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Hydrogen-Bonded Macrocluster Formation of Ethanol on Silica Surfaces in Cyclohexane[1]

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Abstract: Adsorption of ethanol onto silica surfaces from ethanol−cyclohexane binary liquids was investigated by a combination of colloidal probe atomic force microscopy, adsorption excess isotherm measurement, and FTIR spectroscopy using the attenuated total reflection (ATR) mode. An unusually long-range attraction was found between the silica (glass) surfaces in the presence of ethanol in the concentration range of 0.1−1.4 mol % at room temperature. At 0.1 mol % ethanol, the attraction appeared at a distance of 35 ± 3 nm and turned into a repulsion below 3.5 ± 1.5 nm upon compression. Half of the attraction range agreed with the adsorption layer thickness estimated from the adsorption excess amount by assuming that the adsorption layer was composed only of ethanol. This indicated that the observed long-range attraction was caused by the contact of opposed adsorption layers of ethanol on the silica surfaces and that the sharp increase of repulsion at shorter distance was caused by the overlap of structured ethanol clusters adjacent to the surface. ATR-FTIR spectra demonstrated that ethanol adsorbed on the silica (silicon oxide) surfaces formed hydrogen-bonded clusters (polymers). Practically no ethanol clusters were formed on the hydrogen-terminated silicon surface. These results indicated that the cluster formation involved hydrogen-bonding interactions between surface silanol groups and ethanol hydroxyl groups in addition to those between ethanol hydroxyl groups. At higher temperatures (30−50 °C), the range and the strength of attraction decreased owing to the decrease in the hydrogen-bonded clusters monitored by FTIR spectroscopy, reflecting the nature of hydrogen bonding. The range and the strength of the attraction also changed when the ethanol concentration increased: The long-range attraction started to decrease at 0.6 mol % ethanol at room temperature and disappeared at 1.4 mol % while the adsorption excess amount remained almost constant as did the FTIR peak intensity of the hydrogen-bonded OH group of adsorbed ethanol. In the bulk solution, ethanol clusters appeared at 0.5 mol % ethanol; thus, this change in the attraction could be accounted for in terms of the exchange of ethanol molecules between the surface clusters and bulk clusters. The novel self-assembled structure of alcohol on the surface, found in this study may be called a "surface molecular macrocluster" because the hydrogen-bonded clusters extend to distances of ca. 20 nm longer than the typical sizes of common clusters, 2−4 nm, of alcohol (e.g., ethanol).

Introduction

Adsorption from solutions onto solid surfaces is a key in colloid and surface science.[2] It plays important roles in many fundamental and industrial surface processes. Sophisticated application of adsorption have been recently developed such as self-assembled monolayers[3] and alternatively adsorbed layer-by-layer assemblies on solid substrates.[4,5] One of the interesting adsorption systems, from modern and future technological points of views, should be liquid adsorption onto solid surfaces from binary liquids,[2] because elucidation of properties and structures of liquids adjacent to solid surfaces has become increasingly important in advanced materials science and technology which require the downsizing and fine-designing of materials and devices, for example, micro/nanomachines and microchip devices.[6] Surface treatment, catalysis, colloidal stabilization, and wetting are classical examples where liquid adsorption plays a crucial role.[2] Therefore, it is imperative to understand liquid adsorption, more generally liquid structures, at the solid−liquid interface at the molecular level.

The adsorption of one liquid component onto a solid surface from binary liquids has been known and studied generally based on the adsorption excess isotherm, microcalorimetry, and the stability of colloidal dispersions.[7−9] For example, ethanol is

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known to adsorb preferentially to silica surfaces from its mixtures with cyclohexane.[7,9] Adsorption changes the surface (particle−particle) interactions; rheological measurements have demonstrated the attraction between silica particles only at low concentrations of ethanol in cyclohexane. These studies attempted to explain the attraction by the change in van der Waals force in the presence of adsorbed layers. To better understand the phenomenon, several model calculations have been presented to determine the adsorption capacity and thickness of the layer based on adsorption isotherms.[10,11] However, their results were somewhat model-dependent; thus, the unified, concrete features of adsorption layers are missing. More importantly, structures of adsorbed layers and the 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 (AFM), adsorption excess isotherm measurement and infrared spectroscopy in the attenuated total reflection mode (ATR-FTIR), and investigated the adsorption of ethanol onto silica surfaces from its mixtures with cyclohexane, the system previously studied well by conventional methods. Here, we use silica as a general word to call the substrates, glass (for colloidal probe AFM), and oxidized silicon (for ATR-FTIR), chosen on the basis of the experimental requirements. Colloidal probe AFM 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, $F/R = 2\pi G_f$.[12] 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,[12,13] which makes this method a unique tool for surface characterization. The surface forces measurement has been successfully used to study liquid structuring, which is a physically packed, solidlike structuring.[14] The oscillatory forces are observed due to the confinement-induced structuring of liquids, which is regulated by the geometric factors of both surfaces and liquids. 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.

Taking advantage of surface forces measurement combined with ATR-FTIR spectroscopy and adsorption excess isotherm measurement, we found the formation of hydrogen-bonded ethanol clusters (polymers) extending to 10 nm or longer on silica surfaces even at a low ethanol concentration of 0.1 mol %, which brought about the long-range attraction. The ethanol cluster layer was formed through hydrogen-bonding interactions between the surface silanol groups and the ethanol hydroxyl groups, and those between the ethanol hydroxyl groups. This is, to the best of our knowledge, the first direct demonstration at the molecular level of specific liquid structures formed by chemical interactions at solid−liquid interfaces.

Experimental Section

Materials. Reagent grade cyclohexane (Nacalai Tesque) and ethanol were dried with sodium and magnesium, respectively, and distilled immediately prior to use 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.

