

FTIR spectral characterization of thin film coatings of oleic acid on glasses: I. Coatings on glasses from ethyl alcohol

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Oleic acid was coated on soda lime–silicate, soda-silicate, and silica glasses from ethyl alcohol. The coating properties of oleic acid were related to the structure, composition, and dissolution properties of the glasses. The bonding mechanism between the organic coating and the glass surface for each different composition of the glass was revealed by analysis of the diffuse reflectance infrared Fourier transform (DRIFT) spectra. The metal ions on the soda lime–silicate glass surface produced metal-(Na-, Ca-, and Al-) oleates through the formation of metal–carboxylate complexes. Two different structural types were present for calcium-oleate. Some of the oleic acid coated undissociatively on the glass surface through hydrogen bonding. Oleic acid reacted with the surface of the soda-silicate glass, which possessed less Na₂O content than the soda lime–silicate glass did, completely dissociating, producing only sodium-oleate species because of the high diffusion and dissolution rates of Na⁺ ions. Oleic acid formed only hydrogen bonds with silanol groups on silica glass. The coated organic layer on soda lime–silicate glass possessed a more ordered and compact structure than either on silica glass or in pure oleic acid. The metal ions on the soda lime–silicate glass surface strongly coordinated to COO⁻ ions from the oleic acid and made the alkyl chains of the oleates more rigid and oriented, consequently causing the coated layer to be more ordered and compact. This structural result caused the dimeric pairs of COOH groups of undissociatively adsorbed oleic acid molecules to be closer, possessing stronger hydrogen bonds than occurring on the silica glass surface. These results suggest that the composition of the glass is one of the most important factors for determining the coating mechanism involving oleic acid. © 1999 Kluwer Academic Publishers

1. Introduction

Organic compounds have been used to modify the properties of inorganic materials or vice versa [1–5]. For such applications, one of the most important factors is the interaction mechanism between the organic and the inorganic materials, whichever of these materials is the matrix. Another important factor is the durability of the coated or filled organic materials along with the degradation process at the interface. Most studies concerning organic–inorganic interactions have been done with pure or single-component inorganic materials in order to avoid complications involved with a complex system. To the best of our knowledge, it is very rare to investigate interactions between an organic and an inorganic material that contains soluble impurities or consists of multi components, except in the case of clay or soil materials. Most glasses consist of several components, and some of the components such as the network modifiers (even the SiO₂ network portion) can be dissolved and attacked by H₂O or other solvents. Mobile ions on a glass surface also affect the durability of the applied organic coating [3]. Even if a passive layer is applied on a glass surface by forming a pure SiO₂ layer, ions such as Na⁺ ions may diffuse

continuously to the surface due to moisture, temperature, and surface energy and thus interact with the organic molecules. Hence, the interface between an organic and a glass material is very dynamic in service environments. Therefore, it is not easy to predict the interaction mechanisms for coated organic species on glasses in the presence of either humid air or solvents. Studies of organic–glass interactions require the knowledge of the dissolution mechanism of the glass, along with the interactions of the organic species with each component in the glass. Glasses are very good materials for investigations involving interactions with organic species, with particular emphasis on the effects of soluble impurities. In this study, we will investigate the interaction mechanism involving thin films of oleic acid with glass substrates such as soda lime–silicate using DRIFT spectroscopy. The results will be compared with those for soda-silicate and silica glass.

2. Experimental

Of the oleic acid that was used in this study, 99.9% was as received from Aldrich. The investigated glass specimens were soda-lime-silicate and silica slide

glasses along with a soda-silicate glass. The composition of the soda-lime-silicate glass was as follows: 72.2 mol % SiO₂, 14.4% Na₂O, 6.4% CaO, 4.3% MgO, 1.2% Al₂O₃, 1.2% K₂O, 0.3% SO₂. Soda-silicate glass containing 12 mol % Na₂O was fabricated by a melting process in a furnace. The investigated glass powders were obtained by grinding the glasses with a mortar and pestle. Before grinding, the slide glass substrates were washed with acetone, followed by ethanol, and then dried to remove any organic contaminants. After grinding, the glass powders were stored in a desiccator. This routine prevents changes on the glass surfaces that are caused by water adsorption and carbonate formation. Next, 0.5 g of the glass powders were mixed with reagent ethyl alcohol, and then 0.1 mL of oleic acid was added to this solution. In order to reach equilibrium, the solution was aged for 24 h. After centrifuging the aged solution for 20 min, the sediment was separated. The sediment was dried in a vacuum for 24 h and stored in a desiccator before analysing.

