

FTIR spectral characterization of thin film coatings of oleic acid on glasses

Part II *Coatings on glass from different media such as water, alcohol, benzene and air*

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Oleic acid thin film was coated on soda-lime-silicate (SLS) glass from different coating media such as benzene, ethyl alcohol, water and air with different coating times and concentrations. When the coating medium is benzene, relatively more COO-metal ion complexes formed on the substrate surface, resulting in a coating layer with a more rigid and ordered structure. This was caused by a high solubility of oleic acid and a lower metal dissolution rate of the glass substrate in the medium. The coating time was a less important factor on the ordering of molecular chains than the coating medium was. The effect of concentration was more significant when oleic acid is coated from ethyl alcohol or water rather than from benzene. When oleic acid is coated from benzene, the most highly-ordered molecular structure of coating layer was obtained even at lower concentration. This investigation reveals that the dissolution behavior of the substrate, the solubility of the coating material and the dissociation behavior of metal-carboxylate (COO-M) complexes significantly influence the interaction mechanism between the coating material and the substrate. These factors can be controlled by the selection of an appropriate coating medium; thus, we can design organic thin films with optimized properties. © 2000 Kluwer Academic Publishers

1. Introduction

Coatings of organic thin films and hybrid materials have wide range of applications from electronic packaging to bio-medical devices [1–5]. We investigated the effect of the composition of the substrate on its coating by organic materials in a previous study [6]. The coating mechanism involving an organic material on a substrate also depends upon the coating medium (or solvent) along with the composition of the substrate material. The coating medium can affect the surface of the substrate and the solubility of the applied organic materials. Therefore, the selection of the medium is one of the most important factors for the optimized performance of organic thin film layers. Therefore, we must consider the interactions between the substrate, the medium, and the organic material with respect to the coating mechanism.

For this purpose, the coating mechanism for oleic acid onto soda-lime-silicate (SLS) glass was studied using different coating media: benzene, ethyl alcohol, and water along with air. While benzene is very hydrophobic, water is hydrophilic. Ethyl alcohol possesses properties that are between those for the two media. In addition, oleic acid is very hydrophobic while the surface of glass possesses hydrophilic properties. Therefore, each medium can show different capabilities for dissolving

the oleic acid and the glass. Benzene possesses greater solubility of oleic acid but does not cause much dissolution of the glass, while water shows a reversal of these properties between oleic acid and the glass surface. Air can also be considered a coating medium in the wide concept of a medium.

In this study, the coating mechanism was investigated for thin films of the oleic acid on SLS glass substrates using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. The structural interpretation of the resulting spectra will be compared in terms of each coating medium, and we will propose a model for the interaction mechanism of oleic acid coatings in different media onto the surface of a glass that contains various soluble metal ions. This model can be generalized to the materials containing various soluble metal ion impurities. These observations can be applied to the designing of organic thin films with optimized properties.

2. Experimental procedure

The same composition of the SLS glass was used in this study as was used in an earlier investigation [6]. Benzene (Aldrich) was distilled over Na metal to eliminate water. Reagent grade ethyl alcohol (Aldrich) was used without any pre-treatment. The aqueous medium

was distilled water. Usually, 0.5 g of the glass powder was mixed in 10 ml of either benzene, ethyl alcohol or water containing 0.1 ml of added oleic acid (99.9%, Aldrich) to prepare 3.155×10^{-2} M of oleic acid solution.

To investigate the effect of concentration of oleic acid, media possessing different concentrations of oleic acid were prepared. For ethyl alcohol or benzene medium, a solution was first prepared by diluting 1 ml of oleic acid with 100 ml of ethyl alcohol or benzene (3.155×10^{-2} M oleic acid solution), and stirring it vigorously for 1 h. Then, the desired amount of the diluted solution was further diluted with the corresponding medium to prepare a total of 10 ml of ethyl alcohol or benzene solution containing a desired concentration of oleic acid. A very low concentration of oleic acid solution in water was difficult to prepare because oleic acid possesses a strong hydrophobicity, and is not mixable with water and forms droplets. To prepare a 10 ml of aqueous solution containing 0.001 ml of oleic acid, 0.1 ml of 3.155×10^{-2} M oleic acid solution in ethyl alcohol was added to 10 ml of water. For higher concentrations, oleic acid was added to water without dilution. As soon as the glass powders were mixed with water containing oleic acid, the oleic acid droplets disappeared, indicating formation of metal-carboxylate (COO-M) complexes. The coating time was generally 24 h. After centrifuging of the solution, the remaining sediment was dried in vacuum for 24 h for infrared spectral measurement.

To study the effect of coating time, different periods of coating time were selected. In order to investigate the effect of soluble ions from the surface of the glass on the coating, ethyl alcohol/oleic acid solutions containing the glass powders were agitated in a shaker during coating. The glass powder was also washed with distilled water for 19 h before coating. For the coating process involving the oleic acid on to the glass powder from air, the glass powder and oleic acid were placed on separated glass dishes that were stored in the same desiccator. The desiccator was heated in an oven to 110°C for 2 h. During coating in air, the glass powder was mixed one time using a spatula, and then restored into the desiccator for coating.

Infrared spectra were collected using a Nicolet 60SXR infrared spectrometer equipped with a Spectra-Tech diffuse reflectance infrared Fourier transform (DRIFT) accessory. A detailed data collection procedure is found in a previous literature [6].

3. Results and discussion

3.1. The effect of coating medium

3.1.1. The bonding mechanism involving COOH groups

Fig. 1 illustrates the infrared spectra that were obtained for the glass powders on which oleic acid was coated from benzene, ethyl alcohol, distilled water or air. The infrared spectrum that was measured for the sample on which oleic acid was coated from air has been expanded 20 times. Each band in these IR spectra was assigned using the spectra that were measured for either pure oleic acid or the pure oleates involving each of the metal

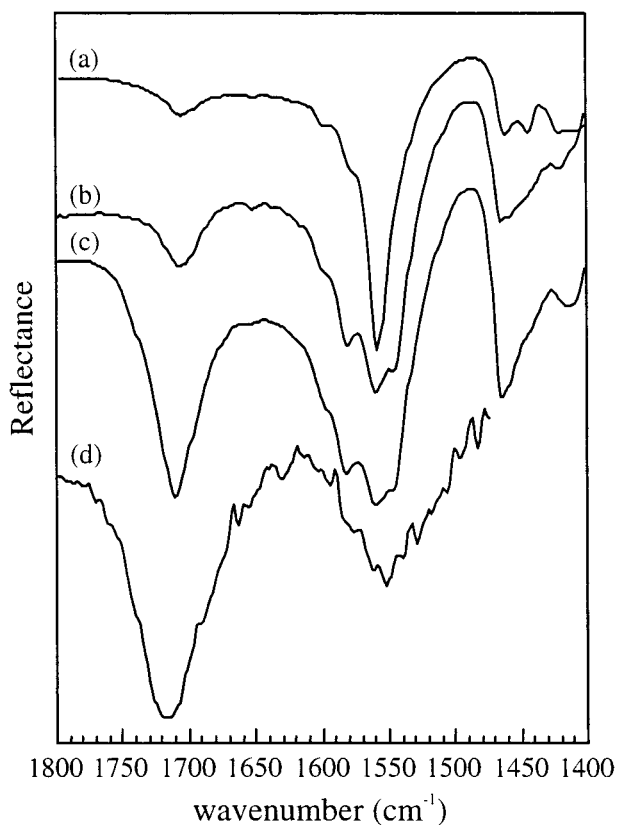


Figure 1 IR reflection spectra for oleic acid coated on the soda-lime-silicate glass from different media (containing 3.155×10^{-2} M of oleic acid): (a) benzene, (b) ethyl alcohol, (c) distilled water, and (d) air (at 110°C for 2 h)-expanded 20 times.

