Long Range Attraction between Glass Surfaces in Cyclohexane-Ethanol Binary Liquids

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Interaction forces between glass surfaces in cyclohexane-ethanol binary mixtures were investigated using colloidal probe atomic force microscopy. An unusually long range attraction was found in the presence of ethanol in the concentration range of 0.1 ~ 1.4 mol%. At 0.1 mol% ethanol, the attraction appeared at a distance of 35 ± 3 nm and turned into a repulsive force below 3.5 ± 1.5 nm upon compression. A possible explanation accounting for this long range attraction is the bridging of opposed adsorption layers of ethanol on the glass surfaces.

The stability of colloidal dispersions in binary liquids changes depending on the composition of the liquids. Therefore, understanding the interactions between colloidal particles is important for regulating their stability. In binary liquids, one component generally adsorbs preferentially onto a solid surface on account of the difference in their affinity with the solid surface, thus complicating the interaction forces. The difference in the stability of colloidal dispersions has been explained in terms of (1) the change in Hamaker constant due to the adsorption layer formation,[1,2] or (2) the change in the zeta potential due to the dissociation of surface ionic groups.[3] However, experimental results were only qualitatively examined for the proposed mechanism, and in some cases, showed inconsistencies.[1] Effects of the adsorption on the interaction forces were not clearly understood. Thus the direct force measurement is essential for elucidating the interactions. In this paper, we report the direct measurement of forces between glass surfaces in cyclohexane-ethanol binary liquid mixtures using the colloidal probe atomic force microscopy (AFM).[4] In cyclohexane-ethanol binary liquids, it is known that ethanol preferentially adsorbs onto hydrophilic glass surfaces.[2] The amount of adsorbed ethanol was determined to study the mechanism of the observed interaction forces.

Ethanol (reagent grade) was distilled prior to use. Cyclohexane from Nacalai Tesque was dried with sodium and distilled immediately prior to use. The interaction force (F) between a glass sphere and a glass plate was measured as a function of the surface distance (D) in cyclohexane-ethanol mixtures 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 (4 ~ 5 μm radius) was then attached to the top 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) for 3 min. just prior to each experiment in order to ensure the existence of silanol groups on glass surfaces.[5] The closed AFM fluid cell constructed in our laboratory was thoroughly washed with distilled ethanol and blown dry with nitrogen, and then rinsed with pure cyclohexane prior to use. The obtained forces were normalized by the radius (R) of the sphere using the Derjaguin approximation.[6]

$$F/R = 2\pi G_f \qquad (1)$$

where G_f is the interaction free energy per unit area between two flat surfaces. The radius (R) was measured by an optical microscope. The individual spring constant of the cantilever was determined following a previously reported procedure.[7]

The adsorption excess isotherm was measured using adsorbent glass spheres (Polyscience) which were washed and water vapor plasma treated in the same manner as for the force measurements. The glass spheres (typically 1.0 g) dispersed in cyclohexane-ethanol mixtures (10 ml) precipitated after they were equilibrated for about 24 h at 20 ± 0.5 °C. The composition of the supernatant was determined using a differential refractometer (Otsuka Electronics, DRM-1021). The adsorption layer thickness (t) was estimated by assuming that only ethanol is present in the adsorption layer using the specific adsorption excess amount ($n_1^{\sigma(n)}$).[8,9]

$$t = n_1^{\sigma(n)} V_1 / a_S \qquad (2)$$

where V_1 is the molar volume of ethanol (0.0970 nm^3/molecule), which was calculated from the density of ethanol[10] at 20 °C, and a_S is the specific surface area of the adsorbent glass spheres (0.60 ± 0.04 m^2/g).[11]