Infrared spectra were recorded for both the oleic acid and the dried glass sediments with a dry air-purged Nicolet 60 SXR FT-IR spectrometer using a DTGS detector. An infrared transmission spectrum was measured for oleic acid on a silicon infrared window that was transparent to the measured infrared range. For the sediments, diffuse infrared reflection spectra were measured by using the Spectra Tech diffuse reflectance infrared accessory. To increase the signal-to-noise ratio, 2048 scans were co-added. The infrared spectrum of the oleic acid that was coated on the glass was subtracted from that of the pure glass. Thus, the illustrated infrared spectra represent those involving changes on the oleic acid after coating on the glasses. For com-

parisons, Na-, Ca-, Al-, and Mg-oleate samples were synthesized. Na-oleate was obtained by reacting oleic acid with a NaOH solution in a stoichiometric ratio. Ca-, Al-, and Mg-oleate specimens were synthesized by mixing an aqueous Na-oleate solution with aqueous CaCl₂, AlCl₃, and Mg(NO₃)₂ solutions, respectively, and precipitating the corresponding metal-oleates. All of these metal-oleates were analysed by infrared transmission spectroscopy using the KBr pellet method.

3. Results and discussion

3.1. The infrared spectrum of oleic acid

Table I lists band assignments related to pure or the coated oleic acid species on the silica or soda lime-silicate glasses. Fig. 1 illustrates the infrared transmission spectrum of pure oleic acid. The infrared bands at 1712 cm⁻¹ and 1743 cm⁻¹ are related to C=O stretching modes for dimeric and monomeric COOH species, respectively [4]. Generally, COOH groups involve hydrogen bonding at higher concentrations to form the dimeric COOH species. Upon hydrogen bonding, the band location for the C=O stretching mode involving the monomeric COOH species shifts to a lower wave number because of the perturbation of the vibrational mode. It is well-known that the amount of the observed wave number shift depends on the strength of the hydrogen bonding [4–7]. The weak shoulder at 1655 cm⁻¹ can be assigned to the C=C stretching mode for oleic acid [8].

3.2. The application of spectral subtraction

Because the amounts of coated organic species on the glasses are usually very small, it is not always easy to

TABLE I Band locations and assignments for the various vibrational modes for pure and coated oleic acid

Band locations (cm ⁻¹)	Band assignments
3006	$\nu(-CH=)$
2958	$\nu_a(-CH_3)$ (coated on fused silica)
2956	(coated on soda lime-silicate glass)
2925	$\nu_a(-CH_2)$ (coated on fused silica or in pure oleic acid)
2923	(coated on soda lime-silicate glass)
2873	$\nu_s(-CH_3)$ (coated on fused silica)
	(coated on soda lime-silicate glass)
2854	$\nu_s(-CH_2)$ (coated on fused silica or pure oleic acid)
2852	(coated on soda lime-silicate glass)
2673	$\nu(OH)$ of dimeric COOH
1747	$\nu(C=O)$ of monomeric COOH (coated on fused silica)
1743	(in pure oleic acid)
1731	(coated on soda lime-silicate glass)
1712	$\nu(C=O)$ of dimeric COOH (coated on fused silica or in pure oleic acid)
1706	(coated on soda lime-silicate glass)
1685	(coated on soda lime-silicate glass)
1655	$\nu(C=C)$
1595	$\nu_a(COO)$ of COO-Al (precipitated)
1589	(coated)
1581	$\nu_a(COO)$ of COO-Mg (precipitated)
1577, 1541	$\nu_a(COO)$ of COO-Ca (precipitated)
1579, 1546	(coated)
1562	$\nu_a(COO)$ of COO-Na (precipitated)
1558	(coated)

