Negative Line Tension for an Ionic Liquid on a Hydrophobic Fluoroalkylsilane Coating

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Contact angles were measured for sub-nanoliter-scale droplets of an ionic liquid on an extremely smooth and homogeneous hydrophobic fluoroalkylsilane coating. Subsequently, line tension values were calculated using a new model considering the direction of hydrostatic pressure. The sign of the line tension obtained from this system was negative. Surface hydrophobicity plays an important role in determining the line tension sign.

Line tension is known to exist near the three-phase contact line for a liquid droplet on a solid surface. The effect of line tension on the interfacial energy balance is described as,

$$\gamma_{\mathrm{LV}} \cos\theta = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} - \frac{\sigma}{r} \qquad (1)$$

where r is the radius of the solid–liquid contact area, θ denotes the contact angle, γ_{SL}, γ_{SV}, and γ_{LV} respectively signify the interfacial free energies per unit area of solid–liquid, solid–gas, and liquid–gas interfaces, and σ stands for the line tension. As is readily apparent from eq 1, the effect of line tension increases with decreasing contact radius, namely, the droplet volume.

Very recently, after preparing an extremely smooth and homogeneous fluoroalkylsilane (trifluoropropyltrimethoxysilane, FAS3) coating, we evaluated contact angles for microliter (µL)-scale and sub-nanoliter (nL)-scale droplets of an ionic liquid (1-hexyl-3-methyl imidazolium/tetrafluoroborate, HMI). The ionic liquid was used to avoid rapid evaporation during measurements.[1] Results revealed that the liquid's hydrostatic pressure markedly affects the line tension measurements from the contact angle when using µL-scale droplets, although the droplet apparently has a spherical cap geometry. For small droplets, e.g., sub-nL-scale droplets, this effect is almost negligible; the precise line tension values are obtainable.[2] The line tension value obtained in the system was $2.0 \times 10^{-8}\,\mathrm{J\,m^{-1}}$.

Recent studies have revealed that the sign of the line tension is not always positive; it is sometimes negative.[3–5] Marmur et al. showed theoretically that the line tension sign changes from positive to negative with increasing contact angle from hydrophilic ($\theta < 90^\circ$) to hydrophobic ($\theta > 90^\circ$).[4] Because FAS3 coating is hydrophilic (static water contact angle of $79 \pm 1^\circ$), we prepared a highly hydrophobic smooth homogeneous coating using a different silane with longer fluoroalkyl moiety in this study. Line tension measurements were then conducted from contact angles for both µL-scale and sub-nL-scale droplets of the same ionic liquid.

A Si plate ((100)) was irradiated using vacuum ultraviolet light for precleaning, and was then heated with 20 µL of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrimethoxysilane (FAS17, $\mathrm{CF_3(CF_2)_7(CH_2)_2Si(OCH_3)_3}$, TSL8233, GE Toshiba Silicones, Tokyo, Japan) in a Petri dish using flowing $\mathrm{N_2}$ at 150 °C for 60 min. The coated surface was rinsed with toluene, acetone, and water, and then dried. The FAS17 coating surface roughness was evaluated in a 5-µm square area using atomic force microscopy (AFM, JSPM-4200; JEOL, Tokyo, Japan) with a Si cantilever (NSC36-c; MikroMasch, Estonia). Static contact angles of 3 µL water droplets were measured using a contact angle meter (Dropmaster 500; Kyowa Interface Science Co., Ltd., Japan) with the sessile drop method. The sliding angle (SA) was evaluated for 30 µL water droplets using an automatic measurement system (SA-20; Kyowa Interface Science Co., Ltd.).

As in a previous study, HMI (density $1.15\,\mathrm{g\,mL^{-1}}$, viscosity $195\,\mathrm{mm\,s^{-1}}$, surface energy $35.8 \pm 1.1\,\mathrm{mJ\,m^{-2}}$; Aldrich) was used as the liquid for line tension measurements. Contact angles of the ultrasmall droplets of HMI were evaluated using an automatic microscopic contact angle meter (MCA-3; Kyowa Interface Science Co., Ltd.) The sub-nL-scale liquid droplets (<5, 10, 20, 50, 100, and 200 pL) were placed on the FAS17 coating. All these evaluations were conducted in ambient air at room temperature (around 25 °C). The relative humidity was approximately 25%. To compare the droplet size dependence, µL-scale droplets (0.2, 0.5, and 1.0 µL) were evaluated under identical conditions using the commercial contact angle meter described above. For each droplet mass, contact angles were evaluated at five points and then averaged.

Figure 1 presents AFM image of the FAS17 coating. No particulate agglomerates were observed in the coating. The surface roughness value (*R*a) was 0.20 nm. The respective static water contact angle and sliding angle of water droplets were 107 ± 1 and $14 \pm 1^\circ$.

