



## Research paper

## Probing the solid-liquid transition of thin propanol and butanol films through interactions with LiI

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## ABSTRACT

This report describes how LiI mixes with thin propanol and butanol films at cryogenic temperatures using time-of-flight secondary ion mass spectrometry and reflection absorption infrared spectroscopy. The glass transition temperature,  $T_g$ , is assignable as the uptake onset of LiI additives in the thin film interior. The uptake rate of LiI in the deeply supercooled region is small for 1-propanol and 2-butanol, but concentrated solutions are formed on a LiI film at temperatures higher than  $1.2\text{--}1.3 T_g$ . The supercooled 2-propanol and 1-butanol are short-lived; their crystallites form complexes at the interface with LiI because of premelting.

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## 1. Introduction

The glass-liquid transition and crystallization of thin glassy films are areas of intense experimental and theoretical interest. Nevertheless, the glass transition remains a mysterious phenomenon because of the coexistence of thermodynamic and kinetic aspects. The slowdown of the dynamics in deeply supercooled liquids has been explained by the formation of cooperatively rearranging regions [1]: spatial fluctuations become increasingly correlated; and the dynamic correlation length diverges near the glass transition temperature,  $T_g$ . The dynamics of a deeply supercooled liquid is spatially heterogeneous because of the correlated motion of groups of neighboring particles, as evidenced by the decoupling of translational diffusion and viscosity [2]. Consequently,  $T_g$  tends to be reduced when molecules are confined in nanoporous media [3] and supported thin films [4–9], where the free surface and substrate interface also play a role in the modification of  $T_g$ .

It is generally considered that crystallization occurs in supercooled liquids. However, some materials appear to crystallize directly from their glasses. An example is glassy water that exhibits no indications of a supercooled liquid before crystallization except for an unusually small endotherm (the heat absorbed during the glass transition) in calorimetry [10–12]. This behavior is explainable as the occurrence of a distinct liquid in the framework of polyamorphism [13]. Supercooled water might be formed via the liquid-liquid (L–L) phase transition [14,15], but this behavior has

not been confirmed explicitly because supercooled water crystallizes immediately. The resulting ice Ic is metastable, behaving similarly to a viscous droplet before it transforms into stable ice Ih [16]. Another example of metastable states is the glacial phase of triphenyl phosphite [17,18]. This material appears to have a distinct amorphous phase resulting from a first-order phase transition of the supercooled liquid, but it might be regarded as an aggregate of nanocrystallites formed via abortive crystallization. In fact, the melting point,  $T_m$ , is expected to be reduced for nanoparticles because ensembles of clusters represent a mixture of solid and liquid phases [19–24]. Solid-liquid phase change of nanoparticles is initiated by surface premelting because weakly bound surface species are less constrained in their thermal motion than those in the interior.

To date, properties of liquid-like phases and their phase transition have been explored using vapor-deposited thin films interacting with various adspecies and substrates [25–35]. Liquid water and simple alcohols form solutions with alkali halides at room temperature. Therefore, their uptake in the thin film interior can be regarded as indicating the solid-liquid transition. For example, thin ethanol [33] and methanol [34] films absorb LiI adspecies at around bulk  $T_g$ , but the development of the supercooled liquid into the normal liquid is not generally accessible because of crystallization. On the other hand, concentrated solutions of LiI are formed after crystallization of methanol and ethanol when they are deposited onto a LiI film. Consequently, liquid-like phases are expected to be formed before and after crystallization of thin molecular solid films, but very little is known about their properties and relations to a normal liquid at room temperature. Apparently, more

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systematic experimental studies must be conducted to elucidate this point. As described herein, we investigate interactions of Lil with vapor-deposited thin films of 1-propanol, 2-propanol, 1-butanol, and 2-butanol using secondary ion mass spectrometry (TOF-SIMS) and reflection absorption infrared spectroscopy (RAIRS) as a function of temperature. Properties of liquid-like phases formed after the glass-liquid transition and crystallization of these alcohols are discussed based on their solvation ability of Lil in comparison with previously reported experimental results for other molecular solids.

## 2. Experiment

The TOF-SIMS experiment was performed in an ultrahigh vacuum (UHV) chamber with base pressure of less than  $2 \times 10^{-10}$  Torr. A primary He<sup>+</sup> beam with kinetic energy of 2.0 keV was extracted from a differentially pumped electron-impact-type ion source. After chopping into pulses, the ion beam was set to be incident onto the sample surface. A grounded stainless-steel mesh was placed 4 mm above the sample that was floated with a bias voltage of +500 V to extract positive secondary ions into a field-free TOF tube. After the ions were detected using a microchannel plate, they were pulse-counted using a multichannel scaler (LN-6500R; Laboratory Equipment). The He<sup>+</sup> beam current was monitored through the backscattered He<sup>0</sup> intensity; it is used for normalization of secondary ion intensities. The TOF-SIMS spectra were taken continuously at a ramping speed of 5 K min<sup>-1</sup>. The fluence of the He<sup>+</sup> ion was kept below  $1 \times 10^{12}$  ions cm<sup>-2</sup> to minimize the sample damage.