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 ethanol−cyclohexane mixtures using AFM (Seiko Instruments, SPI3700-SPA300).[15] 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-1) 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 to ensure the existence of silanol groups on the glass surfaces.[16] After plasma treatment, the cantilever and the glass plate were transferred to the AFM fluid cell while being kept in purified cyclohexane. The closed AFM fluid cell constructed in our laboratory and stored in distilled ethanol was rinsed with distilled ethanol and blown dry with nitrogen before assembling. The inside of the cell was rinsed with pure cyclohexane at least three times to remove ethanol thoroughly before putting samples into the cell. The obtained data of force versus sample displacement (extension of piezo tube) profiles were converted to force (F) versus surface distance (D) profiles by adding (subtracting) the cantilever deflection to (from) the sample displacement and defining the zero of surface distance (D) following the conventional procedure.[15]

The obtained forces were normalized by the radius (R) of the sphere using the Derjaguin approximation, $F/R = 2\pi G_f$.[12] 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.[17] The spring constants of the cantilever used in this study were within the range of 0.8−1.5 N/m. The temperature inside of the AFM fluid cell was controlled by using a rubber heater (OM Heater) for heating within an accuracy of 0.5 °C. The temperature inside of the AFM cell was monitored by a stainless steel-covered thermocouple (almel−chromel) placed in the cell.

Adsorption Excess Isotherm Measurement. The adsorption excess isotherm was measured using adsorbent glass spheres, which were washed and treated with water vapor plasma in the same manner as for the forces measurement. The glass spheres (typically 1 g) dispersed in ethanol−cyclohexane mixtures (10 mL) precipitated after they were equilibrated for about 24 h at 20 ± 0.5 °C. The adsorption excess amounts of ethanol were obtained from the composition change of the supernatant which was determined using a differential refractometer (Otsuka Electronics, DRM-1021). The adsorption layer thickness (t) was estimated from the adsorption excess amount by assuming that only ethanol is present in the adsorption layer and that the density of ethanol in the adsorption layer is equal to that of liquid ethanol (0.789

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g/mL).[18,19] The specific surface area of the adsorbent glass spheres (0.60 ± 0.04 m^2/g) was calculated on the basis of the sizes of the glass spheres by assuming that the spheres were hard and nonporous. The size distribution of the adsorbent glass spheres was determined using an optical microscope equipped with a CCD camera for about 1000 glass spheres. The standard deviation of adsorption excess amount was in the range of 1−6%, depending on the concentrations of the liquid mixtures.

Infrared Spectroscopy in the Transmission and in the Attenuated Total Reflection Mode. Infrared spectra were recorded on a Perkin-Elmer FTIR system 2000 using a TGS detector. All the infrared spectra presented in this study were measured by using the background spectrum of pure cyclohexane. Transmission infrared spectra were obtained using a CaF_2 cell (Nihon Bunko) with an optical path length of 25 μm. For the ATR mode, the ATR attachment from Grasby Specac was used. An ATR flow cell was homemade of stainless steel and sealed with a Teflon O-ring. The ATR prism made of silicon crystal (Nihon PASTEC, 60 mm × 16 mm × 4 mm trapezoid) was used as a solid adsorbent surface. The infrared light was reflected six times with an incident angle of 45°. It is known that on the silicon surface, the oxide layer gradually grows up to 3−5 nm thickness when the surface is exposed to room-temperature air,[20] thus exhibiting similar properties to those of glass. To obtain a clean silicon oxide surface, the silicon crystal was immersed in a mixture of sulfuric acid and hydrogen peroxide (4:1, v/v) and thoroughly rinsed with pure water. The crystal was then treated with water vapor plasma for 20 min immediately prior to each experiment to ensure the formation of silanol groups on the silicon oxide surface. It was kept in pure cyclohexane until assembled into the ATR cell. As a reference, the hydrogen-terminated silicon surface was also prepared by immersing the silicon prism in 0.5% hydrofluoric acid aqueous solution for 30 min. After this treatment, the contact angle of water on the hydrogen-terminated surface became 80 ± 1°, while that on the silicon oxide surface was 0°. The temperature inside of the ATR cell was controlled by using a rubber heater (OM Heater) for heating and ice for cooling within an accuracy of 0.5 °C. The temperature inside of the AFM cell was monitored by a stainless steel-covered thermocouple (almel−chromel) placed in the cell.

The penetration depth (d_p) of the evanescent wave at 3300 cm^{-1} (for the region of hydrogen-bonded OH stretching absorption) was estimated to be 255 nm in cyclohexane using the following parameters: refractive indices for silicon crystal (3.42) and for cyclohexane (1.426), and 45° for the incident angle of the infrared light.[21,22]

In the ATR mode, the orientation of the adsorbed ethanol on the silicon oxide surface was investigated by dichroic analysis of the OH-stretching absorption obtained by using p- and s-polarized infrared light (Figure 1a).[23,24] A three-layer model (silicon prism, adsorption layer, and bulk solution) was applied to calculate the electric field at the interface.[24] A transition moment was assumed to be distributed uniformly around the z axis with the angle γ (Figure 1b). According to this model, the dichroic ratio, A_p/A_s, is given by

$$\frac{A_p}{A_s} = \frac{\left(\frac{E_{0x}}{E_{ix}}\right)^2}{\left(\frac{E_{0y}}{E_{iy}}\right)^2} + \frac{\left(\frac{E_{0z}}{E_{iz}}\right)^2\left\{\frac{1}{3}(1+2f)\right\}}{\left(\frac{E_{0y}}{E_{iy}}\right)^2\left\{\frac{1}{3}(1-f)\right\}} \tag{1}$$

$$f = \frac{3\cos^2\gamma - 1}{2} \tag{2}$$

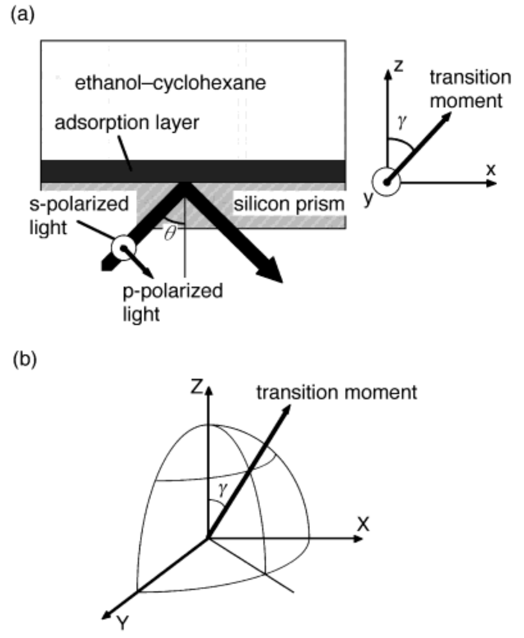

Figure 1. (a) Schematic illustration of FTIR measurement in the ATR mode and the defined coordinate geometry. (b) A uniaxial model to estimate the orientation of the transition moment of an adsorbed molecule on the silicon oxide surface. Here, it was assumed that the transition moment uniformly distributes around the z-axis with an angle of γ.[23]

where (E_{ix}, E_{iy}, E_{iz}) and (E_{0x}, E_{0y}, E_{0z}) are the electric field amplitudes of the incident light and the evanescent wave at the interface, respectively, and f ($-0.5 < f < 1$) is the ordering parameter. In this model, the ideal random orientation ($f = 0$) gives $A_p/A_s = 1.53$ using the parameters presented above (refractive indices and incident angle). When the dichroic ratio is different from the value for the random orientation (1.53), the transition moment has a preferential orientation; it orients more normal to the surface for $A_p/A_s > 1.53$.

