Solvation of Octane at Water− and Methanol−Ice Surfaces and Surfactant Effect of Methanol at Octane−Water Interface Studied by Temperature-Programmed TOF−SIMS

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The interaction of octane with water and methanol ice surfaces has been investigated at molecular level by using TOF−SIMS and TPD. The octane molecules adsorbed on the amorphous D_2O−ice surface dissolve in the bulk completely up to 120 K whereas most of them stay on the CD_3OD−ice surface up to 135 K and then dissolve. The solubility of octane in amorphous solid water is much higher than that in liquid water. The formation of a hydrogen-bonded water cage would be responsible for the hydrophobic hydration of octane as inferred from the local structural similarities between amorphous solid water and crystalline ice. A methanol cage, if any, should not accommodate the octane efficiently because of the presence of the methyl group, so that the lipophilic interaction plays a role for solvation of octane at the methanol surface. The surfactant methanol layer formed on the water−ice surface disturbs the incorporation of the adsorbed octane into the water−ice layer below 130 K. The octane can move on the methyl-group terminated methanol surface and dissolves in the water−ice layer unless the monolayer of surfactant is completed, indicating that the hydrophobic hydration in the bulk water ice is energetically more favorable than the lipophilic interactions at the methanol surface for adsorbed octane molecules.

1. Introduction

Several important processes in aqueous solutions, such as protein folding and formation of micelles and biological membranes, rely on the interactions between water and nonpolar moieties of organic molecules. Amphiphiles have hydrophilic and hydrophobic moieties at the opposite ends and act as surfactants in ternary mixtures with water and hydrocarbons. They preferentially move to the oil−water interface and dramatically lower the surface tension. The research on surfactant systems is important since many phenomena of scientific and technological importance occur at an interface of immiscible liquids. Simple surfactant systems can also be used as models for biological membranes. For the dissolution of solute molecules in liquid water, the hydrogen bonds should be reorganized at the solute−water interface. Indeed, the hydrophobic hydration occurs in such a way that nonpolar molecules sit inside cavities of hydrogen-bonded water molecules, thereby creating icelike or clathratelike structures near the solute molecules.[1,2] However, the exact nature of this structural ordering has remained unclear. The hydration of the nonpolar solutes is energetically unfavorable because the cavitation energy is so high that it may not be compensated by the energy of weak van der Waals interactions at the water−solute interface. For that reason, the aliphatic tail of surfactants prefers a nonpolar phase, such as oil or air.

Amorphous solid water (ASW) is formed by vapor deposition of water molecules in an ultrahigh vacuum environment, and it can be a model system for liquid water and glassy materials. Therefore, insights into solute−water interactions may be gained from the experiment of molecular adsorption on the ASW surface. The dissolution of nonpolar molecules in water ice should be much less likely than in liquid water since large cavity fluctuations are not expected. There is still debate about the

properties of the ASW,[3−5] but an additional effect may arise when the temperature increases with the occurrence of surface melting, which results in the existence of a mobile interfacial liquid water on the ASW or crystalline ice.

To date, molecular level investigations of hydration have been mostly theoretical and computational,[6−12] and probing the interfacial hydrogen bonds presents an enormous challenge to experiment. Very recently, the interaction of polar molecules with the water−ice surface has been investigated on the basis of the temperature-programmed time-of-flight secondary ion mass spectrometry (TP−TOF−SIMS).[13−16] It is demonstrated that the adsorbed CH_3OH molecule completes the hydrogen bond with the D_2O−ice surface up to 100 K and then undergoes the H/D exchange above 140 K because of the evolution of the mobile D_2O molecules on the surface.[14] Thus, the water−ice surface is thought to be highly dynamic in nature. For better understanding of the solute−water interactions at the molecular level, it is apparent that more comprehensive adsorption data on the water−ice surface are indispensable. This paper will report on solvation patterns of adsorption systems consisting of oil (C_8H_{18}), surfactant (CD_3OD), and water (H_2O, D_2O) on the basis of the TP−TOF−SIMS experiments. The transport properties of the C_8H_{18} molecule into the bulk CD_3OD and D_2O layers, as well as the surfactant effects of methanol existing at the oil−water interface, will be discussed as a function of temperature, with particular emphasis placed on the role of the hydrophilic and hydrophobic hydrations in dissolution of solute molecules.