ions that are found in the SLS glass [6]. The spectrum in Fig. 1a for a sample involving oleic acid coated from benzene possesses a very weak shoulder at 1731 cm^{-1} and a band at 1704 cm^{-1} that can be assigned to the asymmetric C=O stretching modes [$\nu_{\text{as}}(\text{C=O})$] for monomeric and dimeric COOH groups, respectively [7]. In addition, bands were observed between $1600\text{--}1540 \text{ cm}^{-1}$, which are related to the asymmetric COO⁻ stretching modes [$\nu_{\text{as}}(\text{COO}^-)$] of COO-M complexes [8]. The band that shows the highest relative intensity (*I*) is located at 1558 cm^{-1} (COO-Na) and weak shoulders at ca. 1581 cm^{-1} (COO-Ca) and ca. 1600 cm^{-1} (COO-Al).

The spectra in Fig. 1b and c were measured for the glass powder samples onto which the oleic acid was coated from ethyl alcohol and water, respectively. These spectra show a relatively strong band at 1558 cm^{-1} (COO-Na) complex, along with two bands at 1579 and 1546 cm^{-1} (COO-Ca) and a weak shoulder at ca. 1600 cm^{-1} (COO-Al). Earlier investigators [9–11] have shown that calcium-oleate species can have one or two different forms depending on deposition or precipitation condition. One complex involves unidentate bonding of the metal ion (1579 cm^{-1}), while the other involves bidentate bonding (1546 cm^{-1}) [9]. In the above-mentioned case, we have also observed two strong bands in this spectral region, indicating that the calcium-oleate species which are produced on the surface possess the two different structural types of complexes. The bands that are related to the $\nu_{\text{as}}(\text{C=O})$ for COOH groups are found at 1706 or 1711 cm^{-1} when

the coating media are either ethyl alcohol or water, respectively.

For a sample onto which oleic acid was coated from air, Fig. 1d illustrates that the total intensity for the reflectance spectrum is so weak that it is not easy to distinguish in detail the corresponding bands that are associated with the each metal carboxylate complex. However, upon comparison with the spectra for the sample coated with the oleic acid from ethyl alcohol and water (see Fig. 1b and c), the location for the band at ca. 1552 cm^{-1} , along with the broadness and shape of the band located at $1620\text{--}1460\text{ cm}^{-1}$ indicates the formation of metal-carboxylate bonds involving COO-Na, COO-Ca, and COO-Al complexes. The relative amounts of the formed metal-complexes are in the same range as those when the coating medium is either ethyl alcohol or water.

Fig. 1 also indicates that the relative intensities between the bands related to the $\nu_{\text{as}}(\text{C}=\text{O})$ and the $\nu_{\text{as}}(\text{COO}^-)$ vary with change in the coating medium. The intensity ratio of the bands, $I_{[\nu_{\text{as}}(\text{C}=\text{O})]}/I_{[\nu_{\text{as}}(\text{COO}^-)]}$, increases in the order of benzene, ethyl alcohol, water and air. At the same time, the relative band intensity for the COO-Na complex increases in the order of water, ethyl alcohol and benzene, as compared to the band intensities for other COO-M complexes. Except in case of the spectrum for the sample coated with oleic acid in air, $I_{(\text{COO-Na})}/I_{(\text{COOH})}$ is large.

When benzene is the coating medium, metal ions are not dissolved from the surface due to the inert nature of benzene in terms of solubility of metal ions from the surface. Therefore, the relative concentration ratio for the each metal ion that is present on the surface of the freshly ground powder is essentially the same as in the initial bulk glass. The investigated SLS glass contains the largest amount of Na^+ ions (14.4 mol% Na_2O), which is more than four times larger than that of Ca^{2+} ions (6.4 mol% CaO). Therefore, significant amounts of Na^+ ions remain on the surface, so that most of the COOH groups for the coated oleic acid interact dissociatively with Na^+ ions. This results in the formation of relatively larger amounts of the COO-Na bonds on the surface of the glass powder.

In contrast, when ethyl alcohol is used as the medium, ethyl alcohol can also extract a small amount of Na^+ ions from the surface. First, this occurs because ethyl alcohol can contain a small amount of adsorbed water. Second, knowing that adsorbed water should be initially present on the surface of the glass powder, these adsorbed water molecules dissolve into the ethyl alcohol near the surface, and thus promote the extraction of Na^+ ions from the surface.

When the coating medium is water, it can extract larger amounts of other metal ions as well as Na^+ ions from the surface. The total concentration of the metal ions (mostly Na^+ ion) on the surface during coating is lowest for samples mixed in water. Thus, relatively smaller amounts of the COOH groups for oleic acid molecules interact with the metal ions on the surface, resulting in a strong infrared band that is related to COOH groups. Ca^{2+} ions from the surface are dissolved less than Na^+ ions in ethyl alcohol or water. Since Ca^{2+} ions

form stronger bonds with silicate groups than Na^+ ions and Al^{3+} (as Al_2O_3) ions are network formers in the glass for the investigated glass composition [12], Ca^{2+} and Al^{3+} ions are relatively stable on the glass. The sodium-oleate species that form at the Na^+ sites on the surface can dissociate in water due to purely the ionic nature of the sodium-associated bonds. Also, because water can attack and leach Na^+ ions from the surface, whole complexes of sodium-oleate can also be easily removed from the surface in to water. In water, bonds between the COO^- ions and either Ca^{2+} or Al^{3+} ions are relatively stable on the surface due to their stronger covalent nature. Metal-oleate species containing Ca^{2+} , Al^{3+} or other metal ions that possess higher valences can be removed from the surface only by leaching the ions from the surface. When the coating medium is benzene rather than water, sodium-oleate species which form on the surface are also stable, because the benzene does not either dissolve the formed COO-Na complexes or leach the Na^+ ions from the surface.