Highly oriented pyrolytic graphite (HOPG) was used as a substrate for TOF-SIMS measurements. It was mounted on a sapphire plate attached to a Cu rod extended from a closed cycle helium refrigerator cooled to 20 K. For cleaning, the substrate was heated to approximately 1200 K by electron bombardment from behind. The sample temperature, which was monitored using Au(Fe) chromel thermocouples attached to the Cu rod close to the sample position, was controlled using a digital temperature controller and a cartridge heater. Liquid samples of 1-propanol, 2-propanol, 1-butanol, and 2-butanol were outgassed via several freeze-pump-thaw cycles. After the gaseous molecules were admitted through high-precision variable leak valves, they were deposited onto the cold substrate to form thin films. The Lil additives were adsorbed onto the film surface by thermal evaporation from a Ta boat placed in front of the HOPG substrate. The coverage of alcohols (Lil) was determined from the evolution curves of secondary ion intensities as a function of exposure (deposition time). One monolayer (ML) of molecules was attained at exposure of approx. 2 L (langmuir; 1 L =  $1 \times 10^{-6}$  Torr s) [35]. The Li<sup>+</sup> yield is high in TOF-SIMS measurements, but it decreases exponentially with increasing thickness of the molecules deposited on Lil [33]. The Li<sup>+</sup> ion is detectable when Lil is embedded underneath a film as thick as 10 ML. These behaviors enable us to explore how Lil adspecies are incorporated into the film interior via the formation of a liquid-like phase [15,32–34].

RAIR spectra were collected in a separate UHV chamber (base pressure of  $3 \times 10^{-10}$  Torr) using a spectrometer (FTS 40A; Bio-Rad Laboratories) with a liquid-nitrogen-cooled mercury cadmium telluride detector. The spectra were taken continuously over a wave number range of 400–4000 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution. Thin alcohol films were deposited onto a polycrystalline Au plate and a polycrystalline Lil film. The latter was deposited onto the former at room temperature by prolonged thermal evaporation of Lil from the Ta boat placed in front of the surface. The substrate was cooled using liquid nitrogen. The sample temperature was monitored using K type thermocouples. The films were deposited at 90 K.

The spectra were taken at the same ramping speed used for TOF-SIMS.

## 3. Experimental results

Fig. 1 presents TOF-SIMS intensities of typical secondary ions sputtered from the 1-propanol film as a function of temperature. The film was formed by deposition of 50 ML 1-propanol onto HOPG at 70 K. Then Lil (0.2–0.3 ML) was adsorbed onto it. Upon heating, the Li<sup>+</sup> ion decreases in intensity at temperatures higher than approximately 110 K because the adspecies is incorporated into the film interior. The translational diffusion of 1-propanol molecules occurs at this temperature as a result of the glass-liquid transition. The TOF-SIMS intensities of Li<sup>+</sup> and H<sup>+</sup>(C<sub>3</sub>H<sub>7</sub>OH) ions obtained using the 1-propanol film annealed to 150 K are also shown as dotted lines. The result is almost identical to that obtained using the film deposited at 70 K, indicating that the 1-propanol film does not crystallize at temperatures up to 150 K.

Fig. 2 depicts OH stretching bands of RAIR spectra for the 200 ML 1-propanol film deposited on (a) the Au substrate and (b) the Lil film at 90 K as a function of temperature. A broad band of OH stretching vibration (3100–3400 cm<sup>-1</sup>) is observed with two broad peaks centered at around 3290 and 3200 cm<sup>-1</sup>. This spectrum is commonly obtained using glassy alcohol films formed after vapor deposition. On the Au substrate, the IR absorption band is almost unchanged until the film evaporates at 180 K, without exhibiting any phase transitions. The result is consistent with the TOF-SIMS observation. On the Lil film, the broad band of amorphous propanol is observable below 140 K. Then the band shifts to the higher frequency side at temperatures up to 150 K. The blue shift of the band results from weakening of the hydrogen bond between molecules. This behavior is explainable as mixing of 1-propanol and Lil at the molecular level to form a concentrated propanolic solution at 140–150 K. Above this temperature, two sharp peaks appear because the solution crystallizes. The peak is broadened again at temperatures higher than 220 K because the composite crystal melts. The physisorbed 1-propanol molecules evaporate completely at temperatures up to 180 K on the metal substrates, but they survive until higher temperatures after complexes are formed with Lil. The concentrated solution is likely to be formed via penetration of liquid-like propanol molecules into the Lil film.