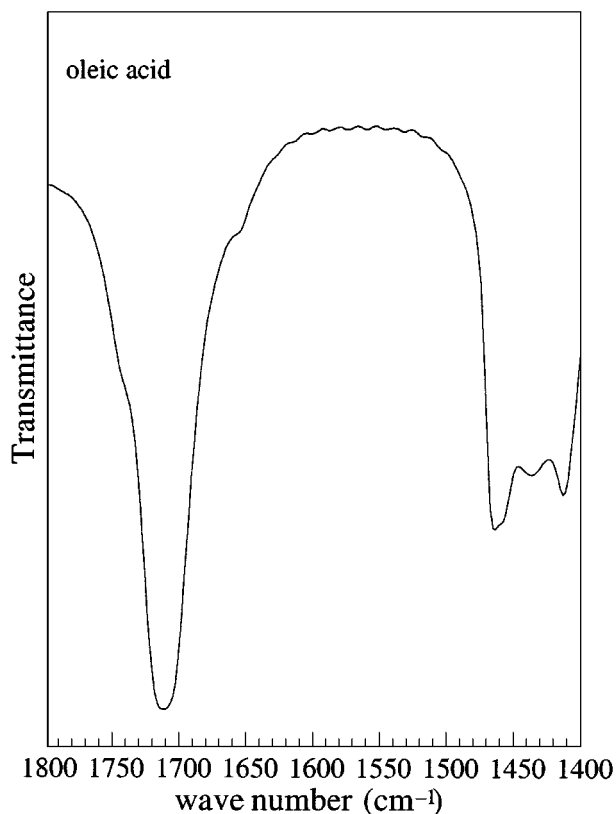


Figure 1 The infrared transmission spectrum for pure oleic acid in a liquid state.

distinguish clearly the infrared bands related to such coated species in the spectrum. Therefore, for most infrared studies of coated organic species on substrates, a subtraction technique is usually convenient. For this study, a subtraction technique was used whenever required. Fig. 2a and b illustrate the infrared spectra measured for a soda lime–silicate slide glass coated with oleic acid after and before subtraction, respectively. The spectrum of the untreated soda lime–silicate glass is illustrated in Fig. 2c. The bands associated with the coated species in the spectrum of the oleic acid–treated soda lime–silicate glass are not clearly distinguishable before spectral subtraction. The resultant spectrum after subtraction, however, reveals very clearly the separate bands related to the coated oleic acid. The resultant difference spectrum represents only the coated oleic acid species. Therefore, the subtracted spectrum can be compared with the spectrum of pure oleic acid in order to identify the new spectral bands that appeared as a result of the interaction of the organic with the glass surface.

3.3. The spectra of coated species

3.3.1. The formation of metal–carboxylate complex bonds

Fig. 3a illustrates the relative intensity of the band at 1706 cm^{-1} due to dimer decreases upon applying of oleic acid on the soda lime–silicate glass. In contrast, several new bands appear over the range from 1610 to 1500 cm^{-1} , indicating the formation of metal–carboxylate species. The band related to the $\text{C}=\text{O}$ stretching mode for a COOH group shifts to a lower

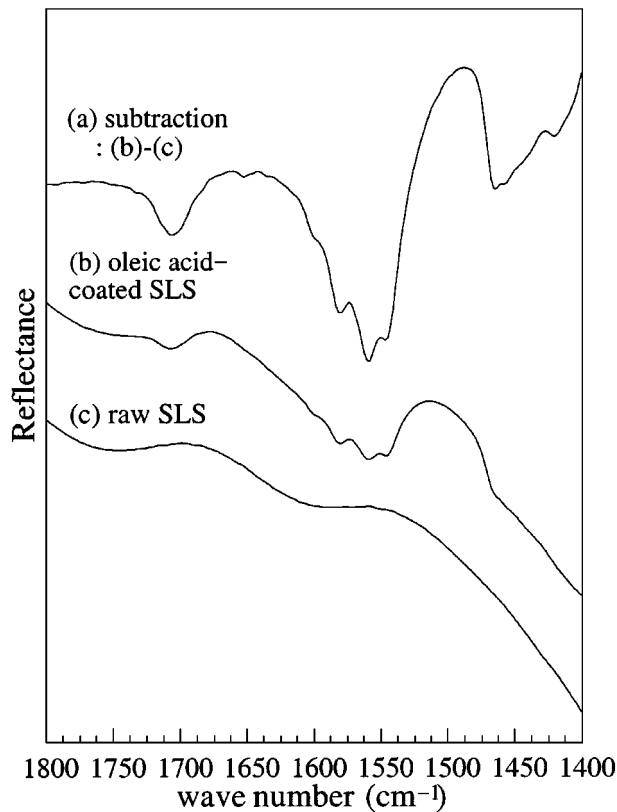


Figure 2 The DRIFT spectra (a) after and (b) before subtraction for the soda lime–silicate (SLS) glass coated with oleic acid and (c) uncoated soda lime–silicate glass.

