Hydrogen-bonded surface macroclusters of carboxylic acid on silica in cyclohexane

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Abstract: The macrocluster formation of propionic acid adsorbed onto silica (glass and silicon oxide) surfaces from propionic acid-cyclohexane mixtures has been studied using surface forces measurement, adsorption excess isotherm measurement and Fourier transform infrared spectroscopy (FTIR) in the attenuated total reflection (ATR) and the transmission (TS) mode. In pure cyclohexane, the interaction extended to only 2-3 nm and described as the van der Waals force. On the other hand, unusually long-range attraction was observed in the presence of propionic acid in the concentration range of 0.1-20 mol%. At 0.5 mol% propionic acid, the attraction appeared at 67 ± 8 nm and turned into repulsion below 2 nm upon compression. This attraction was accounted for in terms of the bridging of opposed adsorption layers of propionic acid on the surfaces. The thickness of the adsorption layer was estimated as half of the attraction range to be 34±4 nm for 0.2-1.0 mol% propionic acid, which agreed well with the thickness calculated from the adsorption excess amount of propionic acid, 38±9 nm, assuming that the adsorption layer consisted of pure propionic acid. Chemical interactions involved in the formation of the adsorption layers of propionic acid were investigated by FTIR-ATR spectroscopy using silicon oxide as a substrate. The hydrogen-bonded OH absorption of propionic acid around 3120 cm⁻¹ was observed at 0.1 mol% propionic acid where the contribution from the bulk solution was small. The linear structure of the surface cluster initiated from the surface silanol groups was demonstrated from the peak position and the dichroic analysis of the hydrogen-bonded OH absorption. An application of this phenomenon with respect to the nano-scale coating technique was demonstrated by the photo-polymerization of the acrylic acid monomer adsorbed on the silica surfaces. Photo-irradiation of the silica substrates for 20 min in 0.1 mol% acrylic acid produced extremely uniform and flat polymer films with a thickness of ≈25 nm, which exhibited an average difference in the height of less than 0.2 nm for a 3 μm × 3 μm area on the surface.

Key words: Macrocluster; carboxylic acid; silica surface; surface force; FTIR-ATR; nano-coating.

Introduction. “Adsorption” is of fundamental importance in many fields of science and technology and attracts increasing attention,1) because surface (interface) effects become essential in such processes of modern and future technology as separation, catalytic reaction and surface nano-fabrication. Nevertheless, relatively little effort has been devoted to the study of the adsorption of one liquid component onto a solid surface from liquid mixtures. The methods employed have been limited and mainly concerned with adsorption isotherms.1)

Recently, we have investigated the adsorption of alcohols (e.g., ethanol) onto the silica surfaces from their mixture with cyclohexane using colloidal probe atomic force microscopy (AFM), Fourier transform infrared spectroscopy in the attenuated total reflection mode (FTIR-ATR) and adsorption excess isotherm measurement, and found the formation of hydrogen-bonded macroclusters of alcohols adsorbed on the silica (glass and silicon oxide) surfaces.2) Here, we use the term “macrocluster”, because the hydrogen-bonded clusters extend to longer distances of ca. 20 nm than the typical sizes of common clusters, 2-4 nm, of liquids (e.g., alcohol).

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In the present study, we investigated the adsorption of propionic acid onto silica surfaces from cyclohexane with the intention of examining the generality of this type of cluster formation. The formation of carboxylic acid macroclusters was demonstrated, and further utilized for fabricating organic nano-films by the in situ photo-polymerization of acrylic acid on the surfaces.