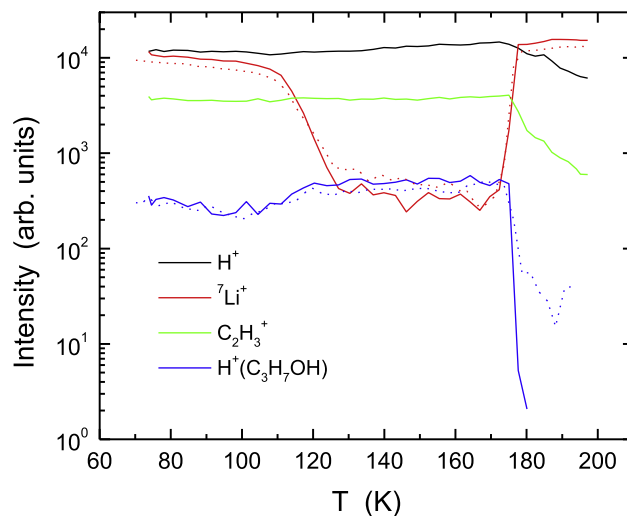
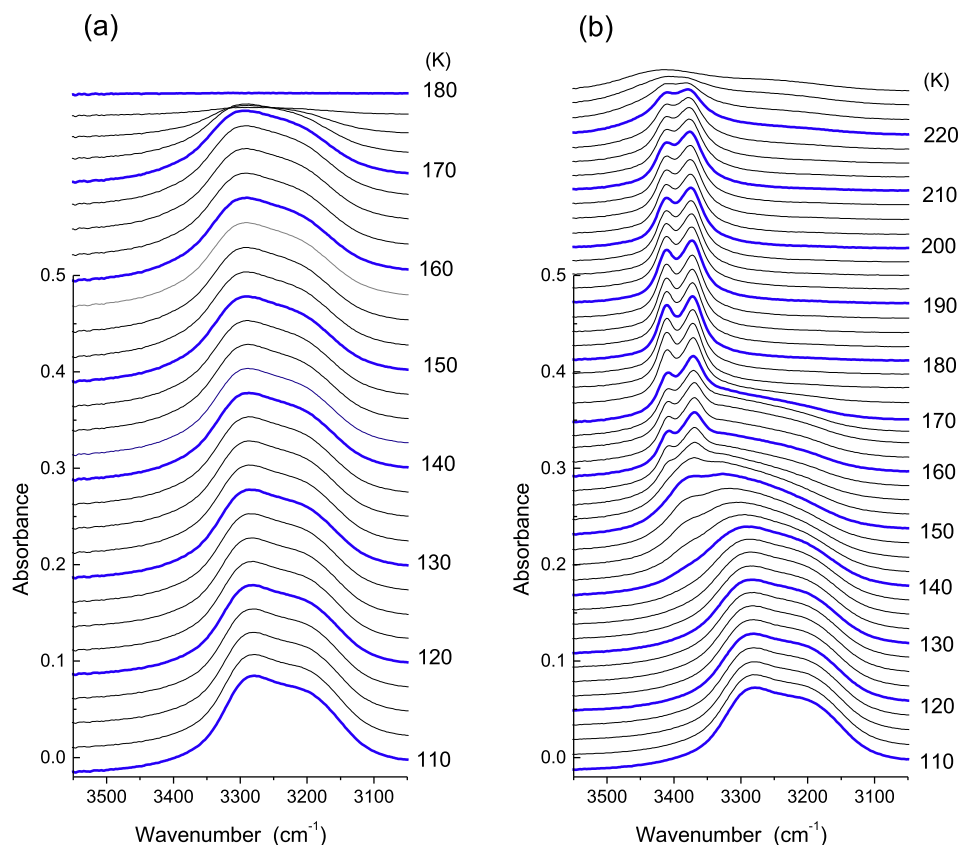
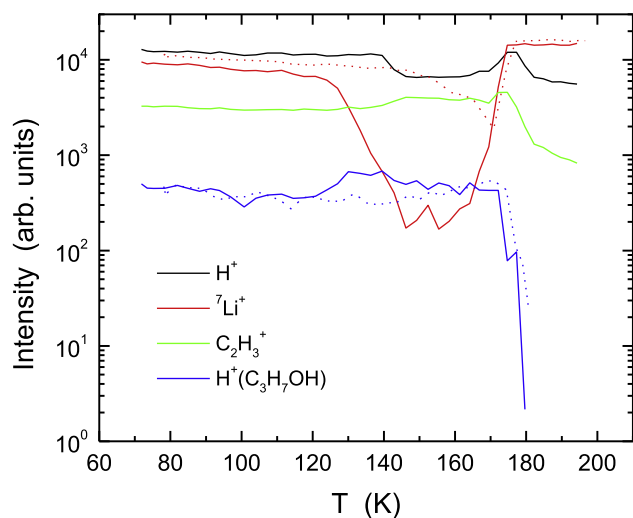


Fig. 1. Temperature-programmed TOF-SIMS intensities of typical ions sputtered from the 1-propanol films (50 ML) on the HOPG substrate, obtained after adsorption of Lil additives (0.2–0.3 ML) on the film surface at 70 K. The result obtained using the film deposited at 70 K (solid lines) is compared with that annealed at 150 K (dotted lines). The temperature was ramped at a rate of 5 K min<sup>-1</sup>.



