

Hydrogen Bonded Molecular Macrocluster Formation on Silica Surfaces in Non-Polar Solvents¹

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Summary

This paper reviews our recent studies on unique organized structures of liquids on silica surfaces. We have recently found that ethanol molecules form linearly hydrogen bonded structures, which are called surface molecular macloclusters, extending ca. 15 nm from the surface silanol groups when they are adsorbed on silica in cyclohexane. A long-ranged attraction appears when these two surfaces approach due to the interfacial energy between the adsorbed layer and the bulk liquid. Similar behavior has been observed for methanol, 1-propanol, but not for 2-propanol. Similarities and differences in properties of these surface molecular macloclusters are discussed.

1. Introduction

The adsorption of one liquid component onto a solid surface from binary liquids has been known for long time and studied generally based on the adsorption excess isotherm, microcalorimetry and the stability of colloidal dispersions [1-3]. For example, ethanol is known to adsorb preferentially to silica surfaces from its mixtures with cyclohexane [1,3]. This attraction was explained by van der Waals force, and several model calculations have been presented to describe the adsorption behaviour. However, their results were somewhat model dependent, and structures of adsorbed layers, nature of adsorbate-surface and adsorbate-adsorbate interactions (or bonding) are not known. Therefore, a novel approach is necessary for characterizing the phenomenon at the molecular level.

In this study, we employed colloidal probe atomic force microscopy, adsorption excess isotherm measurement and infrared spectroscopy in the attenuated total reflection mode (ATR-FTIR), and found ethanol molecules form linearly hydrogen bonded structures, which are called surface molecular macloclusters, extending ca. 15 nm from the surface silanol groups

when they are adsorbed on silica in cyclohexane. Colloidal probe atomic force microscopy can directly monitor the surface forces (F) between a colloidal sphere and a flat plate as a function of surface distance (D). The measured force can be normalized by the sphere radius (R) and related to the interaction free energy between two flat surfaces using the Derjaguin approximation, $F/R = 2\pi G_f$ [4]. Thus, it is naturally a powerful tool to study interactions. In addition, the surface force profiles reflect the distance dependent changes in surface properties from the surface to the bulk [4,5], which makes this method a unique tool for surface characterization. This advantage of the forces measurement could be used for investigating boundaries and structuring of liquids adsorbed on solid surfaces. ATR-FTIR spectroscopy can detect the adsorption species and specify their interaction modes as well as orientations. Here, we review our studies on the macrocluster formation of several alcohols on silica.

2. General Behavior: Ethanol

Surface forces measurement revealed an unusually long-ranged attraction between the silica (glass) surfaces in the presence of ethanol in the concentration range of 0.1-1.4 mol% at room temperature (Fig. 1) [6]. At 0.1 mol% ethanol, the attraction appears at a distance of 35 ± 3 nm and turns into a repulsion be-

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low 3.5-1.5 nm upon compression. Half of the attraction range agrees with the adsorption layer thickness estimated from the adsorption excess amount by assuming that the adsorption layer is composed only of ethanol. This indicates that the observed long-ranged attraction is caused by the contact of opposed adsorption layers of ethanol on the silica surfaces, and the sharp increase of repulsion at shorter distance is caused by the overlap of structured ethanol clusters adjacent to the surface. ATR-FTIR spectroscopy has shown that ethanol molecules adsorbed on the silica (silicon oxide) surfaces form hydrogen-bonded linear clusters (Fig. 2). The range and the strength of the attraction also changes when the ethanol concentration increases: The long-ranged attraction starts to decrease at 0.6 mol% ethanol at the room temperature, and disappears at 1.4 mol% while the adsorption excess amount remains almost constant as well as the FTIR peak intensity of the hydrogen-bonded OH group of adsorbed ethanol. In the bulk solution, ethanol clusters appear at 0.5 mol% ethanol. Therefore, we accounted for this change in the attraction in terms of the exchange of ethanol molecules between the surface clusters and bulk clusters, which has been supported by subsequent NMR spectroscopy [7].