Figure 1 presents the typical interaction forces measured between glass surfaces upon compression in the ethanol-cyclohexane binary liquids (at ethanol concentrations of 0.0~1.4 mol%) and the theoretical van der Waals force using $F/R = -A/6D^2$ (A: nonretarded Hamaker constant).[6] The interaction force in pure cyclohexane agreed with the conventional van der Waals force, and the adhesion force F/R was 10 ± 7 mN/m.[6] At 0.1 mol% ethanol, the interaction remarkably changed, *i.e.*, the long range attraction appeared at a distance of 35 ± 3 nm, reached a maximum (1.5 mN/m) around 10 nm, and turned into repulsion at distances shorter than 3.5 ± 1.5 nm. Half of the

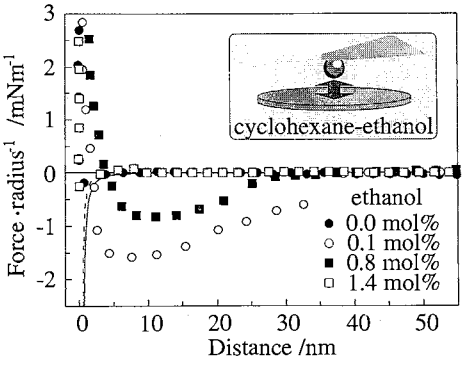

Figure 1. Profiles of interaction forces between glass surfaces upon compression in ethanol-cyclohexane mixtures. Dashed line and solid line represent the van der Waals force calculated using the nonretarded Hamaker constants of 3 x 10^{-21} J for glass/cyclohexane/glass, 6 x 10^{-21} J for glass/ethanol/glass, respectively.[6]

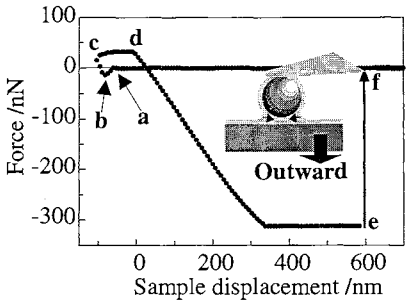

Figure 2. The force profile during one cycle of the measurement: the attraction appeared at **a**, and changed to the repulsion at **b** upon compression. The profile **c-d** shows that the cantilever ramained at the same position although the glass plate retreated. The profile **e-f** indicates the jump-out separation of two surfaces. The insert shows a plausible scheme of liquid influx into the gap during the process **c-d**.

distance where the long range attraction appeared (18 ± 2 nm) was close to the layer thickness of the adsorbed ethanol, 13 ± 1 nm, calculated from the surface excess amount per m^2 (0.23 ± 0.01 mmol/m^2) for the supernatant equilibrium concentration of 0.1 mol% ethanol. This indicates that the attraction might result from the contact of opposed ethanol adsorption layers. The error due to the surface roughness in calculating the adsorption layer thickness should be negligible due to the large layer thickness. The short range repulsion is ascribable to the steric force due to the structure formation of ethanol molecules adjacent to the glass surfaces similar to the hydration force.[4, 12] The observed interactions were identical at various approaching and separating speeds (20 nm/s ~ 500 nm/s).

In order to examine the separation process, the interaction force during one cycle of the measurement at 0.1 mol% ethanol was plotted versus the displacement of the glass plate in Figure 2. At the beginning of the decompression after the contact, the cantilever stayed nearly in the same position (the region c-d in Figure 2) and did not follow the movement of the glass plate retreating about 100 nm although they were practically in contact. 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. The adhesion force was determined to be 140 ± 19 mN/m, which was much higher than that in pure cyclohexane.

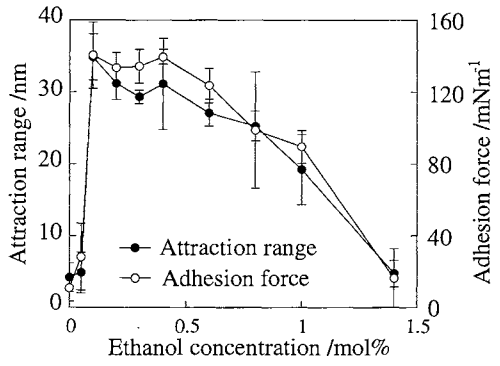

Figure 3. Changes in the attraction range and the adhesion force for the glass surfaces in cyclohexane-ethanol binary liquids.