Other parameters must also be considered regarding the effect of the coating medium on the formation of metal-oleate species, such as the solubilities of oleic acid, the metal ions, or the metal-oleate species in each coating medium. Rather than remaining in water, oleic acid molecules tend to chemically interact at various sites on the surface, due to very low solubility of oleic acid in water. The COOH groups for the oleic acid molecules will interact with metal ions preferentially rather than Si-OH groups, thus forming the COO-M bonds (metal-oleate bonds) rather than hydrogen bonds with Si-OH groups on the surface. The sodium-oleate species possesses higher solubility in water. Calcium-oleate species can be dissolved into water by attack of the Ca^{2+} ion sites on the surface. Higher solubility for some of the metal ions or the metal complexes from the surface into water creates a dealkylized layer on the SLS glass surface, resulting in the creation of new surface Si-OH groups. Then, the COOH groups for oleic acid molecules in the solution have more probability to interact with isolated surface Si-OH groups and form hydrogen bonds with them [13–15]. This process continues until the equilibrium concentrations for every possible species are reached between the surface and the medium. The oleic acid molecules remaining in the aqueous medium also form metal-oleate species with some of the metal ions that are dissolved from the surface. Analysis of the infrared spectra for the dried supernatant solution indicates a significant amount of metal complex formation in the water with respect to the other media (particularly, for Na^+ ions). However, the possibility of re-deposition of the sodium-oleate molecules from water to the surface will be very low because sodium-oleate molecules possess very high solubility in water due to their purely ionic nature.

When oleic acid is coated by evaporation in air at 110°C , the relative intensity for the band related to the COO-Na complex as compared to those related to the other COO-M complexes is weaker than when oleic acid is coated from benzene, (see Fig. 1d). The surface conditions for the coating in air will be more similar to those in benzene than in water. Similar to coating in

benzene, the Na^+ ion concentration on the surface is high when coating occurs in air. In fact, the heating of the glass powder in air can cause some of the mobile ions such as Na^+ ions to diffuse from the glass bulk to the surface. This results in accumulation of Na^+ ions on the surface, with even a higher concentration of Na^+ ions on the surface in air than in benzene. Hence, significantly larger amounts of COO-Na complexes should be formed on the surface in air (also, in benzene). However, the shape and relative intensities of the bands related to the COO-M complexes in the spectrum (see Fig. 1d) is completely different from that in the spectrum for the sample involving the oleic acid coated from benzene (see Fig. 1a). Instead, they are very similar to the case when the coating medium involves either water or ethyl alcohol (see Fig. 1c). This result indicates that reactivities of different metal ions with COOH groups for oleic acid may change with temperature. We cannot rule out that the evaporation of each species in a coating layer would occur in a different manner in such elevated temperature.

3.1.2. The configuration of the coated oleic acid molecules

Fig. 1 shows that $I_{[\nu_{\text{as}}(\text{C}=\text{O})]}$ relatively increases in the order of benzene, ethyl alcohol, water and air. Also, the wavenumber of the infrared band increases systematically from 1704 cm^{-1} for the glass coated from benzene to 1713 cm^{-1} for the glass coated from air, following the same trend as the change in intensity for the band. Fig. 2 illustrates the infrared spectral region associated

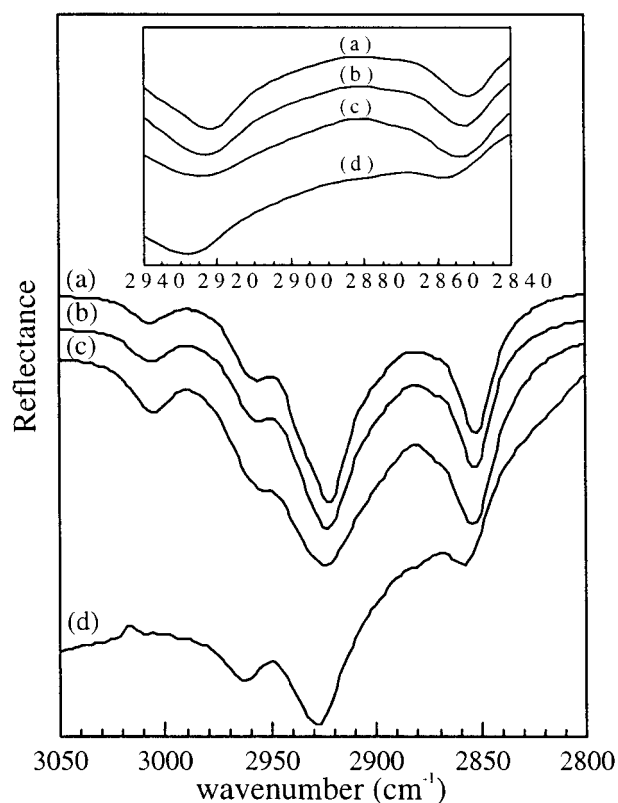


Figure 2 IR reflection spectra for C-H stretching modes of oleic acid coated on the soda-lime-silicate glass from different media (containing 3.155×10^{-2} M of oleic acid): (a) benzene, (b) ethyl alcohol, (c) distilled water, and (d) air (at 110°C for 2 h)-expanded 20 times.

the CH stretching modes. The asymmetric and the symmetric CH_2 stretching modes [$\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$] may be noted at 2923 and 2852 cm^{-1} , respectively, for the oleate coatings from both benzene and ethyl alcohol. These bands shift to 2925 and 2854 cm^{-1} , when the coating medium is water. They further shift to higher wavenumbers (2928 and 2857 cm^{-1}) in the case of coating in air.

The band locations for the $\nu(\text{CH}_2)$ also indicate the strength of the lateral interaction between alkyl chains in adjacent chains due to Van der Waals forces. By increasing the interaction strength, the band locations shift to a lower wavenumber, indicating that the change from a flexible configuration to a more (ordered) rigid configuration of hydrocarbon chains with respect to each other [16–18]. The DRIFT spectra that are illustrated in Fig. 2 indicate that the coated molecules are in a more flexible configuration when oleic acid is coated from air or water than from benzene or ethyl alcohol, resulting in less packing and a more liquid-like state of the coating layer.

This lower ordering of the coated molecules from air and water is also correlated to a reduction in the strength of the hydrogen bond between COOH groups, (see Fig. 1). A previous study [6] demonstrated that oleic acid is coated with higher density involving a more rigid alkyl chain on SLS glass than on silica glass. This is caused by the rigid anchoring of the alkyl molecular chain to the metal ion sites on the SLS glass, which does not occur on silica glass. Such chains lose their flexibility when the COO-M complexes form. The relative amount of the COO-M bond formation decreases when oleic acid is coated from air in comparison from benzene, resulting in a less dense coating layer from air. The infrared spectrum of liquid pure oleic acid possesses bands at 2925 and 2854 cm^{-1} that are associated with the $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$, respectively. This indicates that the distribution of the molecules that are coated from air is even less dense and ordered than that of the liquid pure oleic acid. In addition, the higher deposition temperature in the case of the coating from air may be one of the reasons for the formation of a less dense layer. At higher temperature, the evaporated molecules of oleic acid possess higher mobility during coating, resulting in a more randomly coated molecular layer. *Less amount of coating of oleic acid in air is also one of the reasons for the less dense and random layer of the oleic acid molecules coated in air.* As will be discussed in a later section, the amounts of the various organic molecular species in a coating layer also significantly affect the ordering and the density of a coating layer on the glass.

