG300, and PEG6000. In Fig. 6(a), the water activities of three EG solutions of fixed composition (10, 20, and 30 wt. %) are shown at two temperatures. Unfortunately, no water activity data at temperatures above the melting point curve are available. Despite this shortcoming, the data indicate only a small decrease in \( a_w \) with decreasing temperature for each of the solutions with a maximum change in \( a_w \) of 1.6% for the 30 wt. % solution.

In Fig. 6(b) we show the analogous data for four aqueous PEG300 solutions. Over a large temperature range \( a_w \) is almost constant for the more dilute solutions, but decreases with decreasing temperature for the highly concentrated solutions. There is a smooth change in \( a_w \) as a function of temperature for all four solutions indicating that \( a_w \) in the supercooled metastable temperature range predicted by water-activity-based ice nucleation theory is consistent with the measured trend in \( a_w \) at higher temperature.

The temperature dependence of \( a_w \) for the PEG6000 solutions in Fig. 6(c) is much stronger than the one of PEG300 solutions, in particular for the largest concentrations. In addition, the \( a_w \)-values of the different solutions seem to con-

![FIG. 5. The freezing temperature depression (\( \Delta T_f \)) as a function of the equilibrium melting point depression (\( \Delta T_m \)) in aqueous solutions of EG and PEG. Triangles: ethylene glycol (Ref. 19); squares: PEG300 (this work); diamonds: PEG1000 (this work); open circles: PEG4000 (Ref. 13) and PEG9000 (Ref. 19); solid circles: PEG6000 (this work). The shaded region indicates the range of data for a large number of salts, acids, and simple molecules (Ref. 9).](image-url)
In the following, we will discuss how the thermodynamic properties of aqueous PEG solutions shown in Fig. 6 can be understood by changes in the interaction between PEG and water.

In order to understand the water/PEG phase behavior hydrogen bonding between water and PEG molecules needs to be considered. Slightly above room temperature, PEG is soluble in water at all concentrations over a large molar mass range. In contrast, larger molecules of poly-[methylene glycol] and poly[propylene glycol] are basically insoluble. An interpretation of this behavior was given by Kjellander and Florin, who noted that the average distance between two oxygen atoms in certain conformations of PEG chains is very similar to the oxygen–oxygen distance in a water hydrogen bonding network with local tetrahedral symmetry. They concluded that PEG molecules nicely fit into the water hydrogen bonding network and, hence, are easily dissolved. In contrast, at higher temperatures (≥ 370 K) aqueous PEG solutions have been observed to demix for PEGs with a molar mass larger than about 2200 g mol^{-1} (Ref. 51). With increasing temperature, the number of water molecules bound to PEG molecules via hydrogen bonds decreases and the number of free water molecules increases. Hence, the latter can more easily attain a local bonding symmetry similar to water molecules in pure water. In terms of the thermodynamic properties of aqueous PEG solutions, this might lead to an increase in water activity with increasing temperature, just as observed. This is supported by the fact that both the high temperature measurements by Eliassi et al. for one PEG300 sample and the analysis of our data for another PEG300 sample are consistent with each other. Furthermore, both studies independently reveal that the temperature dependence of PEG300 is smaller than that of PEG1000 and PEG6000, thereby indicating that polydispersity is of second order importance for our analysis.

At this point a discussion is in order of the possible effects that the solute polydispersity of our PEG samples might have on the analysis presented above. We do not have information on the polydispersity of our solutions. However, as discussed above, any effect on $a_w$ of a polydispersity in the PEG6000 samples can be excluded, given the fact that PEG4000 and PEG9000 reveal the same behavior as PEG6000. In contrast, a polydispersity effect on the PEG300 and PEG1000 samples cannot be excluded. In particular, the absolute $a_w$-values for two PEG300 samples of different polydispersity can be different. However, in our treatment we focus on the temperature dependence of $a_w$ rather than its absolute value. We believe that the temperature dependence of $a_w$ is not very sensitive to polydispersity. This is supported by the fact that both the high temperature $a_w$ measurements by Eliassi et al. for one PEG300 sample and the analysis of our data for another PEG300 sample are consistent with each other. Furthermore, both studies independently reveal that the temperature dependence of PEG300 is smaller than that of PEG1000 and PEG6000, thereby indicating that polydispersity is of second order importance for our analysis.

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larity of 0.987 at a temperature of 338 K (Ref. 44). For comparison, the same water activity occurs in aqueous NaCl solutions at a very small concentration of 2.3 wt. % (Ref. 52). This comparison suggests that only weak interactions between the PEG and water molecules exist at these temperatures and, thus, the chemical potential of water is hardly affected by considerable weight fractions of PEG molecules. Furthermore, the data in Fig. 6(c) show that the water activities of the PEG6000 solutions seem to collapse at temperatures \( \geq 340 \, \text{K} \), where all investigated solutions assume a water activity close to 1. This suggests that the water chemical potential is very insensitive to large changes in PEG concentration and might be regarded as an indication that demixing will occur in this system at slightly higher temperatures (\( \geq 390 \, \text{K} \)). The PEG300 data in Fig. 6(b) also show an increase in \( a_w \) for all solutions but not nearly as strong as the PEG6000 data in Fig. 6(c). Also, the data do not collapse to a water activity close to 1. This might indicate that PEG300 and water do not demix at higher temperatures, and indeed, demixing in PEG solutions only occurs for PEGs with a molar mass larger than about 2200 g mol\(^{-1} \) (Ref. 51).

