PHYSICAL REVIEW B **72**, 115414 (2005)

Interaction of alkanes with an amorphous methanol film at 15–180 K

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(Received 13 May 2005; published 13 September 2005)

The hydrogen-bond imperfections and glass-liquid transition of the amorphous methanol film have been investigated on the basis of the film dewetting and the incorporation/desorption of alkane molecules adsorbed on the surface. The butane is incorporated completely in the bulk of the porous methanol film up to 70 K. At least two distinct states exist for the incorporated butane; one is assignable to solvated molecules in the bulk and the other is weakly bound species at the surface or in the subsurface site. For the nonporous methanol film, the uptake of butane in the bulk is quenched but butane forms a surface complex with methanol above 80 K. The butane incorporated in the bulk of the glassy methanol film is released at 120 K, where dewetting of the methanol film occurs simultaneously due to evolution of the supercooled liquid phase.

DOI: 10.1103/PhysRevB.72.115414 PACS number(s): 81.05.Kf, 61.25.Em, 66.30.Pa, 82.80.Ms

I. INTRODUCTION

Physical and chemical properties of condensed molecules have recently attracted considerable attention in diverse research fields such as solution chemistry, biochemistry, environmental science, and astrophysics. The glassy molecular films can be formed by slow accumulation of gas-phase molecules onto cold substrates, and the physical properties of such films depend on the growth conditions. The amorphous molecular films are expected to have a glass transition temperature, T_g, at which the substance becomes a viscous liquid prior to crystallization, but the assignment of the glass transition temperature is still controversial especially for amorphous solid water (ASW).[1–5] The ASW film deposited below 90 K has a considerable amount of bulk cavities and simple molecules such as N_2 and CO, and alkanes are preferentially incorporated in the bulk of ASW.[6–8] From the desorption kinetics of such physisorbed molecules, the film morphology,[6] crystallization,[9–11] and hydrophobic hydration[7] have been discussed extensively. In contrast, very little is known about the thermodynamic properties of other molecular solids. Aliphatic alcohols such as methanol are important solvent used for a wide range of chemical processes and act as surfactants in ternary mixtures with water and hydrocarbons. The glass transition temperature of pure amorphous methanol has been assigned to 103 K,[12] but the properties of a supercooled liquid phase are not clarified. Adsorption of methanol on various metallic substrates has been studied,[13–17] and it has been claimed that crystallization occurs abruptly above 115–120 K, where the shape of the infrared (IR) spectra changes drastically. The water molecule tends to be incorporated into the bulk of the amorphous methanol film in the temperature range 60–120 K,[18] whereas octane stays on the surface up to 135 K.[19] It is still unclear what properties of the methanol film are responsible for the incorporation of these adsorbed molecules.

In this paper, we employ temperature-programed time-of-flight secondary ion mass spectrometry (TP-TOF-SIMS) and temperature programed desorption (TPD) to investigate the interaction of simple alkene molecules such as ethane, propane, and butane with the amorphous methanol film. TOF-SIMS is so sensitive to the outermost surface layer that incorporation of adsorbed molecules in the bulk can be monitored as a function of temperature, whereas TPD can distinguish the solvation of molecules in the bulk from simple adsorption/desorption at the surface unambiguously if combined with TOF-SIMS. Here we demonstrate that the methanol film deposited at 15 K has bulk cavities through which the alkane molecules are incorporated in the bulk and that the incorporation/desorption of the alkane molecules are closely related to the glass-liquid transition of the methanol film.

II. EXPERIMENT

Experiments were conducted in a stainless steel ultrahigh vacuum chamber of base pressure below 1×10^{-8} Pa. The vacuum system was equipped with an electron-impact-type ion source, a linear-TOF tube, and a differentially pumped quadrupole mass spectrometer for TPD. The details of the TOF-SIMS experiments have been described elsewhere.[18] Briefly, a pulsed He^+ ion beam (2 keV) was incident on the sample, which was floated with a bias voltage of +500 eV (ion impact energy was 1.5 keV), and the positive ions extracted into a field-free region of the TOF tube were detected with a channel electron multiplier. The primary ion flux was minimized ($0.1\ nA/cm^2$) to avoid charging and damage of a surface. In each TP-TOF-SIMS measurement, spectra were taken continuously at time intervals of 30 s and the temperature was ramped at a rate of $0.1\ K\,s^{-1}$. The effect of He^+ irradiation on the molecular films was estimated previously by measuring the ion-induced isotope scrambling;[20] the damage was recognized in the TOF-SIMS experiment if the ion dose exceeded $2\times10^{14}\ ions/cm^2$. The TP-TOF-SIMS experiment was completed within the dosage of $5\times10^{12}\ ions/cm^2$, so that no appreciable sample damage should be induced. 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 at around 1200 K. The surface thus prepared exhibited no impurity peaks derived from C and O in the TOF-SIMS experiment, though a trace of Na^+ and K^+ ions was recognized. The CH_3OH, CD_3OD, C_2H_6, C_3H_8, and C_4H_{10} molecules were introduced into the vacuum chamber through variable leak valves and they were deposited on the Ni(111) substrate at