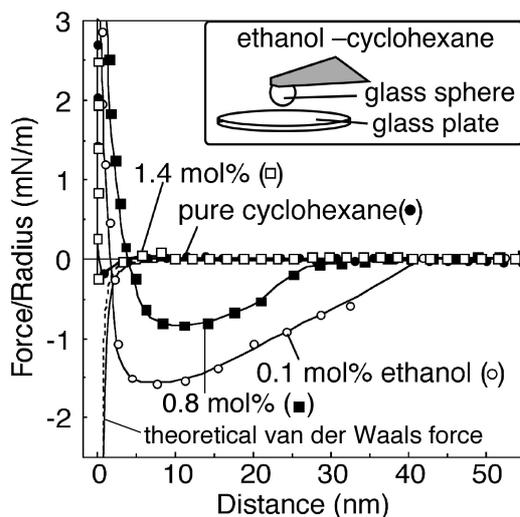


Fig.1 Profiles of interaction forces between glass surfaces upon compression in ethanol-cyclohexane binary liquids.

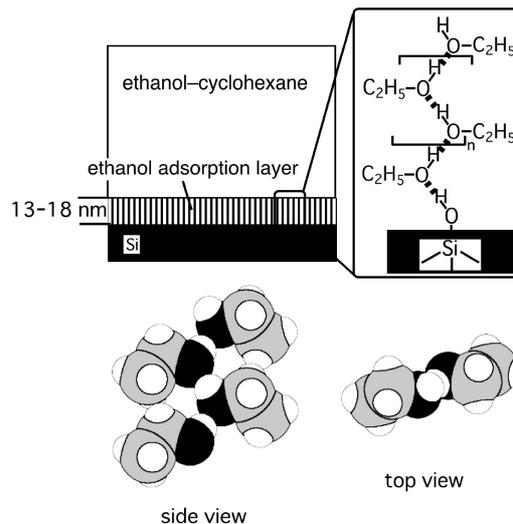


Fig.2 A plausible structure of the adsorption layer of ethanol on the silica surface (top), and the side and top views of ethanol cluster drawn by Chem3D program (bottom); carbon (black), hydrogen (white), oxygen (dark).

3. Surface Induced Wetting vs. Physical Pre-wetting Transition

The effect of the miscibility of liquids on the formation of the surface molecular macroclusters has been investigated for confirming that this is a surface induced phenomenon [8]. The phenomena in methanol-cyclohexane binary liquids, which are immiscible at methanol concentrations of ca. 8-90 mol%, are compared with those in the ethanol-cyclohexane binary liquids, which are miscible at any composition. At a 0.03 mol% methanol, which is far from the critical concentration for the phase separation (LCST), the contact of the methanol macrocluster layers formed on silica surface brought about the attraction from a distance of 42 ± 5 nm which was similar to that observed in ethanol-cyclohexane (Fig. 3(a)). At a methanol concentration of 9.1 mol%, which is above LCST, completely different force profiles are observed (Fig. 3(b)). These results demonstrated that the molecular macrocluster formation is different from the wetting induced by the bulk phase separation, and the perfect wetting of solid surfaces with one liquid component in binary liquids is possible by chemical interaction (hydrogen bonding) independent of their miscibility (Fig. 4).

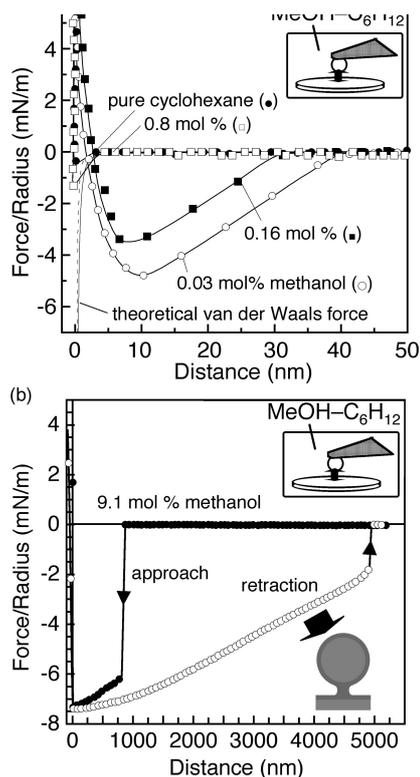


Fig.3 (a) Profiles of interaction forces between glass surfaces upon compression in methanol-cyclohexane binary liquids at 0.0-0.8 mol% methanol. (b) Profiles of interaction forces between glass surfaces upon approach and retraction in methanol-cyclohexane binary liquids at 9.1 mol% methanol (in phase separation).

