



Surface freezing and molecular miscibility of binary fluoroalkanol-alkanol liquid mixture



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ABSTRACT

The surface freezing (SF) of liquid 6-perfluorohexyl hexanol (F₆H₆OH)–1-dodecanol (C₁₂OH) mixture was studied by surface tension, external reflection absorption FTIR (ERA-FTIR), and X-ray reflectivity (XR) measurements. The surface tension vs. temperature curve of pure C₁₂OH liquid shows a sharp break point at the surface liquid (SL)–SF phase transition temperature *T_s*. The surface tension of pure F₆H₆OH, on the other hand, decreases monotonically with increasing temperature. The entropy of surface formation in the SF state of C₁₂OH is large negative due to a well-ordered structure at the surface. The electron density profile determined by XR showed that the C₁₂OH molecules form bilayer stabilized by the hydrogen bonding between hydroxyl groups facing each other through water molecule intercalated in between them. In the F₆H₆OH–C₁₂OH system, the estimation of surface composition indicated that the SL state is enriched in F₆H₆OH compared to bulk liquid. The negative excess entropy in the SL layer suggests that F₆H₆OH molecules form domains at the surface. Furthermore, the surface composition and electron density profile in the SF state indicated that a small amount of F₆H₆OH mix with C₁₂OH in the SF bilayer in which F₆H₆OH molecules preferentially exist in the upper layer of the bilayer.

1. Introduction

The adsorbed films at soft interfaces such as gas/liquid and liquid/liquid interfaces are regarded as a fundamental structure of complicated soft matters including emulsion, liposome, biological membrane and so on. Thus, the study on the structure and property of soft interface is crucial to understand the essential of structure–function relation of various biological and physicochemical phenomena of soft matters. In the mixed component system, particularly, the miscibility of molecules at the interface strongly depends not only on the molecular structure but on the mutual interaction between the adsorbed molecules [1].

It is generally known that the interaction between hydrocarbon (HC) and fluorocarbon (FC) is weaker than those between the same species [2,3]. In our previous studies on the adsorbed film of 1-icosanol (C₂₀OH) and 1H,1H,2H,2H-perfluorodecanol (FC₁₀OH) mixture at the hexane/water interface, the miscibility of molecules in the adsorbed film were examined by constructing the 2D phase diagram (phase

diagram of adsorption; PDA) and evaluating the excess thermodynamic quantities of adsorption [4,5]. An important finding was that the mixing of C₂₀OH and FC₁₀OH molecules in the expanded state is accompanied by a positive excess Gibbs energy and volume. In the condensed state, furthermore, both components are practically immiscible. These results are primarily due to weaker interaction between C₂₀OH and FC₁₀OH molecules than those between the same ones, which is more enhanced in the condensed film in which the molecules are densely packed with each other. The analysis of X-ray reflectivity (XR) data demonstrated that in the expanded state, FC₁₀OH molecules form condensed phase domain coexisting with low density gaseous phase around the expanded–condensed phase transition point [6,7].

Surface freezing (SF) is the phenomena of the two-dimensional condensed film formation at temperature *T_s*, which is a few degrees above the bulk freezing temperature even when the bulk is in liquid state. It was reported by Earnshaw et al. as a break point on the surface tension vs. temperature curve of liquid *n*-heptadecane. The SF phenom-

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ena provide us a lot of experimental and theoretical interests, and many researchers have been studied them in various methods such as simulation, ellipsometry, sum frequency spectroscopy, light scattering, and so on [8–11]. Among others, Deutsch et al. have been investigated the SF of alkane and alkanol systematically by surface tension, X-ray reflectivity (XR), and grazing incidence X-ray diffraction (GIXD) measurements [12–17]. They found that SF phenomena are observed for n -alkane (C_n ; $CH_3(CH_2)_{n-2}CH_3$) with carbon numbers of $16 \leq n \leq 50$, and that the SF layer is monolayer with hexagonal molecular packing. Furthermore, it was claimed that hydrated n -alkanol (C_nOH ; $CH_3(CH_2)_{n-1}OH$) with even carbon number in a range of $10 \leq n \leq 28$ exhibits SF with bilayer structure intercalated water between hydroxyl groups of alkanol facing each other. In addition, the rheological properties of 1-dodecanol ($C_{12}OH$) monolayer at the air/water interface have been studied in relation with the appearance of 2D phase transition [18,19]. In particular, Ortega and Rubio found that the monolayer goes through a 2D liquid–solid phase transition at temperature more than 14 K above the bulk freezing of $C_{12}OH$ [18].

Since the SF is the condensed film formation at the liquid surface, the structure and property of SF layer is expected to be determined by the mutual interaction between the film forming molecules. Therefore, the study on SF at the surface of binary liquid mixtures is highly advantageous to clarifying the miscibility of molecules at the surface mainly from the viewpoint of the mutual interaction between them without taking account of the solute–solvent interaction. In our previous study on SF phenomena of 1-perfluorooctyl decane (F_8H_{10})- n -octadecane (C_{18}) mixture, the surface composition and excess entropy and energy of surface were evaluated in order to examine the miscibility of the molecules at the surface [20]. It was concluded that the mixing of F_8H_{10} and C_{18} at the surface is non-ideal because of weaker mutual interaction between different molecules than those between the same ones. Furthermore, the negative excess entropy of surface suggested that F_8H_{10} molecules form domains in the surface liquid (SL) state.