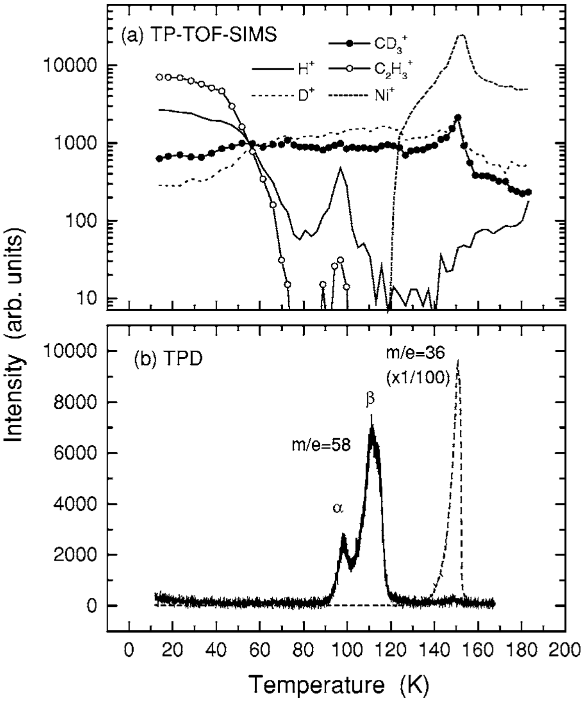

FIG. 1. (a) TP-TOF-SIMS intensities of typical ions and (b) TPD spectra of butane ($me=58$) and heavy methanol (36) from the butane-adsorbed heavy methanol film. The heavy methanol film (50 ML) was deposited on the Ni(111) substrate at 15 K and then 1 ML of butane was adsorbed on it. The temperature was linearly ramped at a rate of 0.1 K s^{-1}.

15 K by backfilling the vacuum chamber. The organic films thus deposited from the gas phase exhibited no impurity molecules in the TOF-SIMS experiment. The growth mode and morphology of molecular films depend on the substrate temperatures, and a layer-by-layer growth occurs at 15 K due to quenching of translational molecular diffusion on the surface. One-monolayer (1 ML) coverage of the adsorbed molecules was determined from the saturation exposures observed in the evolution curves of the sputtered ion intensities, and the film thickness was estimated on the basis of this value. The TPD spectra were taken independently for the methanol films which were prepared under the same procedure as in TP-TOF-SIMS.

III. EXPERIMENTAL RESULTS

Figure 1 shows typical experimental results for (a) TP-TOF-SIMS and (b) TPD on the butane-adsorbed heavy-methanol layer; the CD_3OD film with a thickness of 50 ML was deposited on the Ni(111) substrate and then 1 ML of C_4H_{10} was adsorbed on it at 15 K. The TP-TOF-SIMS spectra and the TPD spectra of C_4H_{10} ($me=58$) and CD_3OD (36) molecules were taken at the same ramping speed. The $C_2H_3^+$ ion from butane decreases in intensity above 45 K and disappears almost completely up to 70 K. This phenomenon should be ascribed to the incorporation of butane in the bulk of the amorphous methanol film rather than desorption. In fact, the butane TPD spectrum exhibits two peaks, α and β, at 97 K and 113 K. It should be noticed that the Ni^+ intensity evolves above 120 K where peak β exhibits a decay edge. The emergence of the sputtered Ni^+ ion should be ascribed to the opening of the methanol film due to the film rupture and dewetting rather than desorption of methanol, as evidenced by the methanol TPD spectrum. The intensities of the D^+ and CD_3^+ ions decrease above 125 K concomitantly with dewetting. The H^+ ion is observed even after the complete decay of the $C_2H_3^+$ ion, indicating that the escape depth of the H^+ ion is larger than the $C_2H_3^+$ ion. The H^+ and $C_2H_3^+$ intensities increase slightly when peak α evolves in the butane TPD spectrum, but no such a correlation is seen in the evolutions between the H^+ ion and peak β. This result can be attributed to the difference in the conformation of the solvated butane, i.e., the butane for peak β is coordinated with a larger number of methanol molecules than that for peak α. It is also likely that the former is incorporated into the bulk and the latter stays closer to the surface. At the evaporation temperature of methanol (150 K), a peak appears in the D^+, CD_3^+, and Ni^+ intensities. As described later, the Ni^+ intensity exhibits a maximum at 1-ML coverage of methanol, so that a peak occurs just before the multilayer desorption. The behaviors of the D^+ and CD_3^+ intensities at 150 K are not fully resolved, but they would be related to the morphology of an evaporating film or the orientation of desorbing molecules. After the multilayer of methanol desorbs, the intensity of H^+ ions increases. They come from chemisorbed butane or impurities such as water. The ions sputtered from chemisorbed molecules undergo efficient resonance neutralization on the metal substrate, so that the faster ions like H^+ are emitted preferentially.