**Experimental section.** Materials. Cyclohexane from Nacalai Tesque was dried with sodium and distilled immediately prior to use. Propionic acid from Nacalai Tesque was distilled prior to use. Acrylic acid from Nacalai Tesque was distilled under the reduced pressure of 4 mmHg. Azobisisobutyronitrile (AIBN) from Nacalai Tesque and poly(acrylic acid) from Wako 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 binary liquids using colloidal probe atomic force microscopy (AFM, Seiko II, SP3700-SPA300) (Fig. 1). 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. The colloidal glass sphere (typically 5 μm in radius) was then attached to the end of a cantilever (Olympus, RC-800P5-1) 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 in order to clean and ensure the existence of silanol groups on the glass surfaces. The closed AFM fluid cell constructed in our laboratory was cleaned with distilled ethanol and blown dry with nitrogen before the assembling.

The interaction forces between the glass surfaces were measured at various propionic acid concentrations (0.0-20.0 mol%). The obtained forces were normalized by the radius (\(R\)) of the sphere using the Derjaguin approximation,

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F/R = 2\pi G_f [1]
\]

where \(G_f\) is the interaction free energy per unit area between two flat surfaces. The individual spring constant of the cantilever was determined following a previously reported procedure. Infrared spectroscopy in transmission (TS) and attenuated total reflection (ATR) modes. All infrared spectra were recorded using Perkin Elmer FT-IR system 2000 with a TGS detector under dry air conditions. Cyclohexane was used to measure the background spectrum for all spectra presented except for that air was used for the KBr tablet. The transmission infrared spectra were obtained using a CaF\(_2\) cell (Nihon Bunko) with the path length of 25 μm. Typically 50 scans were collected with a resolution of 4 cm\(^{-1}\). FTIR-ATR spectra were obtained using a silicon prism (Nihon PASTEC, 60 × 16 × 4 mm trapezoid) as the substrate. The silicon surface is known to be covered by an oxide layer of up to 3-5 nm when exposed to air at room temperature. The silicon prism was cleaned in a mixture of sulfuric acid and hydrogen peroxide (4:1, v/v), and then thoroughly rinsed with pure water. Immediately prior to each experiment, the silicon crystal was treated with water vapor plasma for 20 min. The silicon crystal was assembled into a stainless steel, homemade ATR flow cell sealed with a Teflon O-ring and mounted on the ATR attachment from Grasby Specac. Typically, 200 scans were collected with a resolution of 8 cm\(^{-1}\). The penetration depth (\(d_p\)) of the evanescent wave at 3300 cm\(^{-1}\) 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 degrees for the incident angle of the infrared light. In the ATR mode, the orientation of the adsorbed propionic acid on the silicon oxide surface was investigated by dichroic analysis of the OH stretching peak obtained by using p- and s-polarized infrared light (Fig. 2). A three layer model (silicon prism, adsorption layer and bulk solution) was applied to calculate the electric field at the interface. A transition moment was assumed to be uniformly distributed around the z axis with the angle \(\gamma\). Based on this model, the dichroic ratio, \(A_p/A_s\), was calculated to be 1.46 for the ideal random orientation using refractive indices and
incident angle parameters presented above. For \( A_i/A_s < 1.46 \), the transition moment orients more parallel to the surface.

**Adsorption excess isotherm measurement.** The glass spheres (typically 1.0 g) washed and treated by the water vapor plasma in the same manner described above were dispersed in propionic acid-cyclohexane mixtures (10 ml) then precipitated after being equilibrated for about 24 h at 20 ± 0.5 °C. The adsorption excess amount was determined by measuring the changes in the composition of the supernatants using a differential refractometer (Otsuka Electronics, DRM-1021). The adsorption layer thickness \( (t) \) was estimated by assuming that the adsorption layer was uniform and composed only of propionic acid.

**In situ polymerization of adsorbed layers.** The glass plates (Matsunami, micro cover glass) or silicon prism were treated in the same manner as before, then put into the glass vessel containing cyclohexane. Acrylic acid was added to the vessel at concentrations of 0.1-2.0 mol%. After an equilibration of 1 h, AIBN was added at the molar ratio of AIBN:monomer = 1:1000. The sample plate was irradiated with a Hg lamp (HAMA-MATSU, Model-C940) for the polymerization, then removed from the vessel and dried in a vacuum desiccator. The morphology and the structure of the obtained poly(acrylic acid) films were characterized by AFM imaging and FTIR-ATR spectroscopy.

