Tuning ice nucleation with counterions on polyelectrolyte brush surfaces

Zhiyuan He,1* Wen Jun Xie,2* Zhenqi Liu,1 Guangming Liu,3 Zuowei Wang,4 Yi Qin Gao,2† Jianjun Wang1†

Heterogeneous ice nucleation (HIN) on ionic surfaces is ubiquitous in a wide range of atmospheric aerosols and at biological interfaces. Despite its great importance in cirrus cloud formation and cryopreservation of cells, organs, and tissues, it remains unclear whether the ion-specific effect on ice nucleation exists. Benefiting from the fact that ions at the polyelectrolyte brush (PB)/water interface can be reversibly exchanged, we report the effect of ions on HIN on the PB surface, and we discover that the distinct efficiency of ions in tuning HIN follows the Hofmeister series. Moreover, a large HIN temperature window of up to 7.8°C is demonstrated. By establishing a correlation between the fraction of ice-like water molecules and the kinetics of structural transformation from liquid- to ice-like water molecules at the PB/water interface with different counterions, we show that our molecular dynamics simulation analysis is consistent with the experimental observation of the ion-specific effect on HIN.

INTRODUCTION

Ice formation is ubiquitous and crucial in many fields such as cryobiology, geology, and climate science (1–4). It is believed that the molecular-level understanding of ice formation is essential to predict the future of our planet (5–7). Ions are often involved in the process of ice formation (8–12). Early studies showed that the growth rate of ice in aqueous alkali halide solutions is strongly dependent on the type of salts (8–10). It might be due to the differential incorporation of ions in the ice crystals or selective adsorption of ions at the ice/water interface (11, 12). Particular interests have been focused on ice nucleation because it is the initial and rate-limiting step for ice formation (3, 4, 13–15). Fruppacher and Neiburger (16) and Pruppacher (17) studied the relationship between the supercooling and the structure of aqueous solutions with monovalent ions and found that the nonequilibrium freezing point depression of a solution varied with the type of salts and, for a particular salt, increased with the salt concentration. Recently, Koop et al. (18) revealed that homogeneous ice nucleation in an aqueous solution could be predicted by water activity. Thermodynamic anomalies of water crystallization were investigated by Moore and Molinerio (19) and Hudait and Molinerio (20), who found that the fraction of four coordinated molecules in supercooled liquid water controlled the ice nucleation rate. However, in real systems, ice nucleation occurs more often on foreign surfaces, that is, through heterogeneous ice nucleation (HIN). For example, Ehre et al. (2) and Belitzky et al. (21) found that HIN on charged surfaces was affected by the interfacial water structure, which was also dependent on the amount of surface charges. Abbatt et al. (22) discovered that HIN on the surface of solid ammonium sulfate aerosols was a pathway for the formation of cirrus cloud, which could cover up to 30% of Earth’s atmosphere and greatly affect the global climate. Therefore, it is highly desirable to investigate the effect of ions on HIN.

Although very few theoretical and experimental studies on the ion specificity of HIN have been conducted, the ion-specific effects on the dynamics and structure of interfacial water and other related surface phenomena have been studied for many years (18, 23–27). One pioneering study is the discovery of the Hofmeister series in which ions are ranked according to their ability in salting out proteins from aqueous solutions (28). Note that the Hofmeister series of ions explains many surface phenomena in chemistry and biology (29–32). Recent reports have shown that counterions at various ionic surfaces control the dynamics and structure of interfacial water (23, 33–35). Such observations lead to a reasonable speculation that counterions on solid surfaces can affect HIN because the theoretical analysis shows that the structure transformation in water determines HIN (33–35). Although the prediction is reasonable, it remains an open question whether the ion-specific effect exists for HIN on ionic surfaces.