wave number on its ionization to a carboxylate ion (COO^-). In general, the asymmetric stretching mode of an isolated COO^- ion ($\nu_a[\text{COO}]$) occurs around 1550 cm^{-1} [4, 9]. When a metal ion bonds with a COO^-

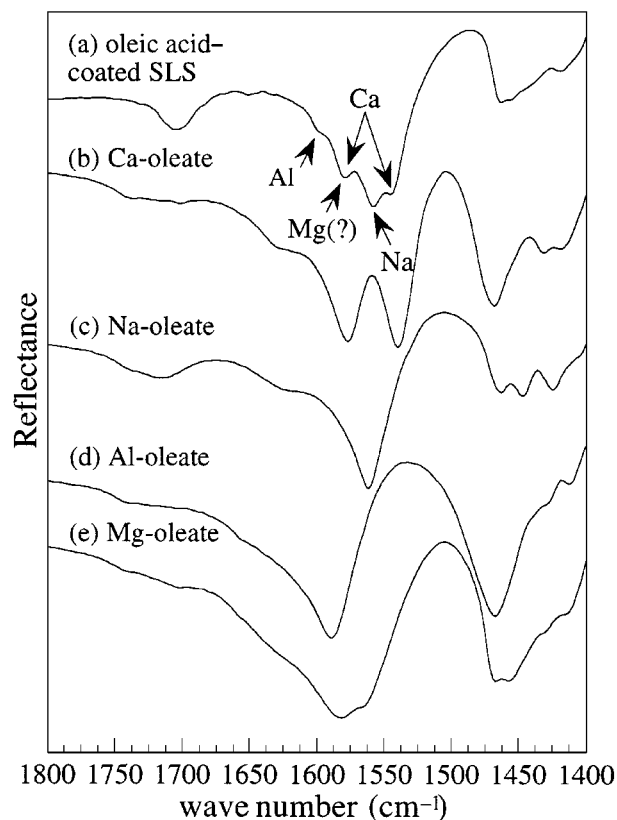


Figure 3 The DRIFT spectra for (a) the soda lime–silicate (SLS) glass coated with oleic acid and (b)–(e) synthesized metal–oleates.

ion, the amount of the shifting of the band depends on the electronegativity [10, 11], the size [12], and the valency of the metal ion associated with the bonded COO^- ions. Also, the symmetry [13, 14], bonding character, and strength [15–19] of the complex are other important parameters that determine the band location for $\nu_a(\text{COO})$ of a COO-M complex. Fig. 3b to e illustrate the infrared spectra measured for metal-oleates such as Ca-, Na-, Al-, and Mg-oleate. The wave numbers of the bands assigned to the asymmetric stretching modes of the COO^- ion group are 1562 cm^{-1} for Na-oleate, 1541 and 1577 cm^{-1} for Ca-oleate, 1589 cm^{-1} for Al-oleate, and 1564 and 1581 cm^{-1} for Mg-oleate. The shoulder at 1564 cm^{-1} in the observed spectrum for the prepared Mg-oleate may be from residual Na-oleate remaining in the final prepared product. Comparing the spectra of the synthesized metal-oleates with that of the oleate-treated soda lime-silicate glass, the presence of at least Na-, Ca-, and Al-oleate was found on the glass surface. The soda lime-silicate glass investigated in this study contains Na^+ , Ca^{2+} , Al^{3+} , and Mg^{2+} and relatively small amounts of several other metal ions. These results indicate that oleic acid interacted dissociatively with these metal ions on the soda lime-silicate glass, forming metal-carboxylate complexes.