2. Experiment

The experiments were carried out in an ultrahigh vacuum chamber (base pressure of 1×10^{-10} mbar) equipped with facilities for standard surface characterization. The He$^+$ ions
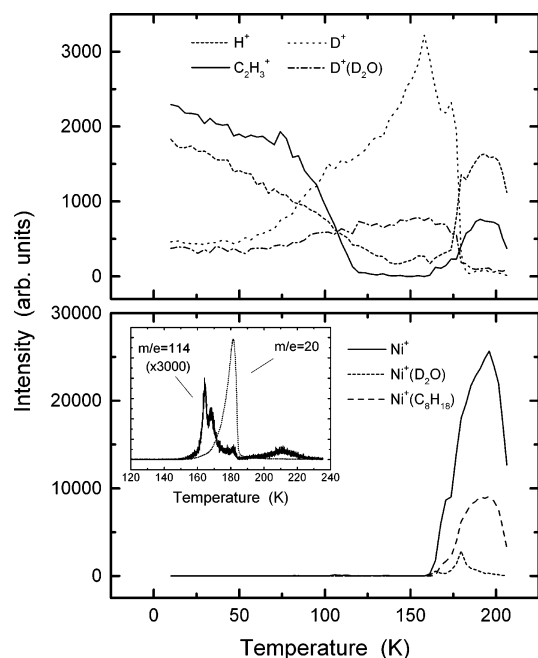
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Figure 1. Evolutions of typical TOF−SIMS intensities from the octane (1 ML) adsorbed D$_2$O layer (50 ML) as a function of temperature. Inset: TPD spectra of octane (*m/e* = 114) and heavy water (20).

with kinetic energy of 2 keV were produced in an electron-impact-type ion source. The TOF−SIMS measurements were made by chopping the primary beam into pulses with width of 60 ns and frequency of 40 kHz. The sample, floated with a bias voltage of +500 eV, was irradiated by the He$^+$ ion through a grounded stainless steel mesh placed 4 mm above the sample surface, and the positive secondary ions extracted into the field-free region of the TOF tube were detected with a channel electron multiplier. To minimize charging and damage of a surface, a pulsed He$^+$ beam with a low incident flux (0.1 nA/cm^2) was used. TOF−SIMS spectra were taken continuously at time intervals of 30 s for a temperature-increasing rate of 0.1 Ks^{-1}. The Ni(111) substrate was mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The surface was cleaned by annealing around 1200 K. The H$_2$O (D$_2$O), C$_8$H$_{18}$, and CD$_3$OD molecules were admitted into the vacuum chamber through independent variable leak valves. One-monolayer (1 ML) coverage of the adsorbed molecules was determined from the decay curve of the sputtered ion intensities from the substrate as a function of exposure, and the film thickness was estimated on the basis of this value. In the present experiment, thin layers (50 ML) of solvent molecules (water and methanol) were deposited at 100 K and then the solute molecule (octane, 1 ML) was adsorbed on them after cooling to 15 K. A thin film of nonporous ASW is formed by this procedure and the cubic water ice is grown by heating above 140 K.[3,4] To the best of my knowledge, however, there exist no literatures about the morphology or crystallinity of the vapor-deposited methanol and octane layers.

3. Experimental Results

Figure 1 shows temperature evolutions of the intensities of typical secondary ions sputtered from the C$_8$H$_{18}$ molecule (1 ML) adsorbed on the D$_2$O−ice surface (50 ML). Fragment ions are emitted from octane while D$^+$ and D$^+$(D$_2$O) are the dominant ion species from the heavy-water layer. With increasing temperatures, the C$_2$H$_3^+$ ion from octane starts to decay at 80 K and disappears almost completely above 120 K. It might