Here, we investigate HIN on polyelectrolyte brush (PB) surfaces. The PB consists of densely end-grafted polyelectrolyte chains, carrying a large number of ionic groups, as shown in Fig. 1. The reversible exchange of counterions in the PB has been explored for a variety of applications, such as designing surfaces with tunable wettability and friction (24, 36–38). Furthermore, the embedded counterions in the PB can provide a unique microenvironment and have been used as carriers for proteins and microreactors to fabricate nanoparticles with high catalytic activity (39, 40). When a drop of pure liquid water is placed atop the PB surface, a fraction of counterions will be released from the PB due to the osmotic pressure, forming a diffusion layer of counterions at the brush/water interface (13, 41). Therefore, the PB surface provides an ideal platform for the investigation of the ion-specific effect on ice nucleation atop ionic surfaces. We have found that HIN can be tuned by exchanging the counterions of the PB, and the distinct efficiency of ions in tuning HIN follows the Hofmeister series. Such phenomena can be well interpreted by the molecular dynamics (MD) simulation analysis. The diffused counterions at the brush/water interface can effectively regulate the dynamics and structure of interfacial water and thus determine the HIN process.

RESULTS

HIN of water drops on the PB surfaces with different counterions was signified by a sudden change in opacity before and after freezing.
range of density can be easily controlled, which can lead to a much broader materials, such as surfactant micelles, is that its thickness and grafting versa. Another significant advantage of the PB over many other given grafting density, the surfaces with various grafting densities is shown in Fig. 2C. At each He et al is −Cl −. We then prepared a series of PMETA brush surfaces with a large variety of charge and Methods), which varied from 5 to 6500 s with the change of anions, as shown in Fig. 3B. The decrease of T0 is consistent with the increase of T11. Cation-specific effect on HIN was also studied on poly(3-sulfopropyl methacrylate potassium) (PSPMA) brush surfaces as well as SO4 2−-terminated SAMs with different counterions for comparison. The T11 of water droplets (Fig. 3C and fig. S8) on PSPMA brush surfaces with different cations shows the order of Ca2+ < Mg2+ < Gdm+ < K+ < Na+ < Cs+ < TMA+ < Li+ < NH4+, which is further confirmed by the results of T0 (Fig. 3D). The sequence of cations is roughly in accordance with the previously proposed Hofmeister series in affecting other properties (29). In contrast, we did not observe ionspecific effect for HIN on SO3 2−-terminated SAM surfaces (fig. S9). In general, the Hofmeister series is more pronounced in anions than in cations (44). Thus, we elucidated the ion-specific effect for HIN on model systems of PMETA brush surfaces with different counterions.

The ion-specific effects on HIN do not explicitly correlate to the change of the macroscopic properties of the PB, such as wettability, viscoelasticity, roughness, or swelling/collapsing behavior, upon the variation of counterions (more details in figs. S10 to S13). To gain molecular-level insight into the ion specificity in tuning HIN, we performed MD simulations to study the ion-specific effect on the structure and dynamics of interfacial water (in fig. S14) (19, 45). Three halide counterions (F−, Cl−, and I−) were chosen as representatives of T11 range of temperature (T11) on the PMETA–I brush surface (0.05 chain/nm2) is −23.8°C, whereas it is −26.4°C on exactly the same brush surface but with SO4 2− as the counterion (fig. S4). Note that we can reversibly tune the T11 on the PB surface through cycling the counterion exchange, as demonstrated in Fig. 2B. Consecutively replacing I− with SO4 2− of the PMETA led to a dropping of the T11 from −23.5 ± 0.4°C to −26.5 ± 0.3°C and vice versa. Another significant advantage of the PB over many other materials, such as surfactant micelles, is that its thickness and grafting density can be easily controlled, which can lead to a much broader range of T11. We then prepared a series of PMETA brush surfaces with the grafting density (σ) varied from 0.03 to 0.50 chain/nm2. The T11 of water drops on PMETA-SO4, PMETA-Cl, and PMETA-I brush surfaces with various grafting densities is shown in Fig. 2C. At each given grafting density, the T11 increases in the same order as SO4 2− < Cl− < I−. On the other hand, for the PB surfaces consisting of the same type of counterion, the T11 increases with the grafting density. The T11 is −26.5 ± 0.3°C on the PMETA-SO4 brush surface with a grafting density of 0.05 chain/nm2 and is −18.7 ± 0.6°C on the PMETA-I brush surface with a grafting density of 0.50 chain/nm2, exhibiting a T11 window as large as 7.8°C, as shown in Fig. 2C.

