

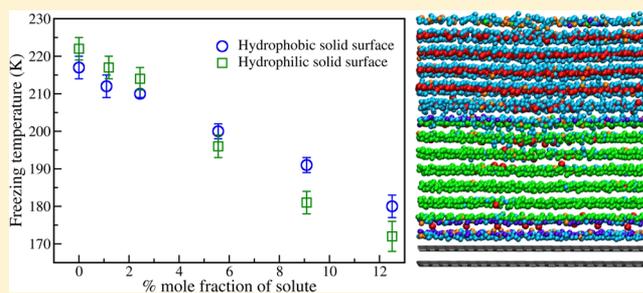
Nucleation of Aqueous Salt Solutions on Solid Surfaces

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Supporting Information

ABSTRACT: The freezing of water in the presence of salts is very common and widely investigated phenomena. However, the role of the substrate during crystallization, and in particular the molecular-level resolution of nucleation mechanism, is still not well-understood. In this work, we investigated the freezing behavior of supercooled water and aqueous lithium chloride solutions on smooth graphitic surfaces. We illustrate the role of solid surfaces in the freezing process of aqueous solutions as a function of mole fraction of a salt exhibiting lowering of freezing temperature, irrespective of a water-binding affinity to the surface. Our molecular dynamics simulations show that the hydrophobic surface is a better nucleating surface when the mole fraction of the salt is over 5%. Our findings reveal that nucleation of ice occurs heterogeneously at the liquid–solid interface. Consequently, propagation of the ice front yields phase-segregated brine near the liquid–vapor interface. Furthermore, we have investigated the effect of salt–surface interaction on the freezing process. We observe lowering of the freezing point with an increase in the water–surface interaction. The simulations demonstrate that nucleation of ice occurs heterogeneously at the liquid–solid interface for low values of interaction, whereas homogeneous nucleation of ice takes place away from the substrate at higher interaction strengths.



INTRODUCTION

Ice nucleation of supercooled water in the presence of various solutes is of great importance to Earth's climate, biology, geology, and many industrial processes.^{1–4} In particular, the addition of solutes to water alters the equilibrium and nonequilibrium properties of the solutions, for example, the freezing point depression of ice in the presence of solute particles. Therefore, the ability to control the kinetics of the liquid–solid phase transition in the presence of solutes, which enhance or prevent nucleation, is important in a variety of natural and industrial processes, such as cloud seeding, prevention of frost and ice formation, cryopreservation of cells, and the survival of living cells.^{5–8} In this direction, the nonequilibrium freezing of water in the presence of different solutes and the effect with increasing solute concentrations have been studied extensively through experiments, theory, and simulations.^{9–17} However, the kinetics of freezing and the equilibrium melting of salt solutions on a substrate is not well-characterized.

Experimental studies have made an effort to understand the effect of solute concentrations on the phase transitions, the melting point, and the internal structure of salt solutions. In 1977, Kanno and Angell⁹ investigated the effects of various salts (LiCl, NaCl, KCl, CsCl, and KI) on the temperature of homogeneous ice nucleation as a function of salt concentration and pressure. They found that although the nucleation temperature of a salt solution depends significantly on solute concentrations, it is independent of the nature of the solute. The homogeneous nucleation temperature and the nucleation rate of aqueous solutions of lithium chloride (LiCl) salt with

increasing salt content have also been studied.¹⁰ Koop et al.¹¹ reported the equilibrium melting and the nonequilibrium freezing temperatures of salt solutions as a function of the solute molality for various salts and organic molecules and expressed the rate of ice nucleation as a function of the activity of water for various solutes in water. Although the addition of solutes to water reduces the homogeneous ice nucleation temperature, there is a significant variation in the melting and freezing temperature at moderate-to-high solute content in water.¹¹ Recently, Bove and co-workers investigated the high-pressure phase diagram of LiCl solutions.^{18–21} It has been reported that the presence of dissolved salts affects the hydrogen bond symmetrization in the crystallization process.²¹

Although rigorous experimental investigations on the liquid–solid phase transitions and the freezing of aqueous solutions as a function of the solute concentration with millimeter- and micrometer-sized droplets have been carried out,^{22–29} there is a limited experimental study on the liquid–solid phase transition of supercooled aqueous solutions on solid surfaces.^{30–32} In laboratory experiments, most of the studies are focused on heterogeneous ice nucleation of an aqueous solution as a function of the solute concentration for different solutes through immersion freezing. These studies have shown that the heterogeneous ice nucleation temperature depends on the activity of water.^{33–38} Anim-Danso et al.³⁰ in a recent work investigated the freezing and melting of water in the presence of

Received: December 20, 2017

Revised: March 28, 2018

Published: March 28, 2018

sodium chloride salt on solid surfaces using infrared–visible sum frequency generation (IR–SFG) spectroscopy. In this work, the authors observed that initially segregation of the concentrated salt solution occurs near the sapphire substrate with the reduction in the temperature of the salt solution. By further reducing the temperature, salt hydrated crystals are formed on the solid surface. Carpenter and Bahadur³² reported an experimental study on the effect of surface and salt concentration on the ice nucleation of supercooled droplets. The authors show that progression of the freezing front of the static droplets on a superhydrophobic surface reduces with an increase in salt concentration.³²

In an experimental framework, the study of crystallization from supercooled water is still extremely challenging, particularly the early stages where the spatial and temporal resolutions are required. Molecular simulations, on the other hand, can unravel the molecular mechanism providing information on the initial stage of ice nuclei formation and its growth dynamics into a crystallite and have been successfully applied to study the nucleation behavior of supercooled liquids.^{39–42} Molecular dynamics (MD),^{43–49} Monte Carlo,^{49–52} and the first-principles^{53–55} simulations have been used to investigate the liquid-to-solid phase change scenarios, structural modification, and free-energy landscapes of ice formation. Although a large number of excellent molecular-level simulation works have been reported in studying the homogeneous ice nucleation of water, few works have been reported on the nucleation behavior and the melting temperature of salt solutions with increasing salt concentrations. Carpenter and Bahadur³² investigated the freezing of a salt solution with the atomistic water model. They found that the freezing process is delayed in the presence of salt and that the nucleation time increases with increasing salt concentrations. Recently, Hudait and Molinero¹⁶ studied the nonequilibrium freezing and equilibrium melting temperatures of water–salt nanodroplets with varying size and salt concentrations using the coarse-grained model of water and a hydrophilic solute mimicking LiCl salt. The simulation studies demonstrated that during the progress of freezing front, ions get rejected into the unfrozen volume.^{12,13} These studies normally focused on the effect of salt with increasing concentrations on the nucleation behavior of ice from liquid water or a nanodroplet. However, nucleation of ice from the salt solution on a solid surface and the effect of salt concentrations on the nonequilibrium freezing temperatures have not yet been investigated using molecular simulations.