Figure 2 shows the TP-TOF-SIMS and TPD experimental

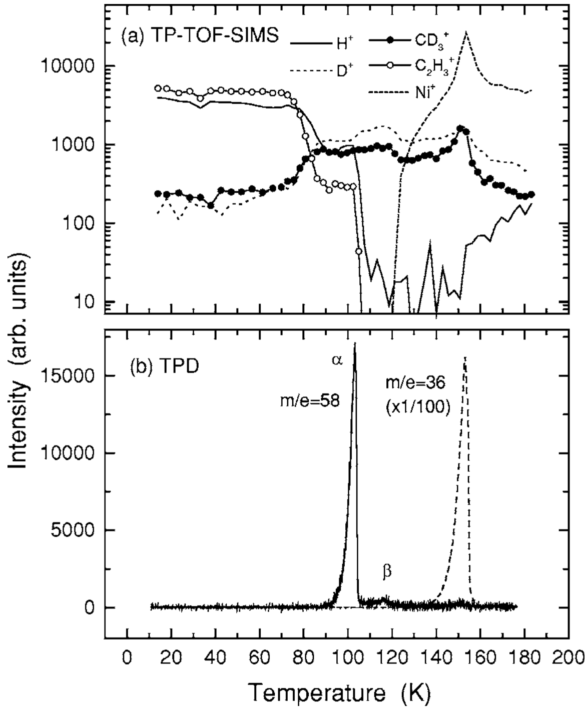

FIG. 2. Same as in Fig. 1, but the heavy methanol film (50 ML) was annealed at 100 K and then 1 ML of butane was adsorbed on it after cooling down to 15 K.

results similar to those in Fig. 1, but the 50-ML CD_3OD film was annealed up to 100 K and then the 1-ML C_4H_{10} molecule was adsorbed on it at 15 K. The $C_2H_3^+$ and H^+ intensities decrease considerably at 78 K and decay completely above 102 K due to the desorption of butane. Thus, the butane molecules can stay on the annealed methanol surface at higher temperatures than on the as-deposited film surface. The decay of the $C_2H_3^+$ and H^+ intensities from butane is not complete above 78 K, suggesting that butane is incorporated in the subsurface sites or forms a complex with methanol at the surface. The butane TPD spectrum exhibits pronounced peak α and considerably smaller peak β, providing a sharp contrast to the result shown in Fig. 1(b). The morphology of the annealed methanol film changes abruptly at 120 K as evidenced by the evolution of the Ni^+ intensity.

Figure 3 shows the TPD spectra of (a) propane and (b) ethane molecules (1 ML) adsorbed on the methanol film (50 ML). The experimental results for the methanol films deposited at 15 K (solid line) and after annealing at 100 K (broken line) are compared to each other. For both molecules, the TPD spectra show peaks α and β from the as-deposited methanol film whereas peak α is predominant from the annealed film. The temperature at which peak α appears depends on the molecular species but peak β occurs basically at the same temperature irrespective of the solute species.

