Hydrogen-bonded Macrocluster Formation of Ethylene Glycol on Silica Surfaces in Ethylene Glycol-Cyclohexane Binary Liquids

Kazue Kurihara,* Yasuhiro Nakagawa, and Masashi Mizukami
Institute for Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577

(Received September 20, 2002; CL-020815)

Adsorption of ethylene glycol on silica surfaces was investigated in cyclohexane. A long-range attraction appeared between the silica surfaces in the presence of ethylene glycol (>0.0005 mol%). ATR-FTIR spectra exhibited an absorption band at 3600–3000 cm^{-1}, ascribed to the hydrogen-bonded hydroxyl groups. The results demonstrated that ethylene glycol adsorbed on the silica surfaces in a thick layer of several tens nm where it formed hydrogen-bonded molecular macroclusters.

The selective adsorption of one liquid component onto a solid surface from binary liquids is well known.[1] However, the molecular level characterization of this type of adsorption layers was practically nonexistent, to the best of our knowledge, until recently when we studied them using a combination of colloidal probe atomic force microscopy (AFM) and Fourier transform infrared spectroscopy in the attenuated total reflection mode (FTIR-ATR).[2–5] We studied the adsorption of alcohol and carboxylic acids onto silica surfaces from their mixtures with cyclohexane, and found the formation of hydrogen-bonded macroclusters by the adsorbed molecules. Here, the term "molecular macrocluster" is used because the hydrogen-bonded clusters extend to longer distances of ca. 20 nm than the typical size of a common cluster, 2–4 nm, for liquids (e.g., alcohol).[4,5] The silanol groups of silica surfaces have been found essential for the macrocluster formation because no macrocluster is formed on hydrogen-terminated silicon surfaces. In this study, to extend the scope of the study on these molecular macroclusters, we examined dihydric alcohol, ethylene glycol, and compared their properties with those of the monohydric alcohol, ethanol.

Cyclohexane from Nacalai Tesque was dried over sodium and distilled immediately prior to use. Ethylene glycol (Nacalai Tesque) was used as received. The measurements were performed similarly to those in previous reports,[2–5] thus only the major parts are described in the following section.

The interaction force (F) between a glass sphere and a glass plate was measured as a function of the surface distance (D) in ethylene glycol-cyclohexane binary liquids using AFM (Seiko II, SPI3700-SPA300). 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 (5–7.5 μm radius) was then attached to the end of a cantilever (Olympus, RC-800PS-1) with epoxy resin (Shell, Epikote1004). The sphere and plate were treated with water vapor plasma (Samco, BP-1) for 3 min[6] just prior to each experiment. The obtained force is normalized by the radius of the sphere (R) using the Derjaguin approximation,[7]

$$F/R = 2\pi G_{\text{f}} \qquad (1)$$

where G_{f} is the interaction free energy per unit area between two flat surfaces.

Infrared spectra were recorded on a Perkin-Elmer FTIR system 2000 using a TGS detector and the ATR attachment from Grasby Specac. The ATR prism made of a silicon crystal (Nihon PASTEC, $60 \times 16 \times 4$ mm trapezoid) was used as a solid adsorbent surface, where the infrared light was reflected six times with an incident angle of 45°. In order 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 then thoroughly rinsed with pure water. The crystal was then treated with water vapor plasma similarly to the glass surfaces. Hydrogen-terminated surfaces were prepared by immersing the silicon prism in 0.5 mol% aqueous hydrofluoric acid for 30 min. The dichroic ratio was calculated from the OH stretching absorption obtained in the ATR mode using p- and s-polarized infrared light.