be presumed that this is caused by the desorption of the C$_8$H$_{18}$ molecule from the surface. To check such a possibility, the experiment of temperature-programmed desorption (TPD) of the C$_8$H$_{18}$ molecule was performed by means of the quadrupole mass analyzer. The TPD spectra for *m/e* = 20 and 114 species (corresponding to the D$_2$O$^+$ and C$_8$H$_{18}^+$ ions, respectively) are shown in the inset. No desorption of the C$_8$H$_{18}$ molecule occurs below 160 K. At least four peaks are clearly discernible in the TPD spectra of octane: in addition to the leading peak (163 K) and the broad peak occurring after evaporation of D$_2$O multilayer (210 K), two humps are seen at 167 and 183 K. Such humps are not observed when the octane is adsorbed directly on the Ni(111) surface and occur simultaneously with the desorption of the D$_2$O molecules, indicating that strong interactions exist between water and octane molecules.

These experimental results clearly show that the observed decay of the TOF−SIMS intensity is caused by the incorporation of the C$_8$H$_{18}$ molecule into the thin-layer bulk of D$_2$O. Such a big molecule as C$_8$H$_{18}$ is readily incorporated in the D$_2$O−ice layer even below 120 K. This result is also remarkable in comparison with the adsorption data of water−soluble molecules such as methanol and ammonia: the CH$_3$OH molecule is hardly incorporated in the D$_2$O layer up to 170 K[14] and the NH$_3$ molecule dissolves in the water layer above 130−140 K.[13] These facts show that the solubility of molecules in water ice is determined by the subtle balance between the hydrophilic and hydrophobic hydrations. It is thus concluded that the hydrophobic hydration of nonpolar molecules is by no means quenched on the water−ice surface. The hydrophobic hydration of amphiphiles is rather disturbed on the water−ice surface because of the preferential formation of hydrogen bonds at the polar group.

In the temperature range above 120 K, the surface is covered with the pure D$_2$O molecules. There exist some interesting features before the D$_2$O multilayer evaporates completely. The D$^+$ intensity increases above 130 K, peaks at 155 K, and then decays, but the D$^+$(D$_2$O) intensity exhibits no such structures. The D$^+$ ions are sputtered from the dangling OD bond of the surface D$_2$O molecules whereas the D$^+$(D$_2$O) ions are emitted from the hydrogen-bonded D$_2$O molecules either via the solvation of D$^+$ by the surrounding D$_2$O molecule or via the proton-transfer reactions during collisions, 2D$_2$O → D$^+$(D$_2$O) + OD$^-$. Therefore, this result can be explained in terms of the increase (130 K < *T* < 160 K) and decrease (*T* > 160 K) of the number of dangling OD bonds at the surface. The hump appears in the Ni$^+$ intensity above 160 K concomitantly with the decay of the D$^+$ ion. The sputtering of Ni$^+$ does not necessarily mean the opening of the D$_2$O layer or the exposure of the clean Ni(111) surface: the Ni$^+$ ion is hardly sputtered from the clean surface and it can be emitted if the thickness of the water layer is less than 4−5 ML.[17] Very small change of the D$^+$(D$_2$O) intensity in this temperature regime also indicates that the hydrogen-bonded D$_2$O multilayer covers the Ni(111) surface. From the TPD spectra of D$_2$O, only 5% of the D$_2$O molecules desorb from the surface up to 165 K. On the basis of these facts, it is concluded that the D$_2$O layer undergoes the abrupt morphological change above 165 K. Essentially the same behavior was observed for the pure D$_2$O layer at this temperature. In this respect, Smith and Kay[5] concluded that the irreversible phase transformation of ASW into crystalline ice occurs at 155−160 K on the basis of the presence of a bump in the TPD spectra of water. Such a bump can be observed clearly in the present TPD spectrum of D$_2$O as well. At the same temperature, Kay and co-workers also observed an explosive
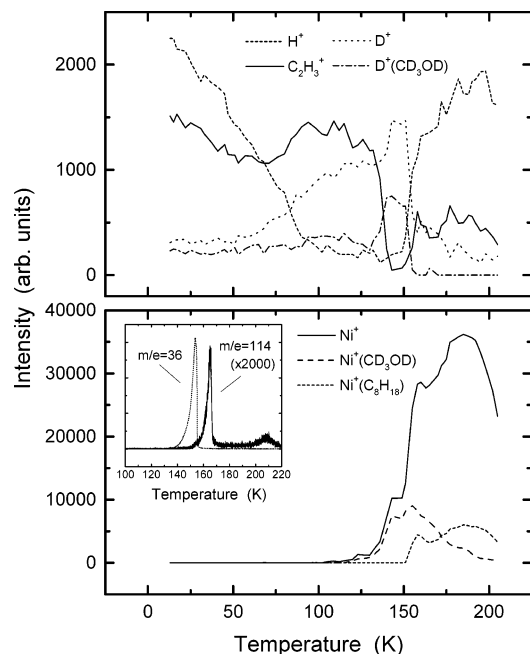
Figure 2. Evolutions of typical TOF−SIMS intensities from the octane (1 ML) adsorbed CD_3OD layer (50 ML) as a function of temperature. Inset: TPD spectra of octane ($m/e = 114$) and heavy methanol (36).