Typically shown in Fig. 4(a) are isothermal TOF-SIMS intensities from the CH_3OH film (50 ML) deposited on the Ni(111) surface. The methanol film was grown at 60 K and the time evolutions of H^+, CH_3^+, and Ni^+ ions were measured at a fixed temperature of 120 K. The Ni(111) substrate is initially covered with a uniform methanol film, and the Ni^+ ions emerge abruptly at 2 min due to dewetting. The film morphology changes continuously after dewetting as revealed from the evolution of the Ni^+ intensity. No saturation behavior was observed within 60 min. This phenomenon cannot be ascribed to the desorption of methanol since the desorption rate of methanol is negligible at 120 K [see also Fig. 1(b)]. Figure 4(b) shows the secondary ion intensities from the Ni(111) surface as a function of coverage of the CH_3OH molecule. The Ni^+ intensity has a maximum at around 1 ML and then decreases gradually with increasing coverage. The Ni^+ ions are not sputtered from the clean Ni(111) surface because they are created during collisions between sputtered Ni atoms and adsorbed methanol. The Ni^+ ion can be emitted through the methanol layer with a thickness up to 7 ML. On the basis of these facts, the continuous evolution of the Ni^+ intensity observed in Fig. 4(a) can be attributed to the viscous flow of the methanol molecules to form droplets. The opened surface is not clean but covered with the molecularly chemisorbed methanol.[21] The gradual increase of the H^+ and CH_3^+ intensities with time suggests that the chemisorbed methanol points its methyl group toward the vacuum side while the physisorbed methanol in multilayer is randomly oriented.

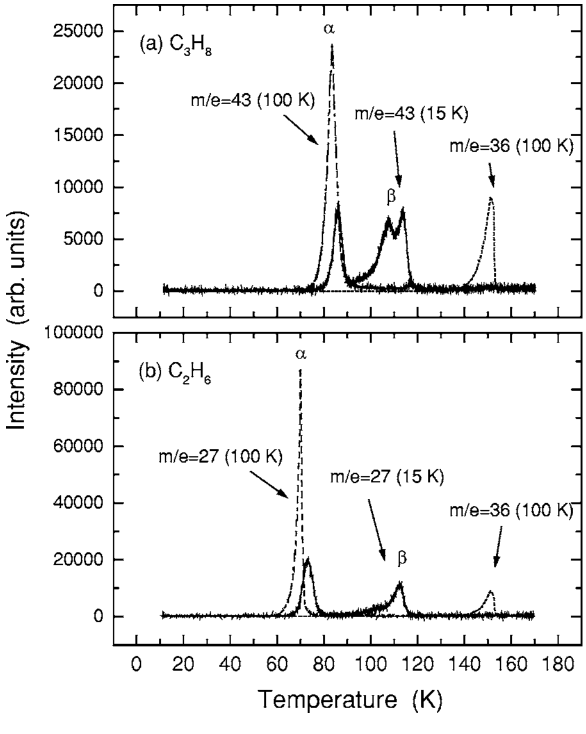

FIG. 3. TPD spectra of (a) propane and (b) ethane adsorbed on the heavy methanol films (50 ML). The 1 ML of propane and ethane molecules was adsorbed at 15 K on the as-deposited (15 K; solid line) and annealed (100 K; broken line) heavy methanol film.