Results and Discussion

Surface Forces between Glass Surfaces in Ethanol−Cyclohexane Binary Liquids. Typical surface force profiles measured between glass surfaces in ethanol−cyclohexane mixtures are shown in Figure 2. In pure cyclohexane, the observed force agreed well with the conventional van der Waals attraction calculated with the nonretarded Hamaker constants for glass/cyclohexane/glass, 3 × 10^{-21} J.[12] Addition of ethanol to cyclohexane changed the interaction. At an ethanol concentration of 0.05 mol %, a slight increase in the pull-off force was observed; however, it agreed with the profile observed in pure cyclohexane within the measurement error. At an ethanol concentration of 0.1 mol %, the interaction forces remarkably changed; the attraction appeared at a distance of 35 ± 3 nm, showed a minimum around 10 nm (−1.6 mN/m), and turned into repulsion at distances shorter than 3.5 ± 1.5 nm. The pull-off force of the contacting surfaces was 140 ± 19 mN/m, which was much higher than that in pure cyclohexane, 10 ± 7 mN/m. It is difficult to explain this long-range attraction in terms of modulation of the van der Waals force by the ethanol adsorption layer, because the van der Waals force calculated for glass/ethanol/glass with a Hamaker constant of 6 × 10^{-21} J was quite similar to the one for glass/cyclohexane/glass. Force profiles

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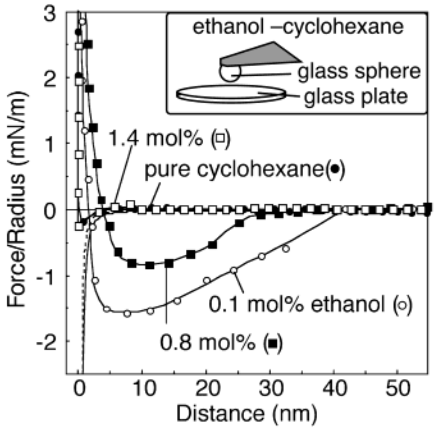

Figure 2. Profiles of interaction forces between glass surfaces upon compression in ethanol−cyclohexane binary liquids at various ethanol concentrations of 0.0, 0.1, 0.8, and 1.4 mol %. Dashed and solid lines represent the van der Waals forces calculated using the nonretarded Hamaker constants of 3×10^{-21} J for glass/cyclohexane/glass and 6×10^{-21} J for glass/ethanol/glass, respectively.[12]

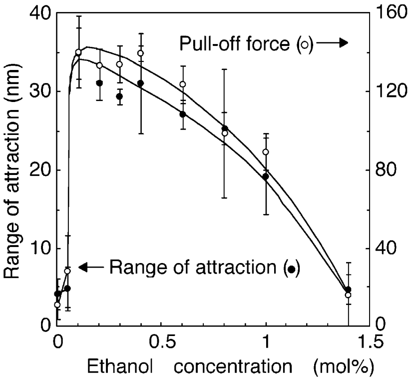

Figure 3. Plots of the range of attraction (●) and the pull-off force (○) as a function of ethanol concentration (ethanol concentration of 0.0−1.4 mol %).

obtained at ethanol concentrations up to 0.6 mol % were similar to each other. A further increase in the concentration decreased the range of attraction. At 0.8 mol % ethanol, attraction appeared at a distance of 25 ± 2 nm, showed a minimum around 11 nm (−0.9 mN/m), and turned into repulsion at distances shorter than 4 nm. The pull-off force decreased to 99 ± 32 mN/m. Finally, at an ethanol concentration of 1.4 mol %, the interaction became practically identical to that observed in pure cyclohexane.

The long-range attraction and the pull-off force are plotted versus the ethanol concentration in Figure 3. The range of the attraction changed parallel to the pull-off force indicating that both forces were associated with the identical phenomenon, most likely the adsorption of ethanol. When ethanol adsorbs to glass surfaces,[7,9] it is natural to ascribe the short-range repulsion to the steric force of structured ethanol molecules adjacent to the surfaces, which should be similar to the hydration force.[25]

A peculiar behavior was seen in the separation process of the force-sample displacement profile. At the beginning of the decompression after the contact, the cantilever stayed nearly at the same position and did not follow the movement of the glass plate retracting about 100 nm (for 0.1 mol % ethanol) although they were practically in contact (the data are shown in the Supporting Information). This unusual behavior could be explained only by the influx of ethanol into the gap between the glass sphere and the plate, indicating the presence of the condensed ethanol layer on and near the glass surfaces. With increasing ethanol concentration, this behavior also weakened in accord with the attraction and the adhesion and finally disappeared at 1.4 mol %. This observation also strongly indicates the close relation of ethanol adsorption on glass surfaces with the interaction forces.

A sharp increase in attraction between silica particles at low concentrations of ethanol in cyclohexane was previously observed in studies by Dékány et al. on stability[9] and rheological[11] properties of the silica dispersions, which qualitatively agreed with the present study, although the concentration range of ethanol for the strong attraction was much higher in the previous study, around 5 mol %. This difference might be attributed to the following different sample preparations: (1) much less water content in our studied liquids because the previous study used a molecular sieve, while we used sodium or magnesium for drying them and (2) the water plasma treatment of surfaces in this work, which ensured the presence of sufficient silanol groups on the surface.