This work aims to unravel the structural and the kinetics of the freezing process of LiCl solutions on a smooth graphitic surface using MD simulations. Here, we investigate the effects of salt concentrations and the hydrophobicity/hydrophilicity of surfaces on the kinetics of ice nucleation in supercooled aqueous solutions. Further, our interest is to provide a broader understanding of the role of interactions between ions and the surface in controlling the nucleation behavior of aqueous solutions.

■ MODEL AND SIMULATION DETAILS

We study the nonequilibrium freezing temperature of aqueous solutions on the atomically smooth graphitic surfaces. The graphite surface consists of two layers of graphene (AB stacking) sheets with an interlayer distance of 0.34 nm and a periodic in the *xy* plane with dimensions of $\sim 5.11 \times 5.16$ nm². An aqueous solution film is placed on top of the graphite

surface. The salt content (% moles) in liquid water (X_S) is defined as

$$X_S = \left(\frac{N_S}{N_S + N_W} \right) \times 100 \quad (1)$$

where N_S and N_W are the number of salt and water molecules in the aqueous solution, respectively. In the present study, we prepared aqueous solutions with $X_S = 1.19, 2.44, 5.56, 9.09,$ and 12.50% . The numbers of water and solute molecules are in the ranges of 4067–4100 and 49–585, respectively, as per the concentration of salt in the aqueous solutions.

In this work, water is represented by the coarse-grained monatomic water model mW.⁵⁶ The interaction between mW water is described by the Stillinger–Weber (SW) potential,⁵⁷ where the functional form consists of a sum of two-body and three-body contributions. This water model has been previously applied to the study of liquid, amorphous, and crystalline systems.^{44,45,48,58–60} Each salt molecule is modeled as a coarse-grained solute S that mimics LiCl salt and interactions are described by the functional form of the SW potential.⁶¹ This coarse-grained model of an aqueous solution of LiCl quantitatively reproduces the structural properties and melting temperature and accurately predicts the relative vapor pressure of water in aqueous solutions close to the experiment.^{15,16,61,62} The water–substrate and solute–substrate interactions are modeled by the two-body contribution of the SW potential. To mimic the hydrophobicity and hydrophilicity of the surface, we have considered the carbon–water interactions (ϵ_{C-W}) = 0.13 and 0.30 kcal/mol, respectively, where interaction parameters of $\epsilon_{C-W} = 0.13$ kcal/mol and $\sigma_{C-W} = 0.32$ nm reproduce the macroscopic contact angle of water on a graphitic surface.⁶³ To see the effect of interaction between ions and the substrate on the crystallization process, we have varied the interaction parameter (ϵ_{C-S}) in the range of 0.13–0.75 kcal/mol with a fixed value of σ_{C-S} (same as σ_{C-W}).

MD simulations are conducted using LAMMPS simulation package⁶⁴ under the canonical ensemble (NVT). A time step of 5 fs is used for integrating the equations of motion using the velocity Verlet algorithm. The temperature in the simulations is controlled by the Nosé–Hoover thermostat with a relaxation time of 1.0 ps. Periodic boundary conditions (PBCs) are applied in all the directions. The atoms in the surface are kept frozen at the bottom of the simulation box, and the height of the system is taken to be 15 nm to avoid unnecessary interaction between a slab and its periodic images under the PBC. The aqueous solution film on a graphite surface is initially equilibrated for 60 ns at a temperature of 300 K. To collect the independent trajectories, additional 40 ns simulations are performed from the equilibrated system at the same temperature. The trajectories are collected after every 2 ns for estimating the freezing temperatures. The freezing process of aqueous solutions is investigated through cooling ramp simulations. A constant value of 1 K amplitude is used for each cooling ramp. The duration of the ramps is 1 ns, and the corresponding rate of change of temperature is 1 K ns⁻¹. The average freezing temperatures are calculated from at least 8 different independent simulations for each salt concentration. The initial temperatures for each simulation are kept at least 50 K above the corresponding freezing temperature reported in this study.

In this study, ice-like and liquid-like molecules are distinguished by evaluating the local order parameter q_{6m} for

individual water molecules using the method of spherical harmonics.⁶⁵ The presence of an ice-like structure along the simulation trajectories is revealed with a cutoff of $q_6 > 0.55$.¹⁶ The size of the largest ice cluster is identified by considering the ice molecules that are connected within a distance of 0.35 nm. The freezing temperature (or crystallization temperature), T_f , is determined by considering a drop in the energy and sharp rise in the fraction of ice particles when the solution is cooled at a rate of 1.0 K ns⁻¹. The detailed description of the order parameters is presented in earlier works.^{43,66} The average tetrahedral order parameter (q_{th}) of each water molecule with respect to its four closest neighbors is calculated using the following equation^{43,67}

$$q_{th} = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \theta_{jk} + \frac{1}{3} \right)^2 \quad (2)$$

where θ_{jk} is the angle formed by a central water molecule with its j and k nearest neighbors. The average value of q_{th} is one for a fully tetrahedral network (perfect tetrahedral crystal), and zero corresponds to a random distribution of these angles.

RESULTS AND DISCUSSION

In this work, we first determine the freezing temperature of the aqueous binary solution as a function of mole fraction of a salt on the graphite-like surfaces for two cases, viz., hydrophobic ($\epsilon_{C-W} = 0.13$ kcal/mol) and hydrophilic ($\epsilon_{C-W} = 0.30$ kcal/mol) water–surface interactions. Figure 1 shows the computed

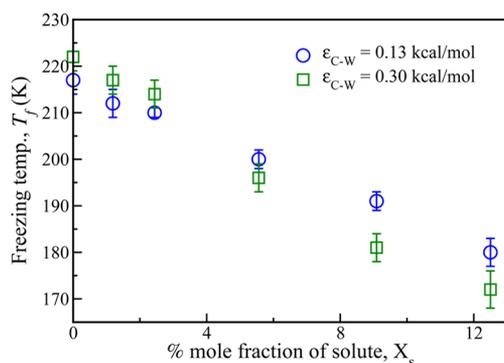


Figure 1. Freezing temperature of aqueous LiCl solutions as a function of percentage mole fraction of a salt at a cooling rate of 1 K ns⁻¹ for both hydrophobic and hydrophilic surfaces, that is, $\epsilon_{C-W} = 0.13$ and 0.30 kcal/mol.