The band at 1558 cm^{-1} in the DRIFT spectra of soda lime-silicate glass (see Fig. 3a) that possesses the strongest intensity is attributed to $\nu_a(\text{COO})$ involving the COO-Na complex. Na_2O is the next major component after SiO_2 in the soda lime-silicate glass investigated in this study. Even though ethyl alcohol may contain some water molecules, and an ethyl alcohol molecule possesses a polar, end hydroxyl group, these are not significant enough factors to remove large amounts of Na^+ ions from the surface. Consequently, this observation indicates that when oleic acid is coated on the soda lime-silicate glass from ethyl alcohol, significant amounts of Na^+ ions are present on the glass surface to form a large amount of Na-oleate complexes.

Many investigators [20–25] have discussed the structure types of metal-carboxylate complexes involving various metal ions on the basis of vibrational spectra. They have shown that the types of the formed complexes could be determined from the splitting amounts (Δ) between the band locations for $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$. The COO-Na bond linkage possesses mainly ionic character. As a result, the C–O and C=O bonds of the COO^- ion group exist in a resonance equilibrium state, showing only one band related to $\nu_a(\text{COO})$ involving the chelated complex [9, 10]. For sodium-oleate, the infrared bands related to $\nu_a(\text{COO})$ and $\nu_s(\text{COO})$ are located at 1562 and 1425 cm^{-1} , respectively (see Fig. 3c). Therefore, the Δ value is 137 cm^{-1} , which would be expected for an ionic bidentate complex [20]. As mentioned earlier, in contrast, when Ca^{2+} ions bond with COO^- ions, the asymmetric stretching mode splits into two bands. At 1419 cm^{-1} , $\nu_s(\text{COO})$ for COO-Ca complexes occurs (see Fig. 3b). The resulting Δ values ($\nu_a[\text{COO}]-\nu_s[\text{COO}]$) are 158 and 122 cm^{-1} for the bands at 1577 and 1541 cm^{-1} , respectively. Considering their wave number splittings and band locations on the basis of Nakamoto's model [20], the bands

at 1577 and 1541 cm^{-1} of the calcium-oleate can be related with unidentate and bidentate complex types, respectively. Calcium ions in the glass stabilize the silicate network containing Na^+ ions and are less soluble than Na^+ ions are [26]. Since Ca^{2+} ions are less affected by the solvent (ethyl alcohol in this study) than Na^+ ions are, sufficient amounts of Ca^{2+} ions can remain on the surface that react with oleic acid.

The band appearing at ca. 1595 cm^{-1} in Fig. 3a may be associated with the COO-Al species. Many other investigators have shown that the bands related to aluminum-carboxylate complex bond appear at ca. 1600 cm^{-1} [27–33]. Most window glasses contain up to several percent of alumina to improve the chemical durability of the glasses. The soda lime-silicate glass investigated in this study contains approximately 1 mol % of alumina. This COO-Al bond linkage is one of the most interesting metal-carboxylate bond linkages since aluminum ions are coordinated strongly to COO^- ion groups [27]. It has been known that when Na-oleate reacts with aluminum salts in an aqueous solution, aluminum ions easily bond with the carboxylate anions, and thus the resultant aluminum oleate precipitates. The COO-Al bond is relatively stronger than the other metal-carboxylate bonds because of its higher covalency. The pK_a value of the carboxylic acid group is approximately 4.5, showing weak acid character. Therefore, for the formation of COO-M bond, an acid-base reaction is one of the crucial reaction steps to form a complex bond. This acid-base reaction requires metal ions that possess Lewis acidic character. It has been observed earlier that soda lime-silicate glasses containing alumina do not show Lewis acidic sites involving aluminum ions [3]. This study shows a relatively weak infrared shoulder related to the formation of aluminum-carboxylate bonds, however. One study involving polyacrylic acid (PAA) adsorption on soda lime-aluminosilicate dental ionomer glass in an aqueous solution [34] showed that calcium ions react quickly with COO^- ions of PAA. In contrast, aluminum ions react relatively slower with isolated COO^- ions. Therefore, oleic acid does not easily react with aluminum ion directly. If sodium-oleate is used, however, aluminum-oleate precipitates relatively easily. Because a Na^+ ion ionically bonds with a COO^- ion, a Na^+ ion rather than a proton that covalently bonds with a COO^- ion would be more easily replaced by metal ions with higher valency, such as Al^{3+} ions. Therefore, in this study, the sodium-oleate species formed on the surface of the glass would help the formation of aluminum-oleate. The relative ratio of $\text{Al}^{3+}/\text{Na}^+$ ions that are present on the surface may be one of the important factors for such formation.

