Ethanol macroclusters adsorbed on glass spheres in ethanol/cyclohexane binary liquids studied by ¹H-NMR spectroscopy

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Ethanol is preferably adsorbed on glass spheres in ethanol/cyclohexane binary liquids. We have recently found that ethanol molecules form a hydrogen-bonded organized structure on the glass surface, which we call an "ethanol macrocluster". In this study, we employed the ¹H-NMR spectroscopy for investigating the ethanol adsorption layer in the binary liquids at 0-2.1 mol% ethanol concentrations in the absence and presence of the glass spheres. The spectra showed resonance lines assigned to the hydroxyl (OH), methylene (CH₂), and methyl (CH₃) protons, respectively. The chemical shifts of these proton resonance lines were similar for two cases, though the line shapes were different especially at ethanol concentrations higher than 0.6 mol%. For example, at 1.94 mol% ethanol, the OH resonance line exhibited shoulders and the CH_2 line was octet in the presence of the spheres, while in the absence of the spheres, the OH and CH_2 lines were singlet and quartet, respectively. These results indicated that there were two types of ethanol clusters in the bulk phase in the presence of the glass spheres at higher ethanol concentrations, resulted from the exchange of ethanol molecules between the bulk and the surface clusters. Key Words: binary liquid/¹H-NMR/adsorption layer/hydrogen bonding/ dynamic motion

1. INTRODUCTION

Recently, we have found that ethanol molecules adsorbed on a glass surface form hydrogen-bonded organized linear chain structure in cyclohexane, which we call "molecular macroclusters" [1-4], and utilized the phenomenon for preparing polymer thin films [5]. It's the cluster axis aligned almost normal to the surface and they extended ca. 15 nm from the surface silanol groups, as shown in Fig. 1

Combination of Fourier transform infrared spectroscopy (FTIR) in the attenuated total reflection (ATR) mode [6] and the colloidal probe atomic force microscopy was used to determine the structure of the ethanol layers adsorbed on the silica surfaces at the molecular level [7-9]. We found that an unusually long-range attraction appeared at about 30 nm between glass surfaces in ethanol/cyclohexane binary liquids. This attraction was much longer than the van der Waals attraction, and was interpreted as a force like the capillary force originating from the interfacial energy between the adsorbed layer and the bulk phase. Therefore, half the range of attraction should correspond to the adsorption layer thickness as shown in Fig. 2 for





the lower ethanol concentration region up to 0.6 mol%. Here, the adsorption layer thickness was estimated from



Fig. 3 ¹H-NMR spectra at (a), (b) 2.1 ethanol in the absence of glass spheres and (c), (d) 1.94 mol % ethanol in the resence of the spheres, respectively, in deuterated cyclohexane.

the surface excess of ethanol assuming that only ethanol was present in the adsorption layer. Beyond 0.6 mol% ethanol, half the attraction range started to decrease while the adsorption layer thickness remained constant. Accounting for this discrepancy between two parameters, we suggested that the exchange of ethanol molecules would occur between the adsorbed layer and the bulk phase. If there were such an exchange, the dynamic properties of ethanol molecules should change [8].

This study aims at elucidating the dynamic properties of ethanol molecules in ethanol/deuterated cyclohexane binary liquids in the presence and the absence of glass spheres by ¹H-NMR spectroscopy. Chemical shifts of the hydroxyl proton (OH), methylene proton (CH₂), and methyl proton (CH₃) resonance lines were similar for both cases. However, the line shapes were different, indicating that there were two kinds of ethanol molecules in the bulk clusters in the presence of the glass spheres at higher ethanol concentrations, and that there was indeed the exchange of ethanol molecules between the surface and the bulk clusters.

2. EXPERIMENTS

Deuterated cyclohexane (Aldrich Chemical Co.) was dried with sodium (nacalai Tesque Inc.), refluxed for above 2 hours and distilled. The content of $C_6D_{11}H$ in C_6D_{12} was 0.3 %. Colloidal glass spheres (Polyscience) were washed in a mixture of sulfuric acid and hydrogen peroxide (4:1, v/v) and thoroughly rinsed with pure water. The glass spheres 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 [8].

¹H-NMR measurements (JEOL, JNM400) were performed for ethanol/deuterated cyclohexane binary liquids in the presence and absence of glass spheres at 21-22.5 °C under the magnetic field of 9.3 T. The glass spheres (0.07 g) were added to an NMR tube containing 0.6 ml of deuterated cyclohexane.

In the case of the binary liquids with glass spheres, ethanol was adsorbed on the glass surfaces. Therefore, it was necessary to determine the final concentration of ethanol in the bulk phase, which was different from the initial value before adding glass spheres. FTIR spectroscopy was used to monitor the ethanol concentration. The absorbance of a peak at 3640 cm⁻¹ assigned to free hydroxyl groups was used to calculate the concentration using the calibration curve obtained for ethanol-cyclohexane binary liquids.

3. RESULTS AND DISCUSSION

Fig. 3 (a), (b) and (c), (d) show ¹H NMR spectra for 2.1 mol% ethanol in the absence of glass spheres and 1.94 mol% ethanol in the presence of the spheres, respectively, in deuterated cyclohexane. Deuterated cyclohexane used exhibited only the $C_6D_{11}H$ resonance line for both absence and presence of glass spheres.

For the former, we observed three resonance lines at chemical shifts of 3.57, 1.38 and 1.14 ppm and assigned them to the CH₂, the proton of $C_6D_{11}H$, and CH₃, respectively. These resonance lines of the latter appeared at similar shift positions to the former. The shifts of CH₂, $C_6D_{11}H$ and CH₃ resonance lines were also independent of the ethanol concentrations studied.

