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APPENDIX

Controversial Phenomena

1 Effect of Naphthalene or N-Hexane on TBOS Adsolubilization

The different surface patterns were observed at low and high tracking force as shown in Figure A1. The maximum height difference of true image was less than that of inverted-contrast image. The edge of patches observed in inverted-contrast image was sharper than that in true image. It was believed that inverted-contrast image was due to strong short-range attractive van der Waals interaction between tip and surface and continuous penetration of the tip through scanned layer (Ceotto *et al.*, 2000).

The effects of naphthalene (99%, Sigma Chemical, St. Louis, MO) and n-hexane (98.5%, EM Science, Darmstadt, Germany) on TBOS adsolubilization were investigated on mica in C₁₆TAB aqueous solution both with and without TBOS. The applied concentration of TBOS, naphthalene and n-hexane were 295, 192 and 180 μM respectively. The penetration dept (Figure A2) through surface aggregates on mica in the system of C₁₆TAB-water, naphthalene-C₁₆TAB-water, n-hexane-C₁₆TAB-water, naphthalene-TBOS-C₁₆TAB-water, and n-hexane-TBOS-C₁₆TAB-water were found as 0.35, 0.6, 0.7, 1.0 and 2.5 nm when tracking force and scan rate are 0.9 nN and 3 Hz respectively. However, droplet pattern (Figure 4.5(b)) was observed on mica in TBOS-C₁₆TAB aqueous solution. The droplet pattern (liquid film instability) was due to reduction of adsorbed film-bulk interfacial tension through the critical interfacial tension value. The addition of n-hexane or naphthalene had less effect on the reduction of adsorbed film-bulk interfacial tension compared to the addition of TBOS, therefore, instability of the film could not be observed.

It was hypothesized that microviscosity inside admicelles changes due to adsolubilization effect when appropriate solute is introduced into surfactant solution. Along with this hypothesis, the viscosity of solute, *i.e.*, TBOS, naphthalene, or n-hexane, were considered. The viscosity of the solution of TBOS-water, naphthalene-water, and n-hexane-water sequentially increase from left to right when mole of each

solute is equal to each other. The same trend is found in the interfacial tension aspect. Consequently, the dept of tip penetration increases when overall microviscosity inside admicelles decreases. This concept led us to suggest that (1) naphthalene and n-hexane improved adsolubilization of TBOS and (2) n-hexane could better improve adsolubilization of TBOS than naphthalene. However, this phenomenon is still controversial because no reasonable forces versus separation curves were investigated.

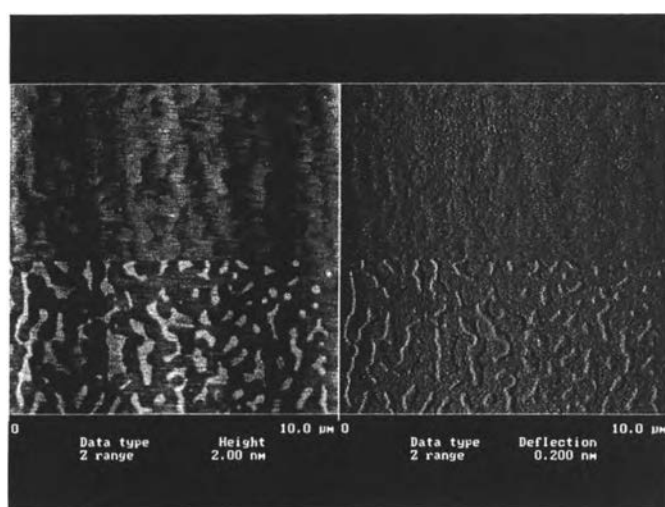


Figure 1 True (upper) and inverted-contrast (lower) images of surface aggregates on mica in naphthalene-295 μM TBOS-700 μM C_{16}TAB aqueous solution at adsorption time of 1 hour (scan rate = 3 Hz, tracking force = 0.9 nN).