freezing temperature on hydrophobic and hydrophilic surfaces with a cooling rate of 1.0 K ns⁻¹. The freezing temperature of the water film on a graphite surface ($T_f = 217 \pm 2$ K) with the original carbon–water interaction strength ($\epsilon_{C-W} = 0.13$ kcal/mol) is higher than the homogeneous freezing temperature of the mW water model.⁴⁵ Our coarse-grain MD simulation shows that the freezing temperature of pure water on the hydrophilic surface is higher than that on the hydrophobic surface (see Figure 1). The freezing temperature obtained in this work is consistent with the prediction of Lupi et al.⁶³ and in agreement with the recent work of Lupi and Molinero,⁶⁸ where the freezing temperature of water on the graphitic surface increases with increase in carbon–water interaction. Recently, Zhang et al.⁶⁹ studied the hydrophilicity-dependent freezing temperature of water using the IR–SFG spectroscopy technique. They found that the freezing temperature increases with increasing

surface hydrophilicity for a small water droplet ($\sim 10 \mu\text{L}$). Furthermore, our results here also support previous studies, which reported that the nucleation ability of a crystalline surface gets enhanced with surface hydrophilicity.^{70–73}

The freezing temperature of water is known to decrease with increasing salt concentrations.^{9,11,16} Interestingly, the effect of salt on the depression behavior of freezing temperature of an aqueous solution is found to be indifferent to the presence of the surface, irrespective of the affinity of water with the surface, as seen in Figure 1. We have also plotted the freezing temperature as a function of the activity of water in solution, as shown in Figure S1. The activity of the solution is calculated from the experimental vapor pressure data at 303.15 K.⁷⁴ The heterogeneous freezing temperature decreases with a decrease in water activity, which is consistent with the experimental observation of water activity-dependent ice nucleation.³⁴ While the qualitative agreement with the activity-dependent freezing temperature model is encouraging, the quantitative comparison is difficult as clearly stated in a recent work of Espinosa et al.⁷⁵ To provide a molecular picture and in particular elucidate the role of the surface, we evaluate the spatial distributions of water and solute at different temperatures during the cooling process. Figure 2 illustrates the water and the solute number density profiles along the direction normal to the surface for $X_s = 2.44$ and 9.09%. Before the onset of freezing, two major distinct peaks close to the graphite surface are observed for both the salt concentrations. Interestingly, no significant difference in the water layering near the surface is noticed for both the salt concentrations, as depicted in Figure 2a,b. However, it is observed that a lower temperature is needed at a higher salt concentration to crystallize the solution. This is evident from the figure corresponding to $X_s = 9.09\%$, where $T = 185$ K shows a signature of crystallinity which is seen at $T = 200$ K for $X_s = 2.44\%$. The number of solute molecules near the surface, on the contrary, is higher for $X_s = 9.09\%$ as compared to that for $X_s = 2.44\%$, as shown in Figure 2c,d. Thus, the solute molecules near the surface play a vital role in controlling the nucleation behavior of water and ice. It should be noted that the first layer of the salt molecules is located at a distance of 0.55 nm from the surface, whereas the first and second layers of the liquid water appear at a distance of 0.29 and 0.59 nm, respectively (at 225 K). In addition, solutes show interior solvation (i.e., solutes are expelled from the vapor–liquid interface), as depicted in Figure S2. However, at a low concentration of the solute, there is a significant enhancement of the solute near the vapor–liquid interface as compared to the bulk region (see the blue solid line in Figure S2). These results are in good agreement with the previous observation of Jungwirth et al.⁷⁶ As the solute content in the solutions increases, the number of solute particles near the surface is found to increase, which inhibits the crystallization of aqueous solutions, leading to drop in the freezing temperature. Figure 3 shows typical snapshots of the nucleation and growth of ice at different temperatures upon cooling at a rate of 1.0 K ns⁻¹ for $X_s = 2.44$ (top panel) and 9.09% (bottom panel). Nucleation is found to initiate at the graphite surface, and with the progression of freezing events (front), the solute particles from the solid–liquid interface are progressively rejected. Finally, the solute molecules get segregated near the vapor–liquid interface, which is also reflected in the density profiles of the solute upon freezing (see Figure 2c,d).

Figure 1 also displays an intriguing effect of the variation in the water–surface interaction strengths (i.e., hydrophobicity/

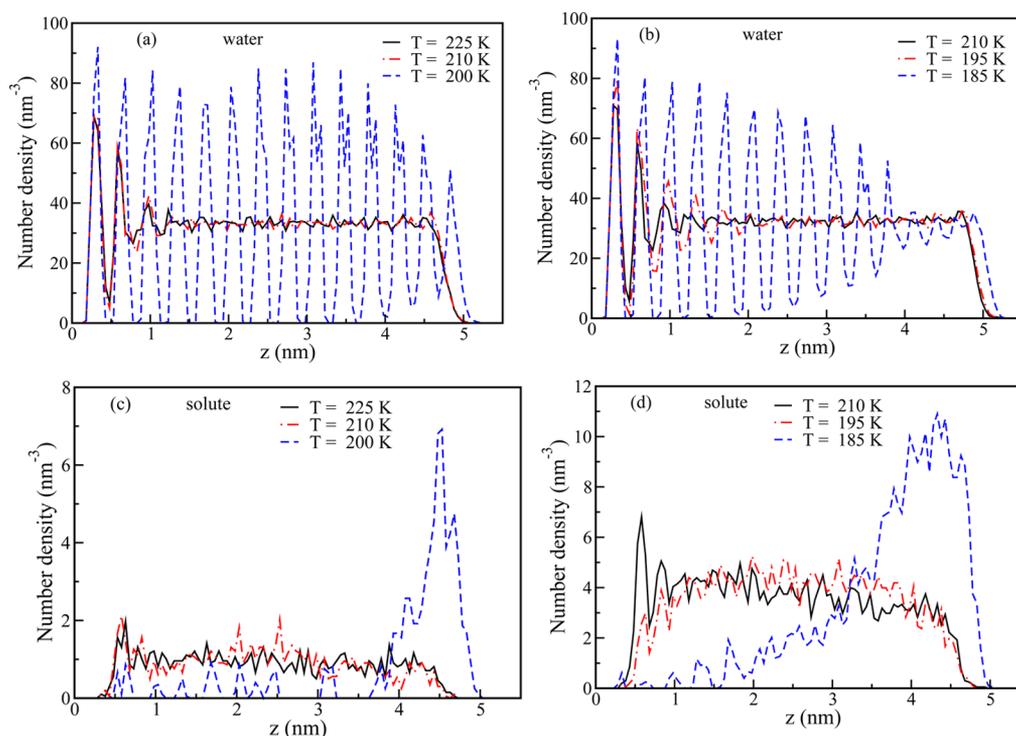


Figure 2. Density of water and solute molecules above the hydrophobic surface ($\epsilon_{C-W} = 0.13$ kcal/mol) at different temperatures during cooling: (a,c) for $X_S = 2.44\%$ and (b,d) for $X_S = 9.09\%$.