Actually, the dryness of cyclohexane altered the results very much. When the cyclohexane without drying and distillation was used in our study, surface forces measured between glass surfaces showed a strong pull-off force of 123 ± 13 mN/m even in a pure cyclohexane although the jump-in attraction appeared only at distances smaller than 5 nm (data not shown). Most probably the strong pull-off forces were caused by the bridging of the water adsorption layers on the glass surfaces similarly to the capillary force. The surface forces showed no significant change when ethanol was added to the unpurified cyclohexane (without drying and distillation). The main features of the results in the presence of water in the unpurified cyclohexane were the large pull-off force and "no" long-range ($D > 5$ nm) attraction on approach. Water in ethanol should bring about the same effect; however, our results were quite different: the long-range attraction and the strong pull-off force changed in parallel when the ethanol concentration was increased (see Figure 3). Therefore, the effect of remaining water in ethanol, even if such water existed, should be negligible in the present study.

Adsorption Layer Thickness of Ethanol and Half the Range of Attraction. To understand the conditions better, we have determined the adsorption excess isotherm by measuring the ethanol concentration changes in binary liquids upon adsorption onto glass particles using a differential refractometer. The apparent adsorption layer thickness can be estimated from the adsorption excess amount of ethanol, assuming that only ethanol is present in the adsorption layer (see Experimental Section). This quantity could be compared with half the attraction range if the attraction were brought about by contact of the adsorbed layers on two opposed surfaces similar to the capillary force.[26,27] Thus, in Figure 4, half the range of the attraction was compared with the apparent adsorption layer thickness as a function of the ethanol concentration. For 0.1 mol % ethanol, half the distance where the long-range attraction appeared, 18 ± 2 nm, was close to the apparent layer thickness of the adsorbed ethanol, 13 ± 1 nm. These results indicated that the most probable explanation for the observed long-range

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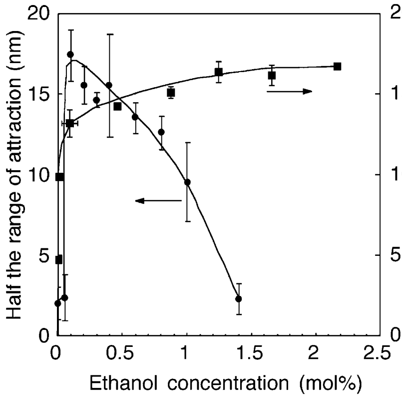

Figure 4. Plots of half the range of attraction (●) and the adsorption layer thickness estimated from the adsorption excess amount of ethanol (■) as a function of the ethanol concentration.

attraction extending over 30 nm is the contact of the ethanol adsorption layer similar to the capillary force,[26,27] and the short-range repulsive force below 5 nm is the steric force owing to the more stable structure of the ethanol adsorption layer similar to the hydration force.[25]

Half the range of attraction was constant up to 0.6 mol % ethanol and decreased with increasing ethanol concentration, while the apparent adsorption layer thickness remained constant at all concentration ranges studied. The discrepancy between the two quantities indicated a change in the structure of the ethanol adsorption layer at concentrations higher than ~0.6 mol %, which will be discussed later on the basis of the results of FTIR spectroscopy.

Adsorption layer thickness obtained for glass spheres without water vapor plasma treatment was 4.2 nm at an equilibrium ethanol concentration of 0.2 mol %. This value was much smaller than those obtained for the spheres with water vapor plasma treatment and close to the layer thickness, 3 nm, obtained in previous studies,[7−9] indicating the strong effect of the surface silanol groups on the ethanol adsorption. The essential role of surface silanol groups in the ethanol adsorption will be demonstrated on the basis of ATR-FTIR spectroscopy on the hydrogen-terminated silicon surface (as an adsorbent).

Here, with the thickness of the adsorption layer known, we may discuss again van der Waals force as a possible origin for the observed attraction because the previous studies, including those by Dékány et al.,[9a] explained the attraction by this mechanism. If this were the case, the sharp increase in the attraction should be observed from a distance of a few nanometers away from the contact of ethanol adsorption layers owing to the van der Waals force between the adsorption layers in cyclohexane (Hamaker constant: 2.2×10^{-21} J). For distances shorter than twice the thickness (contact) of the adsorption layer, the interaction should be approximated by the van der Waals force between glass surfaces in ethanol, which clearly does not accord with the observed surface forces shown in Figure 3.

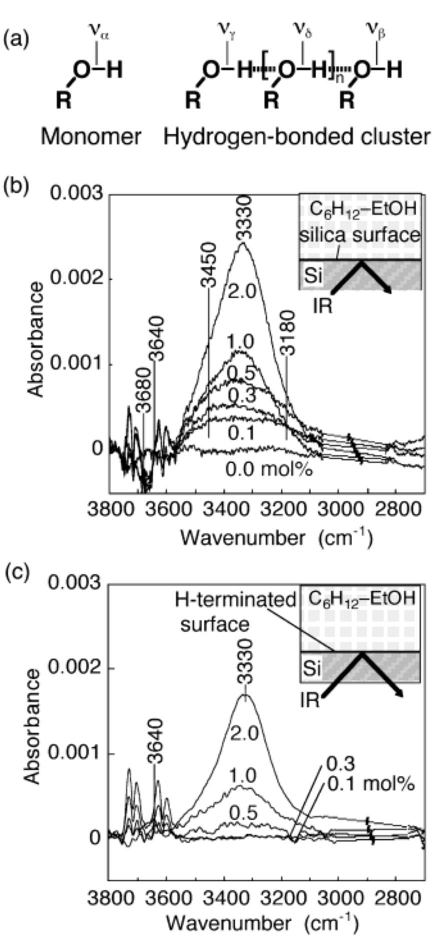

Figure 5. (a) Structures of monomer alcohol and a linear cluster (polymer) of hydrogen-bonded alcohol, and the notation of various OH-stretching modes, $\nu_\alpha \approx \nu_\delta$, which exhibit the absorption peaks at different wavenumbers. (b) ATR-FTIR spectra measured on silicon oxide surface in ethanol−cyclohexane binary liquids at various ethanol concentrations of 0.0, 0.1, 0.3, 0.5, 1.0, and 2.0 mol %. (c) ATR-FTIR spectra measured on a hydrogen-terminated silicon surface in ethanol−cyclohexane binary liquids at various ethanol concentrations of 0.1, 0.3, 0.5, 1.0, and 2.0 mol %. Note that four peaks around 3600−3700 cm^{-1} (3600, 3630, 3705, 3730 cm^{-1} are ascribed to water remaining in a sample compartment of the spectrophotometer.