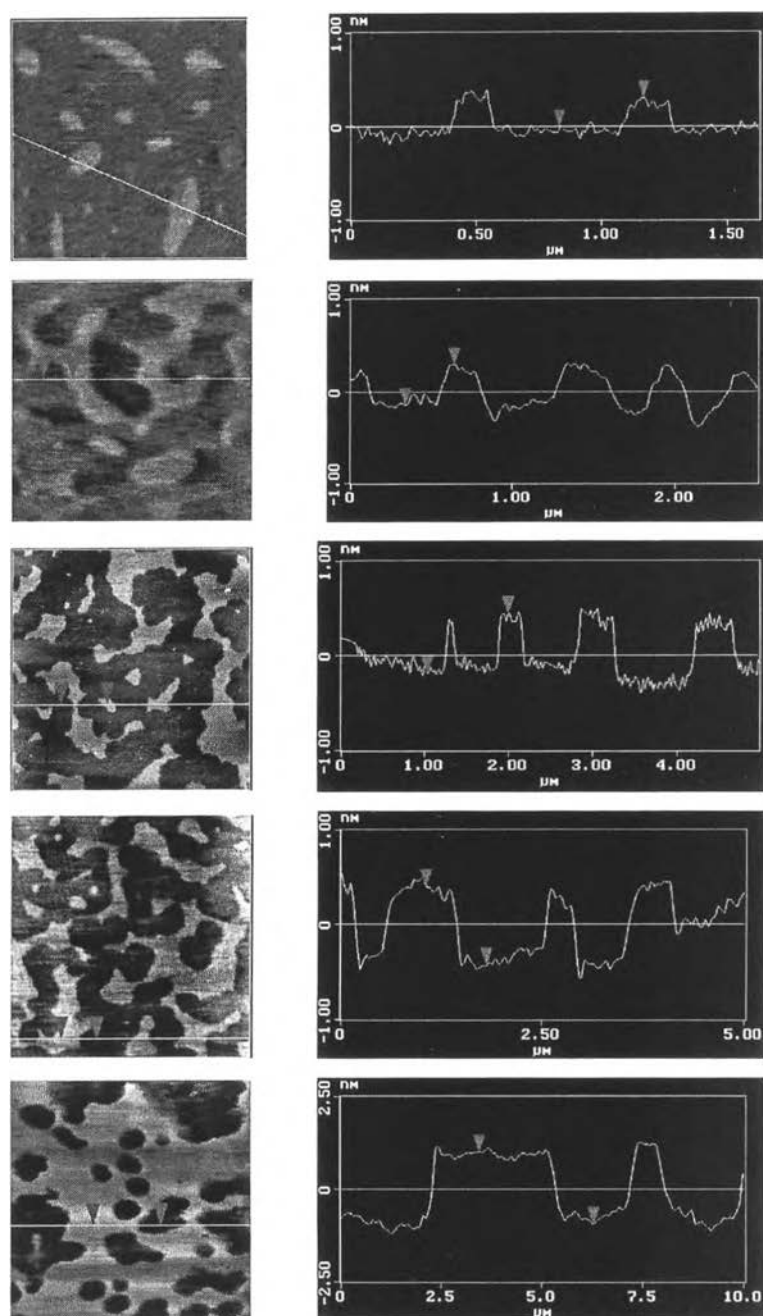


Figure 2 Inverted contrast images of surface aggregates on mica in (a) 700 μM C_{16}TAB (b) 192 μM naphthalene-700 μM C_{16}TAB (c) 180 μM n-hexane-700 μM C_{16}TAB (d) naphthalene-295 μM TBOS-700 μM C_{16}TAB and (e) n-hexane-295 μM TBOS-700 μM C_{16}TAB aqueous solution and their sention analysis (scan rate = 3 Hz, tracking force = 0.9 nN).

2 Non-Uniform Droplet Distribution

Non-uniform droplet distribution was observed on mica in 295 μM TBOS-700 μM C_{16}TAB aqueous solution. Large droplets were believed to be the combination of small droplets. Ordered arrangement of droplets was found in some area.

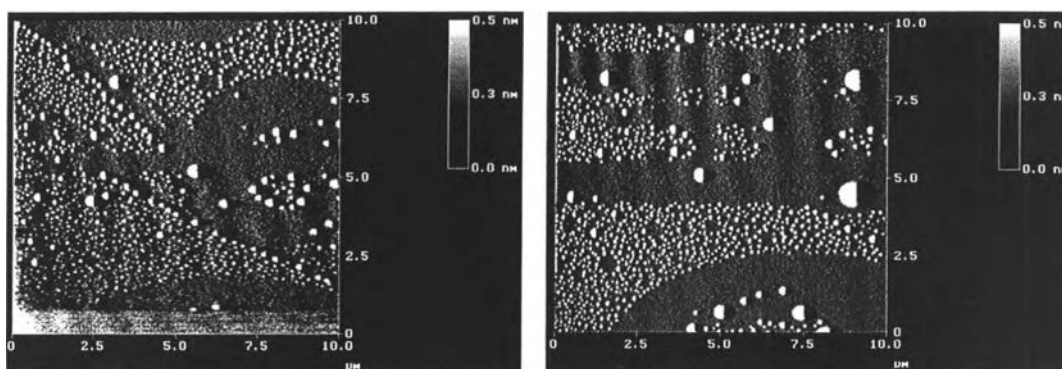


Figure 3 Deflection images of droplet distribution on mica in 295 μM TBOS-700 μM C_{16}TAB aqueous solution.