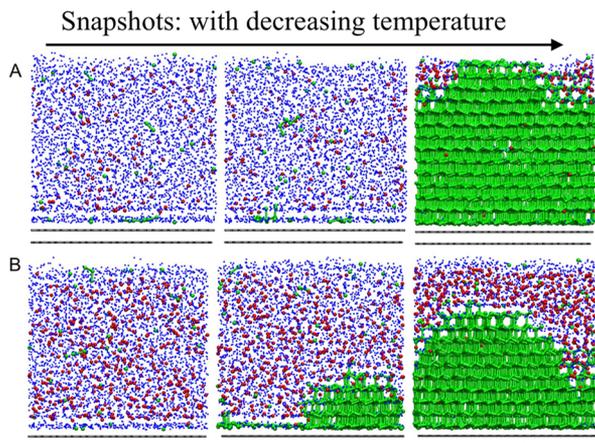


Figure 3. Representative snapshots of crystallization trajectories of aqueous salt solutions on a hydrophobic surface during cooling: (A) $X_S = 2.44\%$ at $T = 225, 210,$ and 200 K (from left to right) and (B) $X_S = 9.09\%$ at $T = 210, 195,$ and 185 K (from left to right). Ice-like molecules distinguished from the aqueous solutions are shown in green balls and connected by sticks that represent hydrogen bonds; liquid water and salt molecules are shown in blue dots and red balls, respectively.

hydrophilicity of the surface) on the freezing temperature of aqueous solutions. Interestingly, at low values of the solute content ($X_S \leq 2.44\%$), the freezing temperature is lower for $\epsilon_{C-W} = 0.13$ kcal/mol compared to $\epsilon_{C-W} = 0.30$ kcal/mol. On the other hand, at high values of the salt content ($X_S \geq 5.56\%$), an opposite trend is found. To understand the unusual behavior of ice nucleation, we evaluate the spatial distributions of water and solute during the cooling process of the aqueous solutions. Figure 4 presents the water and salt distribution on the hydrophilic surface ($\epsilon_{C-W} = 0.30$ kcal/mol) for $X_S = 2.44$ and

9.09%. It is evident from the density profiles of water (see Figures 2a and 4a at $T = 225$ K) that the layering of liquid water in contact with the substrate is higher on the hydrophilic surface ($\epsilon_{C-W} = 0.30$ kcal/mol) than on the hydrophobic surface ($\epsilon_{C-W} = 0.13$ kcal/mol). At a low ϵ_{C-W} , the surface atoms bind water molecules weakly. On the other hand, with an increase in hydrophilicity ($\epsilon_{C-W} = 0.30$ kcal/mol), water molecules bind strongly with the surface atoms, causing enhanced layering at the surface. At this salt concentration, the number of solute particles present near the surface is less (see Figures 2c and 4c at $T = 225$ K), and as a consequence, there is no significant effect of inhibition on the formation and growth of the hexagonal network of ice-like molecules. The results suggest that the existence of strong interfacial water layering at the hydrophilic surface enhances the freezing temperature of a water–salt mixture. Previous molecular simulation results strongly suggest that ordering of interfacial liquid water near the surface plays a role in the kinetics of heterogeneous nucleation of ice from supercooled water.^{63,68,71} With an increase in the concentration of salt, the number of solute molecules near the substrate increases with increasing interaction between the water and surface atoms. At $X_S = 9.09\%$, a greater amount of solutes near the hydrophilic surface (see Figure 4d) is seen as compared to that observed for the hydrophobic surface (see Figure 2d). As a result, the extent of inhibition increases with the solute near the surface and consequently lowers the T_f on the hydrophilic surface. Figure 5 illustrates the snapshot from a freezing simulation upon cooling on a hydrophilic surface with $X_S = 2.44$ and 9.09%. At higher values of X_S , we observe that the hexagonal network of ice-like molecules in contact with the surface is strongly affected by the presence of solute particles near the surface (see Figure 5B, right panel). Thus, at high values of salt concentration, the effect of the water layering on the hydrophilic surface on the ice

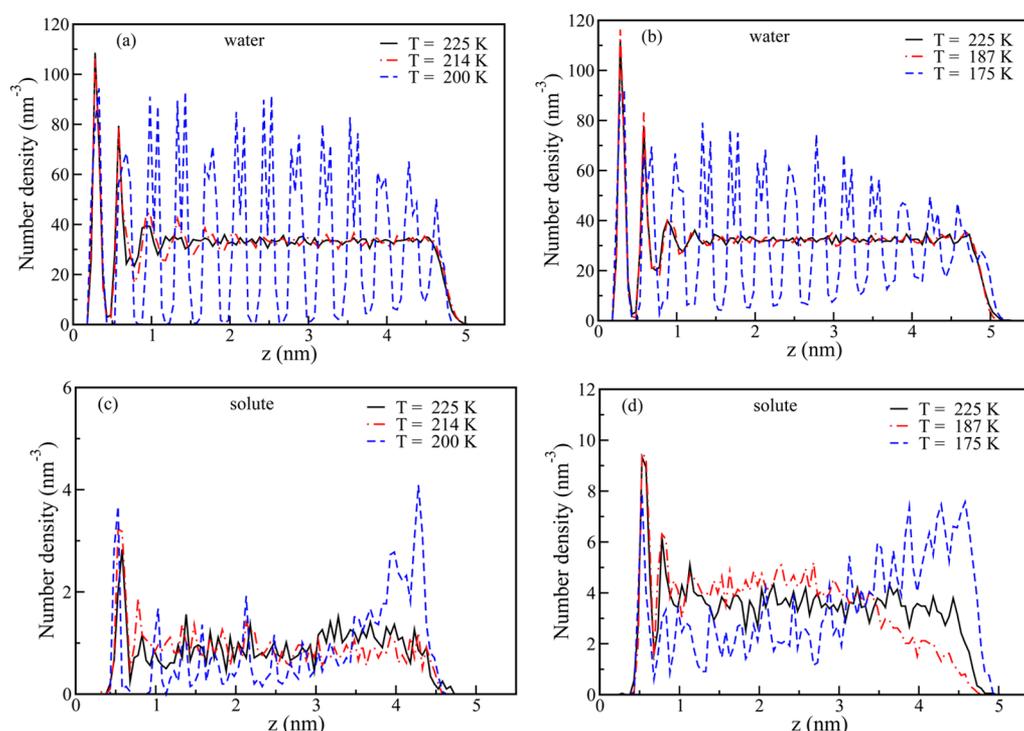


Figure 4. Density of water and solute molecules above the hydrophilic surface ($\epsilon_{C-W} = 0.30$ kcal/mol) at different temperatures during cooling: (a,c) for $X_S = 2.44\%$ and (b,d) for $X_S = 9.09\%$.

