

Ethanol Cluster Formation on Silicon Oxide Surface in Cyclohexane–Ethanol Binary Liquids

Masashi Mizukami and Kazue Kurihara*

Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577

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Adsorption of ethanol onto silicon oxide surfaces from cyclohexane–ethanol binary liquids was investigated by FTIR spectroscopy using the attenuated total reflection (ATR) mode. ATR spectra exhibited that ethanol adsorbed on the surfaces formed clusters even in a low ethanol concentration range of 0.1–0.5 mol% where practically no ethanol cluster formed in the bulk solutions. The spectra 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.

The selective adsorption of one liquid component onto a solid surface from binary liquids is well known.¹ For example, ethanol preferentially adsorbs on silica surfaces from its mixtures with cyclohexane.^{2,3} Nevertheless, relatively few studies have been devoted to study this type of adsorption in spite of its apparent importance in both science and technology because many surface treatments and catalytic reactions are performed in liquid mixtures. Methods employed for the investigation have been limited and mostly based on the adsorption isotherm measurements. The molecular level of characterization is needed for further investigation because such information is essential to elucidate the adsorption phenomena. In the present work, we employed Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR) and demonstrated the cluster formation of ethanol adsorbed on silicon oxide surface.

Infrared spectra were recorded on a Perkin Elmer FTIR system 2000 using a TGS detector. For the ATR mode, the ATR attachment from Grasby Specac was used with a flow cell, homemade of stainless steel and sealed with a Teflon O-ring. Transmission infrared spectra were obtained using a CaF₂ cell (Nihon Bunko) with the path length of 25 μ m. Cyclohexane and ethanol from Nacalai tesque were dried with sodium and magnesium, respectively, and distilled just prior to use.

The ATR prism made of silicon crystal (Nihon PASTEC, 60 \times 16 \times 4 mm trapezoid) was used as a solid adsorbent surface. 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.⁴ In order to clean the 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. Immediately prior to each experiment, the silicon crystal was 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 20 min, in order to ensure the formation of silanol groups on the silicon oxide surface.⁵ The penetration depth of evanescent wave d_p was estimated to be 250 nm at 3300 cm⁻¹ using a refractive indices of the silicon crystal (3.42) and cyclohexane (1.426), and 45° for the incident angle of the light.

Ethanol is known to form hydrogen-bonded dimer and polymers in nonpolar liquids such as CCl₄ and cyclohexane.^{6–8}

The general spectral characteristics of hydrogen-bonded alcohols in the fundamental OH stretching region have been well established.^{6–11} First, as a reference, we examined hydrogen-bonded ethanol cluster formation in bulk cyclohexane–ethanol mixtures. Transmission infrared spectra of ethanol in cyclohexane at various ethanol concentrations (0.3–3.0 mol%) are presented in Figure 1A. Cyclohexane was used for the background spectrum measurement. A spectrum for 0.3 mol% ethanol exhibited a strong peak at 3640 cm⁻¹, assigned to the monomer OH (non bonded), with a shoulder at 3630 cm⁻¹, acceptor end OH group, and a weak peak at 3530 cm⁻¹ attributed to the ethanol cyclic dimers or donor end OH group. With increasing ethanol concentration, a new broad peak appeared at 3330 cm⁻¹ (polymer OH) indicating the formation of ethanol polymers. This peak increased sharply, became comparable to the monomer peak (3640 cm⁻¹) at 1.0 mol% ethanol, then exceeded it in intensity when the ethanol concentration was further increased. On the other hand, only a slight increase in peak intensities at 3640, 3630, and 3530 cm⁻¹ was observed. The observed concentration dependence agreed well with that in CCl₄, and it demonstrated the drastic increase in the number and the size of ethanol clusters in cyclohexane at elevated ethanol concentrations.

Subsequently, we studied ethanol cluster formation on the silicon oxide surface. FTIR-ATR spectra of ethanol in cyclo-

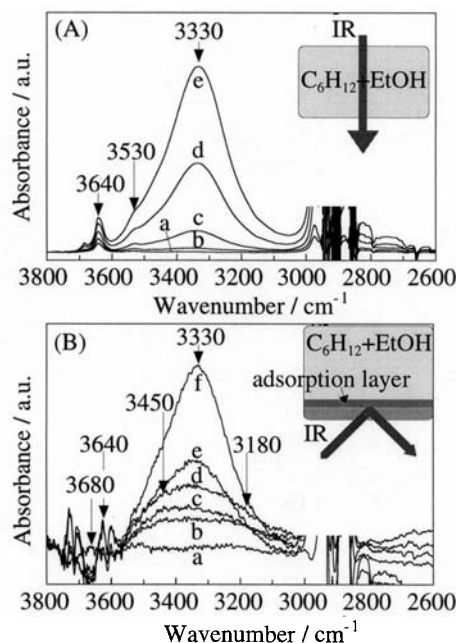


Figure 1. (A) FTIR transmission spectra of ethanol–cyclohexane binary liquids at various ethanol concentrations of 0.3–3.0 mol%:(a) 0.3, (b) 0.5, (c) 1.0, (d) 2.0, and (e) 3.0. (B) FTIR-ATR spectra of ethanol on silicon oxide surface in ethanol–cyclohexane binary liquids at various ethanol concentrations of 0.0–3.0 mol%:(a) 0.0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 1.0, and (f) 2.0.