FTIR Spectra of Ethanol Adsorbed on a Silica Surface and in Bulk Solution. To investigate the structure of adsorbed ethanol on silica surfaces, ATR-FTIR spectroscopy was performed using silicon crystals covered by silicon oxide layers. The surfaces were treated by water vapor plasma to form sufficient silanol groups there (see Experimental Section).

Ethanol is known to form hydrogen-bonded clusters (polymers) in nonpolar solvents such as cyclohexane and tetrachloromethane.[28,29] Therefore, as a reference, we first investigated cluster formation of ethanol in cyclohexane at various ethanol concentrations (0.0−2.0 mol %) by FTIR spectroscopy in the transmission mode (the data are shown in the Supporting Information). In transmission spectra, a peak at 3640 cm^{-1} assigned to the non-hydrogen-bonded OH group (free OH, ν_α) with a shoulder at 3630 cm^{-1} (ν_β) for terminal OH and a weak peak ascribed to dimer or terminal OH at 3530 cm^{-1} (ν_γ) were observed at ethanol concentrations lower than 0.5 mol % (for structures, see Figure 5a).[28,29] No polymer OH peak was

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(27) Here, we used the term “similar to the capillary force” to describe the mechanism of the long-range attraction, i.e., the interfacial energy between the ethanol adsorption layer and the bulk solution caused the long-range attraction similarly to the capillary force. The capillary force is the attraction caused by the bridging of condensed liquid in a capillary between the surfaces close to contact. The condensation of ethanol in our study was caused by hydrogen-bonding interactions between surface silanol groups and ethanol hydroxyl groups as well as between ethanol molecules, which is different from the ordinary mechanism of the capillary condensation.

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observed in this concentration range, indicating that practically no ethanol clusters were formed in the bulk solution. At an ethanol concentration of 0.5 mol %, a polymer OH peak appeared at 3330 cm^{-1}. The intensity of the polymer peak drastically increased with increasing the ethanol concentration further, while only a slight increase was seen in the intensities of other peaks at 3640, 3630, and 3530 cm^{-1}. This indicated that the number of clusters grew as the ethanol concentration increased beyond 0.5 mol %, while those of monomers and dimers remained nearly the same.

ATR-FTIR spectra of ethanol adsorbed on silica surfaces at various ethanol concentrations (0.0−2.0 mol %) in cyclohexane are presented in Figure 5b. The spectrum of reinjected pure cyclohexane (0.0 mol %) was flat, demonstrating the stability of the measurement. At 0.1 mol % ethanol, a narrow negative band at 3680 cm^{-1}, a weak absorption at 3640 cm^{-1} assigned to non-hydrogen-bonded OH groups (free OH, ν_α),[28,29] and a broad strong absorption at 3600−3000 cm^{-1} were observed. This spectrum was clearly different from that observed for the bulk solution at the same ethanol concentration, which showed only a major peak at 3640 cm^{-1}, indicating that adsorbed ethanol adopted a quite different structure from those in the bulk solution (monomer and dimer). The isolated silanol group in nonpolar liquids is known to exhibit an absorption band at 3675−3690 cm^{-1},[30,31] which shifts to a lower wavenumber (3425−3440 cm^{-1}) when the silanol groups hydrogen bond with esters. Therefore, the negative absorption at 3680 cm^{-1} should correspond to a decrease in the isolated silanol groups, and the weak peak at around 3450 cm^{-1}, which formed a part of the broad peak at 3600−3000 cm^{-1}, to the appearance of the silanol groups hydrogen-bonded with the adsorbed ethanol. The major part of the broad absorption at 3600−3000 cm^{-1}, the center of which was around 3300 cm^{-1}, can be assigned to the doubly hydrogen-bonded OH group (polymer OH, ν_δ),[28,29] although the peak was much broader than the polymer OH peak in ethanol−cyclohexane mixtures. These results demonstrated that ethanol formed clusters through hydrogen bonding between the surface silanol groups and the ethanol hydroxyl groups as well as those between the ethanol hydroxyl groups even at 0.1 mol % ethanol. Broadening of the polymer OH peak could be explained by the following: (1) The confined geometry of the surface somewhat restricted the structure of surface species, thus distorting the hydrogen bonding from its most stable form; (2) a weak peak at 3180 cm^{-1}, consisting of the lower part of the broad peak, was similar to that observed for crystallized methanol at −108 and −180 °C,[32] suggesting that a part of the ethanol clusters had somewhat crystalline-like structures because terminals of ethanol clusters were fixed to the surface silanol groups.

With increasing ethanol concentration, the intensity of the polymer OH peak (3330 cm^{-1}) increased, whereas practically no increase in peaks at 3640 cm^{-1} (free OH), 3450 cm^{-1} (hydrogen-bonded silanol OH), and 3180 cm^{-1} (crystalline-like structured OH) was observed. Because of the long penetration depth of an evanescent wave, ca. 255 nm, the absorption attributed to species in the bulk solution could contribute the peaks obtained in the ATR-FTIR spectra. However, the transmission IR spectra of ethanol in cyclohexane showed no polymer OH peak at ethanol concentrations lower than 0.5 mol %. Thus, the contribution from the bulk solution to the polymer OH peak observed in ATR-FTIR spectra was negligible at ethanol concentrations lower than 0.5 mol %. We will discuss later the cases of ethanol concentrations higher than 0.5 mol %.

To examine the effect of the surface silanol groups on formation of the surface macroclusters, the oxidized silicon surface was replaced by the hydrogen-terminated silicon surface, and ATR-FTIR spectroscopy was employed to study possible adsorption of ethanol in cyclohexane. As shown in Figure 5c, spectra measured at 0.1 and 0.3 mol % ethanol displayed no polymer OH peak, but the small peaks around 3640 cm^{-1}, which correspond to free OH, overlapped with the residual peaks of water in air. At 0.5 mol % ethanol, a very small polymer OH peak (ν_δ) appeared and drastically increased with increasing the ethanol concentration beyond 0.5 mol %. The observed dependence of the polymer OH peak intensity on the ethanol concentration was similar to that observed in the transmission IR spectra for the ethanol clusters in the bulk solutions. These results showed that no preferential adsorption of ethanol occurred on the hydrogen-terminated silicon surface, supporting that the silanol groups were essential for the ethanol cluster formation on silica surfaces.