The attraction remained the same up to the ethanol concentration of 0.4 mol%, then decreased both in the distance range and intensity, and adhesion force (see Figure 3). In 1.4 mol% ethanol, the interaction became identical to that in pure cyclohexane. Both the long range attraction and the adhesion force simultaneously changed with increasing ethanol concentration, indicating that the interactions share the same origin: contact of the adsorbed ethanol layers. The decrease in the attraction range demonstrates that the pure ethanol adsorption layer is thinning and a clear boundary to the bulk solution disappears at 1.4 mol% ethanol. One may note, however, that the surface excess ethanol remained nearly the same for the concentration range of 0.1 ~ 2.0 mol% ethanol (data not shown). The mechanism to explain the difference in these concentration dependencies is currently under investigation in our laboratory.

This work demonstrates for the first time the presence of the long range attraction in miscible binary liquids, which could be explained by contact of the adsorption layer. A similar attraction was observed between mica in water saturated octamethylcyclotetrasiloxane (near the critical point) and was explained by bridging of the capillary condensed water on surfaces in inmiscible liquids.[13] On the other hand, in our case, cyclohexane and ethanol are completely miscible at 20 °C, thus the pure ethanol layer formation is a surface induced phenomenon. Further investigations are needed to understand how such a thick ethanol adsorption layer can be formed and modify the surface interactions depending on the ethanol concentration in the bulk liquids. Elucidation of these mechanisms may provide novel information on the structure of the ethanol adsorption layer at the molecular level.

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References and Notes

1 G. Machula, I. Dékány, and L. G. Nagy, *Colloids Surf. A: Physicochem. Eng. Asp.*, **71**, 241 (1993).
2 Z. Király, L. Turi, I. Dékány, K. Bean, and B. Vincent, *Colloid Polym. Sci.*, **274**, 779 (1996).
3 B. Vincent, Z. Király, S. Emmet, and A. Beaver, *Colloids Surfaces*, **49**, 121 (1990).
4 W. A. Ducker, T. J. Senden, and R. M. Pashley, *Langmuir*, **8**, 1831 (1992).
5 H. Okusa, K. Kurihara, and T. Kunitake, *Langmuir*, **10**, 3577 (1994).
6 J. N. Israelachvili, "Interemolecular and surface forces," 2nd ed, Academic Press, London (1991).
7 J. P. Cleveland, S. Manne, D. Bocek, and P. K. Hansma, *Rev.Sci.Instrum.*, **64**, 403 (1993).
8 I. Dékány, F. Szántó, and L. G. Nagy, *Prog. Colloid & Polymer Sci.*, **65**, 125 (1978).
9 I. Dékány, L. Túri, E. Tombácz, and J. H. Fendler, *Langmuir*, **11**, 2285 (1995).
10 J. A. Riddick, W. B. Bunger, and T. K. Sakano, "Organic Solvents," in "Techniques of Chemistry," ed. by A. Weissberger, John Wiley & Sons, New York, (1986), Vol. 2, p. 192.
11 The standard deviation of $n_1^{\sigma(n)}$ was in the range of 1 ~ 6% depending on the concentrations of the liquid mixtures. The specific surface area a_S was calculated by assuming that the sphere was hard and nonporous. The size distribution of the adsorbent glass sphere was determined using an optical microscope equipped with a CCD camera using 1000 glass spheres.
12 A. Grabbe, and R. G. Horn, *J. Colloid Interface Sci.*, **157**, 375 (1993).
13 H. K. Christenson, *J. Colloid Interface Sci.*, **104**, 234 (1985).