The investigated glass also contains Mg^{2+} ions. The band due to the $\nu_a(\text{COO})$ for a COO-Mg complex, however, overlaps with that for a COO-Ca complex, as indicated in Fig. 3b and e. Therefore, the possibility of the contribution of the Mg-oleate to the band at 1579 cm^{-1} for Ca-oleate cannot be ruled out. The relative band intensities for the two $\nu_a(\text{COO})$ modes involving COO-Ca complexes, however, are very close for the spectra of the pure Ca-oleate and the surface

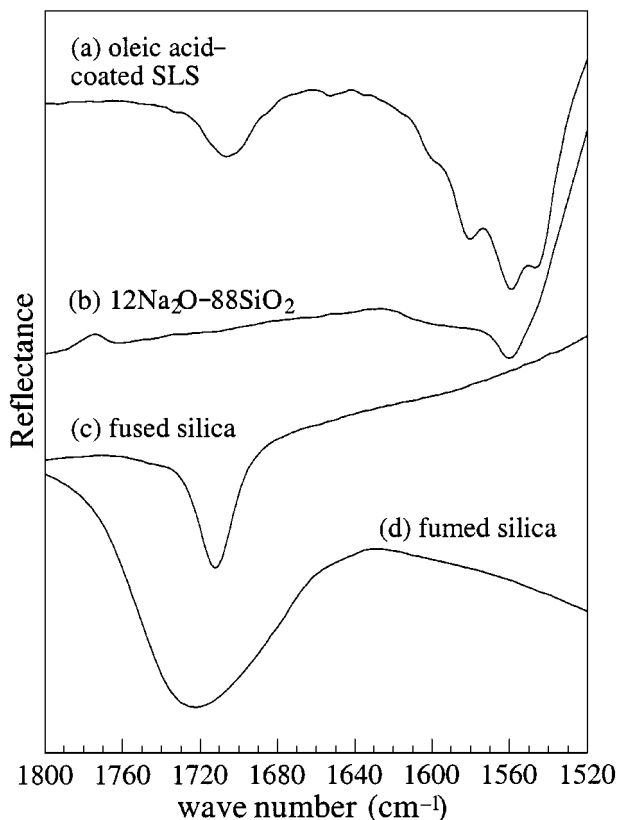


Figure 4 The DRIFT spectra for (a) the soda lime–silicate glass, (b) the soda-silicate glass, (c) the fused silica, and (d) the fumed silica coated with oleic acid.

Ca-oleate that is formed as a result of coating on the glass surface. This intensity observation may indicate that only a small amount of Mg-oleate is produced on the glass surface, regardless of the amount of Mg^{2+} ions present on the surface of the soda lime–silicate glass.

3.3.2. The effect of glass composition

Fig. 4 illustrates the effect of the glass composition on the coating of oleic acid. For all of the investigated samples, the same amount of oleic acid was applied in ethyl alcohol. The infrared spectrum for the soda-silicate glass containing 12 mol% Na_2O does not possess any bands related to the C=O stretching modes for COOH groups of oleic acid. Only the band attributed to the COO–Na complex species appeared at 1563 cm^{-1} , as shown in Fig. 4b. The soda lime–silicate glass in Fig. 4a contains 14.4 mol% Na_2O , which is more than the above-mentioned soda-silicate glass contains. The soda lime–silicate glass shows a significantly strong band because of the C=O stretching mode for COOH groups, however. This result suggests that the composition of the glass is a very important factor for the interaction of oleic acid with the glass surface. The soda-silicate glass has a significantly lower durability than the soda lime–silicate glass has, in which components such as Ca and Al oxides stabilize the SiO_2 network and consequently reduce the amounts of leachable metal ions (mainly, sodium ions) [26]. Hence, the amounts of sodium ions available on a glass surface and in a solution are significantly higher in the case of the soda-silicate glass than in the soda lime–silicate glass. This results in dissociating more