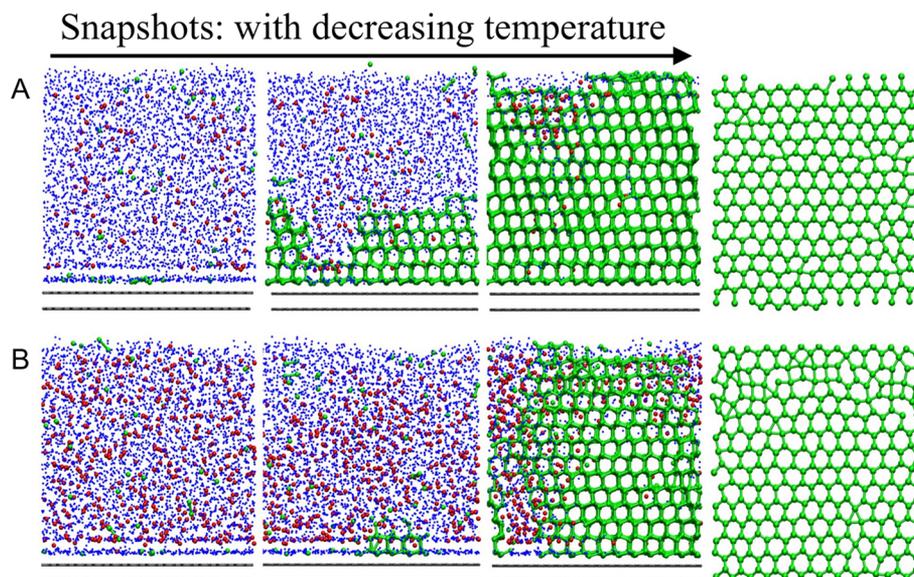


Figure 5. Representative snapshots of crystallization trajectories of aqueous salt solutions on a hydrophilic surface ($\epsilon_{C-W} = 0.30$ kcal/mol) during cooling: (A) $X_S = 2.44\%$ at $T = 225, 214,$ and 200 K (from left to right) and (B) $X_S = 9.09\%$ at $T = 210, 187,$ and 175 K (from left to right). Ice-like molecules distinguished from the aqueous solutions are shown in green balls and connected by sticks that represent hydrogen bonds; liquid water and salt molecules are shown in blue dots and red balls, respectively.

crystallization is less prominent. This is mainly due to the significant presence of the solute molecules near the surface, which prevents the heterogeneous nucleation of ice on the hydrophilic surface.

Figure 6 shows the temperature dependence of the average tetrahedral order parameter in the direction perpendicular to the surface. The water molecules near the surface as well as in the bulk region become less tetrahedrally ordered during cooling with an increase in the solute content (see Figure 6a,b). The results demonstrate that the tetrahedral water environment

at the solid–liquid interface and the bulk region is reduced with an increase in the solute content in an aqueous solution. Thus, the data clearly support the results on the inhibition of freezing temperature with increasing salt content in an aqueous solution. At a low solute content ($X_S = 2.44\%$), the contact layer water molecules are more ordered on the hydrophilic surface than on the hydrophobic surface, which is indicative of higher freezing temperature on the hydrophilic surface. On the other hand, at a higher concentration of salt ($X_S = 9.09\%$), the contact layer water molecules show more tetrahedral environment on the

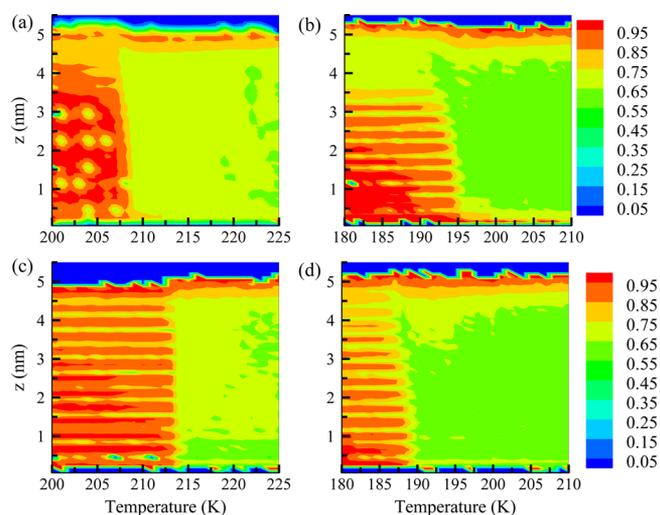


Figure 6. Temperature dependence of the average tetrahedral order parameter of water along the direction normal to the surface for $\epsilon_{C-W} = 0.13$ kcal/mol and (a,b) correspond to $X_S = 2.44$ and 9.09% , respectively, and for $\epsilon_{C-W} = 0.30$ kcal/mol and (c,d) correspond to $X_S = 2.44$ and 9.09% , respectively. In color bar, red color corresponds to solid-state values and blue to liquid-state values.

hydrophobic surface than on the hydrophilic surface (see Figure 6b,d). It seems reasonable to indicate that the solute molecules near the solid surface reduce the orientational ordering of water molecules, and as a consequence, a lower value of freezing temperature is observed.

We now focus on the nucleation behavior and the structure of crystalline ice obtained through an isothermal crystallization of the water–salt solution. Here, we have considered temperature above the freezing points of salt solutions on the graphitic surface. Figure 7 shows the structure of a crystallized water–salt on the hydrophobic and hydrophilic surfaces at 200 ns for $X_S = 2.44$ and 9.09% at 215 and 195 K, respectively. We observe that nucleation takes place at the solid–liquid interface, followed by the propagation of the ice front in the supercooled aqueous salt solutions. As the ice front progresses, the solute molecules are mostly expelled from the crystallite, though few

solute molecules get trapped in the bilayer of ice-like molecules. It is observed from the simulation trajectories that few solute particles replace water from one of the lattice points of the hexagonal network of the ice structure (see the top view of Figure 7A, bottom panel). Surprisingly, for nucleation on the hydrophilic graphitic surface at $X_S = 9.09\%$, we observe more ordering of solute molecules in a salt-rich solution, which possibly indicate the crystallization of salt hydrates. It is noted that the solute molecules are located at positions either within the hexagon or at the position of water molecules in a six-member network, as depicted in Figure 7B (top view, right panel). Recent MD simulation studies^{77,78} describe the effect of ice polymorphism in both homogeneous and heterogeneous nucleations. The higher nucleation is observed for stacking-disordered ice compared to pure hexagonal crystallites. In our investigation, we have observed stacking-disordered ice on the graphite surface, as shown in Figure S3. Thus, we expect that the formation of different polymorph crystallites will have effect on the freezing temperature.