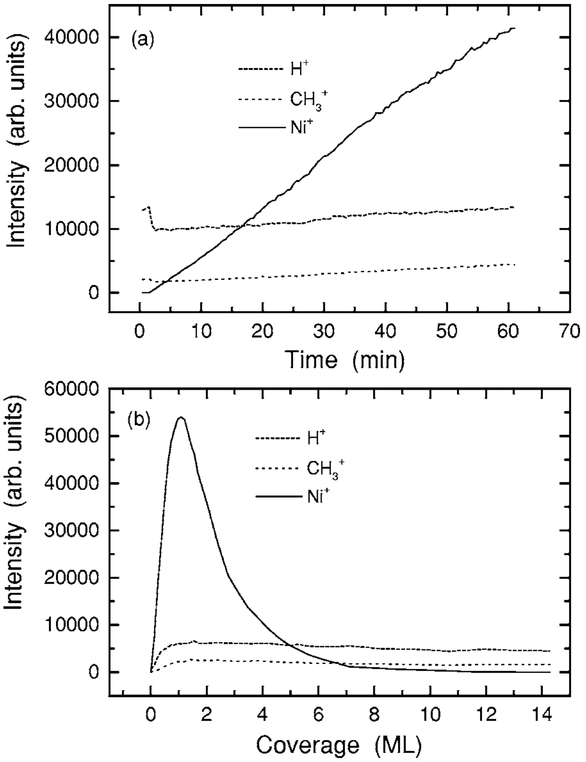

FIG. 4. (a) Isothermal TOF-SIMS intensities of typical secondary ions sputtered from the methanol-adsorbed Ni(111) surface. The CH_3OH film with a thickness of 50 ML was deposited on the Ni(111) substrate at 60 K, and time evolutions of the sputtered H^+, CH_3^+, and Ni^+ intensities were measured at a fixed temperature of 120 K. After the film dewetting at 2 min, the morphology of the film changes continuously over an hour, as evidenced by the evolution of the Ni^+ intensity. (b) TOF-SIMS intensities from the Ni(111) surface as a function of coverage of the CH_3OH molecules. The measurements were made at 15 K.

IV. DISCUSSION

The methanol film deposited at 15 K should contain a considerable amount of cavities through which the adsorbed alkane molecules can permeate into the bulk. The cavities collapse by heating, and some of the alkane molecules are trapped in the bulk, thereby resulting in peak β in the TPD spectra. Although the exact temperature at which the cavities are quenched is not determined in the present study, this assumption is consistent with the fact that the heavier molecules with higher desorption temperatures are trapped more efficiently in the bulk. Thus, peak β is attributable to the solvated alkanes in the bulk. The bulk cavities disappear considerably by annealing the film at 100 K, but the alkane molecules are incorporated in the subsurface sites or form a complex at the surface, as evidenced by the decrease in intensity of secondary ions from butane above 80 K (see Fig. 2).

The uptake of alkanes in the porous methanol film indicates that alkane is mobile on the cavity walls at considerably low temperatures ($T > 60$ K). On the other hand, the incorporation of the alkane molecules in the annealed methanol film should be caused by the restructuring of the methanol molecules to form a complex. The high diffusivity of alkanes is characterized by weak van der Waals interactions between alkanes and methanol, whereas the rotational and translational diffusions of the methanol molecules require higher activation energies to reorganize the hydrogen bonds. The incorporation of alkane molecules in the bulk or subsurface sites should be caused by the imperfections of the hydrogen bonds in the methanol film. Such imperfections still exist in the film annealed at 100 K, so that the adsorbed butane can form a complex with methanol due to reorganization of the hydrogen bonds. The complete desorption of alkanes up to 120 K should be caused by the phase transition of methanol associated with drastic reorganization of the hydrogen bonds.

In the previous paper,[22] we have demonstrated that the self-diffusion of molecules in the pure methanol film commences at 80–90 K prior to the film dewetting at 115–120 K. Note that the butane uptake (80 K) and film dewetting (120 K) in the present study take place at around these temperatures, suggesting that the presence of the alkane additives has no significant effect on the properties of the methanol matrix. The increased mobility of the methanol molecules above 80 K may accelerate the formation of a surface complex with butane, and the morphological change of the film (120 K) can be attributed to the emergence of the liquidlike phase. These two temperatures do not agree with the calorimetric glass transition temperature of methanol (103 K). In deeply supercooled liquid ($T > 1.2T_g$), it is well known that the self-diffusion of molecules and the viscosity of the film are decoupled, resulting in the breakdown of the Stokes-Einstein relation.[23] This phenomenon has been explained in terms of the spatial heterogeneity due to the formation of the fluidized domains dispersed throughout an essentially solid matrix. These two domains are expected to vary in size and shape. It should be noted that not all of the mobile molecules can contribute to the structural relaxation immediately since the fluidity arises from a correlated, long-range motion of the molecules. Probably, the slow evolution of the cooperatively rearranging molecules in the fluidized domains is responsible for the delay of the structural relaxation (120 K) relative to the self-diffusion onset (80–90 K) in the temperature-programed experiments. The deviation of the structural relaxation temperature from the calorimetric T_g can be ascribed to the kinetic effects associated with the heating and cooling rate of the experiment.[24]

