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Role of the electric double layer in the ice nucleation of water droplets under an electric field

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ABSTRACT

Figuring out the mechanism of ice nucleation on charged aerosols or in thunderstorms is of fundamental importance in atmospheric science. However, findings on whether the electric field promotes or suppresses heterogeneous ice nucleation are conflicting. In this work, we design an apparatus and test the influence of the electric field on ice nucleation by freezing a series of deionized water droplets resting on solid surfaces with an electric field perpendicular to the substrates. Results show that ice nucleation is obviously promoted under the electric field and is independent of the field direction. Theoretic analyses show that the promotion is due to the reduction of Gibbs free energy which can be partially rationalized by the electric field sustained in the electric double layer at the solid-water interface, with strength about two orders higher than that of the external electric field. Moreover, water-droplet deformation under the electric field is not expected to be the cause of the ice-nucleation promotion.

1. Introduction

Supercooled water droplets experience strong electric fields under many conditions, such as in clouds (Winn et al., 1974), near the surface of high-voltage transmission lines (Laforte et al., 1998), and in acid cracks (Gavish et al., 1992). As a kind of polar molecule (dipole moment = 2.95 ± 0.2(Gubskaya and Kusalik, 2002)), ice nucleation is expected to be affected by the external electric field. Since the 1950s, a number of mechanisms have been presented to reveal the influence of an external electric field on ice nucleation, including discharge (Mandal and Pradeep Kumar, 2002; Schaefer, 1968), bubble perturbation (Smith et al., 1971), electrical current (Shichiri and Araki, 1986), ions in solution (Petersen et al., 2006b) and electrode ionization (Hozumi et al., 2003). However, many questions remain unanswered. Two of the most basic questions are as follows: First, in what way does the electric field affect ice nucleation (promotes, suppresses or has no effect)? Second, what is the lower limit of strength of an external electric field under which a change in ice-nucleation rate is detectable?

For homogeneous nucleation, both theory (Kashchiev, 1972) and simulation results (Jung et al., 1999; Sun et al., 2005; Svishchev and Kusalik, 1994, 1996) indicate that ice nucleation is promoted upon exposure to an external electric field, which is known as electrofreezing (Pruppacher, 1973). The lower limit should be higher than 10^5 V/m (Dawson and Cardell, 1973; Stan et al., 2011). For heterogeneous nucleation (HEN), in which ice nucleation occurs near foreign surfaces, simulation and experiment results are conflicting, whereas a theoretic model has not yet been established. In simulations, the external electric field near solid surfaces reportedly benefits ice nucleation without exception (Yan and Patey, 2011, 2012; Yan and Patey, 2013; Zhang et al., 2014a, 2014b; Zhang et al., 2013). However, the electric-field strength used in the simulations (≥10^9 V/m) is much higher than that in practical application. In experiments, ice nucleation is reportedly promoted (Choi et al., 2005; Gavish et al., 1992; Orlowska et al., 2009; Sun et al., 2008), suppressed (Nakajima et al., 2007), or unaffected (Doolittle and Vali, 1975) by electric fields with strength ranging from 10^3 V/m to 10^6 V/m. Ehre et al. (2010) even reported that icing can be promoted or suppressed depending on the direction of the electric field perpendicular to a solid surface with strength around 10^5 V/m.

Given the contradictions among the few available experimental data, in this work, we carry out experiments to examine the influence of the electric field on the ice nucleation by freezing a series of deionized water droplets resting on solid surfaces under an electric field perpendicular to the substrates. Given that all tests resulting in unexpected inhibition of ice nucleation under an electric field are from droplet-nucleation tests (Ehre et al., 2010; Nakajima et al., 2007), water droplets instead of bulk water (Orlowska et al., 2009; Sun et al., 2008) are used in the present work. Results show that ice nucleation is obviously promoted by the electric field, and the promotion is independent of the field direction. The lower limit of the strength of the external electric field for HEN should be in the order of 10^5 V/m. These findings indicate that ice nucleation can indeed be manipulated by the electric field in many fields, such as in freeze-drying (Woo and Mujumdar, 2010),

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cryopreservation (Petersen et al., 2006a) and energy storage (Inada et al., 2001).

2. Experiments

2.1. Preparation of samples

To avoid electrode ionization (Hozumi et al., 2003) and to determine whether the property of a solid surface is important for ice nucleation under an electric field, we prepared two kinds of surfaces with different surface chemistries. One is a copper foil coated with stearic acid (SA) and the other is a copper foil coated with polyethylene (PE). We will name the corresponding samples as SA and PE surfaces in following discussion for convenience. The SA surface was prepared by a two-step method (Liu et al., 2012), in which the wettability can be manipulated easily and the plate uniformity is satisfactory. First, a copper foil (2×2 cm^2; 99.9% purity) was abraded using silicon carbide papers (800 and 2000 grade) and then carefully polished with 0.5 M diamond polishing paste. The foil was then dipped in acetone and deionized water (18 MΩ cm) and cleaned ultrasonically for 30 min, respectively. After dried in the air, the foil was immersed into 100 mL of mixed solution (0.5 wt.% H_2O_2 + 2 M HCl) and etched for 1 h at 333.2 K. Second, after repeating the cleaning process, the foil was immersed into an ethanol solution of SA (0.5 mM) for 15 min at 295.7 K and then dried in ambient air. To prepare PE surface, a thin layer of PE powder (diameter ≈ 80 μm) was deposited onto a copper foil (2×2 cm^2). The mass density of the PE layer was about 3.03×10^{-4} g/cm^2. PE was melted at 428.2 K for 1.5 h and then crystallized at ambient temperature. The wettability was represented by the contact angle (CA) and the rolling angle, which were measured on a POWERACH stage at ambient temperature (295.2 ± 1 K). The CA and rolling angle on SA (PE) surface were 155 ± 2° and 3–4° (99 ± 2° and >90°) for a 10 μL water droplet. The difference in wettability can be rationalized by their different surface morphologies analyzed by scanning electron microscopy (SEM). As shown in Fig. 1, the SA surface had two levels of hierarchy, which was essential to its perfect hydrophobic performance (Liu et al., 2012). Conversely, the PE surface was smoother and had poor hydrophobicity.