3.2. The effect of coating time

Fig. 3 illustrates the effect of coating time on the coating of oleic acid onto the glass from ethyl alcohol. The main large spectral changes in Fig. 3 occur in the infrared spectral region that is associated with the metal-carboxylate bonds. After less than 4 h of coating, the related infrared spectrum possesses a very strong band at 1558 cm^{-1} (COO-Na), along with shoulders at 1581 and 1545 cm^{-1} (COO-Ca). In contrast, after more than

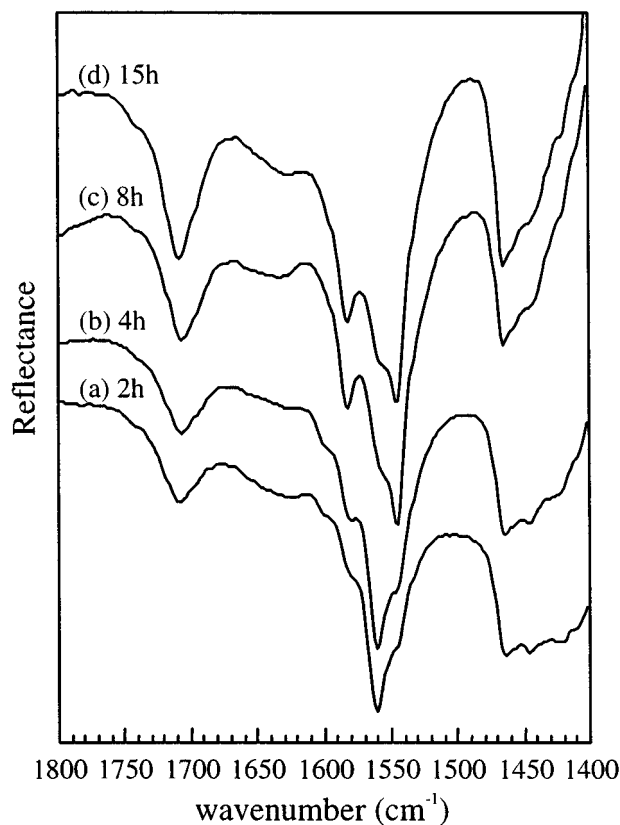


Figure 3 IR reflection spectra for oleic acid coated on the soda-lime-silicate glass for different treatment time (3.155×10^{-2} M of oleic acid).

8 h, $I_{(\text{COO-Ca})}/I_{(\text{COO-Na})}$ significantly increases. Since Na^+ ions are more easily extracted than Ca^{2+} ions from the surface, the metal ions extracted from the surfaces will be dominantly Na^+ ions with increasing coating time. In contrast to aging in air, a more calcium-rich layer with respect to Na^+ ions forms on the surface during coating from ethyl alcohol. This results in the formation of relatively larger amounts of calcium-oleate on the surface with increasing coating time, as compared to sodium-oleate.

The infrared spectra also indicate the COOH groups have different reactivities with different sites on the surface. Those differences are related to the reaction sequence with respect to coating time. 1) Initially, COOH groups of oleic acid preferentially bond to Na^+ ion sites on the surface, forming COO-Na complexes. 2) Later, as dissolution of Na^+ ions or formation of COO-Na complexes reduces the amounts of available Na^+ ions, the COOH groups react with Ca^{2+} ions, forming COO-Ca complexes, and also form hydrogen-bonded complexes with Si-OH groups. 3) Following these reactions on the surface, condensation of oleic acid molecules occurs above or between the organic molecular chains in the first coating layer. Hydrogen bonds can only occur between the COOH groups of these condensed molecules, forming dimeric COOH groups. 4) Na^+ ions in the COO-Na bonds on the surface can be replaced in the presence of water by other ions that possess higher valence.

The relative intensity for the band at ca. 1705 cm^{-1} increases a little with increasing coating time. This increase is caused by the dissolution of more and more Na^+ ions from the surface that are anchored or unan-

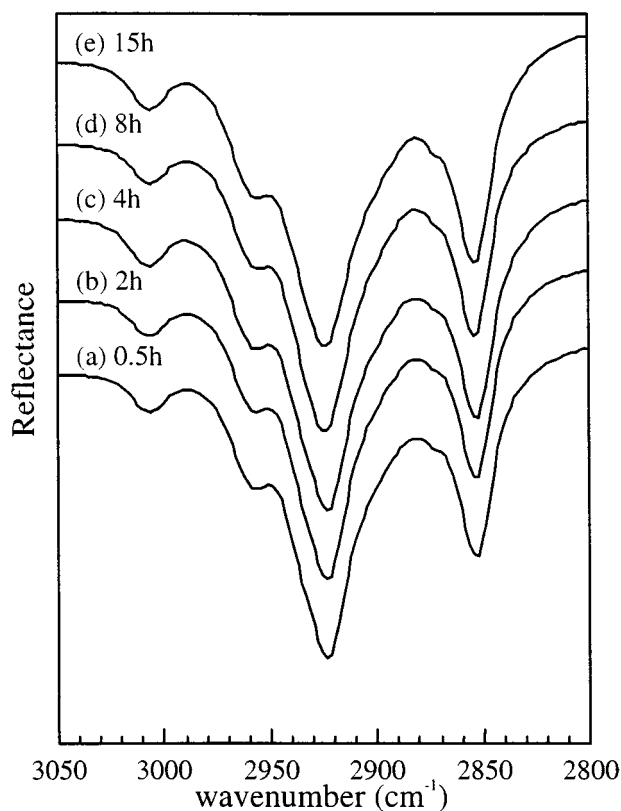


Figure 4 IR reflection spectra for C-H stretching modes of oleic acid coated on the soda-lime-silicate glass for different treatment time (3.155×10^{-2} M of oleic acid).

chored to COO^- groups, generating more Si-OH sites. At these Na^+ ion-depleted sites, COOH groups of the oleic acid molecules approach and form hydrogen bonds with the Si-OH groups that are now present there. Thus, more and more oleic acid molecules are coated onto the surface by either hydrogen bonding to the isolated Si-OH groups, or condensing onto the oleate species already on the surface.