In the discussion above, the crystallization of aqueous solutions of varying salt concentrations on hydrophobic/hydrophilic graphitic surfaces is studied at a constant cooling rate or at a constant temperature. The freezing temperature reduces with increasing mole fraction of the solute for both the surfaces. We found a lower freezing temperature on the hydrophilic surface at high salt concentrations. The solute molecules considered in this simulation are highly hydrophilic in nature, and the solute–surface interaction is equivalent to the original carbon–water interaction. We now investigate the effect of enhancing carbon–solute attractive interaction on the freezing of aqueous solutions. To this end, we systematically vary the carbon–solute interaction strength over a broad range and compute the crystallization temperature of aqueous solutions on the graphite surface. Figure 8 shows the freezing temperature of a salt–water mixture as a function of the interaction between the solute molecules and the carbon atoms of the graphite surface with a cooling rate of 1.0 K ns^{-1} . At a low value of the solute content ($X_S = 2.44$), T_f decreases with an increase in the interaction strength. On the other hand, at a higher concentration of salt ($X_S = 5.56\%$), a noticeable variation

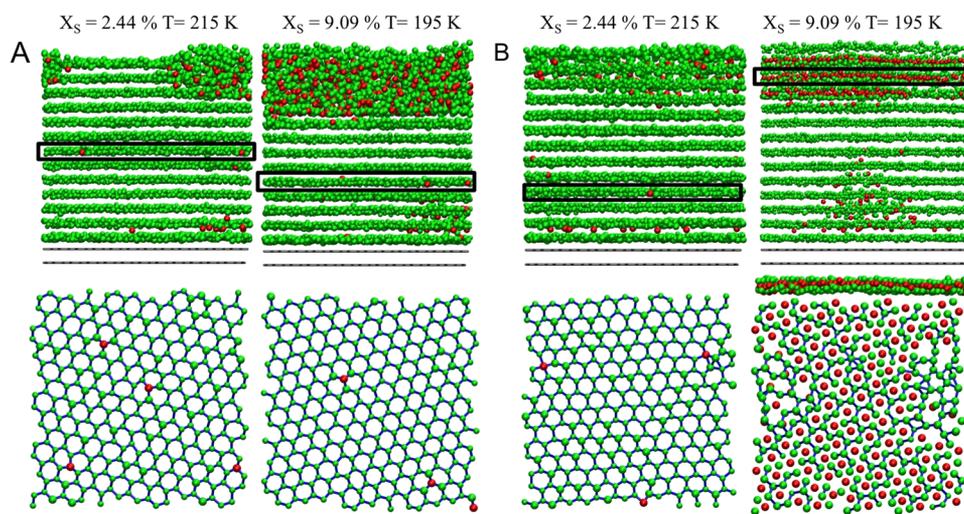


Figure 7. Isothermal crystallization of aqueous salt solutions at 215 K for $X_S = 2.44\%$ and at 195 K for $X_S = 9.09\%$: (A) hydrophobic ($\epsilon_{C-W} = 0.13$ kcal/mol) and (B) hydrophilic ($\epsilon_{C-W} = 0.30$ kcal/mol) graphitic surfaces. Water and salt molecules are represented by green and red balls, respectively.

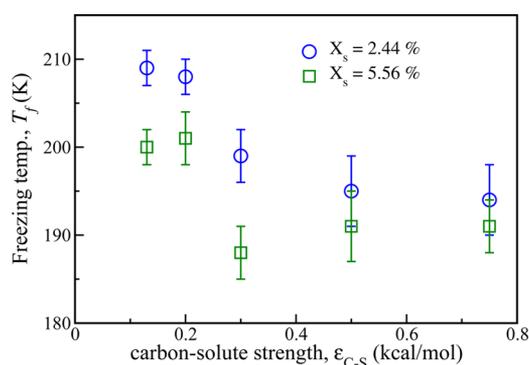


Figure 8. Freezing temperature of aqueous LiCl solutions as a function of carbon-solute interaction strengths on a hydrophobic surface ($\epsilon_{C-W} = 0.13$ kcal/mol) at a cooling rate of 1 K ns^{-1} for $X_S = 2.44$ and 9.09% .

in the freezing temperature is found with ϵ_{C-S} . As the salt-surface interaction strength increases, the T_f reaches a minimum at $\epsilon_{C-S} = 0.30$ kcal/mol. Further increase in ϵ_{C-S} enhances the freezing temperature slightly.

To understand the carbon-solute interaction strength-dependent reduction of the crystallization temperature, we analyze the distribution of water and solutes in the direction perpendicular to the surface. Figure 9 shows the number density of water and solutes on a hydrophobic surface upon cooling at a constant rate for $X_S = 2.44\%$. With an increase in the interaction strength, a substantial change in the distribution of solute molecules in the aqueous solution (i.e., before freezing) is noticed along the direction normal to the surface. In particular, the location of the first peak of density is shifted from ≈ 0.57 to ≈ 0.29 nm. Furthermore, the density profile shows an intense peak for $\epsilon_{C-S} \geq 0.30$ kcal/mol (see Figure

9c,d at $T = 225$ K). As a consequence, the positions of the first and second peaks of the number density of water (i.e., contact water layers) are shifted slightly toward the substrate. It should be noted that the first peak position of water appears at a distance ≈ 0.29 nm from the substrate. Therefore, the number of water molecules at the contact layers reduces with increasing ϵ_{C-S} . On the other hand, the number of solutes adsorbed on the substrate increases with increasing ϵ_{C-S} , as depicted in Figure 9c,d, which is indicative of a decrease in the structural ordering of water with increasing ϵ_{C-S} . Thus, the solute molecules near the substrate inhibit the formation of a six-member network of water and result in the drop of T_f with an increase in ϵ_{C-S} . Although at $\epsilon_{C-S} = 0.30$ kcal/mol, the solute exhibits an intense peak at the surface in the density profile, a significant amount of solutes is also present in the bulk phase (see Figure 9d $T = 225$ K). This might be due to the competitive interaction between the water-solute and the carbon-solute. To this end, the solute adsorption energy (i.e., potential energy after geometry minimization) to the surface is compared with the water-solute potential energy. We find that the adsorption energy of a solute on the substrate (≈ -4.0 kcal/mol) is greater than the water-solute interaction energy (≈ -2.3 kcal/mol, corresponding to the potential energy of one solute molecule and two water molecules). Thus, at low values of the salt content, less number of solutes are present at the solid-liquid interface, and the first water layer (i.e., in contact with the substrate) becomes active. Consequently, heterogeneous nucleation occurs at the solid-liquid interface (see Figure 10A for $X_S = 2.44\%$) at $\epsilon_{C-S} = 0.30$ kcal/mol. As the interaction strength increases, the solutes mostly adsorb on the surface. This causes a reduction in the number of water molecules in the contact layer, and thus, water molecules at the solid-liquid interface become inactive and are unable to form a