Figure 1 shows the typical interaction forces measured between glass surfaces upon compression in the ethylene glycol-cyclohexane binary liquids (at the ethylene glycol concentrations of 0–0.005 mol%) and the theoretical van der Waals force using $F/R = -A/6D^2$ (A: nonretarded Hamaker constant). The interaction force in pure cyclohexane agreed with the conventional van der Waals force. The addition of ethylene glycol to cyclohexane changed the interaction, i.e., the long-range attraction appeared at a distance of 19 ± 4 nm at 0.0005 mol%. This distance became longer with the increasing ethylene glycol concentration, and the maximum attraction range was 349 ± 11 nm at 0.005 mol%. The pull-off force changed also depended on the ethylene glycol concentration in parallel with the long-range attraction, and exhibited the maximum, $F/R = 182 \pm 9$ mN/m, at 0.005 mol%. Previous studies[2–5] have

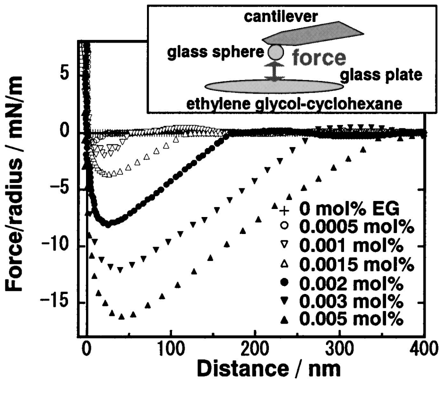

Figure 1. Force profiles of interactions between glass surfaces upon compression in ethylene glycol(EG)-cyclohexane binary liquids at various EG concentrations. Solid line represents the van der Waals force calculated using the nonretarded Hamaker constant of 3×10^{-21} J for glass/cyclohexane/glass.

indicated that the long-range attraction is caused by the contact (the bridging) of opposed adsorption layers, and the pull-off force corresponds to the force required for separating these contacted adsorption layers. The same mechanism should likely operate in the case of ethylene glycol. Thus, the adsorption of ethylene glycol was studied by ATR-FTIR spectroscopy.

ATR-FTIR spectra measured on silica (oxidized silicon) surfaces at various ethylene glycol concentrations (0–0.005 mol%) in cyclohexane are shown in Figure 2. At 0.0005 mol%, a broad absorption at 3600–3000 cm^{-1} and a narrow negative band at around 3660 cm^{-1} were observed. This spectrum is very similar to ATR spectra measured in ethanol-cyclohexane binary liquids, though the alcohol concentration range is much higher in the case of ethanol (>0.1 mol%). The former peak was ascribed to the hydrogen-bonded OH groups (νOH),[8,9] indicating the presence of hydrogen-bonded ethylene glycol on the silica surface probably by adsorption. On the other hand, the latter corresponded to decrease in the isolated (non-hydrogen bonded) silanol groups,[10,11] i.e., the surface silanol groups were hydrogen-bonded with ethylene glycol molecules. The intensity of the broad absorption at 3600–3000 cm^{-1} increased with the increasing ethylene glycol concentration.

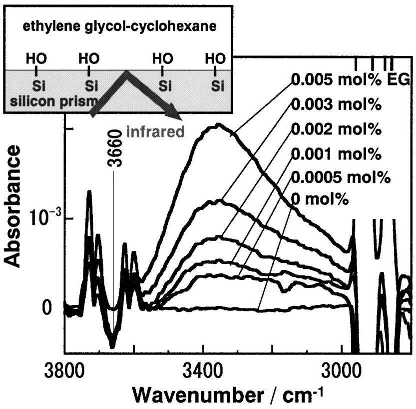

Figure 2. ATR-FTIR spectra measured on silicon oxide surface in ethylene glycol(EG)-cyclohexane binary liquids at various EG concentrations.