To confirm the ethanol concentration dependence of the cluster formation both on the surface and in the bulk solution, the integrated peak intensities of polymer OH absorption obtained from ATR-FTIR spectra measured on the silica surface (A_{ATR-OH}) and the hydrogen-terminated silicon surface (A_{ATR-H}) and those from the transmission spectra (A_{TS}) were plotted as a function of the ethanol concentration in Figure 6a. The A_{TS} value, which represented the cluster formation in the bulk solution, showed no significant increase at ethanol concentrations lower than 0.5 mol %. The drastic increase in A_{TS} occurred at ethanol concentrations higher than 0.5 mol %. The A_{ATR-H} value showed a concentration dependence similar to A_{TS}, indicating that A_{ATR-H} was ascribed only to the ethanol clusters formed in bulk solution. On the other hand, the A_{ATR-OH} value, which monitored the cluster formation on the silica surface, started to increase sharply at ca. 0.1 mol % ethanol, where there was only negligible absorption in the case of the hydrogen-terminated surfaces as well as in the bulk. A_{ATR-OH} increased almost proportionally to an ethanol concentration higher than 0.5 mol % ethanol. Comparison of A_{ATR-OH} with A_{TS} and A_{ATR-H} confirmed that A_{ATR-OH} contained absorption only from the ethanol clusters on the surface at ethanol concentrations lower than 0.5 mol %, while it contained absorption both from ethanol clusters on the surface and in bulk solution at concentrations higher than 0.5 mol %. The subtraction of A_{ATR-H} from A_{ATR-OH} should provide the net absorption due only to the surface cluster. The values of ($A_{ATR-OH} - A_{ATR-H}$) are plotted against the ethanol concentration in Figure 6b and compared with the adsorption layer thickness obtained from the adsorption excess isotherm. Two values changed in parallel, and sharp increases were seen at ethanol concentrations lower than ca. 0.5 mol %, supporting that ethanol molecules in the adsorbed layer existed in a form of hydrogen-bonded clusters.

The surface force profiles showed the decrease in the long-range attraction between glass surfaces at ethanol concentrations higher than 0.6 mol % as shown in Figure 3. However, there is no particular change in both the adsorption layer thickness and

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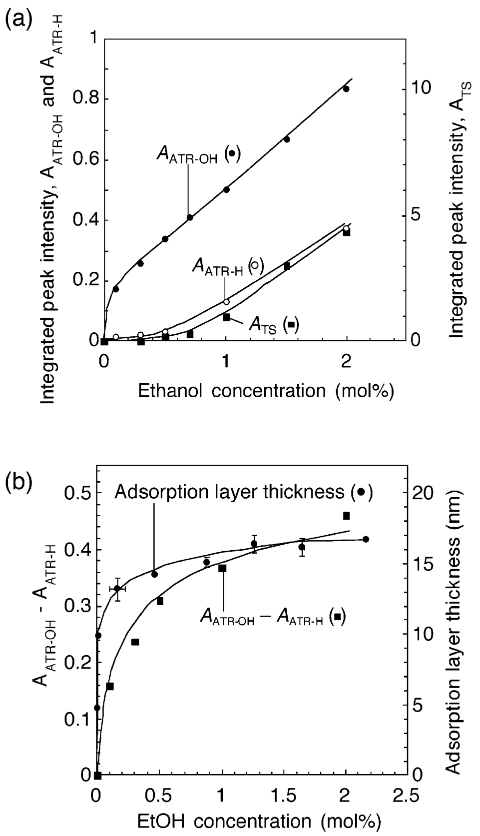

Figure 6. (a) Ethanol concentration dependencies of the integrated peak intensity of polymer OH absorption: (●) represents the intensity obtained in ATR spectra measured on silicon oxide surface (A_{ATR-OH}), and (○) represents the intensity obtained in ATR spectra measured on a hydrogen-terminated silicon surface (A_{ATR-H}). (■) represents the intensity obtained in transmission spectra (A_{TS}). (b) Ethanol concentration dependencies of the polymer OH absorption due to adsorbed ethanol (●) obtained by subtracting A_{ATR-H} from A_{ATR-OH}, and of the adsorption layer thickness (■) estimated from the adsorption excess amount of ethanol.

polymer OH peak intensity around this concentration, although one may note that the drastic increase in the ethanol cluster concentration in bulk solution occurred at ca. 0.5 mol % ethanol.

Orientation of Ethanol Molecules on a Silica Surface Based on Dichroic Analysis. Subsequently, the orientation of ethanol in the surface adsorption layer was examined by measuring the dichroic ratios of polymer OH absorption in ATR-FTIR spectra on the silicon oxide surface. The polymer OH absorption obtained by using p-polarized light was more than twice as large as that obtained by using s-polarized light at 3300 cm^{-1} (the data are shown in the Supporting Information). This indicated that the adsorbed ethanol has a preferential orientation. Therefore, the dichroic ratio of the integrated peak intensity of polymer OH, A_p/A_s, was plotted together with the dichroic ratio calculated for the random orientation as a function of the ethanol concentration in Figure 7a. Dichroic ratios of the ethanol polymer OH peak were 2.9 ± 0.6 and 3.0 ± 0.3 at ethanol concentrations of 0.1 and 0.3 mol %, respectively. These values were substantially higher than the value calculated for the random orientation (1.53). The mean orientation of OH groups (γ) in the surface cluster was 40 ± 4° at 0.1 mol % ethanol based on the model presented in Figure 1b.

With an increase in the ethanol concentration, the dichroic ratio started to decrease at 0.5 mol % and reached a constant value for the random orientation at ethanol concentrations higher than 3.0 mol %. This was reasonably explained by the contribution from the bulk solution, which was dominant at higher ethanol concentrations, and perhaps by changes in the orientation of ethanol in clusters formed on the surface.