We next studied the ion-specific effect as a function of the brush thickness. When the PMETA brush height is increased from 2 to 50 nm (measured in air) at a fixed grafting density of 0.50 chain/nm2, the differences among the T11 on the PMETA-SO4, PMETA-Cl, and PMETA-I surfaces are significantly amplified, whereas the order remains the same, as shown in Fig. 2D. The absence of ion-specific effect on PMETA brush surfaces with a low thickness of 2 nm was also verified by investigations of HIN on the NMe3 + -terminated self-assembled monolayers (SAMs) with various counterions (fig. S6) (29). The absence of ion specificity in HIN should be related to the low concentration of diffused ions at the interfaces, which agrees with other ion-specific phenomena (29, 43). The influence of the cooling rate (from 1.0 to 10.0°C/min) in the T11 was also studied, and the trend of the ion-specific effect on HIN is the same, as shown in fig. S7.

To have a more complete series of ions on tuning HIN, we investigated the HIN on the PB brush surfaces with a large variety of counterions, as shown in Fig. 3A. The T11 increases in the anion sequence of SO4 2− < Ac− < HPO4 2− < Cl− < Br− < SCN− < NO3− < I−, which matches well with the Hofmeister series. To further consolidate the specific effect of anion on HIN, we studied the corresponding nucleation delay time (tD) at −20.0°C (details in Materials and Methods), which varied from 5 to 6500 s with the change of anions, as shown in Fig. 3B. The decrease of tD is consistent with the increase of T11.
in the Hofmeister series, in which Cl\(^-\) situates in the middle and F\(^-\) and I\(^-\) belong to the two ends. The PMETA brush swells in water, and its counterions can diffuse into the surrounding water [above the outermost quaternary ammonium–positive (QA\(^+\)) group]. The diffused halide anions are defined as the ions at the brush/water interface that are not in direct contact with any outermost QA\(^+\) groups. As shown in Fig. 4A, an important feature is that the concentrations of all three counterions approach zero at about 15 Å away from the outermost QA\(^+\) group (fig. S15). The numbers of the diffused counterions of F\(^-\), Cl\(^-\), and I\(^-\) at the brush/water interface differ significantly, and the concentration of F\(^-\) is almost three times that of I\(^-\).

The diffused counteranions at the brush/water interface also have a profound ion-specific effect on the relaxation of OH bond orientation and the formation rate of ice-like water molecules. The orientation of interfacial water molecules relaxes in the order of F\(^-\)<Cl\(^-\)<I\(^-\) because anions with high charge density (F\(^-\), in this case) tend to slave the surrounding water molecules and slow down their rotational dynamics (in Fig. 4C). The reorientation of water molecules plays a crucial role in the hydrogen bonding dynamics (48). The kinetics of making and breaking hydrogen bonds of ice-like water molecules in different PMETA-anion systems was also studied (see MD method and Fig. 4, D and E). The formation of ice-like water molecules is determined by the interplay between making rate constant (k) and breaking rate constant (k\(^'\)) of ice-like water.

**DISCUSSION**

Recently, Tielrooij et al. (26) reported that the effect of cations and anions on water structure is nonadditive, exhibiting a long-range feature.
beyond the first hydration shell of ions. It was found that ions are not independent species in aqueous solutions, and ion-ion interactions are important. Collins (44) has proposed an empirical law of matching water affinities (LMWA). According to the LMWA, the oppositely charged ions tend to associate into compact ion pairs if their hydration free energies are close to each other (27, 28, 44). In particular, both the specific long-range electrostatic interactions between oppositely charged ions and the short-range hydration of ion pairs may strongly affect the dynamics and structure of the interfacial water.