A shift in the locations for $\nu(\text{CH}_2)$ (2923 and 2852 cm^{-1}) is not observed (see Fig. 4), indicating that the molecular density and the configurations (ordering) of the chains are not affected with coating time in these experimental conditions. The bands related to $\nu(\text{CH}_2)$ for coated oleic acid are located at higher wavenumbers when the molecules are coated from air for 2 h (2928 and 2857 cm^{-1}) rather than from ethyl alcohol for 0.5 or 2 h (2923 and 2852 cm^{-1}) (see Figs 2d and 4a and b). These results indicate that the nature of coating medium affects more significantly the density and the ordering in the coating layer than the coating time does.

3.3. The effect of pre-washing of powder and agitation of the suspension

During the coating process involving oleic acid on the surface, mixtures of the glass powder, oleic acid and medium were agitated moderately in a shaker. Also, before being coated with oleic acid, some of the glass powders were washed with water. The infrared spectra for these samples are illustrated in Fig. 5. As compared to the spectra that were obtained for the oleic acid coated from benzene or ethyl alcohol without agitation

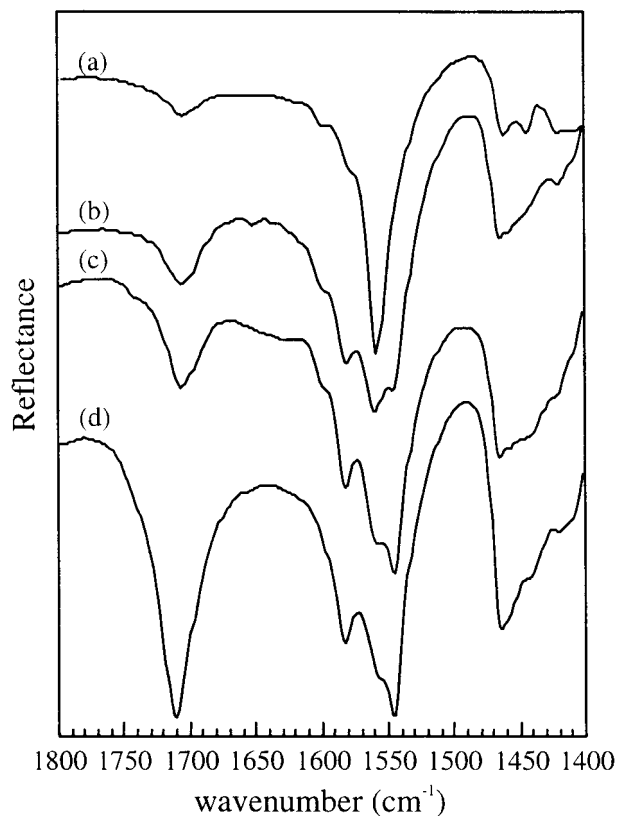


Figure 5 IR reflection spectra for oleic acid coated on the soda-lime-silicate glass from (a) benzene, (b) ethyl alcohol without agitation, (c) ethyl alcohol with agitation, and (d) ethyl alcohol after washing the glass with water for 19 h (3.155×10^{-2} M of oleic acid).

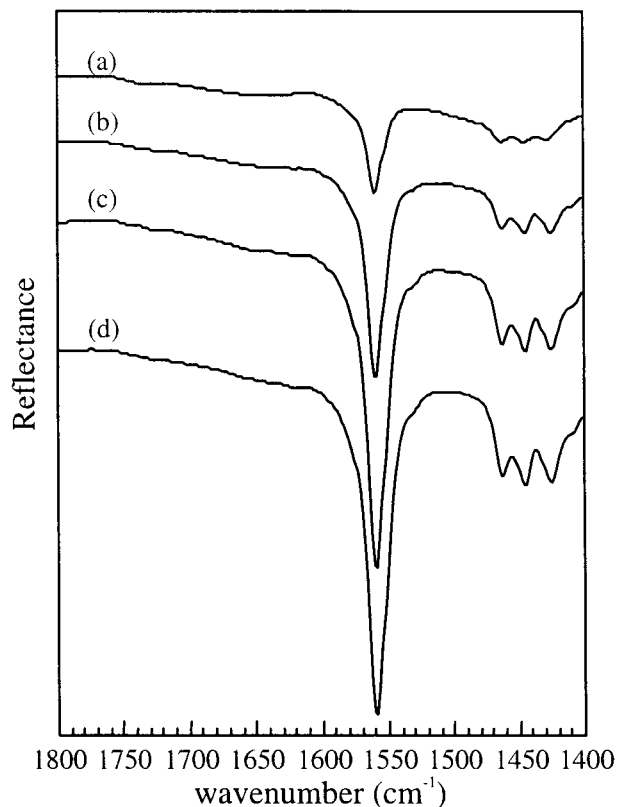


Figure 6 IR reflection spectra for oleic acid coated on the soda-lime-silicate glass from benzene (10 ml) containing different amounts of oleic acid: (a) 0.001 (3.155×10^{-4} M), (b) 0.005 (1.577×10^{-3} M), (c) 0.01 (3.155×10^{-3} M), and (d) 0.02 ml (6.309×10^{-3} M).

(see Fig. 5a and b), the perusal of the spectrum for the agitated sample (see Fig. 5c) indicates an increased $I_{(1707 \text{ cm}^{-1})}/I_{(1558 \text{ cm}^{-1})}$. The band at 1707 cm^{-1} for the agitated samples shifts to 1711 cm^{-1} for the washed samples, and its intensity becomes stronger. During agitation, the rate of dissolution of Na^+ ions or COO-Na species from the surface is accelerated, resulting in less COO-Na complex on the surface. The spectrum for oleic acid that was coated on the glass after washing the glass possesses similar trends (see Fig. 5d). However, with the formation of a highly Na^+ ion-depleted layer, the intensity for the band associated with the COOH groups becomes very strong relative to those of the other species. An aging test of the coated samples in air shows that for the pre-washed glass samples, the COOH groups still remain on the surface even after several months. In contrast, for the samples on which oleic acid is coated without pre-washing the glass, most of the COOH groups disappear, and mainly only sodium-oleate species were found on the coating layer after aging for the same period of time.