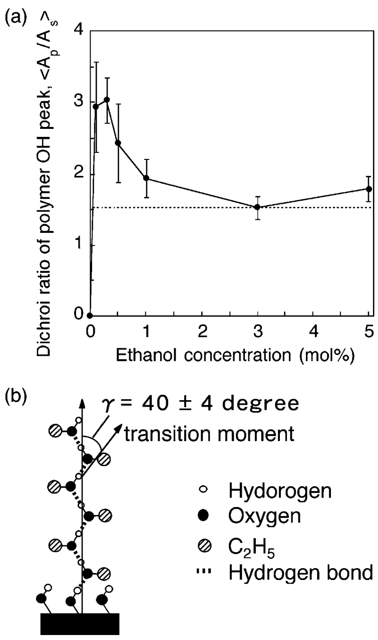

Figure 7. (a) A plot of the dichroic ratio of polymer OH absorption, obtained from the ATR-FTIR spectra measured on silicon oxide surface, as a function of ethanol concentration. A dashed horizontal line represents the dichroic ratio expected for the random orientation (1.53). (b) A plausible structure of an ethanol cluster on silica surface based on dichroic analysis of ATR-FTIR spectra.

A plausible structure of ethanol clusters on the silica surface at low concentrations is drawn in Figure 7b: the hydroxyl groups hydrogen-bond in the form of a linear zigzag chain (angle between OH groups and the chain axis is about 36°), and the axis of the chain is aligned almost normal to the surface. We may call this novel self-assembled structure of alcohol on the surface as the "surface macrocluster", because the hydrogen-bonded clusters extend to distances of ca. 20 nm longer than the typical sizes of common clusters, 2−4 nm, of alcohol (e.g., ethanol).

Temperature Dependence of Ethanol Adsorption on a Silica Surface. If the hydrogen-bonding interaction is playing a crucial role in ethanol adsorption, it should be sensitive to changes in temperature.[28] Therefore, we measured the surface forces and ATR-FTIR spectra in ethanol−cyclohexane binary liquids in the temperature range of 20−50 °C. Figure 8a shows the temperature dependence of the interaction forces between glass surfaces in 0.5 mol % ethanol. Long-range attraction was observed from a distance of 40 ± 3 nm at 20 °C which agreed with the results presented in Figure 2. At 30 °C, the range of the attraction decreased to 32 ± 2 nm. With increasing temperature further, it monotonically decreased and became 27 ± 3 nm at 50 °C.

The ATR-FTIR spectra were also measured in 0.5 mol % ethanol at various temperatures (12, 20, and 30 °C) using the silicon oxide surface (Figure 8b). A clear decrease, by about a half, was seen in the polymer OH absorption at 3350 cm^{-1} as well as those corresponding to dimer or terminal OH (3530 cm^{-1}) when the sample temperature was increased from 12 to 20 °C. This agreed with the thinning of the ethanol adsorption

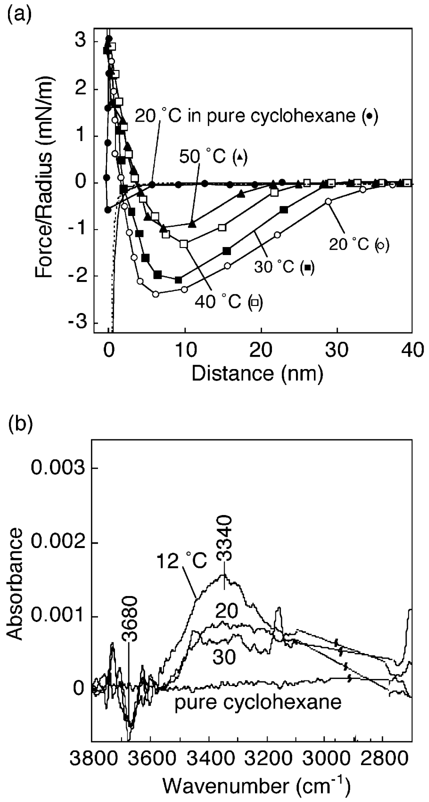

Figure 8. (a) Profiles of interaction forces between glass surfaces upon compression in 0.5 mol % ethanol in cyclohexane measured at various solution temperatures of 20, 30, 40, and 50 °C and that in pure cyclohexane at 20 °C. Dashed and solid lines represent the van der Waals force calculated using the nonretarded Hamaker constants of 3×10^{-21} J for glass/cyclohexane/glass and 6×10^{-21} J for glass/ethanol/glass, respectively.[12] (b) ATR-FTIR spectra on silicon oxide surface in 0.5 mol % ethanol in cyclohexane at various solution temperatures of 12, 20, and 30 °C.

layer, observed by the forces measurement, due to the lower stability of macroclusters at higher temperatures. When the temperature was further increased to 30 °C, the polymer OH absorption decreased to a certain extent, and the observed spectrum was similar to that for 0.1 mol % ethanol at room temperature. This indicated that clusters close to the silica surface remained at a higher temperature. No clear increase in other OH peaks corresponding to free OH (3640 cm^{-1}), dimer, or terminal OH (3530 cm^{-1}) was detected; thus, ethanol should have escaped from the surface to the bulk solution, which was natural from the model that ethanol adsorbed through hydrogen bonding. One may note that two peaks appearing at 3450 and 3160 cm^{-1} were artifacts due to the residual (not compensated by the background) peaks of cyclohexane, which occasionally appeared even in pure cyclohexane, and had no effect on the baselines.

The obtained temperature dependence is reasonably expected from the model of ethanol macroclusters formed through hydrogen bonding. Adsorption of ethanol on silica surface is known to be exothermic,[11] agreeing with our results of temperature dependence. The present observation also indicated the potential to regulate the cluster thickness by varying temperature.

Plausible Structure of the Ethanol Adsorption Layer and Origin of Long-Range Attraction. A plausible structure of ethanol macroclusters adsorbed on the silica surface is presented in Figure 9 based on the ATR-FTIR spectroscopy with dichroic analysis. The surface macrocluster of ethanol has an ordered linear chain structure with the cluster axis aligned almost normal to the surface. The side and the top view of the ethanol clusters drawn by the Chem 3D program are shown also in Figure 9. The density of ethanol in the adsorption layer was calculated to be 0.75 g/mL by assuming that the hydrogen-bonded ethanol dimer occupied a volume of 0.46 nm^2 (cross section from the top) × 0.25 nm (height from the side). This value agreed well with the density of bulk ethanol, 0.79 g/mL, supporting the assumption that the density of adsorbed ethanol layers was equal to the bulk value for the estimation of the thickness of the adsorbed layer. In Figure 9, non-hydrogen-bonded OH groups of terminal ethanol molecules are facing the bulk solution dominated by cyclohexane. Thus, the certain level of the interfacial energy should be raised between the surface layer and the bulk solution, and the contact of the ethanol layers formed on opposed glass surfaces should bring about the long-range attraction. This mechanism bears similarity to the capillary force that acts between hydrophilic surfaces due to water condensation.[26, 27]