In this respect, the IR absorption studies claimed that the amorphous methanol film crystallizes irreversibly at around 116–120 K;[13–15,17] at this temperature, a broad OH band splits into two sharp components within minutes. They have been assigned to the in-phase and out-of-phase vibrations of the hydroxyl group of crystalline methanol. It might be presumed that the abrupt dewetting of the methanol film is related to the crystallization. However, such a possibility is denied by the fact that the viscous flow of the methanol film continues for an hour even after dewetting, as typically seen in Fig. 4(a). Recent experiments[25] and simulations[26,27] of supercooled liquid revealed that particles with similar mobility are spatially correlated, resulting in the coexisting at any instant of the caged clusters of nondiffusing molecules with cooperatively rearranging stringlike clusters.[26] In pure liquid methanol, moreover, the hydrogen-bonded molecular chains are known to exist.[28] Therefore, such chains may be formed in the supercooled liquid methanol as well. The OH vibrational components observed in the IR spectra above 120 K[13–15,17] might be caused by such molecular chains. In any case, a long-range order like crystallization is hardly discussed without reliable diffraction data. The liquid phase is dominant above 120 K and the crystallites would grow in the liquid phase rather gradually. The coexistence of supercooled liquid and crystallites is likely in light of spatial heterogeneity.

The present results remind us of the hydration of alkanes in the ASW film.[8] The onset temperature for the translational molecular diffusion has been determined as 136 K and the film morphology changes at 165 K due to the increased fluidity.[22] The alkane molecules are incorporated in the bulk of ASW up to 100 K, and the formation of the bulk hydrates is concluded from the explosive alkane TPD peak at 160–165 K.[8] The water TPD spectra from the ASW film exhibit a characteristic bump at 165 K. This phenomenon has been explained in terms of the abrupt crystallization of the ASW film,[29,30] but it is better ascribed to the morphological change of the liquidlike film induced by the surface tension.[8,22] No such a bump is observed in the methanol TPD spectra, since the morphology of the methanol film changes well below the desorption onset. There exist significant debates concerning the assignment of water's T_g either to 136 K or to 165 K.[1–5] As already mentioned, this arises from the kinetic effect associated with the delay of the structural relaxation relative to the self-diffusion onset, which is characteristic of supercooled liquid.[24] The hydrophobic hydration of alkanes in the bulk of ASW is basically caused by the restructuring of the waters' hydrogen-bond network,[31] so that it is facilitated if the cavities or imperfections of hydrogen bonds exist in the bulk. For the solvation of alkanes in the methanol film, the reorganization of hydrogen bonds should play a more decisive role than the hydrophobic interactions between alkanes and the methyl group. This provides a reason why the properties of methanol films are quite similar to water films in terms of the solvation and glass-liquid transition.

The number of bulk cavities and hydrogen-bond defects decreases considerably by annealing the film. The annealing temperature of 100 K is above (below) the onset temperature for self-diffusion of methanol (water) molecules, so that alkanes are incorporated (not incorporated) in the bulk of the water (methanol) film annealed at 100 K. Regarding the water adsorption on the amorphous methanol film, the monolayer of water tends to dissolve in the bulk of the methanol film up to 120 K[18] and the closed water film is hardly created on the methanol film when water is deposited at 100 K.[32] These phenomena can be explained by the presence of the mobile methanol molecules (above 80 K) and the hydrogen-bond imperfections. Indeed, water incorporated in the methanol film preferentially bridges the hydrogen bonds of methanol.[28] In contrast to the small alkane molecules discussed here, the monolayer of octane desorbs above 160 K, which enables us to discuss the alkane-methanol interactions at higher temperatures. It was revealed that the octane basically stays on the surface of the annealed methanol film up to 135 K, though the formation of some complexes with the methanol molecules is suggested at 70–90 K.[19] This result clearly indicates that the structural relaxation of the methanol film at 120 K has no significant effect on the incorporation of adsorbed octane in the bulk.

V. SUMMARY

The solvation and desorption of alkane molecules adsorbed on the amorphous methanol film have been investigated in order to gain information about the morphology, hydrogen-bond imperfections, and glass-liquid transition of the film. At least two distinct states are found to exist for the incorporated alkanes; one is assignable to solvated molecules in the bulk that desorb at 110–120 K irrespective of the solute molecules, and the other is due to the weakly bound species. The former is created in such a manner that the molecules that diffuse into the porous methanol film are trapped during pore collapse. On the nonporous methanol film prepared by annealing at 100 K, the alkanes are incorporated in the subsurface sites or form a complex with methanol above 80 K due to the presence of mobile molecules. The alkanes confined in cavities of the glassy methanol film are hardly detached, but they are released up to 120 K due to the occurrence of the glass-liquid transition of the methanol film. The translational diffusion and viscous flow of molecules are decoupled in the supercooled liquid phase, so that the onset of the latter (120 K) is delayed considerably relative to the former (80–90 K) in the temperature-programed experiments.

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