We performed MD simulations to investigate the interactions between PMETA brushes and three representative counterions, F\(^-\), Cl\(^-\), and I\(^-\). Because of excluded volume effect and electrostatic repulsion between the charged groups of the PB (36, 49), the PB chains are heavily stretched in water. At the same time, the dissociation of QA halide pairs occurs, and free halide ions diffuse to the brush/water interface, forming a counterion-rich interfacial water layer. According to the LMWA, the capability of F\(^-\), Cl\(^-\), and I\(^-\) to form compact ion pairs with the QA\(^+\) group increases because the charge density decreases in the sequence of F\(^-\) > Cl\(^-\) > I\(^-\), and the QA\(^+\) ion has a low charge density. Thus, the concentrations of diffused counterions at the water/brush interfaces decrease in the order of F\(^-\) > Cl\(^-\) > I\(^-\), which agrees well with the simulation results. When the grafting density or the thickness of the PB is higher, the electric field generated by the QA\(^+\) groups is also stronger, which imposes higher attractive potential to the counterions and so prevents them from escaping into the brush/water interface. This effect is more evident for the weakly hydrated ions (here, I\(^-\)), which prefer to stay inside the PB due to the LMWA and so effectively amplify the difference, as shown in Fig. 2 (C and D).

The orientational relaxation of interfacial water molecules decays more slowly with the increase of the anion charge density, as shown in Fig. 4C. Meanwhile, the hydrogen bond making rate of ice-like water molecules increases in the order of F\(^-\) < Cl\(^-\) < I\(^-\), whereas the difference of the hydrogen bond breaking rate of ice-like water molecules is minimal (see inset of Fig. 4D). Note that the hydrogen bond making rate and the fraction of ice-like water molecules, which were calculated through independent analysis from MD simulation (see MD method), follow the same increment trend as a function of the distance (within 15 Å) from the brush/water interface. This is in agreement with the classical relationship between the concentration and the rate constant in a dynamic equilibrium state,

\[
\frac{C_{\text{ice-like water}}}{C_{\text{liquid-like water}}} = \frac{k}{k}'
\]

We also compared the fraction and the making rate constant of ice-like water molecules at the local brush/water interface with the same concentration of counterions (see table S1). The results in Fig. 4 (B and D) demonstrate the amplified ion-specific effect due to the increase of counterion concentration in the Hofmeister order. Consequently, the total numbers of ice-like water molecules on the surface of PMETA-I and PMETA-Cl are 8 and 6% higher than that on the PMETA-F surface. Because the rate of ice formation is strongly controlled by the fraction of ice-like water, HIN is more likely to occur on the brush surface with a low charge density counterion (here, PMETA-I) (19, 45). Also note that HIN is also influenced by the effective contact area between the water and the PB. For the PB with the same thickness and grafting density but different counterions (F\(^-\), Cl\(^-\), and I\(^-\)), the effective contact area is almost the same (figs. S15 and S18A). Therefore, the structure and dynamics of interfacial water dominate HIN. In contrast, the effective contact area increases with...
the grafting densities and/or thicknesses of the PB, which leads to an increased statistical probability of HIN. Consequently, the \( T_{th} \) increases, as shown in Fig. 2 (C and D). In principle, one can consider to characterize the HIN phenomenon by calculating the thermodynamic properties, such as enthalpy, entropy, and heat capacity in MD simulations. However, the complicated composition of the PB system and the nonequilibrium feature of the ice nucleation process make the interpretation of the results very difficult. Therefore, we will leave this for later study.

To our knowledge, these results are the first to show that ion specificity in tuning HIN on ionic surfaces follows the Hofmeister series. This finding not only shed new light on the ion-specific effect on ice nucleation but can also stimulate future studies involving the design of anti-icing material. The physical principle behind this work will further motivate the ongoing interest in exploring the origins of Hofmeister effects.

**MATERIALS AND METHODS**

**Materials**

Cationic PMETA and anionic PSPMA brushes were prepared on gold surface, modified by either initiator or methyl-terminated monolayers. The subsequent polymerizations were based on surface-initiated atom transfer radical polymerization (SI-ATRP) in a 2:1 (v/v) oxygen-free water/methanol mixture. The samples were then washed with Milli-Q water and dried under N\(_2\) flow. The different grafting densities of PMETA brushes were tuned by adjusting the mixing ratio of unreacted CH\(_3\)-terminated functionalities and ATRP initiator. The grafting density (\( s \)) is calculated by

\[
s = \frac{N_A r_{\text{dry}}}{M_n},
\]

where \( N_A \) is the Avogadro number, \( r_{\text{dry}} \) is the dry thickness of polymer measured by ellipsometer, \( M_n \) is the number average molecular weight, and \( r \) is the density of PMETA (1.0 g/cm\(^3\)) (50).