Figure 3. Evolutions of typical TOF−SIMS intensities from the thin film of C_8H_{18} (1 ML)/CD_3OD (0.5 ML)/H_2O (50 ML) as a function of temperature.

desorption of the CCl_4 molecules, which are embedded underneath the thick water−ice layer, and concluded that it is caused by the formation of connected desorption pathways by the crystallization.[18] The TPD spectrum of octane exhibits the corresponding peak at 167 K though the molecules in the present case are incorporated from the surface. As described here, these phenomena should be related to the morphological change of the water−ice layer rather than crystallization. Indeed, the possibility of irreversible crystallization is denied from the experiment of the $H_2{}^{16}O-H_2{}^{18}O$ isotope exchange at the water−ice surface: this phenomenon is more likely to be ascribed to the droplet formation of liquidlike water.[17] After the evaporation of the D_2O multilayer, the intensity of the fragment ions from the C_8H_{18} molecule increases again. They are emitted from the chemisorbed species on the Ni(111) surface. The presence of the chemisorbed C_8H_{18} and D_2O molecules on the surface can also be confirmed from the emission of the $Ni^+(C_8H_{18})$ and $Ni^+(D_2O)$ ions, respectively.

Figure 2 displays the TP−TOF−SIMS intensities of typical secondary ions sputtered from the C_8H_{18} (1 ML) adsorbed CD_3OD−ice surface (50 ML). The C_8H_{18} molecule stays on the surface up to 135 K, above which temperature an almost pure CD_3OD layer appears as revealed from the evolution (decay) of the D^+ and $D^+(CD_3OD)$ ions (the $C_2H_3^+$ ion). The adsorption of the C_8H_{18} molecule on the CD_3OD surface is not simple for $T < 135$ K: the D^+ (H^+) intensity increases (decreases) monotonically with increasing temperature, implying a strong solvation of octane by methanol, whereas the intensity of $C_2H_3^+$, as well as $D^+(CD_3OD)$, is not changed significantly. The origin of this behavior is not fully understood, but it should be related to the ionization/neutralization of sputtered particles as well as the conformation of the complex between octane and methanol. The octane is thought to stay at the surface or subsurface layer, without incorporation in the bulk, suggesting the incompletion of the first solvation shell of methanol. The chemisorbed CD_3OD and C_8H_{18} molecules remain on the Ni(111) surface after the evaporation of the CD_3OD multilayer, as revealed from the emission not only of the fragment $C_2H_3^+$
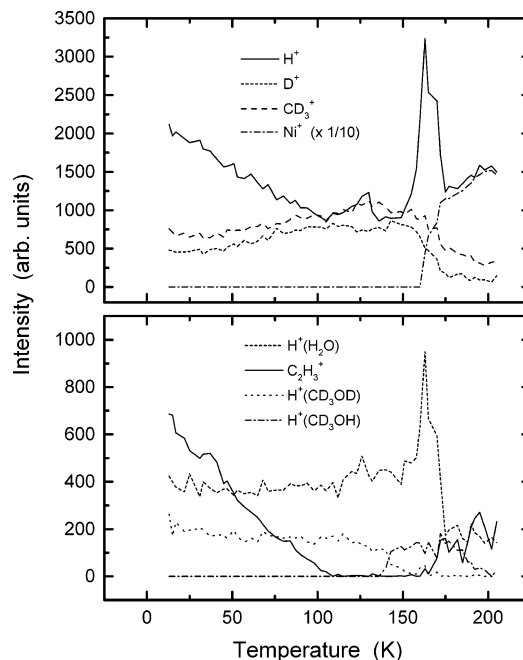
ion but also of the molecular ions such as $Ni^+(CD_3OD)$ and $Ni^+(C_8H_{18})$. The $Ni^+(C_8H_{18})$ ion appears only after the complete evaporation of the CD_3OD multilayer.