2.2. Instruments and nucleation-rate tests

As shown in Fig. 2(a), to monitor the nucleation conveniently, we designed an apparatus composed of a cylindrical shell electrode and a cylinder electrode. The shell electrode was connected to the positive/negative electrode of a DC voltage generator (0–50 kV; accuracy, 0.1 kV) to change the electric-field direction. To observe obvious alterations in ice nucleation, we chose 10 kV as the operational voltage. Further increase of the voltage will cause break down between electrodes (threshold value ≈ 11 kV). The electric discharge can result in coalescence of small droplets on the surface and affect the ice-nucleation behavior (Hortal et al., 2012). As shown in Fig. 2(b), the electric field near the surface was perpendicular to the surface. The magnitude of the electric field in the area of placing water droplets was $4.28 \pm 0.13 \times 10^5$ V/m, which was estimated by the COMSOL simulator. The maximum difference between the strength of total electric field and the component of the electric field perpendicular to the surface was 5.0×10^3 V/m. The cylinder electrode was buried in a cooling cabinet and grounded. The tested sample was stuck to the cylinder electrode by silver-epoxy adhesive, and the electrode was cooled through oxygen flow. Temperature was detected by a T-type thermocouple buried in the cylinder electrode, with accuracy 0.1 K. Although Tao and Hua (2002) pointed out that a metal thermocouple cannot work properly under an electric field, we have not observed obvious temperature shifts before and after applying the electric field (with difference smaller than 0.2 K). The temperature difference between the buried thermocouple and the tested surface was about 1.5 ± 0.1 K. To facilitate placing water droplets and reduce evaporation (Castellano et al., 2014), the cylinder electrode was cooled down to 263.2 K and then, about 40 deionized water droplets (0.5 μL, 18 MΩ cm) were placed on the tested sample. Afterwards, the droplets were sealed with an O-ring and a coverslip containing albolene. Droplet sizes were consistent with those used in previous studies (Ehre et al., 2010; Nakajima et al., 2007). During the freezing-melting cycles, the stage was cooled from 278.2 K at a cooling rate of 1.0 ± 0.2 K/min until all droplets froze and then naturally heated. During the freezing-melting cycles, to reduce the influence of the residual effects of applying an electric field (Doolittle and Vali, 1975), the sequences were interleaved, that is "without electric field ⇨ positive electric potential on the cylindrical shell ⇨ negative electric potential on the cylindrical shell ⇨ without electric field…". Besides, the electric field was applied only during the freezing process and was turned off during melting. The alignment change of the ice crystals while changing electric-field direction was not observed due to the restriction of observation condition (Foster and Hallett, 2002). The corona phenomenon around the water droplets was also not observed (Kinsey, 2012). The freezing events were optically monitored with a camera from the top of the device. For each case, at least 250 nucleation events were collected by cooling a series of drops various times on the same surface to get satisfactory statistics.

3. Results and discussion

Given that ice nucleation is a stochastic phenomenon (Supporting information), the freezing temperatures of the droplets distribute within a range. The distributions of the freezing temperatures are shown in Fig. 3. The average freezing temperatures of the droplets on SA (PE) surface are 255.4, 256.5 and 256.5 K (254.4, 255.0 and 255.1 K) when the potential of the cylindrical shell electrode is 0, −10 and 10 kV, respectively. The average freezing temperatures under an

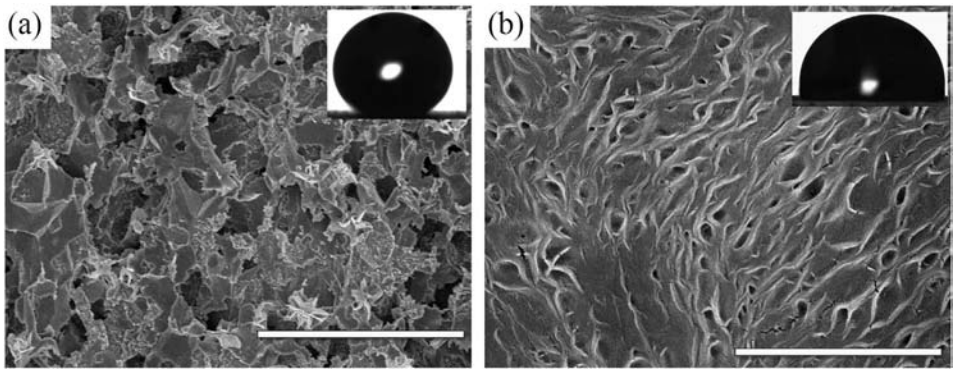

Fig. 1. SEM images of sample surfaces coated with (a) SA and (b) PE (scale bar = 5 μm). The insets are representative photographs of a 10 μL deionized water droplet without an electric field.