Conversely, a chemical shift of the OH resonance line gradually increased with the increasing ethanol concentration as shown in Fig. 4, in which Δ shift was plotted against the ethanol concentration. Here, Δ shift is the difference between the chemical shifts, δ (OH) and δ (CH₂), of the OH and CH₂ resonance lines as δ (OH) $-\delta$ (CH₂). Δ shift gradually changed from -2.85 ppm at 0.3 mol% to 0.36 ppm at 3.3 mol%. It is known that such increase is due to developing the formation of hydrogen-bonded polymers (clusters) of ethanol in a non-polar solvent with increasing the ethanol concentration [10].

To examine how the ethanol adsorption on glass spheres affected the OH resonance peak, the chemical shift of the OH resonance line for both the absence and the presence of the spheres were compared in Fig. 3. These plots in filled triangles and circles showed that the difference between them was very little. The previous study has revealed that ethanol is adsorbed onto glass surfaces by hydrogen bonding extending ca. 15 nm from the surface silanol groups [8]. The density of ethanol in the adsorbed layer has been found to be similar to that of the bulk ethanol. The OH resonance for the bulk ethanol is observed at a chemical shift of about 4 ppm [12], which is very different from the shift in a diluted ethanol solution. Therefore, if the adsorbed ethanol contributed to the observed resonance line, the chemical shift should be different for two cases of the absence and presence of glass spheres, which was not the case of the current observation. It is most likely that we could only detect the OH attributed to the ethanol molecules existing in the bulk phase, but not those adsorbed on the glass surfaces. As we know, NMR spectra attributed chemical species adsorbed on a solid surface show very broad peaks, sometimes too broad and weak to detect, which might be the case of our present system [15].



Fig. 4 Δ shift is plotted vs. the ethanol concentration. Here, Δ shift is $\delta(OH) - \delta(CH_2)$, where $\delta(OH)$ and $\delta(CH_2)$ are the chemical shift of the proton resonances of the hydroxyl and the methylene group, respectively. Filled circles and triangles correspond to the data of ethanol-deuterized cyclohexane mixtures without and with glass spheres in this work, respectively. Open circles correspond to the data without glass spheres by Chandler and Dinus [10].

We will now discuss the NMR line shapes in both cases of the absence and presence of glass spheres. For the former, as shown in Fig. 2 (a), the CH₂, CH₃, and OH resonance line gave quartet, triplet and singlet, respectively [11, 12]. These line shapes were independent of the ethanol concentration studied. However, in the case of the latter (with the spheres), their line shapes depended on the ethanol concentration. For the line shape of the OH, the singlet peak at 0.24 mol% changed with increasing ethanol concentration; i.e., a peak with shoulders at both sides was observed at This shoulder was analyzed by the 1.94 mol%. Gaussian deconvolution with the combination of one singlet and one triplet component [11]. This indicated that there were two types of ethanol clusters in the bulk phase in the presence of the glass spheres at higher ethanol concentrations, possibly resulted from the exchange of ethanol molecules between the bulk and the surface adsorbed layer. As mentioned in the previous paragraph about the OH resonance lines, even in the presence of glass spheres, ethanol molecules in the bulk phase were likely contributing to the observed resonance. Therefore, the change in the line shape of the OH resonance line implied that two kinds of dynamic motions existed in the hydroxyl protons of the ethanol

molecules in the bulk phase in the presence of glass spheres as well as at higher ethanol concentrations. Some hydroxyl protons showed relatively free dynamic motions similar to those in the binary liquids without the spheres, and others displayed suppressed dynamic motions corresponding to a broad line. The existence of two different dynamic motions for the hydroxyl proton must influence the resonance of the CH_2 group that locates next to the OH group.

The CH₂ resonance line was a quartet in the absence of glass spheres (see Fig. 3 (a) for 2.10 mol% ethanol), and it changed to an octet by the addition of the spheres (Fig. 3 (b) for 1.94 mol% ethanol) [13]. Such a change was not observed without the glass spheres for a similar ethanol concentration range. The chemical shift of the CH₂ resonance lines was independent of the ethanol concentration, thus, it should be natural to expect that both adsorbed ethanol on the glass spheres and the bulk ethanol contribute to the CH₂ line. In order to estimate the contribution of the adsorbed ethanol, the ratio of ethanol adsorbed on the surface to that in the bulk phase was calculated. The ratio was 1: 32 at 1.94 mol% ethanol, indicating that the bulk ethanol mainly contributes to the NMR spectra in Fig. 3. The change in the line shape to the octet should be brought about by the spin couplings between the OH and CH₂ and between the CH3 and CH2 due to the suppressed dynamic motions of the CH_2 in the bulk [13, 14]. This suppression should be caused by the presence of adsorbed ethanol molecules on glass, quite likely through the interaction between ethanol molecules in the bulk and in the adsorbed layers.

We measured ¹H NMR spectra of ethanol /deuterated cyclohexane binary liquids in the presence and absence of glass spheres. Observed spectra were mainly attributable to ethanol molecules in the bulk phase, and remarkably influenced by the presence of glass spheres: the broadening and additional splitting were observed in the OH and CH_2 resonance lines by the addition of the spheres at ca. 2 mol% ethanol. These changes indicated the interaction between the bulk ethanol and those in the adsorbed macroclusters. The interfacial energy should be decreased by these interactions

because it would become difficult to define a clear interface. It is interesting to find such dynamic behavior exists between the adsorbed species and the bulk phase, which should be important for designing novel materials utilizing adsorption phenomena.

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