**Fig. 2.** Temperature evolution of RAIR spectra for the OH stretching region of the 1-propanol film (200 ML) deposited onto the (a) Au substrate and (b) Lil film at 90 K. The temperature was ramped at a rate of 5 K min<sup>-1</sup>.

The interaction of Lil adspecies with the 2-propanol film (50 ML) is examined using TOF-SIMS. The experimentally obtained results are shown in Fig. 3. The adspecies are incorporated into the film interior at approximately 125 K because a liquid-like phase occurs. The Li<sup>+</sup> intensity tends to plateau at approximately 140 K, where the H<sup>+</sup> intensity decreases. This behavior is ascribable to crystallization ( $T_c = 140$  K). In fact, when Lil is adsorbed onto the



**Fig. 3.** Temperature-programmed TOF-SIMS intensities of typical ions sputtered from the 2-propanol films (50 ML) on the HOPG substrate, obtained after adsorption of Lil additives (0.2–0.3 ML) on the film surface at 70 K. The result obtained using the film deposited at 70 K (solid lines) is compared with that annealed at 150 K (dotted lines).

2-propanol film annealed to 150 K, the uptake of adspecies at 125 K is quenched, as depicted by a red dotted line for Li<sup>+</sup>. On the crystalline film surface, the Li<sup>+</sup> intensity starts to decrease at higher temperatures. It reaches its minimum value at 170 K immediately before the film evaporates. This result indicates that a liquid-like state is formed even after crystallization of 2-propanol.

Fig. 4 shows RAIR spectra obtained using the 200 ML 2-propanol film. On the Au substrate (a), narrow peaks emerge from the broad OH stretching band at temperatures higher than 140 K because of crystallization. This behavior agrees with the TOF-SIMS result. For the 2-propanol film deposited on the Lil film (b), crystallization occurs at the same temperature. However, the molecules tend to remain after evaporation of the physisorbed species at 170 K, as revealed from occurrence of a band at 3400 cm<sup>-1</sup>. This species is assignable to a complex between Lil and 2-propanol. It might be amorphous because no sharp peak is identifiable. This band tends to grow after crystallization at  $T > 160$  K, with uptake of the Lil adspecies in the crystalline film is enhanced, as revealed from the decay curve of the Li<sup>+</sup> intensity in Fig. 3.

Similar measurements were made using thin films of 1-butanol and 2-butanol. The experimental results of TOF-SIMS for uptake of the Lil adspecies (0.2–0.3 ML) on the glassy and crystalline 1-butanol films (50 ML) are displayed in Fig. 5. The Li<sup>+</sup> intensity from the glassy film decreases gradually with increasing temperature and decays at  $T > 125$  K as displayed by a red solid line, because of the glass-liquid transition. The Li<sup>+</sup> intensity obtained using the film formed by heating the glassy film to 150 K exhibits no such behavior (a red<sup>1</sup> dotted line) because of crystallization.

<sup>1</sup> For interpretation of color in Figs. 3, 5, 7, the reader is referred to the web version of this article.