COOH groups of the applied oleic acid on the surface and in the solution of this glass, as compared with the soda lime–silicate glass. This result also suggests that sodium ions play a major role in dissociating COOH groups of the applied oleic acid. The infrared spectra in Fig. 4c and d are illustrated for fused silica and fumed silica, respectively, which were treated with oleic acid. As expected, the spectra reveal only the band associated with the C=O stretching mode for COOH groups on the coated oleic acid. The infrared spectrum for fumed silica powder possesses a band that is broader and is located at a higher wave number than that for the fused silica. This may be the result of a particle size effect due to the smaller particle sizes in fumed silica powder.

3.3.3. The presence of hydrogen bonding and oriented conformation in the hydrocarbon chain of the oleate group on the glass surface

Fig. 5 illustrates the infrared spectral region associated with the C=O stretching modes for COOH groups of pure oleic acid and coated oleic acid on fused silica and soda lime–silicate glass. When oleic acid molecule is coated on the surface of the soda lime–silicate glass, a relatively strong band at 1706 cm^{-1} along with a shoulder at 1685 cm^{-1} that are associated with dimers and a shoulder at 1731 cm^{-1} that is related to monomers of COOH groups are observed (Fig. 5a). This observation indicates that some of oleic acid has not dissociatively interacted with metal ions on the soda lime–silicate glass surface and that some of the oleic acid is adsorbed

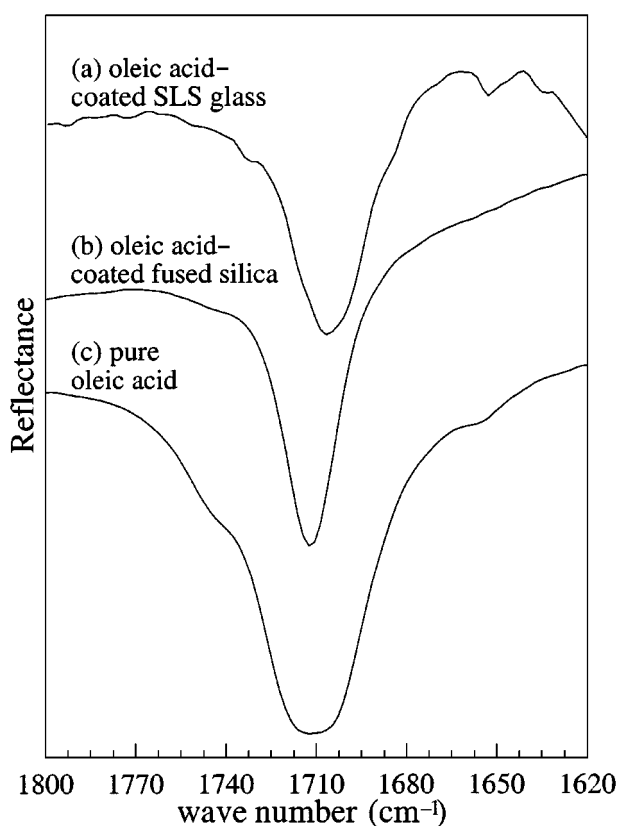


Figure 5 The DRIFT spectra for ν_a (C=O) of COOH of oleic acid coated on (a) the soda lime–silicate glass and (b) the fused silica and (c) pure oleic acid.