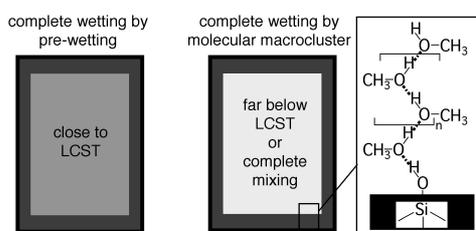


Fig.4 Schematic of wetting of solid surface through pre-wetting (left) and through the molecular macrocluster formation (right).

4. Effect of Molecular Structure: 1-Propanol and 2-Propanol

Isomers, 1-propanol and 2-propanol, have been studied [9]. 1-Propanol forms macrocluster similar to that of ethanol macrocluster, and the long range attraction appeared from a distance 69 ± 9 nm (Fig 5(a)). On the other hand, no long range attraction appears for 2-propanol (Fig. 5(b)), although a similar amount of 1-propanol and 2-propanol are adsorbed on

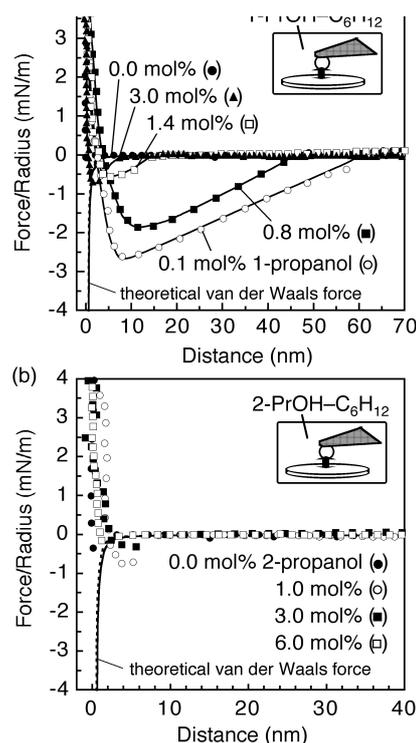


Fig.5 Profiles of interaction forces between glass surfaces upon compression, (a) in 1-propanol-cyclohexane binary liquids, (b) in 2-propanol-cyclohexane binary liquids.

the silica surfaces. The absence of a long-range attraction can be explained by the cyclic aggregation structure of 2-propanol on the surface which was revealed by transmission and ATR-FTIR spectroscopy.

5. Interfacial Energy between Macrocluster Adsorption Layer and Bulk Solution

Surface forces measurement has revealed that the long range attraction appearing 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 (γ) between the adsorption layer of molecular macroclusters and the bulk solution. The γ values are evaluated by analyzing the long range attraction as well as pull-off force in methanol-cyclohexane binary liquid mixtures by using the equation derived based on the model shown in Fig. 6 [10].

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

The value thus obtained is 7.2 ± 0.3 mN/m for

Table 1 Interfacial energies between macrocluster layer and bulk.

	methanol	ethanol	1-propanol
γ (mN/m)	7.2 ± 0.3	3.3 ± 0.6	3.2 ± 0.9

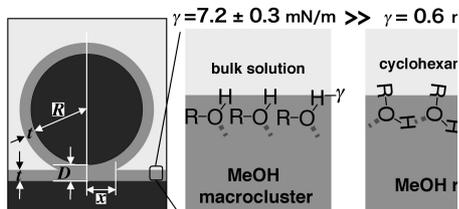


Fig.6 The geometry used for the model analysis, and the schematic of the interface between methanol macrocluster layer and bulk (left). The schematic of interface between methanol-cyclohexane in phase separation (right).

methanol, which is more than 10 times larger than that for methanol/cyclohexane interface at the phase separation (0.6 mN/m). In case of completely miscible binary liquids such as ethanol-cyclohexane and 1-propanol-cyclohexane, γ values larger than 3 mN/m are obtained (Table 1). This larger interfacial energy should be attributable to the rather fixed orientation of methanol molecules at the interface due to the ordered structure of methanol molecules in a macrocluster (Fig. 6).

6. Summary

It is surprising that simple molecules such as ethanol could form an ordered structure extending so long distance of tens nm. For generalization, it is necessary to establish theoretical foundation toward which we are currently making efforts. Surface macroclusters should also be important in advanced technology where the surface effect becomes more and more significant in the course of downsizing systems and fine designing of surfaces. An example of application is modification of surfaces and/or designing functionalized materials using on molecular macroclusters: we have prepared polymer thin films by in-situ polymerization of macroclusters of acrylic acid adsorbed on glass surfaces [11].

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