Macrocluster Formation of Alcohol on Silica Surface in Cyclohexane:
Analysis of Interfacial Energy between Adsorption Layer and Bulk Solution*

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Recently, we have found that alcohols adsorbed on the silica surface in non-polar liquids (cyclohexane, etc.) form ordered structures extending to several tens of nanometer through hydrogen bonding between the surface silanol groups and the adsorbed alcohols as well as between the adsorbed alcohols. We call this structure the surface molecular macrocluster. Surface forces measurement has revealed that the long range attraction appears from distances about twice of the macrocluster layer thickness. The bridging of the adsorption layers brings about the long range attraction due to the interfacial energy between the adsorption layer of molecular macroclusters and the bulk solution. In this study, the interfacial energies ($\gamma$) between the methanol adsorption layer and the bulk solution were evaluated by analyzing the long range attraction as well as pull-off force in methanol-cyclohexane binary liquid mixtures. The interfacial energy ($\gamma$) was evaluated to be 7.2 $\pm$ 0.3 mN/m, which was more than 10 times larger than that for methanol/cyclohexane interface at the phase separation (0.6 mN/m). This larger interfacial energy should be caused by the rather fixed orientation of methanol molecules at the interface due to the ordered structure of methanol molecules in a macrocluster. [DOI: 10.1380/ejssnt.2006.244]

Keywords: Atomic Force Microscopy; Alcohols; Solid-liquid interfaces; Clusters; Self-assembly

I. INTRODUCTION

It is well known that the properties of liquids adjacent to the solid surfaces or confined in nanometer spaces are different from those of bulk liquids [1-6]. This confinement and surface effects are becoming more important in the micrometer or nanometer scale devices such as micromachine, nanomachine, microchip, micro and nano particle assemblies, and so on. In the past decade, well designed porous materials [7], surface forces apparatus equipped with the shear force measuring systems [1-6, 8-13] and computer simulations [14-16] have been developed to study the structuring of confined liquids. However, these studies have been limited to the rather simple systems.

An interesting subject to study is the liquid adsorption onto solid-liquid interfaces from binary liquids, however, its study has been limited mainly to the adsorption isotherm measurement and its model analysis in spite of its basic and technological importance [17-19]. Recently, we have succeeded in identifying the structure of ethanol adsorbed on a silica surface in cyclohexane by employing the combination of surface forces measurement, adsorption excess isotherm measurement and infrared spectroscopy in the attenuated total reflection mode (ATR-FTIR) [20-22]. It has been found that ethanol forms a linearly associated polymer extending to ca. 15 nm from the surface through hydrogen-bonding between the surface silanol group and the hydroxy group of ethanol as well as between the hydroxy groups of the ethanol molecules. We use the term “surface molecular macrocluster” for this novel organized liquid structure. The adsorption layer consists of practically pure ethanol. Surface forces measurement has demonstrated the long range attractions from distances about twice of the macrocluster layer thickness (e.g. 35 $\pm$ 3 nm at 0.1 mol% ethanol). This indicated that the interfacial energy was generated between the bulk solution and the ethanol macrocluster layer, and the contact and overlap of the adsorption layers brought about the long range attraction to reduce the interface between the ethanol adsorption layer and bulk solution. Similar molecular macrocluster and long range attraction were also found for the 1-propanol and methanol on the silica surface in cyclohexane [23, 24]. This indicated that the molecular macrocluster formation induced the interfacial energy between the alcohol adsorption layer and the bulk solution even for the alcohols completely miscible with cyclohexane. In this study, we derived the equation for the long range attraction in terms of the interfacial energy $\gamma$. The $\gamma$ values for macroclusters of methanol was estimated by analyzing the long range attraction. The $\gamma$ value for the methanol-cyclohexane interface in bulk phase separation was also estimated from the attraction at $D = 0$ measured in methanol-cyclohexane binary liquid at methanol concentration of 9.1 mol% (above the critical concentration ca. 8.0 mol%) [25-27]. The obtained $\gamma$ values 7.2 $\pm$ 0.3 mN/m for methanol macrocluster at methanol concentration of 0.03-0.16 mol% was 10 times larger than the value $\gamma$ for bulk methanol-cyclohexane interface in phase separation (0.6 mN/m).