3.4. The effect of the concentration of oleic acid

3.4.1. In benzene

Figs 6 and 7 illustrate the infrared spectra measured for oleic acid coated on the glass from benzene. In the investigated range of concentration, the band related to the $\nu_{\text{as}}(\text{C}=\text{O})$ for the COOH is hardly observed. The spectra indicate that in the range of concentration, most of the carboxylate groups in the coating bond with metal

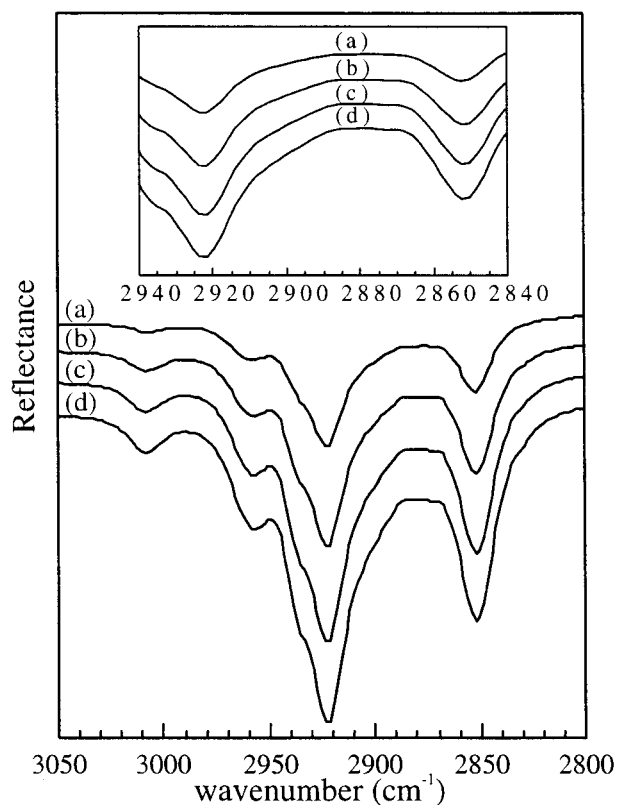


Figure 7 IR reflection spectra for C-H stretching modes of oleic acid coated on the soda-lime-silicate glass from benzene (10 ml) containing different amounts of oleic acid: (a) 0.001 (3.155×10^{-4} M), (b) 0.005 (1.577×10^{-3} M), (c) 0.01 (3.155×10^{-3} M), and (d) 0.02 ml (6.309×10^{-3} M).

ions and form mostly COO-Na complexes (1558 cm^{-1}). Because benzene medium does not significantly alter the surface, abundant amounts of Na^+ ions remain on the surface. Also, because carboxylate groups prefer strong bonding with Na^+ ions (even at higher concentrations of oleic acid), the presence of oleic acid species involving COOH groups and other COO-M species are not indicated in the infrared spectra.

As illustrated in Fig. 7, the concentration of oleic acid in benzene generally does not affect the locations for the bands attributed to the $\nu_{\text{as}}(\text{CH}_2)$ and $\nu_{\text{s}}(\text{CH}_2)$ (2923 and 2852 cm^{-1}). This result indicates that the coating layer is considerably dense and ordered even at lower concentrations of oleic acid. These band locations are closely related to the relative amounts of the COO-M complexes and COOH groups on the surface (see Figs 1 and 2). As mentioned earlier, COO-M complexes possess highly rigid and oriented alkyl chains due to the lower mobility of the chains on the surface. In contrast, COOH groups possess flexible chains on the organic molecules.

3.4.2. In ethyl alcohol

Figs 8 and 9 illustrate the infrared spectra that were measured for oleic acid coated on the glass from ethyl alcohol. As illustrated in Fig. 8a (0.001 ml of oleic acid ($3.155 \times 10^{-4}\text{ M}$)), bands associated with COO-M or COOH species are not observed in the spectra, in contrast to the spectrum for sample involving oleic acid

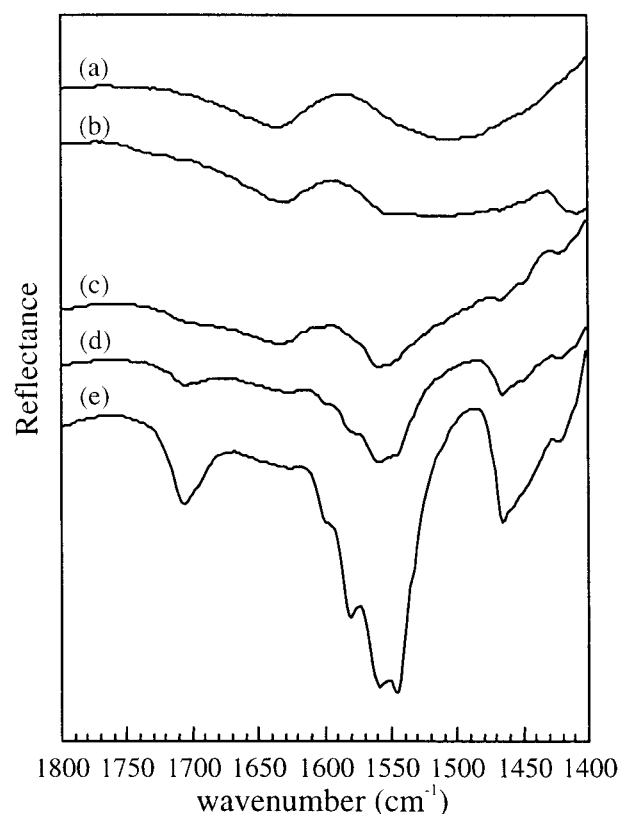


Figure 8 IR reflection spectra for oleic acid coated on the soda-lime-silicate glass from ethyl alcohol (10 ml) containing different amounts of oleic acid: (a) 0.001 ($3.155 \times 10^{-4}\text{ M}$), (b) 0.005 ($1.577 \times 10^{-3}\text{ M}$), (c) 0.01 ($3.155 \times 10^{-3}\text{ M}$), (d) 0.05 ($1.577 \times 10^{-2}\text{ M}$), and (e) 0.1 ml ($3.155 \times 10^{-2}\text{ M}$).

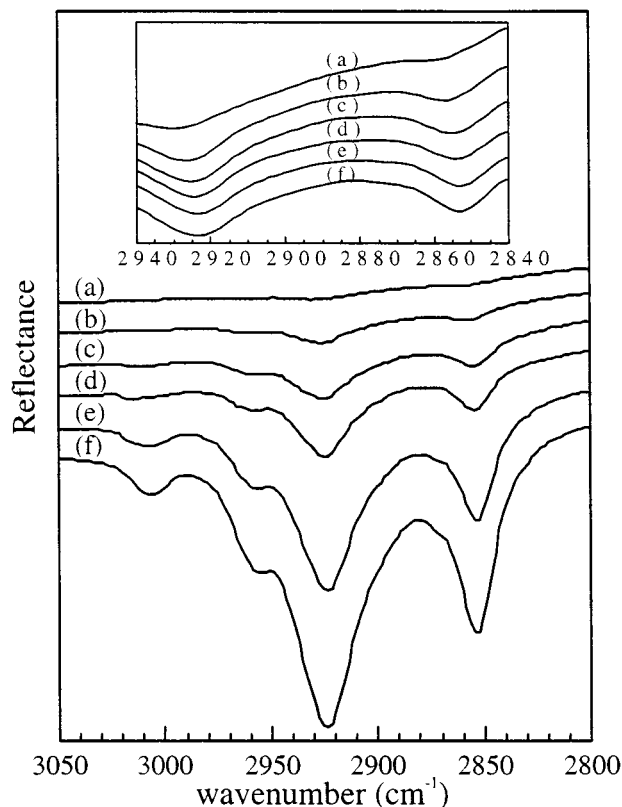


Figure 9 IR reflection spectra for C-H stretching modes of oleic acid coated on the soda-lime-silicate glass from ethyl alcohol (10 ml) containing different amounts of oleic acid: (a) 0.001 ($3.155 \times 10^{-4}\text{ M}$), (b) 0.005 ($1.577 \times 10^{-3}\text{ M}$), (c) 0.01 ($3.155 \times 10^{-3}\text{ M}$), (d) 0.02 ($6.309 \times 10^{-3}\text{ M}$), (e) 0.05 ($1.577 \times 10^{-2}\text{ M}$), and (f) 0.1 ml ($3.155 \times 10^{-2}\text{ M}$).