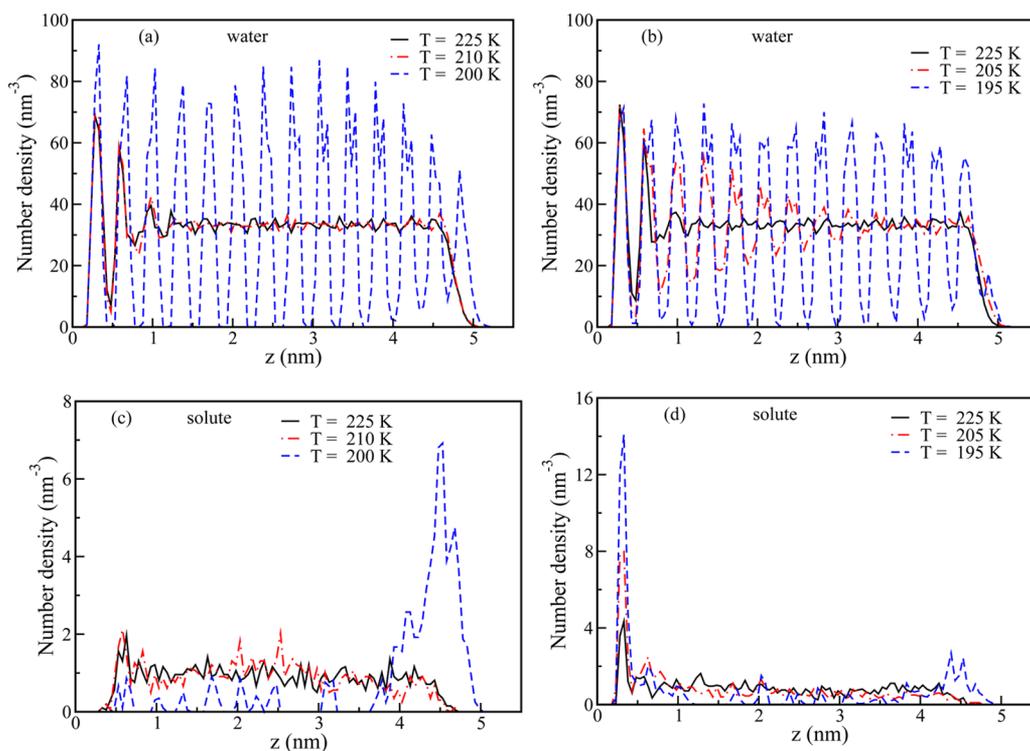


Figure 9. Density of water and solute molecules above the surface ($\epsilon_{C-W} = 0.13$ kcal/mol) at different temperatures during cooling at $X_S = 2.44\%$: (a,c) and (b,d) for $\epsilon_{C-S} = 0.13$ and 0.30 kcal/mol, respectively.

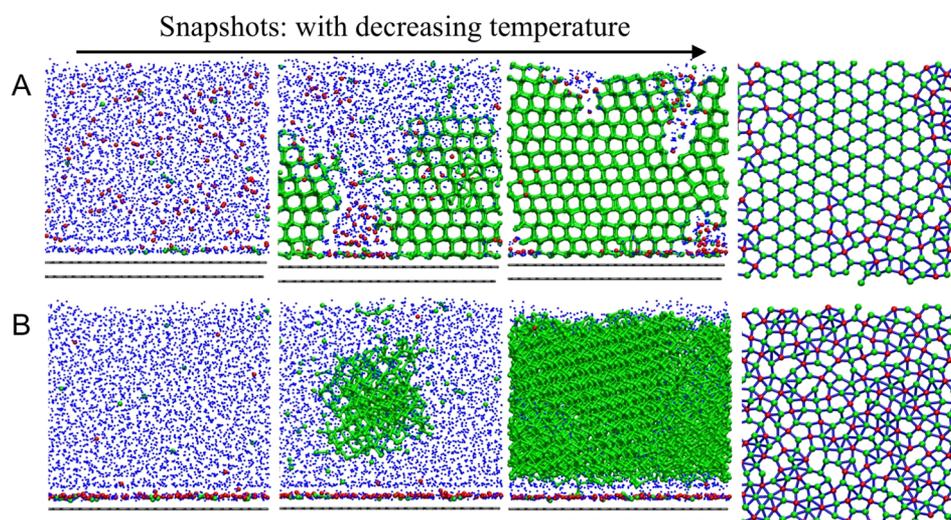


Figure 10. Representative snapshots of crystallization trajectories of an aqueous salt solution ($X_S = 2.24\%$) at different temperatures during cooling: (A) $\epsilon_{C-S} = 0.30$ kcal/mol at $T = 225, 205,$ and 195 K (from left to right) and (B) $\epsilon_{C-S} = 0.50$ kcal/mol at $T = 225, 198,$ and 190 K (from left to right). The right panel shows the water and solute molecules in the contact layer on the graphite surface. The water molecules classified as ice-like molecules in aqueous solutions are shown in green balls and connected by sticks that represent the bonds; liquid water and salt molecules are shown in blue dots and red balls, respectively.

six-member ring on the surface. Further, we have plotted the freezing temperature of solutions at a solute content of 2.24% (see Figure S4). From the figure, it is clear that at a high value of the carbon–water interaction, the freezing temperature is closer to the homogeneous freezing line. Thus, nucleation is initiated away from the surface particularly at a higher substrate–solute interaction (see Figure 10B for $\epsilon_{C-S} = 0.50$ kcal/mol).

On the other hand, at a higher value of the solute content ($X_S = 5.56\%$), an unusual behavior in the freezing temperature is observed with increasing carbon–solute interaction strength (see Figure 8). The results imply that the solute particles play a significant role in the crystallization mechanism of water–salt mixtures. To address this intriguing dependence of freezing temperature on carbon–solute interaction strengths, we examine the distribution of solutes and water molecules along the direction normal to the surface. The data in Figure 11 (before the onset of freezing) show that as the ϵ_{C-S} increases the number of water molecules in the vicinity of the surface (i.e., within the first layer) reduces, whereas the number of solutes near the surface increases with ϵ_{C-S} . Increasing ϵ_{C-S} enhances the binding of the solute with the surface atoms, and

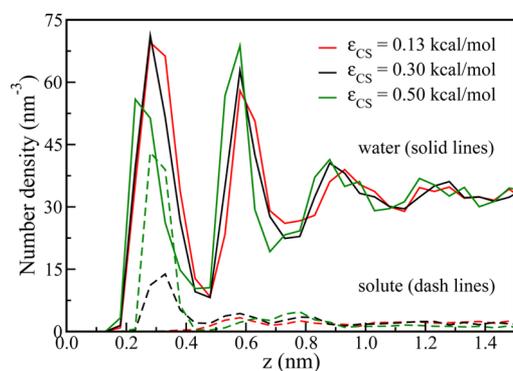


Figure 11. Density of water and solute molecules above the surface ($\epsilon_{C-W} = 0.13$ kcal/mol) before crystallization for $X_S = 5.56\%$.

as a consequence, a greater number of solutes adsorb on the surface. At $\epsilon_{C-S} < 0.30$ kcal/mol, nucleation is initiated at the surface (i.e., heterogeneous nucleation takes place, see Figure 12A) because of the presence of insignificant solutes on the surface, leading to the strong ordering of water molecules at the surface. Thus, solutes near the surface are unable to inhibit nucleation, which gives rise to higher T_f as compared to the