II. EXPERIMENTAL SECTION

A. Materials

Reagent grade cyclohexane (Nacalai Tesque) and methanol were dried with sodium and magnesium, respectively, and distilled immediately prior to use in order to avoid the influence of water. Reagent grade hydrofluoric acid from Stella Chemifa, sulfuric acid from Nacalai Tesque and hydrogen peroxide from Santoku Chemical were used as received.

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B. Surface forces measurement

The interaction forces \((F)\) between a glass sphere and a glass plate were measured as a function of the surface distance \((D)\) in methanol-cyclohexane mixtures using atomic force microscope (AFM, Seiko Instruments, SPI3700-SPA300) (Fig. 1) [28]. Colloidal glass spheres (Polyscience) and glass plates (Matsunami, micro cover glass) were washed in a mixture of sulfuric acid and hydrogen peroxide (4:1, v/v), and thoroughly rinsed with pure water. A colloidal glass sphere (4-5 µm in radius) was then attached to the end of a cantilever (Olympus, RC-800PS) with epoxy resin (Shell, Epikote1004). The spheres and the plates were treated with water vapor plasma (Samco, BP-1, 20 W, 13.56 MHz rf source in 0.6 Torr of argon and water, 50 mL/min flow rate) for 3 min just prior to each experiment in order to ensure the existence of silanol groups on the glass surfaces [29]. After plasma treatment, the cantilever and the glass plate were transferred to a homemade AFM fluid cell [20–22], while being kept in purified cyclohexane. The obtained data of force versus sample displacement (extension of piezo tube) profiles were converted to force \((F)\) versus surface distance \((D)\) profiles following the conventional procedure [28].

The obtained forces were normalized by the radius \((R)\) of the sphere using the Derjaguin approximation, \(F/R = 2\pi G_f\) [30]. Here, \(G_f\) is the interaction free energy per unit area between two flat surfaces. The radius \((R)\) was measured by an optical microscope equipped with a CCD camera. The individual spring constant of the cantilever was determined by measuring the resonant frequency of the cantilever before and after adding the mass (glass sphere) at the end of the cantilever [31]. The spring constants of the cantilever used in this study were within the range of 0.8-1.5 N/m.

III. ANALYSIS OF LONG RANGE ATTRACTION

Figure 2 shows the schematic illustration of the glass sphere (radius \(R)\) and plate which has adsorption layer of thickness \(t\), separated at the distance \(D\), together with the plausible structure of alcohol macrocluster in the adsorption layer. Here, the parameter \(x\) is the radius of overlapping area of the adsorption layers formed on the opposed surfaces.

Assume that no deformation occurs in the adsorption layers besides the overlapping area when they are in contact, and the interface between the adsorption layer and bulk solution has the energy per unit area \(\gamma\). The interfacial energy \(\gamma\) disappears inside of the overlapping area, and the attractive force due to the interfacial energy \(\gamma\) acts only along the perimeter of the overlapping area. Thus the total attraction \(F_\gamma\) caused by the interfacial energy becomes \(2\pi x\gamma\). Based on the geometry shown in Fig. 2, the normalized attractive force \(F_\gamma/R\) was described as follows.

\[
\frac{F_\gamma}{R} = -2\pi x\gamma = -\frac{2\pi\gamma\sqrt{(2t-D)(2R+D)}}{R}.
\]

In addition to the long range attraction, the short range repulsive force was observed and the interaction force profile exhibited the minimum at ca. 10 nm or less. This short range repulsion can be ascribed to the steric repulsion due to the stable molecular macroclusters adjacent to the surface similarly to the solvation force. Empirically, it is known that the solvation force can follow the exponential function [30, 32, 33]. Thus, we employed a single exponential function for the short range repulsive force. Combining Eq. (1) with the single exponential function
TABLE I: The methanol adsorption layer thickness $t$ and the interfacial energy between methanol macrocluster layer and the bulk solution $\gamma$, estimated through the analysis of the long range interaction force by Eq. (2).

| concentration (mol%) | $t$ (nm) | $\gamma$ (mN/m) |
|----------------------|----------|-----------------|
| 0.03                 | 16       | 7.7             |
| 0.04                 | 14       | 7               |
| 0.05                 | 15       | 7.4             |
| 0.07                 | 12.2     | 7.0             |
| 0.09                 | 13.5     | 7.0             |
| Average (0.03-0.09)   | 14.1 ± 1.4 | 7.2 ± 0.3 |

for repulsion, we obtained Eq. (2):

$$\frac{F_{\text{total}}}{R} = -\frac{2\pi \gamma \sqrt{(2t - D)(2R + D)}}{R} + A \exp \left( -\frac{D}{B} \right).$$

(2)

Here, $A$ and $B$ are the strength factor and the decay length of the solvation force, respectively. The measured interaction forces on approaching the surfaces were analyzed by Eq. (2) and the interfacial energies $\gamma$ were estimated.