**Results and discussion.** Surface forces and adsorption isotherm measurements. Fig. 3 shows the typical profiles of the interaction forces between the glass surfaces upon compression in propionic acid-cyclohexane binary liquids at various propionic acid concentrations of 0.0, 0.1, 0.5, 5.0, 10.0 and 20.0 mol%. Solid line represent the van der Waals force calculated using the nonretarded Hamaker constants of \( 3 \times 10^{-21} \) J for glass/cyclohexane/glass.

![Fig. 2. Schematic illustration of FTIR-ATR spectroscopy, the defined coordinates, and a uniaxial model used to estimate the orientation of a transition moment of carboxylic acids adsorbed on the silicon oxide surface. Here, it was assumed that the transition moment distributes uniformly around the z axis with the angle of \( \gamma \).](image1)

![Fig. 3. Profiles of interaction forces between glass surfaces upon compression in propionic acid-cyclohexane binary liquids at various propionic acid concentrations of 0.0, 0.1, 0.5, 5.0, 10.0 and 20.0 mol%.](image2)
acid concentrations of 0.2-1.0 mol%. Here, values obtained at different concentrations were averaged because they nearly agreed with each other within the experimental error. Thus, we may conclude that the adsorption layers were composed of nearly pure propionic acid in this concentration range, and bridging of opposed adsorption layers should produce the long range attraction. The attraction remained the same up to 5.0 mol% propionic acid, then gradually decreased and almost disappeared at 20.0 mol%. We interpreted this change as a result of acid molecules being exchanging between the interface and the bulk solution (to be reported later). The short range repulsion was ascribable to the steric force due to the more stable structure of the propionic acid adjacent to the glass surfaces similar to the hydration force.\(^7\)\(^20\)

**Infrared spectroscopy of adsorbed propionic acid.** Chemical interactions involved in the formation of the adsorption layers of propionic acid were investigated by FTIR-ATR spectroscopy. FTIR-ATR spectra of propionic acid in cyclohexane at various propionic acid concentrations (0.0-0.5 mol%) are presented in Fig. 5. At 0.1 mol% propionic acid, a broad absorption around 3120 cm\(^{-1}\), which was assigned to the hydrogen-bonded OH stretching, was observed. This peak was located at a higher wavenumber compared with that of the hydrogen-bonded OH observed in the transmission spectrum (TS) of the bulk solution (see inset). The difference in the peak position of the hydrogen-bonded OH absorption indicated that the structure of the hydrogen bonding of propionic acids on the silicon oxide surface should differ from those in the bulk, where cyclic dimers are dominant. The hydrogen-bonded OH stretching absorption of oxalic acid was reported for two different crystalline structures of \(\alpha\) and \(\beta\) (Fig. 6).\(^21\) In the \(\alpha\) form, the C=O and OH bonds of a single carboxyl group are associated with different oxalic acid molecules, exhibiting the OH stretching absorption at 3114 cm\(^{-1}\). In the \(\beta\) form, the carboxyl groups form cyclic dimers through hydrogen bonding, exhibiting an absorption at 2890 cm\(^{-1}\). Therefore, the broad OH stretching absorption observed at \(-3120\) cm\(^{-1}\) in the ATR mode indicated that the propionic acids form a linear hydrogen-bonded structure, which we may call a “macrocluster”. With increasing the propionic acid concentration, the position of the hydrogen-bonded OH peak was gradually shifted to a lower wavenumber. At 1.0 mol% propionic acid, it became identical to that for the bulk solution, indicating that the measurement detected more contribution from the bulk due to the long penetration depth of the infrared light of 255 nm.