As the previous study showed, the force based on the hydrostatic pressure in the liquid is described as $\rho g h^2/2\,\mathrm{N\,m^{-1}}$ (ρ, liquid density; g, gravitational acceleration; and h, droplet height). We obtained the following equation as the relation between $\cos\theta$ and contact radius r in the previous study.[2]

$$\cos\theta = \frac{\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}}{\gamma_{\mathrm{LV}}} - \frac{\sigma}{\gamma_{\mathrm{LV}}} \cdot \frac{1}{r} + \frac{\rho g}{2\gamma_{\mathrm{LV}}} \left(\frac{(1-\cos\theta)}{\sin\theta} r \right)^2 \qquad (2)$$

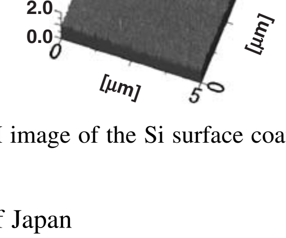

Figure 1. AFM image of the Si surface coated with FAS17.

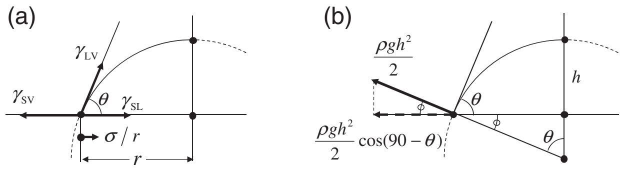

Figure 2. (a) Balance between line tension and surface tension at the three-phase contact line. (b) Contribution of hydrostatic pressure with consideration of its direction at the three-phase contact line.

The third term on the right side of eq 2 was regarded as the hydrostatic pressure term. However, it is more appropriate to consider its direction for practical application to Young's equation (Figures 2a and 2b). Therefore, we multipled $\cos(90-\theta)$ to this term to obtain the horizontal element of hydrostatic pressure and reconstructed this equation because the angle formed by the radius from the center of the circle (liquid–air interface) and the solid surface is estimated as $90-\theta$. The new relation between $\cos\theta$ and contact radius r is given as shown below.

$$\cos\theta = \frac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}} - \frac{\sigma}{\gamma_{LV}}\frac{1}{r} + \frac{\rho g}{2\gamma_{LV}}\frac{((1-\cos\theta)r)^2}{\sin\theta} \quad (3)$$

The result of application of this equation to a sample used in a previous study (the case of FAS3) is presented in Supporting Information.[6] The values obtained from the new model show better agreement with previous results, especially in the microliter range. Moreover, values obtained from eq 3 by summing static pressure term to the approximate line of sub-nL-scale area (▲) correspond better with experimental data than the previously calculated values (×). These results imply that consideration of the hydrostatic pressure direction provides a better account of the contact angle liquid mass dependence.

Figure 3 shows $\cos\theta$ and $1/r$ plots for µL-scale and sub-nL-scale droplets. In the sub-nL-scale area, where the effect of hydrostatic pressure is almost negligible, all plots exhibited a linear relation between $\cos\theta$ and $1/r$. However, its slope is positive; the calculated line tension value was $-1.5 \times 10^{-8}\,\mathrm{J\,m^{-1}}$. For µL-scale droplets, the slope was negative, similar to that of FAS3. This slope value is probably attributable to the large contribution of hydrostatic pressure terms. The sign of line tension on the FAS3 coating is positive. However, it was negative for the FAS17 coating. It is noteworthy that no remarkable difference in contact angle hysteresis exists between FAS3 and FAS17.[6]

Although the contact angles of FAS17 coating for HMI are around 85° and less than 90°, its line tension sign was negative. A plausible explanation of this result is the self-assembled monolayer coating surface. Marmur's model includes the assumption of a rigid homogeneous solid surface.[4] However, de Gennes et al. found theoretically that substrate materials affect the wettability of liquid on the coating when the liquid thickness is sufficiently larger than that of the coating.[7] The thicknesses of fluoroalkylsilanes used in our study are 0.42 (FAS3) and 1.33 nm (FAS17), respectively.[8] These are much smaller than the liquid thickness. Therefore, it is expected that the Si substrate affects macroscopic wetting phenomena such as the contact angle to some degree. On the other hand, line tension exists only near the three-phase contact line,[9] and the liquid is not thick. Consequently, the contribution of the substrate will be negligible, and interaction between liquid molecules and fluoroalkyl moiety in FAS17 will determine the line tension magnitude and sign. This difference might provide switching of the line tension sign at a contact angle less than 90°. Results of this study demonstrate that highly hydrophobic fluoroalkylsilane provides negative line tension. Detailed investigations of the coating thickness effects on switching of the line tension sign will be undertaken as future work.

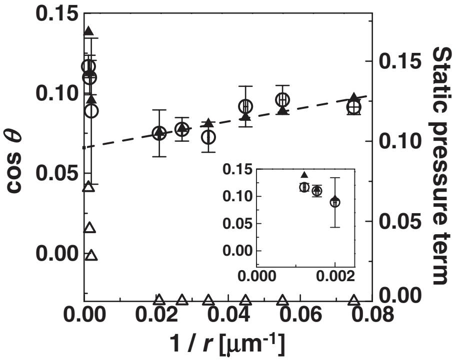

Figure 3. Relation between $\cos\theta$ and $1/r$ for µL-scale and sub-nL-scale droplets on the FAS17 coating (○, experimental values; △, improved hydrostatic pressure terms in eq 3; and ▲, improved calculated values in eq 2).

References and Notes

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