The pull-off force measured on separation after the contact was also analyzed, and the interfacial energy $\gamma$ between molecular macrocluster layer and the bulk solution was estimated. It is known that the attraction at $D = 0$ (pull-off force) caused by the capillary bridge, e.g., the condensed water between hydrophilic surfaces in air, can be described by the following Eq. (3) [30]:

$$\frac{F_{\text{capillary}}}{R} = -4\pi \gamma \cos \theta.$$  

(3)

IV. RESULTS AND DISCUSSION

Figure 3 shows the example of the surface forces measured in methanol-cyclohexane binary liquids together with fitting curves drawn using Eq. (2). In pure cyclohexane, attractions appeared from a distance of 4 ± 2 nm which agreed well with the conventional van der Waals attraction calculated with the non-retarded Hamaker constants [30]. Addition of methanol drastically changed the interaction force. For 0.03 mol% methanol, the long-range attraction, which extended to 42 ± 5 nm, appeared and turned into repulsion at distances shorter than 2.3 ± 1.2 nm. The pull-off force also increased to 179 ± 10 mN/m. The shape of this long range interaction force profiles were similar to those observed in ethanol-cyclohexane as well as in 1-propanol-cyclohexane, indicating that the long range attraction was similarly caused by the contact of opposed adsorption layers and the short range repulsion was ascribed to a steric force caused by the overlap of structured layers [20–22]. This was confirmed by measuring the adsorption excess amount of methanol onto the glass surfaces [24]. At methanol concentration of 0.03-0.12 mol%, the methanol adsorption layer thickness was 13.0±2.7 nm, and was comparable to the half of the attraction range, 19.2 ± 1.9 nm. This supported that the adsorption layers on glass surfaces consisted of almost pure methanol and the long-range attraction was caused by the contact of these methanol adsorption layers. The long range interaction forces measured at 0.03-0.16 mol% methanol were well fitted using Eq. (2), and the parameters of the thickness $t$ and the interfacial energy $\gamma$ were evaluated. Table 1 summarizes the parameters $t$ and $\gamma$ obtained for the methanol molecular macrocluster layer at methanol concentrations of 0.03-0.09 mol%. Here, we limited our analysis to the data below 0.09 mol% methanol where the attraction started to decrease in spite of the constant amount of adsorption excess methanol. The decrease in the attraction above 0.09 mol% indicated that the interface might be no longer sharp enough possibly due to the exchange of methanol molecules between the adsorption
layers on the surface and those in the bulk solution [20–
22, 34].

The interfacial energies $\gamma$ at 0.03-0.09 mol% were almost constant and the averaged $\gamma$ was 7.2 ± 0.3 mN/m. The mean adsorption layer thickness $t = 14.1 \pm 1.4$ nm thus obtained agreed well with the value calculated based on the adsorption excess isotherm measurement 13.0 ± 2.7 nm [24]. One interesting point is that the measured attraction range was 6-7 nm longer than the attraction range obtained by fitting of Eq. (2). This difference in the attraction range between the measured and the calculated value ($\Delta D$, see Fig. 3a) could be explained by the bridging of the methanol adsorption layers formed on opposite two surfaces due to the deformation induced by the van der Waals force between methanol adsorption layers. The possible range of bridging of the methanol adsorption layers due to the van der Waals force is now under consideration.

The interfacial energies $\gamma$ between the methanol adsorption layer and the bulk solution at 0.03-0.09 mol% methanol were also evaluated from the pull-off force using Eq. (3). Table 2 shows the interfacial energies obtained from the pull-off force. The obtained mean interfacial energy, $\gamma = 15.8 \pm 1.6$ mN/m, was much larger than those estimated by the analysis of the attraction upon approaching. Here, the peculiar force profile was observed as shown in Fig. 4. At the beginning of decompression of the surface (c-d), the repulsive force increased although the lower surfaces were retracted. This might indicate the further growing of methanol adsorption layer during the decompression, which increases the overlapping area of adsorbed macrocluster layers, and increases the total work of adhesion, i.e., pull-off force.