In order to confirm a role of the surface silanol groups, a hydrogen-terminated silicon surface was used as a substrate for ATR-FTIR spectroscopy. The ATR-FTIR spectra thus obtained displayed no absorption at 3600–3000 cm^{-1} for 0.0005–0.005 mol% ethylene glycol (data not shown), demonstrating that the silanol groups are essential to the adsorption of ethylene glycol. The adsorption of ethylene glycol occurred at concentrations higher than ca. 0.0005 mol% through hydrogen-bonding between the surface silanol groups and ethylene glycol and that between ethylene glycol. The spectra also indicated that there was not enough ethylene glycol in the bulk that could provide detectable contribution to the ATR spectrum, though the penetration depth of the evanescent wave was ca. 250 nm at 3300 cm^{-1}.[3] Therefore, the ATR-FTIR spectra in Figure 2 did not show any contribution from the hydrogen-bonded clusters possibly existing in the bulk phase, and only reflected the amount of the adsorbed ethylene glycol thus the adsorption layer thickness. Actually, the integrated peak intensity of the absorption at 3600–3000 cm^{-1} increased similarly to the range of the long-range attraction when the ethylene glycol concentration increased (these data will be reported in the future). These results support the mechanism that the long-range attraction is caused, also for ethylene glycol, by the contact (bridging) of the opposed adsorption layers.

Polarized ATR-FTIR spectra were obtained using p- and s-polarized light, and provided the mean orientation angle of the OH group to be 36 ± 2° from the dichroic ratio.[5,12] A plausible model for ethylene glycol macroclusters is shown in Figure 3.

This study has demonstrated that ethylene glycol (dihydric alcohol) forms hydrogen-bonded molecular macroclusters on silica surfaces in cyclohexane as does monohydric alcohol. However, the concentration ranges where macroclusters are formed are very different, higher than 0.0005 mol% for ethylene glycol and 0.1 mol% for ethanol.[3,5] The maximum range of the attraction, which seems to correspond to twice the maximum thickness of the adsorption layer of alcohol, is also different, ~350 nm for ethylene glycol and ~40 nm for ethanol.[2,5] Ethylene glycol, which bears two hydrogen bonding hydroxyl groups, seems to efficiently form molecular macroclusters on surfaces. This study opens the door for the fine regulation of structures of hydrogen-bonded molecular maclоclusters in adsorbed layers, which could be used as a novel surface molecular organization in nanomaterials science.

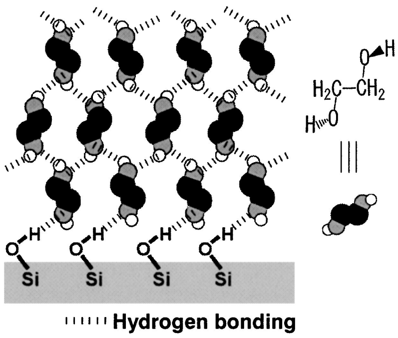

Figure 3. A plausible model of ethylene glycol macroclusters on glass surface in cyclohexane.

This work was supported by a Grant-in-Aid for Scientific Research (No. 13022204, 14340214) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 Z. Király, L. Turi, I. Dékány, K. Bean, and B. Vincent, *Colloid Polym. Sci.*, **274**, 779 (1996).
2 M. Mizukami and K. Kurihara, *Chem. Lett.*, **1990**, 1005.
3 M. Mizukami and K. Kurihara, *Chem. Lett.*, **2000**, 256.
4 M. Mizukami, M. Moteki, and K. Kurihara, *J. Am. Chem. Soc.*, **124**, 12889 (2002).
5 K. Kurihara and M. Mizukami, *Proc. Jpn. Acad.*, **77B**, 115 (2001).
6 H. Okusa, K. Kurihara, and T. Kunitake, *Langmuir*, **10**, 3577 (1994).
7 J. N. Israelachivili, “Intermolecular and Surface Forces,” 2nd ed., Academic Press, London (1991).
8 U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).
9 L. J. Bellamy, “Advances in Infrared Group Frequencies,” Methuen & Co. Ltd., London (1968).
10 S. N. W. Cross and C. H. Rochester, *J. Chem. Soc., Faraday Trans.*, **75**, 2865 (1979).
11 J.-M. Berquiner and H. Arribart, *Langmuir*, **14**, 3716 (1998).
12 The mean orientation angle was obtained as an average of the data measured for five different concentrations. A typical orientation angle was 35.1 ± 0.2° calculated from the dichroic ratio of 3.15 ± 0.05 at 0.003 mol%.