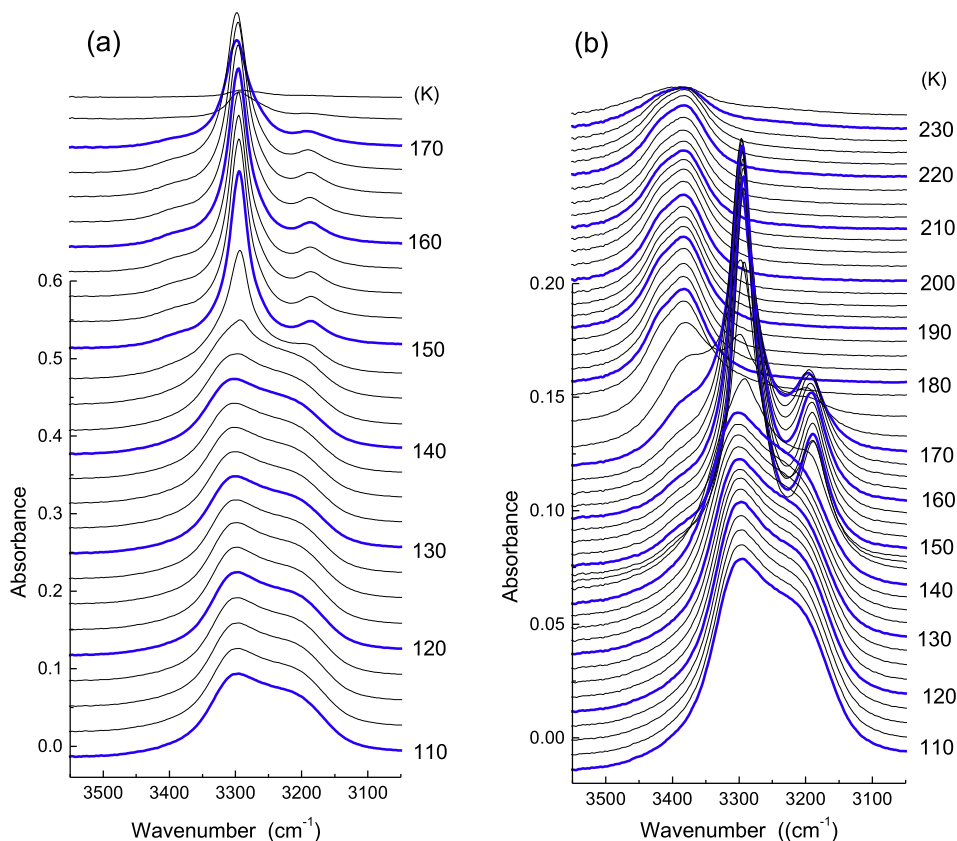


Fig. 4. Temperature evolution of RAIR spectra for the OH stretching region of the 2-propanol film (200 ML) deposited onto the (a) Au substrate and (b) Lil film at 90 K.

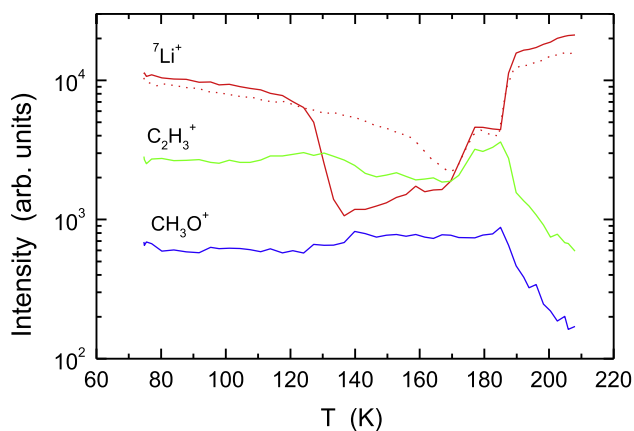


Fig. 5. Temperature-programmed TOF-SIMS intensities of typical ions sputtered from the 1-butanol films (50 ML) on the HOPG substrate, obtained after adsorption of Lil additives (0.2–0.3 ML) on the film surface at 70 K. The result obtained using the film deposited at 70 K (solid lines) is compared with that annealed at 150 K (dotted lines).

Instead, the  $\text{Li}^+$  intensity tends to decrease gradually at approximately 160 K, suggesting that a liquid-like state occurs at higher temperatures for the crystalline 1-butanol film.

Fig. 6 presents temperature evolutions of the OH stretching band of 1-butanol films (200 ML) deposited onto the (a) Au and (b) Lil film surfaces at 90 K. The crystallization commences at approximately 145 K, as revealed by the presence of two sharp peaks at 3320 and 3390  $\text{cm}^{-1}$ . The 1-butanol molecules evaporate completely from the Au substrate at temperatures up to 190 K. The crystallization kinetics of 1-butanol on the Lil film is almost iden-

tical to that on Au. However, complexes remain after evaporation of the physisorbed species, as revealed from the peak at 3380  $\text{cm}^{-1}$ . This peak starts to develop at approximately 160 K, which corresponds to the decay onset of the  $\text{Li}^+$  intensity observed using the crystalline 1-butanol film, as depicted in Fig. 5. Consequently, the liquid-like phase formed after crystallization is responsible for the complex formation.

In Fig. 7 is displayed the experimental result of TOF-SIMS obtained using 2-butanol films (50 ML) on which Lil (0.2–0.3 ML) is adsorbed. The uptake of Lil occurs quite similarly between the films deposited at 70 K (a red solid line) and annealed to 150 K (a red dotted line), indicating that 2-butanol film does not crystallize in this temperature range. The Lil adspecies are incorporated into the film interior at  $T > 135$  K because the liquid-like phase is formed via the glass-liquid transition.

Fig. 8 depicts the OH stretching band obtained using the 200 ML 2-butanol film deposited on (a) the Au substrate and (b) the Lil film as a function of temperature. The crystallization of 2-butanol is not identified on the Au substrate until the film evaporates, in agreement with the TOF-SIMS result. On the Lil film surface, the band shifts to the higher-frequency side at temperatures higher than 160 K because a concentrated solution is formed with Lil. The complex appears to remain amorphous at higher temperatures, as inferred from the absence of sharp peaks.