3 Effect of Excess Reaction Time

Dried silica films modified in 295 μM TBOS-700 μM C_{16}TAB aqueous solution and 295 μM TBOS aqueous solution were investigated. Mica was removed from modifying solution to water or C_{16}TAB aqueous solution in the case that modifying solution is TBOS-water or TBOS- C_{16}TAB -water until desired time. Excess reaction time was defined as the time counted after removing mica substrate from modifying solution until desired time. The excess reaction time was 24 hours for all experiments. For this excess reaction time, fibrous texture (Figure A4) was observed on dried silica film modified in 295 μM TBOS aqueous solution at both reaction time of 15 minutes and 2 hours. Whereas, droplet pattern (Figure A5) was observed on dried silica film modified in 295 μM TBOS-700 μM C_{16}TAB aqueous solution. Without excess reaction time, fibrous texture (Figure 4.8(c)) and droplet pattern (Figure 4.10(c)) were observed at 24-hour reaction time. It was believed that the structures observed after 24-hour reaction time was possible due to the further reaction of residual TBOS or TBOS- C_{16}TAB molecular cluster on surface.

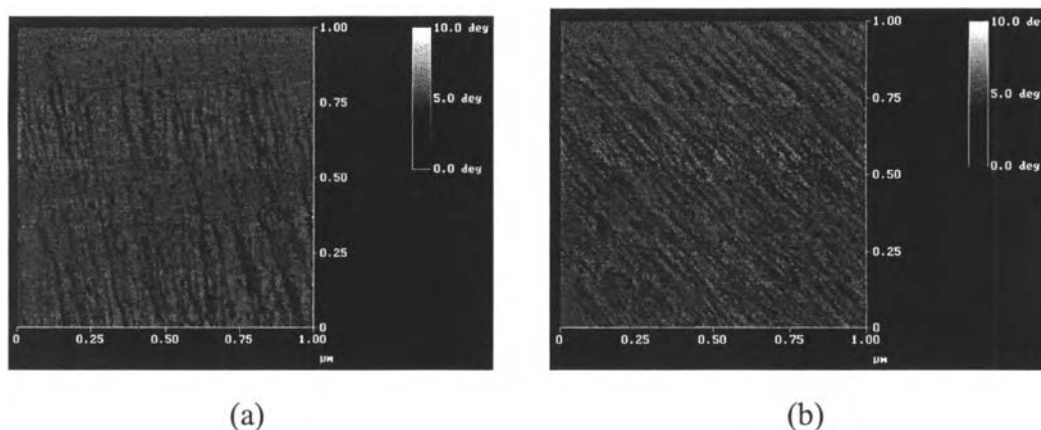


Figure 4 Phase images of dried silica films on mica modified within 295 μM TBOS aqueous solution with reaction time of (a) 15 minutes and (b) 2 hours and excess reaction time of 24 hours for both cases.

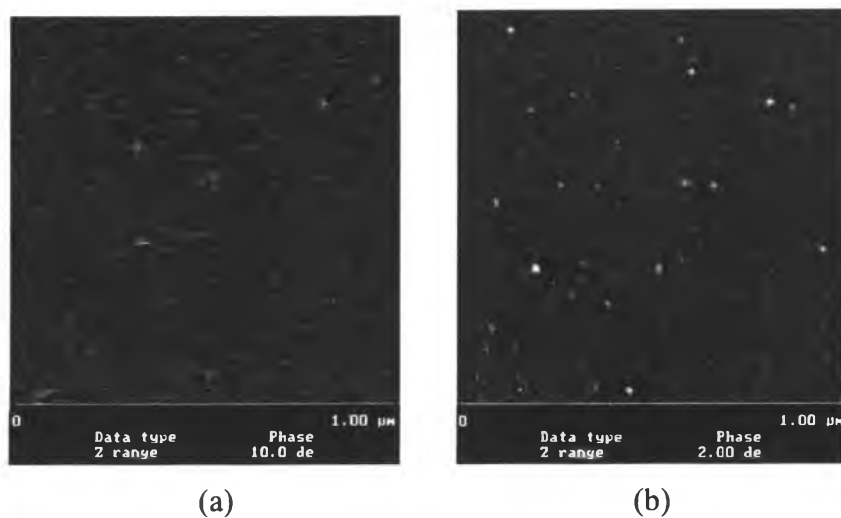


Figure 5 Phase images of dried silica films on mica modified within 295 μM TBOS- 700 μM C_{16}TAB aqueous solution with reaction time of (a) 15 minutes and (b) 2 hours and excess reaction time of 24 hours for both cases.

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