Droplet Size Dependence of Line Tension for an Ionic Liquid on a Smooth Silane Coating

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Line tension was measured for microliter-scale and subnanoliter-scale droplets of an ionic liquid on a highly smooth and homogeneous fluoroalkylsilane coating. Values for microliter-scale droplets were two orders larger than those for subnanoliter-scale droplets despite their identical combinations of solid surfaces and liquid. Scale factors related to this measurement and hydrostatic pressure from the liquid play an important role in the discrepancy.

Line tension derives from the curvature of the three-phase contact line for a liquid droplet on a solid surface. When effects of surface stains or adsorption of molecular substances are negligible, the wettability on a smooth solid surface is commonly evaluated by the contact angle (θ) given by Young's equation:

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

where r is the radius of the solid–liquid contact area, and 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. The line tension is described as σ in the equation. This value is quite small compared to other interfacial free energies. Therefore, the effect of this tension is generally ignored.

The values of line tension and other interfacial free energies are constant in a solid–liquid system. Therefore, a linear relation is obtainable between $\cos\theta$ and $1/r$. By measuring contact angles with different masses of the liquid droplet and plotting $\cos\theta$ and $1/r$, we can obtain the line tension value from the slope ($-\sigma/\gamma_{\mathrm{LV}}$). The practical value of the line tension measured using this method ranges from 10^{-9} to 10^{-5} J·m^{-1}.[1–4]

As might be readily apparent from Young's equation, the effect of line tension increases concomitantly with decreasing contact radius, namely, the droplet mass. Various previous studies were performed using microliter-scale droplets for this measurement, but those using subnanoliter-scale droplets are few.[5] In the present study, we measured and compared line tension values using microliter-scale droplets and subnanoliter-scale droplets. The problem of rapid evaporation for subnanoliter-scale droplets was avoided using ionic liquids. For this study, we prepared a highly smooth and homogeneous fluoroalkylsilane coating on a silicon surface using chemical vapor deposition (CVD). Then, line tension measurements were performed on the coating.

A Si plate ((100), 15×40 mm^2) was precleaned using vacuum ultraviolet light irradiation. The Si plate was set into a glass container (Petri dish) with 0.02 µL of trifluoropropyltrimethoxysilane (FAS3, $CF_3(CH_2)_2Si(OCH_3)_3$, GE Toshiba Silicones, Tokyo, Japan) and sealed with a glass cap under dry N_2 conditions. Then, the container was heated in an oven to 100 °C for 90 min with flowing dry N_2. After that heat treatment, the plates' surfaces were rinsed using flowing toluene, acetone, and water; then they were dried at 80 °C in air.

Surface roughness of FAS3 coating was evaluated in a 5-µm square area using atomic force microscopy (AFM, JSPM-4200; JEOL, Tokyo, Japan) with a Si cantilever. Static contact angles of 3-µL water droplets were measured with a contact angle meter (Dropmaster 500; Kyowa Interface Science Co. Ltd., Saitama, Japan) using 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.).

In this study, an ionic liquid, 1-hexyl-3-methylimidazolium tetrafluoroborate (HMI, density 1.15 g·mL^{-1}, viscosity 195 mm·s^{-1}; Aldrich Chemical Co., Inc.) was used for measurement of the line tension. The surface energy of the liquid was evaluated using pendant drop method. Contact angles of ultrasmall droplets of HMI were evaluated using an automatic microscopic contact angle meter (MCA-3; Kyowa Interface Science Co., Ltd.). Liquid droplets of subnanoliter-scale (<5, 10, 20, 50, 100, 200, and 500 pL) were placed on the FAS3 coating. The contact angle, the droplet radius, and their height were obtained by analyzing the recorded image. 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, microliter-scale droplets (0.2, 0.5, 1.0, and 2.5 µL) were also evaluated under identical conditions using the commercial contact angle meter described above. Contact angles were evaluated at 7 points for each droplet mass, and then averaged.

Figure 1 portrays AFM images of the FAS3 coating. No particulate agglomerates were observed in the coating; the surface roughness value (R_a) was 0.20 nm. Static water contact angle and sliding angle of water droplets were respectively $79 \pm 1^\circ$ and $16 \pm 2^\circ$. The surface energy of HMI was 35.8 ± 1.1 mJ·m^{-2}.