**Counterions exchange**

The Cl\(^-\) in PMETA and K\(^+\) in PSPMA were exchanged by immersing the brushes into 0.1 M solutions of target counterions for 60 min. The samples were subsequently washed with Milli-Q water to remove excess surface free salt. The completeness of ion exchange was further confirmed by x-ray photoelectron spectroscopy (XPS) (fig. S1). Replacing the original Cl\(^-\) with I\(^-\) and SO\(_4\)\(^{2-}\) resulted in the appearance of new peaks of binding energies at 618.4 eV (13d) and at 168.6 eV (S2p), whereas the signal of Cl\(^-\) at 196.7 eV (Cl2p) disappeared. The absence of the signal of Na\(^+\) atom indicated that free salt inside the brushes has been removed.

**Water freezing procedure**

The \( T_{th} \) and \( t_{D} \) were measured by the homemade experimental apparatus (fig. S2). The sample cell was composed of a rubber O-ring sandwiched
between two cover glasses (42). The $t_D$ of ice nucleation is defined as the time interval between the time when the substrate reaches a target temperature and the time when the ice nucleus appears. Water droplets can be deposited at $-20.0^\circ\text{C}$ (target temperature) for several hours without a noticeable water condensation or evaporation.

**MD method**

Sixteen (META)$_{12}$ polycation chains were homogeneously grafted perpendicular to a Si(1 0 0) surface, leading to a grafting density of 0.69 chains/nm$^2$. Counterions of $\text{F}^-$, $\text{Cl}^-$, and $\Gamma^-$ (192) were added near QA$^-$ groups to neutralize the system. Water molecules (18,551) were also added to each system. The force fields and simulation details of the brushes with different counterions are reported in the Supplementary Materials. The structural order parameter (tetrahedrality) of the interfacial water was calculated by

$$q_i = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=j+1}^{4} (\cos\psi_{jik} + \frac{1}{3})^2$$

where $i$ represents the central water molecule, $j$ and $k$ represent the four nearest water molecules around water $i$, and $\psi_{jik}$ is the angle formed by $jik$ (51). We regard the water molecule with $q = 1$ to 0.9 as ice-like water ($q = 1$ corresponds to a water in a perfect tetrahedral ice crystal), which acts as the precursor of ice nucleus. The fraction of ice-like water (tetrahedrality above 0.9) in bulk water is about 14%. More simulation details are presented in the Supplementary Materials.

Water dynamics can be noted by water orientational time correlation functions (TCFs)

$$C_2(t) = <P_2[\mu_{\text{OH}}(0) \cdot \mu_{\text{OH}}(t)]>$$

where $P_2$ is the second-order Legendre polynomial and $\mu_{\text{OH}}$ is the direction vector of the OH bond of water molecules. Similar to the calculation of the kinetics of hydrogen bonds in liquid water, we computed the time constants of the formation of ice-like water molecules (48). The function $p_i(t + t_0, t_0)$ is defined as 1 if the water molecule $i$ is ice-like (liquid-like) during the time from $t_0$ to $t + t_0$ and within this interval, it does not transform into liquid-like (ice-like). Otherwise, it is defined as 0. The TCF $C(t)$ can be calculated from the simulation data

$$C(t) = <p_i(t + t_0, t_0)> / <p_i(t_0, t_0)>$$

It is assumed that $C(t)$ decays exponentially as

$$C(t) = \exp(-kt)$$

where $k$ is the rate constant.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/6/e1600345/DC1

**REFERENCES AND NOTES**


Tuning ice nucleation with counterions on polyelectrolyte brush surfaces
Zhiyuan He, Wen Jun Xie, Zhenqi Liu, Guangming Liu, Zuowei Wang, Yi Qin Gao and Jianjun Wang

Sci Adv 2 (6), e1600345.
DOI: 10.1126/sciadv.1600345