At low temperatures an increasing number of water molecules in pure water are hydrogen bonded\(^{50} \) and attain a tetrahedral symmetry within the water hydrogen bonding network.\(^ {53} \) Since this is predicted to occur also in aqueous PEG solutions,\(^ {50} \) it facilitates the formation of hydrogen bonds between PEG molecules and water at lower temperature. The larger number of PEG–water hydrogen bonds leads to a reduction of the solution water activity,\(^ {54} \) just as observed in Figs. 6(b) and 6(c). This picture is supported by the results of a physical model of aqueous PEG solutions.\(^ {50} \) That model includes competitive hydrogen bonding between water–water and water–polymer molecules. The model results agree qualitatively very well with the behavior seen in Fig. 6, i.e., a very strong change in water activity of PEG solutions in the supercooled temperature range is predicted. More detailed calculations are needed in order to allow a quantitative comparison between data and model, in particular because the model was mainly aimed at predicting the behavior of PEG solutions at temperatures above 273 K (Ref. 50).

Comparing the three different data sets in Fig. 6 and the one for PEG1000 (not shown in Fig. 6) there is a clear trend: the larger the molar mass of the solute the stronger is the change in \( a_w \) for a fixed solution concentration with decreasing temperature. This behavior can easily explain, at least qualitatively, the different slopes of \( \lambda \) for the various solutions shown in Fig. 5. The simple molecules like EG do not show a strong decrease in \( a_w \), thus allowing only a supercooling similar to the one of salts. As a result only a small \( \lambda \)-value of about 2 is observed. The large PEG molecules show a strong decrease in \( a_w \) between the melting and freezing temperature leading to a larger supercooling and, hence, larger \( \lambda \)-values. Unfortunately, the present analysis is not quantitative because the lack of \( a_w \)-data for supercooled PEG solutions. Exact numerical values for \( a_w \) can be provided only by direct measurements or comprehensive thermodynamic models of PEG solutions such as the one discussed above.\(^ {50} \) Nevertheless, the current analysis strongly supports water-activity-based ice nucleation theory, since the latter is consistent with all available experimental data in the stable and metastable range. Also, it provides a qualitative physical explanation of why polymer solutions exhibit a much larger supercooling than do solutions of simple molecules or salts. Finally, our data are in agreement with the suggestion\(^ {17,18,42} \) that ice nucleation in aqueous solutions is controlled entirely by thermodynamic parameters due to the existence of a liquid phase spinodal.

IV. CONCLUSION

The equilibrium and nonequilibrium phase transitions in aqueous PEG solutions have been determined and compared to literature values. All observed equilibrium transitions could be assigned to specific phase equilibrium temperatures. In particular, the occurrence of two eutectic temperatures in the system water/PEG6000 can be attributed to the formation of metastable and stable PEG crystals. Also, the measured homogeneous ice nucleation temperatures have been analyzed for various PEG solutions. For each PEG, the supercooling with respect to ice increases with increasing solution concentration and can be represented by the magnitude of \( \lambda = \Delta T_f / \Delta T_m \). The data show that \( \lambda \) increases as a function of the PEG molar mass. In order to understand this freezing behavior, the water activities of the different PEG solutions were compared in the stable and supercooled temperature range. It was found that the water activity of PEG solutions decreases with decreasing temperature. This trend is stronger for the PEG with a greater molar mass. The analysis of the freezing behavior and the \( a_w \)-data of the different solutions within the framework of water-activity-based ice nucleation theory reveals that the greater supercooling of solutions of large PEGs can be well understood. The present study thus provides strong support for water-activity-based ice nucleation theory,\(^ {9} \) because its predictions are consistent with all experimental data. Our study is also in agreement with the suggestion\(^ {17,18,42} \) of a thermodynamic control of ice nucleation in aqueous systems due to the existence of a liquid phase spinodal.

ACKNOWLEDGMENTS

The authors thank P. Isler and D. Knopf for technical support, and U. Krieger and D. H. Rasmussen for helpful comments on the manuscript.

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20 The so-called stability-limit scenario is one of three hypotheses currently discussed to explain the behavior of water in the supercooled metastable range (Ref. 4).
23 To compare the data of this study with Eliassi et al. (Ref. 44), the measured data in Fig. 3 were fitted to polynomial functions, in order to calculate the appropriate freezing and melting temperature for each concentration (Ref. 24).
24 Water-activity-based ice nucleation theory (Ref. 9) predicts an unambiguous relationship between the freezing temperature of a solution, $T_f$, and the solution water activity at $T_f$ (solid lines in Fig. 6). We have used this relation in order to predict the water activity of PEG solutions at their respective freezing temperature (open symbols in Fig. 6).