Figure 2 depicts $\cos\theta$ and $1/r$ plots for microliter-scale and subnanoliter-scale droplets. In this area, plots in Figure 2 exhibit a linear relation between $\cos\theta$ and $1/r$ in each range. However, the calculated line tension values from the plots were 1.4×10^{-6} J·m^{-1} for microliter-scale droplets, and 2.0×10^{-8} J·m^{-1} for subnanoliter-scale droplets. Values for microliter-scale droplets were two orders larger than those for subnanoliter-scale droplets despite their identical combinations of solid surfaces and liquid. This large discrepancy is difficult to explain simply by the difference of relative surface roughness dimension

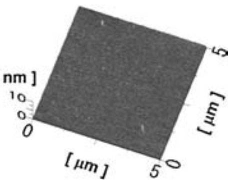

Figure 1. AFM image of the Si surface coated with FAS-3.

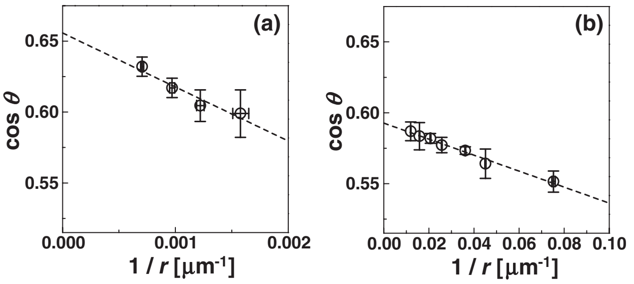

Figure 2. Relation between $\cos\theta$ and $1/r$ for (a), microliter-scale droplets and (b), subnanoliter-scale droplets.

or nanoscale heterogeneity in the surface. Calculations from the practical contact radius and height revealed that the droplet on the FAS3 coating could be assumed to have spherical cap geometry (see Supporting Information).[6] The shape deformation by gravity is apparently not remarkable for either microliter-scale or subnanoliter-scale droplets. A similar result was obtained using a different ionic liquid.[6] Therefore, this trend is not a special case of this solid–liquid combination.

McHale et al. pointed out that the effect of gravity becomes remarkable when the droplet radius is more than 10% of its capillary length.[7] Based on the obtained surface energy of HMI, the length was calculated as 1.76 mm. Therefore, 10% of the capillary length corresponds to 176 μm; this value is almost intermediate between microliter-scale and subnanoliter-scale droplets in this study.

We turned over the FAS3 coating and examined the droplet size dependence of line tension by setting microliter-scale droplets using a three-phase syringe to the reverse side.[6] In this alignment, the direction of gravity was opposite to the usual direction. The result of this line tension was $2.6 \times 10^{-6}\,\mathrm{J{\cdot}m^{-1}}$, the sign was changed to negative and the absolute value was of almost identical order. Shape analysis revealed that the droplet could be assumed as having spherical cap geometry, even in this alignment.[6] This result suggests that gravity affects the line tension value for microliter-scale droplets.

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; h, droplet height).[8] Therefore, Young's equation is redescribed as follows:

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

Consequently, the relation between $\cos\theta$ and contact radius r is given as

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

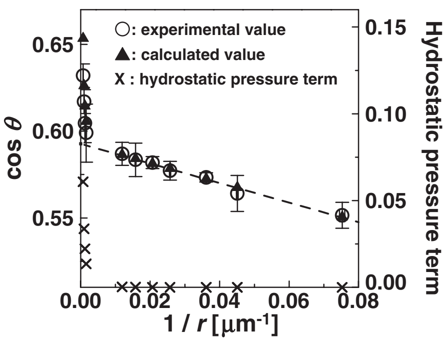

Figure 3. Relation between $\cos\theta$ and $1/r$: ○, experimental value; ▲, calculated value; ×, hydrostatic pressure term in eq 3.

Triangle plots in Figure 3 are those obtained from eq 3 by summing the static pressure term to the approximate line of the subnanoliter-scale area. As might be readily apparent from Figure 3, these plots correspond well with the experimental data trend in this droplet size range. This result suggests that hydrostatic pressure by liquid plays an important role in the line tension measurement from the contact angle using microliter-scale droplets.

When a droplet is sufficiently small, such as a subnanoliter-scale droplet, this effect is almost negligible (the plot of × is quite small in this range, as shown in Figure 3). Although the droplet shape apparently has a spherical cap geometry, the line tension measurement from the contact angle using microliter-scale droplets includes ambiguity. Precise line tension values are obtainable using smaller droplets such as subnanoliter-scale ones.

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