#### 4. Discussion

The solid-liquid transitions of thin alcohol films are clearly identifiable from the uptake of the Lil adspecies in the film interior. The Lil additives with coverage of as little as 0.2–0.3 ML are not expected to influence the crystallization and melting kinetics of the alcohol films as thick as 50 ML. In contrast, a concentrated



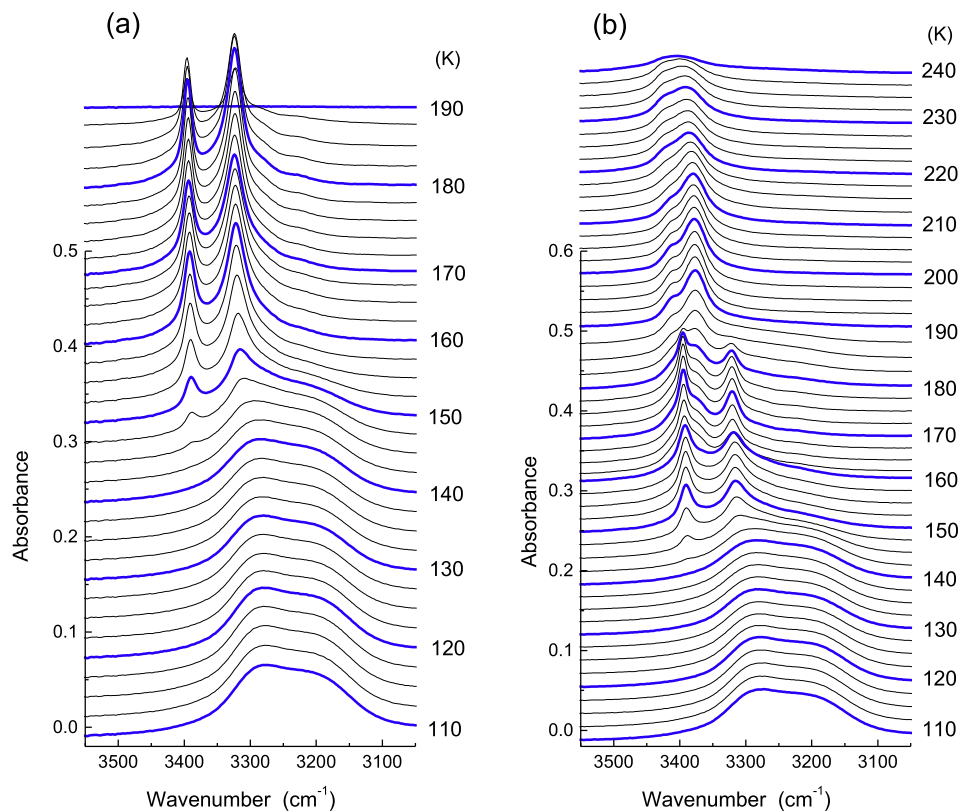


Fig. 6. Temperature evolution of RAIR spectra for the OH stretching region of the 1-butanol film (200 ML) deposited onto the (a) Au substrate and (b) Lil film at 90 K.

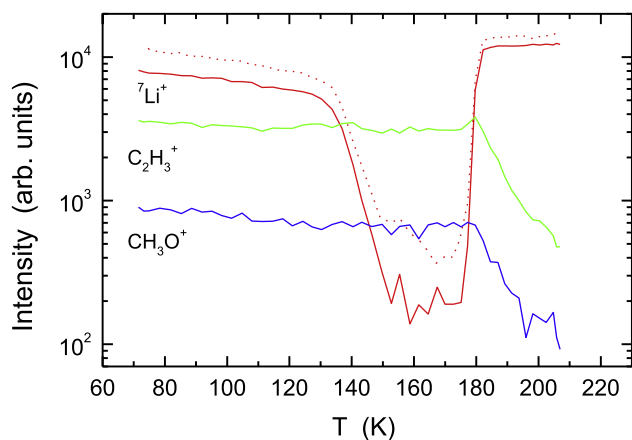


Fig. 7. Temperature-programmed TOF-SIMS intensities of typical ions sputtered from the 2-butanol films (50 ML) on the HOPG substrate, obtained after adsorption of Lil additives (0.2–0.3 ML) on the film surface at 70 K. The result obtained using the film deposited at 70 K (solid lines) is compared with that using the film annealed at 150 K (dotted lines).

solution or an eutectic melt is formed at the interface with the Lil film via penetration of liquid-like alcohols. The thin films'  $T_g$  is determined from the uptake onset of the Lil adspecies on the initially glassy films because Lil is incorporated into the film interior via translational diffusivity of the alcohol molecules. The stability of supercooled liquid against crystallization depends on the alcohol species. The thin films of 1-propanol and 2-butanol avoid crystallization, so that properties of the supercooled liquid can be explored in a wide temperature range. On the other hand, liquid-like properties are identifiable for 2-propanol and 1-butanol, after crystallization. The uptake onsets of the Lil adspecies (approx-

mately 160 K) for crystalline 2-propanol and 1-butanol films, which agree with the onsets of the complex (i.e., eutectoid) formation at the interface with the Lil film, are apparently lower than their respective bulk melting points of 183.5 and 182 K. This occurs because a liquid-like phase is formed below  $T_m$  as a result of premelting.