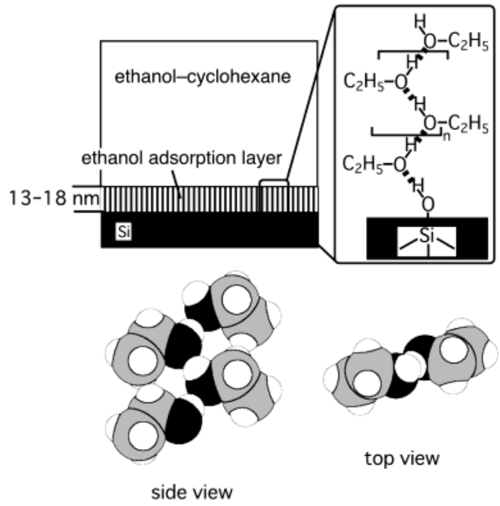

Figure 9. A plausible structure of the adsorption layer of ethanol on the silica surface (top), and the side and top views of ethanol cluster drawn by ChemBats3D program (bottom); carbon (black), hydrogen (white), oxygen (dark).

A decrease in the long-range attraction at ethanol concentrations higher than 0.6 mol % was peculiar, because there was no particular change in both the adsorbed layer thickness and polymer OH peak intensity around this concentration (see Figures 4 and 6b). Actually, the latter two quantities were nearly constant at concentrations higher than 0.6 mol %. One drastic change occurring around 0.6 mol % ethanol was that the ethanol clusters in the bulk solution started to grow drastically at ethanol concentrations higher than 0.5 mol %. It is conceivable that the cluster formation in the bulk solution influences the structure of the ethanol macrocluster on the silica surface. We suppose that the exchange of ethanol molecules between clusters on the surface and in the bulk solution occurs when the ethanol cluster formed in the bulk solution. This should result in the decrease in the interfacial energy between the surface macrocluster and the bulk solution, leading to the decrease in the attraction. We observed the decrease in the dichroic ratio at 0.5 mol % ethanol, which might be caused by the decrease in the ordering of surface ethanol macrocluster due to exchange of molecules. However, unfortunately, the contribution from the bulk solution cannot be neglected at present, which prevents us from clearly discussing the exchange effect.

Conclusions

Adsorption of ethanol from cyclohexane on silica surfaces was studied by employing a novel approach, and the following results were obtained.

(1) A novel molecular assembly, that is, surface macroclusters of ethanol, was found on the silica surface at low concentrations of ethanol. This structure was formed through the hydrogen-bonding interactions between the surface silanol groups and the ethanol hydroxyl groups as well as those between the ethanol hydroxyl groups.

(2) The dichroic analysis in ATR-FTIR spectroscopy revealed that the surface macrocluster of ethanol had an ordered linear chain structure with the cluster axis aligned almost normal to the surface.

(3) Forces acting between glass surfaces were a long-range attraction extending to 35 ± 3 nm at 0.1 mol % ethanol and a shorter-range repulsion which could be ascribed to a steric repulsion of structured ethanol molecules adjacent to the silica surface. Agreement of half the range of attraction and the adsorption layer thickness estimated from the adsorption excess isotherm clearly indicated that the contact of the surface macrocluster formed on two opposed glass surfaces brought about the long-range attraction.

(4) Long-range attraction and the amount of adsorbed ethanol decreased at higher temperatures. This is in good accordance with the characteristic of hydrogen-bonding interactions.

(5) The range of long-range attraction decreased with increasing the ethanol concentrations beyond 0.6 mol %, and the interaction became practically identical to that observed in pure cyclohexane at 1.4 mol % ethanol. On the other hand, no decrease in the adsorption layer thickness was observed, which was confirmed on the basis of the adsorption excess isotherm measurement and ATR-FTIR spectroscopy. We proposed that such decrease in the attraction might be related to the dynamics of ethanol molecules within the adsorbed layer: ethanol molecules could exchange between ethanol clusters on the surface and those in bulk solution at higher ethanol concentrations where ethanol clusters formed in the bulk solution. The mechanism of the decrease in the attraction is under further investigation at our laboratory.

Similar hydrogen-bonded macroclusters were found on silica surfaces in binary mixtures of other alcohols (methanol and propanol) as well as carboxylic acid with cyclohexane. These systems also exhibited long-range attraction.[33] Our results indicated that the surface macrocluster formation should be a general phenomena for surfaces bearing hydrogen-bonding groups such as the silanol group in binary mixtures of hydrogen-bonding liquids and nonpolar liquids. The present study is, to the best of our knowledge, the first demonstration of a specific molecular structure of a liquid adsorbed at the solid−liquid interface. A combination of colloidal probe atomic force microscopy, adsorption excess isotherm measurement, and ATR-FTIR spectroscopy was a powerful tool for characterizing such a phenomenon. We think that this study of hydrogen-bonded macrocluster formation bears significance for the general understanding of the behavior of liquids, such as structuring, on solid surfaces at the molecular level, which has not yet been well achieved. In the mesoscopic scale, where the macroscopic and molecular concepts meet, we should be able to connect two concepts by describing a macroscopic behavior by molecular term. In our study, this is realized as “the long-range attraction appeared when the hydrogen-bonded clusters of ethanol formed”.

Surface molecular macroclusters should also be important in advanced technology where the surface effect becomes more and more significant in the course of downsizing of systems and fine-designing of surfaces. Examples of advanced technology where the surface effect is large include: liquid flow on the solid surface, tribology, micro/nano machine. Further, this unique structure can be utilized for modifying surfaces or designing functionalized materials based on molecular self-organization. To demonstrate this potential, we have prepared polymer thin films by in situ polymerization of macroclusters of acrylic acid adsorbed on glass surfaces.[34]

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Supporting Information Available: Figures showing the one cycle of force profile observed between glass surfaces at ethanol 0.1 mol % in cyclohexane by plotting force against sample displacement, transmission FTIR spectra of ethanol−cyclohexane binary liquids at ethanol concentrations of 0.3, 0.5, 1.0, and 2.0 mol %, and ATR-FTIR spectra measured on silicon oxide surface in ethanol−cyclohexane binary liquids using p- and s-polarized light at 0.1 mol % ethanol (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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