coated from benzene (see Fig. 6a). However, Fig. 9a shows weak bands related to the $\nu(\text{CH}_2)$. Thus, the amounts of oleic acid molecules coated on the glass are so small that the bands related to COO-M or COOH species could not be detected on the spectrum. The infrared transmission spectrum measured for the supernatant solution for the coating medium mixture involving 0.001 ml of oleic acid also indicates the presence of the COO-Na complex. This observation indicates that the Na^+ ions that are dissolved from the surface react with oleic acid in the solution. Another interpretation is that the COO-Na complex formed on the surface are dissolved into the ethyl alcohol due to water impurity contained in the ethyl alcohol or on the surface of the glass. As the concentration of oleic acid increases, bands at 1579 and 1546 cm^{-1} (COO-Ca) are observed, along with a weak band at 1600 cm^{-1} (COO-Al) and a medium intensity band at 1705 cm^{-1} (COOH). $I_{(\text{COO-Ca})}$ and $I_{(\text{COOH})}$ also increase, as compared to $I_{(\text{COO-Na})}$. This result indicates that within the given coating time, more oleic acid is required to form the COO-Ca complexes and the COOH species rather than the COO-Na complexes.

The density and ordering of the coating layer are more dramatically affected by concentration in ethyl alcohol than in benzene. As shown in Fig. 9, the band related to the $\nu_{\text{as}}(\text{CH}_2)$ are found at 2931 and 2927 cm^{-1} for 0.001 and 0.005 ml additions of oleic acid to the mixture, respectively. At this concentration, the surface coverage of the oleic acid is still too low to

achieve a very compact layer. Increasing the concentration of oleic acid from 3.155×10^{-4} M (0.001 ml) to 3.155×10^{-3} M (0.01 ml), the location for the band related to the $\nu_{\text{as}}(\text{CH}_2)$ changes from 2931 cm^{-1} to 2925 cm^{-1} , indicating that the density of the coating layer increases dramatically. In contrast, upon increasing the concentration from 3.155×10^{-3} M (0.01 ml), to 3.155×10^{-2} M (0.1 ml), the location for this band changes only from 2925 cm^{-1} to 2923 cm^{-1} . This result indicates that above this concentration, the coverage of the coated organic material reaches monolayer, and the density and ordering of the coating layer are little affected.

3.4.3. In water

Figs 10 and 11 illustrates the infrared spectra that were measured for the glass sample involving oleic acid coated from water. Perusal of the spectra in Fig. 10 indicates that $I_{(\text{COOH})}$ is relatively very strong over the whole concentration range applied for oleic acid, as compared to the spectral results when benzene or ethyl alcohol was used as a coating medium. As the concentration of the applied oleic acid in the solution increases, $I_{(1707-1713 \text{ cm}^{-1})}$ greatly increases due to the higher dissolution rate of metal ions from the glasses, and the lower solubility of oleic acid in water. Also, Na^+ ions in the COO-M complexes are replaced easily by Ca^{2+} ions, or the COO-Na complexes on the surface are dissolved into water, as indicated by the decreased

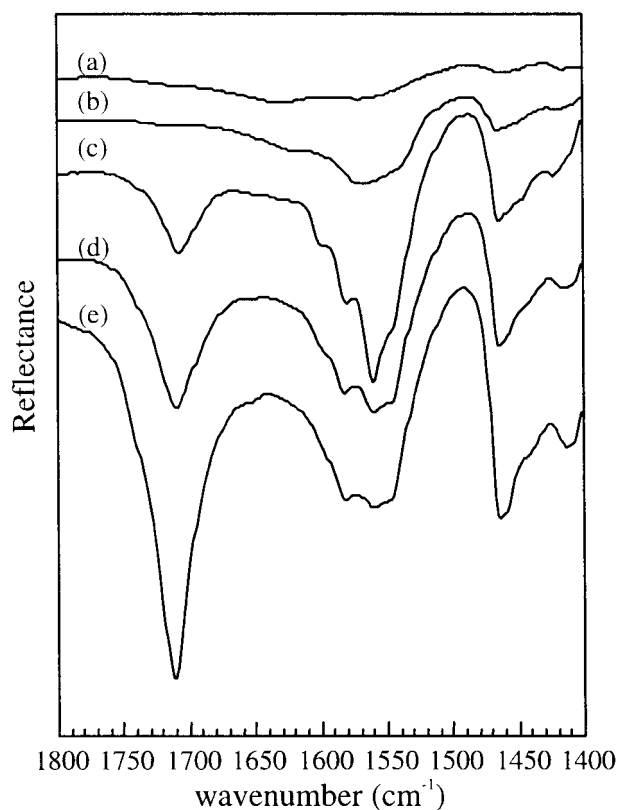


Figure 10 IR reflection spectra for oleic acid coated on the soda-lime-silicate glass from distilled water (10 ml) containing different amounts of oleic acid: (a) 0.001 (3.155×10^{-4} M), (b) 0.01 (3.155×10^{-3} M), (c) 0.05 (1.577×10^{-2} M), (d) 0.1 ml (3.155×10^{-2} M), and (e) 0.2 ml (6.309×10^{-2} M).