Some interesting features are observed prior to the evaporation of the CD_3OD multilayer. The disappearance of the C_8H_{18} molecule from the surface above 135 K cannot be ascribed to the desorption of octane from the surface as revealed from the TPD spectrum shown in the inset: the desorption of octane occurs above 160 K after the evaporation of the methanol multilayer. The octane TPD spectrum exhibits two peaks, which is basically the same as that for the octane adsorbed directly on the Ni(111) surface. Thus, octane dissolves in methanol completely above 135 K. A hump appears in the Ni^+ and $Ni^+(CD_3OD)$ intensities when the pure CD_3OD layer evolves. The roughening of the methanol layer should be responsible for this behavior. Such a morphological change was not observed clearly in desorption of the pure methanol layer,[14] suggesting that the interaction with octane modifies the film morphology.

It is thus found that octane is more soluble in water than methanol at cryogenic temperatures. Of interest in this respect is the surfactant effect of methanol existing at the octane/water interface. Figure 3 shows the TP−TOF−SIMS intensities from the $C_8H_{18}/CD_3OD/H_2O$ system. A thin layer of the H_2O molecules (ASW: 50 ML) was first grown on the Ni(111) substrate and then the CD_3OD molecules (0.5 ML) were adsorbed on it at 100 K. At this temperature, the methanol stays on the surface by pointing the methyl group toward the vacuum side and forming the hydrogen bonds with the water layer. This is manifested by the fact that only the H^+ attached CD_3OD molecule is sputtered via the proton-transfer reaction, $CD_3OD + H_2O \rightarrow H^+(CD_3OD) + OH^-$. If the islanded methanol existed, the D^+-attached heavy methanol should be sputtered (see also Figure 2 and ref 14). The octane was adsorbed on this surface at 15 K. The $C_2H_3^+$ ion from C_8H_{18} decays monotonically in intensity and disappears completely above 120 K. Thus, the C_8H_{18} molecule tends to be incorporated in the H_2O layer without appreciable interactions with the coadsorbed CD_3OD
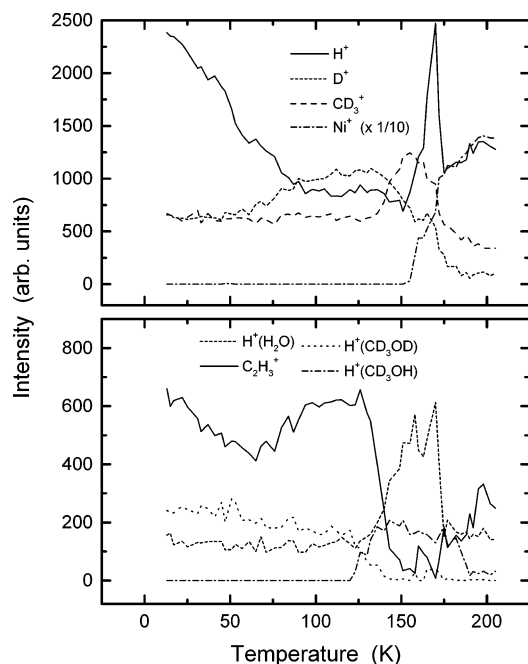
Figure 4. Evolutions of typical TOF−SIMS intensities from the thin film of C_8H_{18} (1 ML)/CD_3OD (1 ML)/H_2O (50 ML) as a function of temperature.

molecules. The CD_3OD molecule stays on the surface up to the evaporation temperature of water. It undergoes the H/D exchange with the water layer above 140 K as revealed from the dominance of the $H^+(CD_3OH)$ ion. The evolution of the mobile water molecules on the surface would be responsible for this phenomenon,[14] as inferred from the fact that the water molecules evolve on the surface above 150 K.