The Lil is expected to be incorporated in the film interior from both the free surface and the substrate interface. However, no concentrated solution develops for all alcohols at  $T_g$ , as revealed from invariance of the OH stretching band frequencies before and after the Lil uptake, indicating that a dilute solution is formed. A concentrated Lil solution can be formed for 1-propanol and 2-butanol with increasing temperature, as evidenced by a blue shift of the broad OH stretching band. It is therefore suggested that the solvation ability of nascent liquids formed at  $T_g$  is lower than that of the liquid at higher temperatures. Probably, this behavior is associated with dynamical heterogeneity characteristic of the supercooled liquid [2]: the correlated motion of groups of neighboring molecules results in domain structures in the deeply supercooled region ( $T < 1.2 T_g$ ). The overall fluidity is given by an average of the dominant caged domain and the minor domain exhibiting high fluidity. Because of the coexistence of liquid-like and solid-like domains, decoupling occurs between self-diffusion coefficient and viscosity [36]. The molecules move forming clusters or strings in liquid-like domains [37–39], so that reorganization of molecules to form concentrated Lil solutions tends to be quenched in the deeply supercooled region, thereby resulting in poor solubility of Lil. In fact, the concentrated Lil solutions of 1-propanol and 2-butanol evolve at ca.  $1.2–1.3 T_g$ , as revealed from the RAIR spectra in Figs. 2 (b) and 8(b). Probably, domain structures disappear above this temperature, and properties of the normal liquid become evident.

The 2-propanol and 1-butanol crystallizes in the deeply supercooled region, so that no concentrated solution develops on the Lil film before crystallization occurs. The Lil additives deposited onto

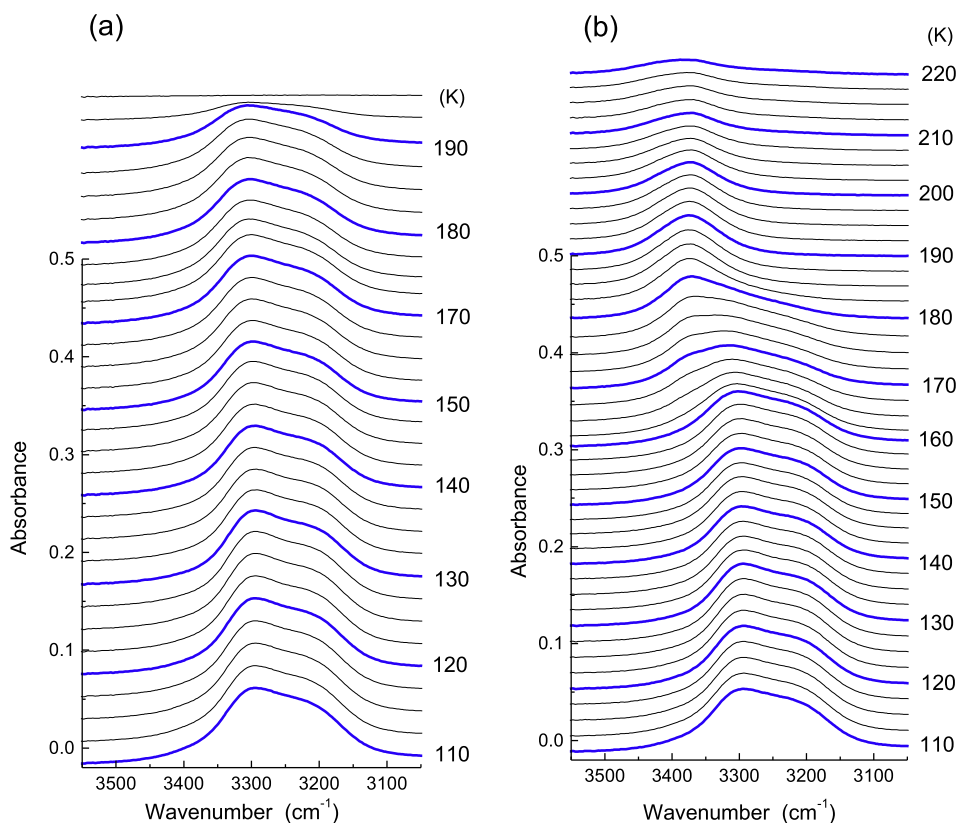


Fig. 8. Temperature evolution of RAIR spectra for the OH stretching region of the 2-butanol film (200 ML) deposited onto the (a) Au substrate and (b) Lil film at 90 K.