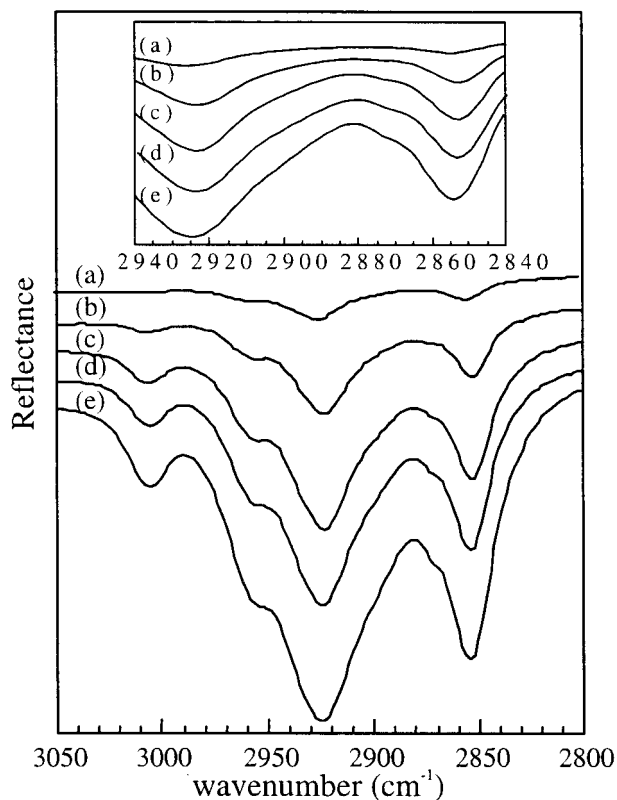


Figure 11 IR reflection spectra for C-H stretching modes of oleic acid coated on the soda-lime-silicate glass from distilled water (10 ml) containing different amounts of oleic acid: (a) 0.001 (3.155×10^{-4} M), (b) 0.01 (3.155×10^{-3} M), (c) 0.05 (1.577×10^{-2} M), (d) 0.1 ml (3.155×10^{-2} M), and (e) 0.2 ml (6.309×10^{-2} M).

$I_{(\text{COO-Na})}$ and the increased $I_{(\text{COO-Ca})}$. As can be seen in Fig. 11, the concentration of oleic acid does not much affect the location for the band at 2925 cm^{-1} [$\nu_{\text{as}}(\text{CH}_2)$]. This result indicates that the coverage does not affect the lateral interactions of the alkyl chains in this case.

Table I lists that the concentrations of metal ions in supernatant solutions from the glass, water and oleic acid mixtures. Except in the case of Al^{3+} ions, the resulting concentrations of the metal ions dissolved from the glass significantly reduced with increasing oleic acid concentration. The extracted amounts of Ca^{2+} ions that possess higher valence have been most significantly reduced. As indicated by the interpretation of the infrared spectra in Fig. 11, increasing the concentration of oleic acid increases the amount of oleic acid (COOH) species coated on the surface with respect to the metal-oleate complexes (COO-M). Thus, the surface layer of the glass is protected somewhat from the water molecules by the formation of a hydrophobic layer of oleic acid molecules that have long hydrocarbon chains.

We must also consider the strength of bonds, which occur either between metal ions and COO^- or COOH groups, or between metal ions and the glass matrix. Na^+ ions on the surface form COO-Na complexes that are soluble in water, so that some of the Na^+ ions can be dissolved from the surface of the glass. In contrast to Na^+ ions, Ca^{2+} ions form essentially water-insoluble COO-Ca complexes. COO-Ca complex can be removed only if Ca^{2+} ions are leached (detached) from the surface by water molecules. Fig. 10 shows that

TABLE I The concentration (ppm) of metal ions extracted from the soda-lime-silicate glass (0.5 g) in a distilled water (10 ml) containing different amounts of oleic acid (ml) after 24 h aging

oleic acid conc. (ml/10 ml H ₂ O)	0.001 (3.155 × 10 ⁻⁴ M)	0.01 (3.155 × 10 ⁻³ M)	0.05 (1.577 × 10 ⁻² M)	0.2 (6.309 × 10 ⁻² M)
Si ⁴⁺	11.70 ± 0.10	8.03 ± 0.02	6.62 ± 0.12	3.86 ± 0.01
Na ⁺	34.40 ± 0.40	30.40 ± 0.10	23.70 ± 0.10	18.70 ± 0.20
Ca ²⁺	4.13 ± 0.10	4.03 ± 0.03	2.41 ± 0.08	0.32 ± 0.01
Mg ²⁺	1.36 ± 0.01	0.94 ± 0.01	0.55 ± 0.05	0.06 ± 0.01
Al ³⁺	0.50 ± 0.01	0.44 ± 0.02	0.58 ± 0.03	0.46 ± 0.02

with increasing concentration of oleic acid, the relative amount of the COO-Ca complexes increases relative to the COO-Na complexes. Therefore, oleic acid suppresses the dissolution of metal ions that possess higher valence, such as Ca²⁺ and Mg²⁺ ions. Because Al₂O₃ acts as a network former in the investigated SLS glass, Al³⁺ ions are very stable in the glass matrix. Thus, Al³⁺ ions are essentially not leached from the glass matrix. Moreover, COO-Al bonds are very strong. Therefore, the leached amounts of Al-containing species do not change by increasing the amount of oleic acid added in solution. In the case of silicate groups, the amount of the hydrogen-bonded species formed between COOH groups and Si-OH groups increases with the further addition of oleic acid in solution. These hydrogen bonds may also be responsible for the lowering of the dissolution of the Si⁴⁺ ions into water.

4. Conclusions

The results obtained from this FTIR spectral study indicate that the coating mechanism for oleic acid on SLS glass from different media depends on 1) the dissolution behavior for the glass, 2) the dissociation mechanism involving the COO-M bonds, and 3) the surface composition of the glass, along with the relative amounts of oleic acid and metal ion sites or isolated Si-OH groups which are available for the formation of the COO-M complexes or the hydrogen-bonded species, and 4) the solubility of the oleic acid in each coating medium. Therefore, we must consider the interactions between the glass substrates, the media and oleic acid. Further conclusions can also be drawn:

1. When oleic acid is coated from the benzene, the COO-Na and COO-Ca complexes formed on the surface is not affected and dissolution of the metal ions from the glass does not occur during its coating process. Therefore, the initial surface composition plays an important role in the coating mechanism involving oleic acid. This condition explains why larger amounts of COO-Na complexes and more rigid (ordered) molecular chains form in the organic layer coated on the glass from benzene.

2. When ethyl alcohol is used as the coating medium, water molecules which can be found as an impurity in the medium or adsorbed on the surface can extract some of the metal ions, dissociate COO-Na bond and remove some of COO-Na complexes from the surface. Thus, the dissolution mechanism involving metal ions and the dissociation mechanism involving COO-M complexes from the surface are important with respect to

the coating mechanism involving oleic acid. Thus, the coating layers in the case of ethyl alcohol medium contain mostly COO-Na and COO-Ca complexes along with relatively small amounts of COOH groups.

3. If water is the coating medium, metal ions and COO-Na complexes are easily removed from the surface. The solubility of oleic acid is very low in water. In this case, the coating layer contains relatively larger amounts of oleic acid species and smaller amounts of COO-M complexes.

4. If COO-M complex is unstable in the coating medium (such as COO-Na in water), a metal ion in the complex that possesses a lower valence can be replaced with a metal ion that possesses a higher valence (i.e., exchange reaction).

5. The packing state of oleic acid coating layer was very close related with the relative amounts of COO-M complexes to COOH groups. Formation of relatively more COO-M complexes leads to a more rigid and ordered (compact) coating layer. Such ordered coating layer was obtained using the coating media such as benzene which possesses high solubility for oleic acid and less metal dissolution power for the substrate.

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