Figure 4 shows the experimental result of the same system but with the 1-ML CD_3OD molecules existing at the interface. In contrast to the result shown in Figure 3, the C_8H_{18} molecule stays on the surface without incorporation into the bulk of H_2O for T < 130 K. The $C_2H_3^+$ ion evolves quite similarly to that in Figure 2, indicating that octane interacts preferentially with methanol. The same result is obtained for a thicker (2 ML) CD_3OD layer, in which the hydrogen-bonded CD_3OD molecules exist considerably as revealed from the emission of $D^+(CD_3OD)$. Thus, a critical thickness (1 ML) exists for methanol to separate octane from the water layer as a surfactant. The onset temperature for the H/D exchange between the CD_3OD and H_2O molecules (125 K) is significantly lowered compared to that in Figure 3. The hydrophobic (or lipophilic) interactions between octane and methanol may affect the hydrogen bond at the water−methanol interface. It is more likely that the H/D exchange is induced by the perturbation of the interface water molecules during the dissolution of octane.

4. Discussion

In the previous section, the variations in ion yields have been ascribed to changes in the surface concentration or hydrogen-bond formation but very little is discussed in terms of the ionization/neutralization processes of sputtered particles. The D_2O and CD_3OD species chemisorbed on the Ni(111) surface are hardly detectable as fragment and protonated ions because of the efficient resonance neutralization during departure from the metal surface, whereas the bare-Ni^+ and Ni^+-attached molecular ions are sputtered considerably even from the chemisorbed species. Probably, this is because the transient complex formation with chemisorbed molecules is necessary

for the ionization of sputtered Ni, in which the Ni(111) surface plays a role as an acceptor of electrons via the resonant tunneling to the open conduction band. This assumption is supported by the fact that very few Ni^+ ions are sputtered from the clean Ni(111) surface and the Ni^+ and $Ni^+(H_2O)_n$ intensities exhibit a peak at around 1-ML coverage of water molecules.[17] When the surface is covered with the multilayer of water and alcohol, the resonance processes played by the metal substrate are quenched and the ionization occurs during molecular collisions at the surface. The intensity of the protonated molecular ions is determined by the proton-transfer reactions so that it is altered by heating because of the reorganization of hydrogen bonds, thereby enabling us to explore the occurrence of hydration and H/D exchange as a function of temperature. The ion intensities are largely enhanced if the partially ionic salts or charge-transfer complexes are formed at the surface since the long-lived anion− cation pairs are created during molecular collisions.[13] The formation of molecular ions has been elucidated in terms of the "hydrogen-bond-breaking" mechanism on the analogy of the conventional bond-breaking mechanism, where the transfer of protons rather than electrons is responsible for the ion-pair formation. In the present case, no such charge-transfer complexes are formed in the combinations of water, methanol, and octane, so that the sputtered ion intensities are not largely altered by the surface compositional change. The charge-transfer processes described above is completely independent of the thermally activated processes, such as hydration and H/D exchange: the effects of the He^+ bombardment on these processes can be ignored in the present experiment because the ion beam current is minimized. SIMS is quite sensitive to the outermost surface layer, but the probing depth seems to be dependent on the sputtered ion species (see, e.g., Figures 1 and 2 in which the decay curves from octane are different between H^+ and $C_2H_3^+$). This phenomenon will be discussed elsewhere.