In this study, we aim at clarifying the effect of molecular interaction on the mixing of molecules at liquid surfaces of binary fluoroalkanol-alkanol mixture and thus 6-perfluorohexyl hexanol (F_6H_6OH)-1-dodecanol ($C_{12}OH$) mixture was employed. The surface tension of the liquid mixture was measured as a function of temperature, and then the surface composition and the excess entropy and energy of surface were evaluated. XR measurement was applied to the SF state to discuss the interfacial structure in terms of the electron density profile along surface normal. The results obtained were compared with those of 1-undecanol ($C_{11}OH$)- $C_{12}OH$ mixture to discuss the effect of the mutual interaction between FC and HC chains on the structure and the miscibility of molecules at the surface. The effect of SF structure and hydroxyl group on the miscibility of molecules at the surface is further examined by comparing the surface phase diagram (2D diagram) with that of F_8H_{10} - C_{18} mixture.

2. Experimental

2.1. Materials

1-Dodecanol ($C_{12}OH$) purchased from Aldrich Co. Ltd. was purified by fractional distillation under reduced pressure. 6-perfluorohexyl hexanol (F_6H_6OH) purchased from Daikin Kogyo was purified by fractional distillation under reduced pressure and recrystallization twice from chloroform solution. Their purities were estimated to be more than 99% by gas-liquid chromatography and checked by observing no time dependence of surface tension of pure liquid during 60 min (less than 0.1 mN m^{-1}). Water used in this study was produced from a Millipore Milli-Q system.

Before surface tension and X-ray reflectivity measurements, each alcohol was stirred with water for 1 hour by magnetic rotor at desired temperatures and allowed to stand for one day in order to saturate them

with each other until the mixtures separate completely into two transparent phases.

2.2. Methods

2.2.1. Surface tensiometry

The surface tension γ of F_6H_6OH - $C_{12}OH$ liquid mixture was measured as a function of temperature T and the mole fraction x_2 of $C_{12}OH$ in the mixture under atmospheric pressure by the pendant drop method based on the shape analysis of liquid drops [21]. The experimental error in γ value was estimated within $\pm 0.05 \text{ mN m}^{-1}$.

2.2.2. X-ray reflection

X-ray reflectivity from liquid surface was measured at the beamline BL37XU in SPring-8 by using a liquid surface spectrometer [22]. X-ray beam introduced into the experimental hut was diffracted by a Ge (111) crystal to select the energy (25 keV) and adjust the incident angle of the beam. A slit placed in front of the sample cell determines the beam size. The slit gaps were $10 \mu\text{m}$ in vertical and $200 \mu\text{m}$ in horizontal. The footprint on the interface was around 2 cm along the beam path. A N_2 gas ion chamber was put between the slit and sample cell to measure the flux of incident beam. The intensity of reflected beam was detected by two-dimensional detector (PILATUS) equipped with a copper-aluminum absorber to reduce the X-ray photons to optimum amounts.

The cell is made of stainless steel and equipped with Mylar windows. In the specular reflection condition, the scattering vector $\mathbf{Q} = \mathbf{k}_{\text{scat}} - \mathbf{k}_{\text{in}}$ is only in normal to the interface (z -direction) and given by $Q_z = (4\pi/\lambda)\sin\alpha$, where $\lambda (= 0.496 \text{ \AA})$ is the X-ray wavelength used in present study, and α is the incident angle. The measurement was carried out at given T and x_2 under atmospheric pressure. Temperature was controlled by the Peltier device equipped to the cell.

X-ray reflectivity $R(Q_z)$ measured as a function of the scattering vector Q_z can be interpreted to yield the electron density profile normal to the interface. Under the first Born approximation, $R(Q_z)$ is expressed as

$$\frac{R(Q_z)}{R_F(Q_z)} \cong \left| \frac{1}{\rho_0} \int \frac{d\langle \rho(z) \rangle}{dz} \exp(-iQ_z z) dz \right|^2, \quad (1)$$

where $\rho(z)$ is the electron density profile averaged over the interfacial plane along with z -direction which is normal to the interface, ρ_0 is the electron density of bulk liquid phase, and Fresnel reflectivity $R_F(Q_z)$ for an ideally smooth interface is expressed as

$$R_F(Q_z) \approx \left| \frac{Q_z - Q_z^T}{Q_z + Q_z^T} \right|^2, \quad (2)$$

where Q_z^T is the z -component of the wave vector transfer with respect to the lower phase given by

$$Q_z^T = \sqrt{Q_z^2 - Q_c^2}. \quad (3)$$

Here, the total reflection of X-ray from the lower phase occurs for $Q_z < Q_c$. Here, the scattering vector at critical angle Q_c is calculated by using

$$Q_c = 4\sqrt{\pi\rho_0 r_e}, \quad (4)$$

where r_e is the classical electron radius $r_e = 2.818 \text{ fm}$.

The SF layer is modeled by n slabs. Interfaces at the top and bottom of each slab will be fluctuated with thermally excited capillary waves [23,24], which broadens the interface with an error function of interfacial roughness σ . Thus, the electron density for n -slab model is given by [6,25]

$$\frac{\langle \rho(z) \rangle}{\rho_0} = \frac{1}{2} \sum_{i=1}^n (\rho_i - \rho_{i+1}) \left\{ 1 + \text{erf} \left(\frac{z + \sum_{j=1}^i L_j}{\sigma\sqrt{2}} \right) \right\}, \quad (5)$$

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