As a comparison, the surface forces between glass surfaces were measured at methanol concentration of 9.1 mol%, which is higher than the critical concentration of phase separation of the methanol/cyclohexane mixtures (Fig. 5). It is known that the thick methanol rich layers start to grow on solid surfaces when the conditions approaches to the phase separation (pre-wetting transition) [25–27]. Figure 5 shows that the attraction appeared from a distance ca. 800 nm on approaching, and gradually increased with decreasing distance, and became $7.4 \pm 0.2$ mN/m at $D = 0$. On the decompression process, the attraction at $D = 0$ was similar to the value on approach, $7.4 \pm 0.2$ mN/m. On further decompression, the attraction gradually decreased and jumped to zero at $D \sim 5000$ nm (jump out). The attraction from ca. 800 nm observed on approach should be caused by the contact of the adsorbed layers, and indicating the formation of the methanol adsorption layers with a thickness of ca. 400 nm. The agreement of the attraction at $D = 0$ on approach and decompression ($7.4 \pm 0.2$ mN/m) indicates that no change occurred in the adsorption layer after contact. The gradual decrease in the attraction on the decompression process up to $D \sim 5000$ nm indicated that the deformation of the bridging of the adsorption layers. The profile of the attraction measured on approach could not be reproduced by Eq. (2), most probably due to the deformation of the methanol adsorption layer after bridging. Thus, the interfacial energy $\gamma$ was estimated from the attraction at $D = 0$, $7.4 \pm 0.2$ mN/m using Eq. (3) ($\gamma = F_{\text{pull-off}}/4\pi R$) [30] to be 0.6 mN/m. This $\gamma$ value agreed well with the literature value of $\gamma$ for the methanol-cyclohexane interface in the phase separation.

The interfacial energy $\gamma$ obtained for molecular macroclusters formed on the surfaces at 0.03-0.09 mol%, 7.2±0.3
The interfacial energy between methanol adsorption layer and the bulk solution $\gamma$, estimated through the analysis of pull-off force by Eq. (3).

| concentration (mol%) | pull-off force (nm) | $\gamma$ (mN/m) |
|---------------------|--------------------|-----------------|
| 0.03                | 179 ± 10           | 14.3 ± 0.8      |
| 0.04                | 194 ± 2            | 15.4 ± 0.2      |
| 0.05                | 216 ± 10           | 17.2 ± 0.8      |
| 0.07                | 216 ± 12           | 17.2 ± 1.0      |
| 0.09                | 212 ± 11           | 16.9 ± 0.9      |
| Average (0.03-0.09) | 199 ± 20           | 15.8 ± 1.6      |
| 0.8                 | 7 ± 4              | 0.6 ± 0.3       |
| 9.1                 | 7.4 ± 0.2          | 0.6             |

mN/m was more than 10 times larger than that obtained for the phase separation at 9.1 mol% methanol (0.6 mN/m). This must be related to the fixed orientation of methanol molecules in the methanol macrocluster layer, while the methanol molecules at the interface between the separated phases of methanol/cyclohexane can take favorable orientation to reduce the interfacial energy. In addition, the concentration difference is larger in case of the methanol macrocluster layer (almost pure methanol layer) and bulk solution (0.03-0.09 mol% methanol).

V. CONCLUSIONS

In conclusion, we have derived the equation for long range attractions caused by the contact of the adsorption layers of molecular macrocluster formed on glass surfaces. The long range attractions observed at 0.03-0.09 mol% methanol were well reproduced taking account of the force acting at the perimeter of the overlapping area of adsorption layers. By the curve fitting, the interfacial energy $\gamma$ between the adsorbed methanol layer and the bulk solution was evaluated to be $7.2 \pm 0.3$ mN/m for 0.03-0.09 mol% methanol. This $\gamma$ value was more than 10 times larger than that for methanol/cyclohexane interface at the phase separation (0.6 mN/m). This larger interfacial energy at 0.03-0.09 mol% methanol should be related to the rather fixed orientation of methanol molecules which causes the larger density of free hydroxy group at the interface. Thus, the surface molecular macrocluster formation can induce the drastic change in the interaction force as well as adhesion force, and can be utilized for regulation of colloidal dispersion, rheology of colloidal dispersion, accumulation and ordering of particles.

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