



## 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 LiI 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 LiI 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 LiI 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 (LiI) 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 LiI [33]. The Li<sup>+</sup> ion is detectable when LiI is embedded underneath a film as thick as 10 ML. These behaviors enable us to explore how LiI 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 LiI film. The latter was deposited onto the former at room temperature by prolonged thermal evaporation of LiI 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 LiI (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 LiI 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 LiI 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 LiI 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 LiI. The concentrated solution is likely to be formed via penetration of liquid-like propanol molecules into the LiI film.

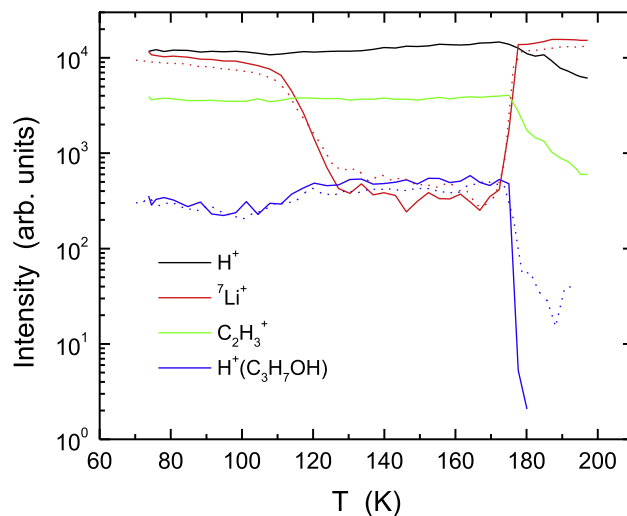


Fig. 1. Temperature-programmed TOF-SIMS intensities of typical ions sputtered from the 1-propanol films (50 ML) on the HOPG substrate, obtained after adsorption of LiI additives (0.2–0.3 ML) on the film surface at 70 K. The result obtained using the film deposited at 70 K (solid lines) is compared with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

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