the crystalline film surface are thought to be incorporated in the interior through grain boundaries. Consequently, a quasi-liquid is formed on the surface and boundary of crystal grains because of premelting. Premelting is known to occur near bulk  $T_m$  (approximately  $T > 0.9 T_m$ ) on macroscopic metal surfaces [40–42], where the premelting layer thickness diverges upon reaching  $T_m$ . In this study, the quasi-liquid also develops at approximately  $0.9 T_m$  for both 2-propanol and 1-butanol to form complexes with the Lil film (Figs. 4(b) and 6(b)), but no broad OH stretching band characteristic of the liquid phase is recognizable on the Au substrate (Figs. 4(a) and 6(a)). Probably, the premelting layer is so thin (monolayer thickness) that its contribution to the RAIR spectra is negligible relative to that of the crystal grains. Moreover, a quasi-liquid layer is expected to be inseparable from the underlying crystal grains because it can be regarded as a layer with large-amplitude vibrations at the free surface of crystallites [43]. Molecular dynamics (MD) simulations [20] also revealed that a few atoms popped out from a quasi-liquid layer of free clusters. They migrate as “floaters” on the surface during premelting. The molecules in the quasi-liquid layer might diffuse independently without forming clusters or tagged species in contrast to the molecules in the deeply supercooled liquid, thereby facilitating mixing with Lil and the formation of complexes.

The glass transition and (pre) melting behaviors of water and ethanol are unique in comparison with those of propanol and butanol described here. The 200 ML water ( $T_m = 273$  K) [32] and ethanol (158.5 K) [33] films, respectively, transformed thoroughly to concentrated Lil solutions on the Lil film during or immediately after crystallization at approximately 165 K ( $0.6 T_m$ ) and 130 K ( $0.8 T_m$ ), as revealed from blue shift of the OH stretching band. The glass transition behavior of water is also anomalous in comparison with that of alcohols [15,32]: The alkali halide adspecies survive on the film surface across the glass-liquid transition and then incorporated steeply during crystallization. Probably, this

occurs because supercooled water can be formed transiently via the L-L phase transition [15]. No such a behavior is observed in the case of alcohols because the liquid phase formed in the deeply supercooled region is thermodynamically connected to normal liquid. This is evidenced by the experimental results of 1-propanol and 2-butanol that avoid crystallization.

The polycrystalline films comprised of smaller grains are expected to be created during nucleation in thin films. The smaller the grain size, the lower the premelting temperature becomes. In fact, reduction of the premelting temperature for thinner films is identified for methanol [34]. The interface with high curvature has higher free energy, so that the curved interface or smaller grain tends to disappear by heating (the Gibbs-Thomson effect). The premelting layer is equilibrated with such crystal grains, so that smaller grains are expected to be converted preferentially to concentrated solutions at the interface with the Lil film if the solutions are thermodynamically more stable. Probably, such is the case for interactions of crystalline ethanol [33] and methanol [34] with Lil during premelting. In the case of 2-propanol and 1-butanol, the interface with Lil appears to be more stable, as evidenced by the survival of crystal grains. The incomplete mixing with Lil also implies that solid complexes are formed at the interface rather than liquid solutions. Consequently, the occurrence of a solid-liquid transition at the free surface, substrate interface, and boundaries of crystallites is demonstrated above a certain critical temperature through interactions with Lil, although premelting is not explicitly observable when using pure crystalline films.

## 5. Conclusion

The solid-liquid transitions and solvation properties of liquid-like phases are examined through interactions of thin alcohol films with Lil. The glass-liquid transition is explored based on the uptake

of LiI adspecies into the thin film interior. Results show the  $T_g$  of thin films as approximately 110, 127, 125, and 132 K, respectively, for 1-propanol, 2-propanol, 1-butanol, and 2-butanol. Crystallization is avoided for the 1-propanol and 2-butanol films, whereas 2-propanol and 1-butanol crystallize at approximately 145 K. The mixing occurs with LiI after the supercooled liquid is formed, but the uptake of LiI in the deeply supercooled region is not significant for any alcohol examined here. The concentrated LiI solution is formed for 1-propanol and 2-butanol at temperatures higher than 1.2–1.3  $T_g$ , as revealed from the blue shift of the OH stretching band. The poor solubility of LiI in the deeply supercooled liquid is explainable in terms of dynamical heterogeneity or the coexistence of solid-like and liquid-like domains. Mixing occurs between LiI and the crystalline 2-propanol and 1-butanol films at approximately 0.9  $T_m$  because premelting layers are formed at the free surface, grain boundaries, and substrate interface. The premelting layer is expected to be equilibrated with crystal grains, as evidenced by the fact that the crystalline methanol and ethanol films can be converted thoroughly to concentrated solutions on LiI. For 2-propanol and 1-butanol, however, solid-like complexes might be formed at the interface, playing a role as a separator between crystallites and LiI.

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