Surface Freezing of Binary Liquid Mixtures

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Almost all substances melt from the surface (surface melting). However, it was found that liquid normal alkanes with 15~50 carbon atoms form solid monolayer at the temperature $T_s$, which is a few degrees above the bulk freezing temperature $T_f$, corresponding to surface freezing (SF). The aim of this study is to clarify the relation between miscibility and molecular interaction in SF layers formed on the binary liquid mixture. We employed $n$-alkane ($C_nH_{2n+2} : C_n$) and $n$-alkanol ($C_nH_{2n+1}OH : C_nOH$) as hydrocarbon (HC) substances and 1-(perfluorooctyl)decane (F$_{8}H_{10}$) as fluorocarbon (FC) one, and investigated the SF phenomenon in the mixed C$_{17}$-C$_{18}$, C$_{11}OH$-C$_{12}OH$, and F$_{8}H_{10}$-C$_{18}$ systems by the surface tension measurement and thermodynamic data analysis.

The surface tensions $\gamma$ of the liquid mixtures were measured as a function of temperature $T$ and the mole fraction of C$_{18}$ or C$_{12}OH$ in the mixtures $x_2$ under atmospheric pressure by the pendant drop method. Bulk freezing temperature $T_f$ was determined by differential scanning calorimeter (Parkin-Elmer Pyris1). Two alcohols and their mixture were saturated with water at desired temperatures before measurements.

**Pure component systems:**

The $\gamma$ vs. $T$ curves of pure C$_{17}$, C$_{18}$, and F$_{8}H_{10}$ systems show a distinct break point at $T_s$ corresponding to SF. The $\gamma$ value increases with increasing $T$ below $T_s$, indicating large negative entropy of interface formation $\Delta s$. The larger $\Delta s$ of F$_{8}H_{10}$ than C$_{18}$ in the SF state comes from that the packing of HC chain of F$_{8}H_{10}$ is a little loose due to the difference in cross sectional area of HC and FC chains, which was confirmed by the external reflection absorption FTIR (ERA-FTIR) spectra.

**Binary component systems:**

In the C$_{17}$-C$_{18}$ mixture, SF occurred at all $x_2$. The $\Delta s$ value is around $-0.9$ mJ K$^{-1}$ m$^{-2}$ below $T_s$, indicating the formation of two dimensional solid monolayer at the surface of liquid. The estimation of surface composition of C$_{18}$ $x_2^{\sigma}$ and the excess entropy of mixing at the surface $s^{\sigma,E}$ suggests that C$_{17}$ and C$_{18}$ molecules mix almost ideally both in the surface liquid (SL) and SF states.

In case of F$_{8}H_{10}$-C$_{18}$ system, on the other hand, SL layer is enriched in F$_{8}H_{10}$ with lower surface tension than C$_{18}$ compared to bulk liquid. The $s^{\sigma,E}$ value is negative which is due to the domain formation of F$_{8}H_{10}$ molecules in the SM layer. Furthermore, the $x_2^{\sigma}$ value in SF state is close to zero or unity, indicating that F$_{8}H_{10}$ and C$_{18}$ are practically immiscible mainly due to the weak interaction between different components.

The $\gamma$ vs. $T$ curves of pure C$_{11}OH$ and C$_{12}OH$ systems also show a break, and the $\Delta s$ value below $T_s$ (ca. $-0.9$ mJ K$^{-1}$ m$^{-2}$) is much smaller than that of the condensed monolayer at the liquid C$_{9}OH$/water interface (ca. $-0.45$ mJ K$^{-1}$ m$^{-2}$). This difference suggests the bilayer formation in the SF state of C$_{9}OH$. The mixing of C$_{11}OH$ and C$_{12}OH$ at the surface of liquid mixture will be discussed in terms of surface composition and excess entropy of mixing at the surface.