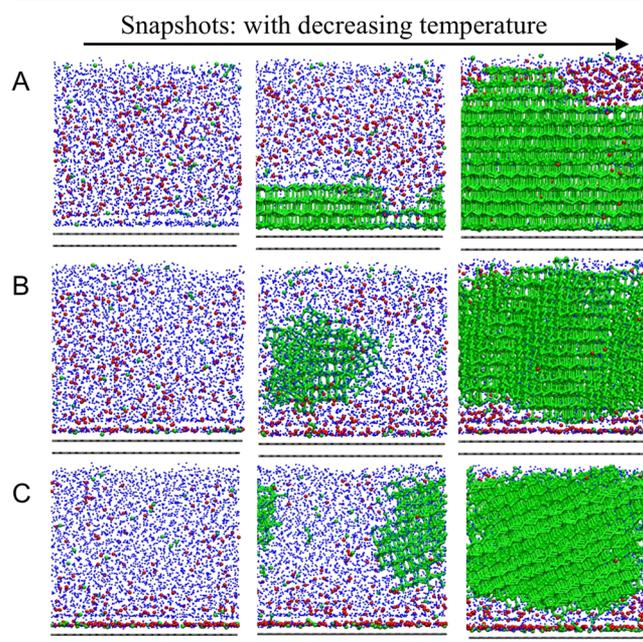


Figure 12. Representative snapshots of crystallization trajectories of aqueous salt solution ($X_S = 5.56\%$) at different temperatures during cooling: (A) $\epsilon_{C-S} = 0.13$ kcal/mol at $T = 225, 202,$ and 195 K (from left to right); (B,C) for $\epsilon_{C-S} = 0.30$ and 0.50 kcal/mol, respectively, at $T = 210, 193,$ and 185 K (from left to right). Ice-like molecules distinguished from aqueous solutions are shown in green balls and connected with bonds; liquid water and salt molecules are shown in blue dots and red balls, respectively.

case of higher values of ϵ_{C-S} . Interestingly, at a strength of 0.30 kcal/mol, we found T_f to be the lowest. At this ϵ_{C-S} , there is a competitive interaction between water–solute and carbon–solute pairs. As a result, a significant number of solute particles get adsorbed at the surface. Nevertheless, a substantial amount of solute particles are still present in the bulk region (see the density profile in Figure 11). The water molecules in the contact layer become inactive to promote nucleation from the solid–liquid interface because of the substantial amount of solutes accumulated closer to the surface. As a result, nucleation events are initiated away from the surface similar to the case of homogeneous nucleation (see Figure 12B). This is in contrast to the nucleation behavior observed at the lower salt content ($X_S = 2.44\%$) where nucleation occurs in the heterogeneous manner (see Figure 10A). This is due to a large number of solutes adsorbed on the surface compared to a lower mole fraction of solutes in the solution (i.e., $X_S = 2.44\%$). On the other hand, a greater amount of solutes is also present in the bulk region at this concentration of salt in the solution. Consequently, ice nucleation is further inhibited, leading to a very low freezing temperature. Further increase in the carbon–solute interaction strength ($\epsilon_{C-S} > 0.30$ kcal/mol) enhances strong adsorption of solutes on the substrate. As a result, the contact layer water molecules become insensitive to nucleation at the surface, and homogeneous nucleation is favored at higher values of ϵ_{C-S} , as shown in Figure 12. Furthermore, we have observed immobilized solute molecules in the contact layer with the surface, which acts almost as an atomically rough surface. On the other hand, the solute content in the bulk region reduces with increasing ϵ_{C-S} , and therefore, we found that the freezing temperature slightly enhances ($\epsilon_{C-S} > 0.30$ kcal/mol).

In this work, we have shown that solute adsorption on the substrate can lead to different mechanisms of nucleation. Solute adsorption on the surface can change the nature of the substrate from hydrophobic to hydrophilic and vice versa. Zhang et al.⁶⁹ have recently reported an experimental work where hydrophobicity of the surface is modified by functionalization using different organic molecules. Similarly, Papagiannakopoulos and co-workers^{79,80} studied ice nucleation on bare and organic molecule-covered graphite using the deposition mode. The authors report that the adsorption of methanol and butanol provides hydrophilic and hydrophobic surface sites, respectively. This modification allowed the formation and growth of smooth crystalline and rough ice on hydrophilic and hydrophobic surfaces, respectively. While the current work is based on a model salt, the results at low concentration (where most of the experiments are usually conducted) are interestingly similar to a certain extent to that observed for different surfaces studied in experiments. Thus, we believe that our results, based on a wide range of solute concentrations and surface–solute interaction strengths, could be valuable in the understanding of the heterogeneous nucleation of complex systems.

CONCLUSIONS

This study addresses the effect of surface and salt concentration in controlling the nucleation of ice from an aqueous solution. We systematically investigated the freezing behavior of aqueous solutions up to 12.5% mole fraction of a salt on hydrophobic and hydrophilic surfaces. Our simulation results indicate that the freezing temperature decreases with increasing mole fraction of the solute and that the behavior is indifferent to

the nature of the substrate. This work elucidates an intriguing effect of hydrophobicity/hydrophilicity of the surfaces on the freezing mechanism of water–salt solutions. We find the higher freezing point on the hydrophilic surface as compared to the hydrophobic surface for low values of solute content ($X_S \leq 2.44\%$), while opposite trend is observed at the higher salt content ($X_S > 2.44\%$) for a weak carbon–solute interaction strength of 0.13 kcal/mol. The results display that the freezing temperature depends on the hydrophilicity of the surface at low salt concentrations. On the other hand, at high salt concentrations, the solute near the surface plays a significant role in the crystallization process. Further, we investigated the nucleation behavior and the internal structure of ice through isothermal crystallization of water–salt solutions. We find that nucleation of ice occurs heterogeneously at the solid–liquid interface. The isothermal simulations demonstrate that the presence of the solute in the hexagonal network of the ice structure suggests the formation of salt hydrate crystals. Finally, the sensitivity of the freezing temperature to the carbon–solute interaction has also been studied. The results of our simulations suggest that the freezing temperature usually decreases with increase in the carbon–solute interaction strength. We observe heterogeneous nucleation at the solid–liquid interface at a weak carbon–solute interaction, whereas homogeneous nucleation is initiated away from the substrate at a strong carbon–solute interaction. Interestingly, at $X_S = 5.56\%$, the lowest T_f is obtained for an interaction of 0.30 kcal/mol. This is because of competitive interactions between the carbon–solute and the water–solute pairs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b12495.

Additional simulation results of the freezing temperature as a function of water activity, density profile, and snapshot (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the Department of Science and Technology (DST), Government of India. The computational resources are provided by the HPC cluster of the Computer Center (CC), Indian Institute of Technology, Kanpur.

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