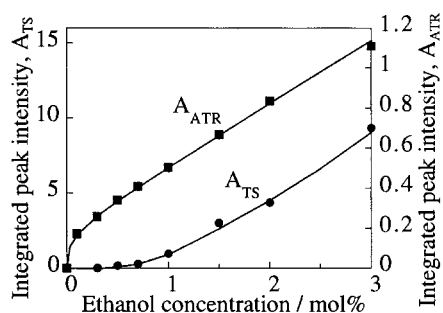


Figure 2. Plots of integrated peak intensities of polymer OH (3600–3000 cm^{-1}) as a function of the ethanol concentration. Filled circles represent the values obtained from transmission spectra (A_{TS}), while filled squares represent those from ATR (A_{ATR}).

hexane at various ethanol concentrations (0.0–2.0 mol%) are presented in Figure 1B. Cyclohexane was also used to measure a background spectrum. The spectrum of reinjected pure cyclohexane (0.0 mol% ethanol) was flat demonstrating the stability of the measurement. At 0.1 mol% ethanol, a narrow negative peak at 3680 cm^{-1} , a weak peak at 3640 cm^{-1} (free OH), and a broad strong peak at 3600–3000 cm^{-1} were observed. This broad peak at 3600–3000 cm^{-1} were composed of the peak at 3450 cm^{-1} , 3330 cm^{-1} (polymer OH) and 3180 cm^{-1} which became apparent at higher ethanol concentrations (0.3 and 0.5 mol%). It is known that the isolated silanol group exhibits the absorption band at 3675–3690 cm^{-1} in a nonpolar liquid, e.g., CCl_4 , and when the silanol groups hydrogen bond with esters, the absorption band shifts to a lower wavenumber (3425–3440 cm^{-1}).^{12–15} Thus, the negative absorption at 3680 cm^{-1} and the positive peak at 3450 cm^{-1} should correspond to the decrease in the isolated silanol groups and the appearance of the silanol groups hydrogen bonded with the adsorbed ethanol, respectively. The strong broad peak ascribed to the polymer OH appeared at 3600–3000 cm^{-1} together with the relatively weak monomer OH peak at 3640 cm^{-1} at 0.1 mol% ethanol where no polymer peak appeared in the spectrum of the bulk solution. This demonstrated the cluster formation of ethanol adsorbed on the silicon oxide surface. The bandwidth corresponding to the half absorbance of the polymer peak (390 cm^{-1}) at 0.1 mol% was rather broad compared with the half-bandwidth of the transmission peak (207 \pm 4 cm^{-1}) which well agreed with the reported value for ethanol in CCl_4 .⁷ Ethanol clusters at the solid-liquid interface should be in a greater variety of forms than those in the bulk, i.e., various oligomers, linear polymers with distorted hydrogen bonds due to two dimensional confinement, and crystalline-like structures. One may also note that a weak peak at 3180 cm^{-1} observed in the ATR spectrum similarly to spectra observed for ethanol crystallized at -108 $^\circ\text{C}$.¹⁶ This suggested 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 monomer OH (3640 cm^{-1}) and the polymer OH peak (3330 cm^{-1}) increased, while absorption at 3450 and 3180 cm^{-1} remained the same. At higher ethanol concentrations, bulk species should have contributed to ATR spectra because of the long penetration depth of the evanescent wave, 250 nm. To examine the bulk contribution, the integrated peak intensities of polymer OH peaks of transmission (A_{TS}) and ATR (A_{ATR}) spectra are plotted as a function of the ethanol

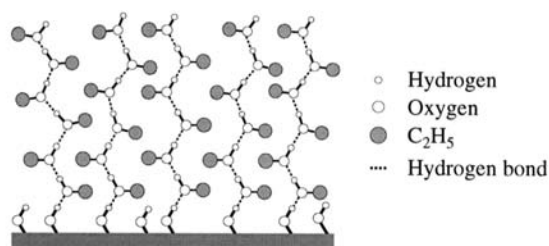


Figure 3. A plausible structure of the adsorption layer composed of ethanol clusters.

concentration in Figure 2. The former monitors cluster formation in the bulk liquid, while the latter contains contributions of clusters both on the surface and in the bulk. A comparison of A_{TS} and A_{ATR} clearly indicated that ethanol clusters formed locally on the surface at low concentrations of ethanol up to \approx 0.5 mol% where practically only a negligible number of clusters existed in the bulk. Previously we estimated the ethanol adsorption layer thickness to be 13 ± 1 nm for the glass surface, treated in a similar manner as the present work, at 0.1 mol% ethanol (in cyclohexane) based on the adsorption excess measurement assuming that only ethanol was present in the adsorption layer.³ The present work demonstrated that the thick adsorption layer most likely consisted of ethanol clusters formed through hydrogen bonding between surface silanol groups and ethanol as well as those between ethanol molecules. A plausible structure of the ethanol adsorption layer is presented in Figure 3.

This is, as far as we know, the first demonstration of alcohol cluster formation locally on solid (silicon oxide in this work) surfaces upon adsorption. We believe that our approach will shed light on the molecular level of understanding of liquid adsorption, which can be important for designing many surface processes, such as surface modifications and reactions, and the stabilization of colloidal dispersions.

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