The incorporation of octane into water ice occurs completely even below 120 K. This phenomenon should be explained in terms of the hydrophobic hydration. According to the so-called "iceberg" model,[1,2] hydrophobic solutes increase the hydrogen-bonding structure of water in the first hydration shell and the cavity formation is the important first step for solvating any nonpolar solutes in water. However, the formation of a highly ordered cage of water molecules around the nonpolar solute is not supported by the recent experiments,[19−21] that is, the hydration cage existing in the liquid is more loosely defined than in the solid system. A poor solubility of nonpolar solutes may also be caused by the excluded volume effect, which is amplified by the small size of water molecules themselves.[22,23] In the framework of these existing models, it seems remarkable that such a large molecule as octane readily dissolves in water ice at temperatures as low as below 120 K. The cavity formation or the incorporation of solute molecules into the bulk may not be induced under the condition of the quenched bulk diffusion of water molecules. There exist many hydrogen-bond defects in the bulk ASW, so that it is possible that the hydrogen-bond reorganization is induced by the rotation of the D_2O molecules without diffusion. As far as the short-range orders are concerned, moreover, there exist significant similarities between ASW and ice Ih.[24] Therefore, the formation of crystalline ice or clath-ratelike hydration shell would be facilitated in the bulk ASW with a relatively open structure, in which the nonpolar solute may play a role as a nucleus for the ice crystallization. The molar fraction of octane dissolved in liquid water is about 10^{-6} at room temperature,[25] which should be much smaller than that in ASW. This fact strongly suggests that ASW and liquid water

are completely distinct phases. Probably, the formation of water cage presumed in the conventional iceberg model of hydrophobic hydration is realized in ASW but the imperfect hydration shell in liquid water causes a much poorer solubility of nonpolar molecules.

The solvation of octane at the methanol−ice surface is less effective than the water−ice surface. The octane forms a complex with methanol at the surface but is never incorporated into the bulk below 135 K. The hydrogen-bond cage of methanol, if formed, may not lead to the cavity formation because of the presence of the methyl group. Probably, this is one of the reasons for the octane's less solubility in methanol than water. The solvation complex should be formed via the lipophilic interactions between octane and methanol. If this is the case, the hydroxyl group of methanol should exist at the "surface" of the complex. Such a conformation may be realized as inferred from the experimental results shown in Figure 2: the $D^+(CD_3OD)$ ion, arising from the hydrogen-bonded molecules, does not evolve relative to D^+ for $T < 135$ K, whereas it occurs considerably when the pure methanol layer appears ($T > 140$ K), suggesting that the hydrogen bond of methanol at the fist solvation shell of octane is less completed than that of the pure methanol layer.

The surfactant effect of the methanol at the octane−water interface is quenched unless the methanol nonolayer covers the water surface completely. This is because the octane−water interaction is stronger than the octane−methanol one. The octane can undergo the lipophilic interaction with the surfactant methanol layer since it is terminated with the methyl group. The octane diffuses on the surface and can penetrate into the water ice through the opening of the methanol layer. The similarity of the temperature evolutions of $C_2H_3^+$ between Figures 2 and 4 shows that the octane−methanol interactions are basically lipophilic even at the pure methanol surface.

It is thus concluded that the hydrophobic hydration plays an important role in dissolution of nonpolar solute molecules in water ice especially at cryogenic temperatures ($T < 120$ K). The monolayer of amphiphilic solutes basically stays on the water−ice surface without dissolution since the hydrophilic and hydrophobic hydration shells are hardly compatible in the bulk water ice. The hydrophilic solutes can be incorporated in water ice above 140 K provided that the bulk diffusion of water molecules is enabled.[13,17]

5. Summary

It is demonstrated that TP−TOF−SIMS is a quite powerful tool for the analysis of solvation of nonpolar molecules adsorbed on the water− and methanol−ice surfaces. The octane molecules

adsorbed on the D_2O−ice surface are incorporated completely in the bulk up to 120 K. A part of them undergo hydrophobic hydration in the bulk, as evidenced by the occurrence of dehydration at temperatures where the liquidlike water evolves (167 K) and the multilayer of water evaporates (183 K). The octane is hydrated or incorporated more efficiently in the bulk of ASW than liquid water since the cage structure of crystalline ice is thought to be created more preferentially in ASW, as inferred from the local structural similarities between ASW and crystalline ice. The octane adsorbed on the methanol−ice surface undergoes lipophilic interactions and stays on the surface up to 135 K. The monolayer of methanol adsorbed on the ASW surface suppresses the dissolution of the octane into the bulk of ASW, but the octane tends to be incorporated in the ASW if the monolayer of methanol is not completed, suggesting that the hydrophobic hydration of octane is energetically more favorable than the lipophilic interactions between octane and methanol.

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