Dichroic analysis of the hydrogen-bonded OH absorption in the ATR mode has been performed in order to confirm the structure of the propionic acid cluster. The dichroic ratio of the integrated peak intensity of the hydrogen-bonded OH, \(A_\parallel/A_\perp\), was 0.91 ± 0.09 at a propionic acid concentration of 0.1 mol%. This value gave the average orientation angle of the OH bond (\(\gamma\)) to be 74 ±
8 degree to the surface normal. This indicated that the OH bonds of the propionic acid on the surface are aligned almost parallel to the surface. With increasing the propionic acid concentration, the dichroic ratio gradually increased and became ca. 1.6 at 1.0 mol% then remained almost constant.

*Adsorption polymerization of acrylic acid.* It should be interesting to utilize this phenomenon for preparing materials. We substituted propionic acid by acrylic acid and performed *in situ* polymerization of the acrylic acid adsorbed on the silica surfaces. The AFM image in Fig. 7 was obtained for a film prepared at 0.1 mol% acrylic acid by photo-irradiation for 20 min. It showed that the film was quasi-atomically flat and had no detectable defect. The average difference in the height was less than 0.2 nm in a 3 μm x 3 μm area. This surface morphology was quite reproducible. The film thickness was estimated to be ca. 25 nm from the forces measurement, agreeing with the thickness of the adsorption layer of propionic acid, 26 ± 1 nm, at 0.1 mol% (Fig. 4). We have no corresponding data for acrylic acid because it could contaminate the measurement cells. The poly(acrylic acid) film must be formed by the polymerization of the acrylic acid adsorption layer not by an adsorption of polymers produced in the bulk solution.

Fig. 8 shows an FTIR-ATR spectrum (ATR) of a poly(acrylic acid) film formed on a silicon prism surface together with a transmission spectrum (TS) of commercial poly(acrylic acid) in a KBr tablet. The ATR spectrum exhibited a broad absorption peak at ~3300 cm⁻¹, which was similar to the peak obtained for propionic acid adsorbed on a silica surface, and ascribed to a linear chain of hydrogen-bonded carboxylic acids. The linear chain cluster structures were still maintained in the poly(acrylic acid) films (Fig. 9). On the other hand, the transmission spectrum of poly(acrylic acid) in a KBr tablet showed a peak at ~3000 cm⁻¹, indicating the presence of various structures such as cyclic dimers and linear forms in the tablet. A regulated structure of the poly(acrylic acid) films formed by the combination of hydrogen bonding and polymerization may produce unique properties for the films. Indeed, it was very difficult to make a small pit in the film by an AFM tip. Films with different morphologies were obtained when we prolonged the irradiation time and/or increased the monomer concentration. We will report them in a separate paper.

**Conclusion.** In this study, we studied the adsorption of propionic acid (or acrylic acid) onto silica surfaces, and obtained the following results.

1. Unusually long-range attraction was found between glass surfaces in propionic acid-cyclohexane binary liquids, which was accounted for in terms of the bridging of opposed adsorption layers.

2. Hydrogen-bonded clusters of propionic acid were found in its adsorbed layer on silica surfaces in cyclohexane. Previously, we have found the formation of similar hydrogen-bonded clusters of alcohols (e.g., methanol, ethanol and 1-propanol) adsorbed on silica surfaces from cyclohexane. The current study demonstrated that the cluster formation is not limited to alcohols, and is a more general phenomenon.

3. Application of this adsorption phenomenon to fabricate the polymer nano-films has been performed.
Poly(acrylic acid) nano-films, 25 nm in thickness, were obtained with high reproducibility. They were quasi-atomically flat and uniform and exhibited practically no defect. Compared to other methods such as the spin coating and the LB method for preparing thin-films on solid surfaces, the adsorption method is simple, cost-efficient and highly applicable to substrates of different shapes. The preparation of uniquely ordered and/or structured films on solid surfaces should be possible. With these advantages, this method should be applicable in many areas of material science, which require thin-film preparation and nano-coatings.

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