in the form of dimeric molecules. In the pure state, oleic acid possesses C=O stretching modes related to dimer and monomer COOH groups at 1712 and 1743 cm^{-1} , respectively (Fig. 5c). In a very dilute solution in CCl_4 , a monomeric COOH group possesses a C=O stretching mode at around 1760 cm^{-1} [4]. Each band due to the dimeric or monomeric COOH of the oleic acid coated on the soda lime–silicate glass appears at a slightly lower wave number than those corresponding to the dimers or the monomers of pure oleic acid. It has been known that the COOH groups of oleic acid molecules can bond onto a silica surface through hydrogen bonds with surface silanol (Si–OH) groups [30, 35–38]. This results in the perturbation of the C=O stretching mode for a monomeric COOH group and OH stretching mode for a surface Si–OH group. Consequently, this interaction causes their band locations to shift to lower wave numbers. An experiment was carried out to find the related spectral band shift of OH stretching vibration of Si–OH groups due to hydrogen bonding on coating of oleic acid. Oleic acid was coated on the fused silica or soda lime–silicate glass with different concentration. We could not, however, identify a new band appearing as a result of shifting of the band for the isolated surface OH stretching mode, which was due to the formation of hydrogen bonds with COOH groups, because the bands for internally contained OH groups in the glass possess very high intensities in this spectral region. Instead, the infrared spectra (not shown in Fig. 5) revealed that the band intensity for the OH stretching mode decreases gradually, as one increases concentration of applied oleic acid in the solution. These observations suggest that monomeric COOH groups of the oleic acid form hydrogen bonds with the Si–OH groups that are present on the soda lime–silicate glass surface (Fig. 5a).

The band associated with the C=O stretching mode belonging to monomeric COOH groups is located at a higher wave number for fused silica (1747 cm^{-1}) than for soda lime–silicate glass (1731 cm^{-1}) (Fig. 5a and b). This result suggests that the COOH groups of the oleic acid molecules bond relatively weakly with the surface hydroxyl groups on the fused silica than on soda lime–silicate glass. The band related to the dimeric COOH groups is located at the same wave number (1712 cm^{-1}) for both pure oleic acid and coated oleic acid on the fused silica. This similarity indicates that in coated oleic acid, the oleate species that are present above the first hydrogen-bonded molecular layer on the glass surface cannot be much different than they are in pure oleic acid.

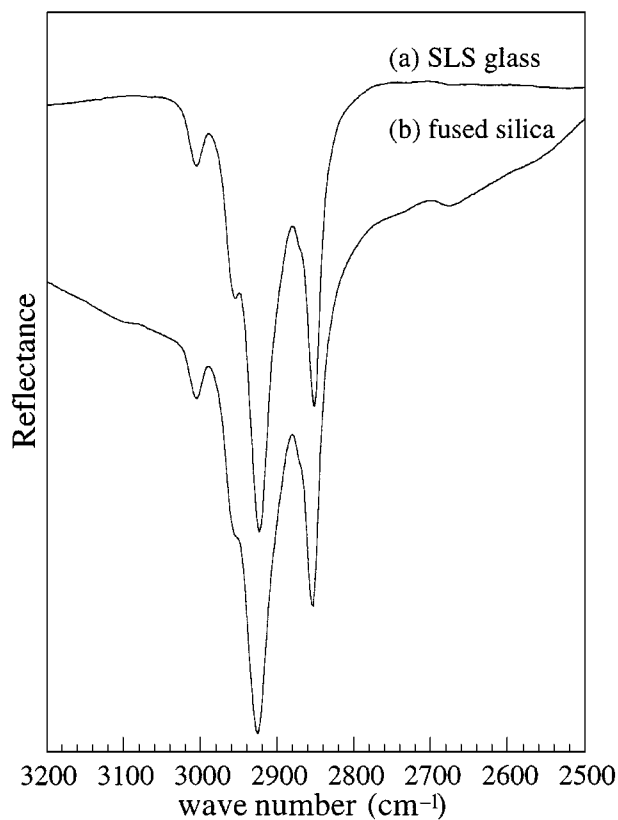
For the oleic acid coated on the soda lime–silicate glass, the band attributed to the C=O stretching mode associated with dimer species appears at 1706 cm^{-1} , which is at a slightly lower wave number than for both oleic acid coated on fused silica and pure oleic acid. There may be two reasons for the lower band location for dimeric COOH groups of oleic acid coated on the soda lime–silicate glass than in pure oleic acid. First, dimers could also form hydrogen bonds with surface Si–OH groups on the soda lime–silicate glass. This results in a stronger hydrogen bond (more perturbation of the C=O stretching vibration) than for the dimer in pure oleic acid or in coated oleic acid on fused silica. Second,

coated oleic molecules may have a more ordered (compact) structure than oleic acid on fused silica or in pure oleic acid has. The band locations for dimeric COOH groups of the coated oleic acid can be affected by the conformation and the structure of the coated oleic acid. An explanation regarding the packing density and the orientation of the alkyl chains of oleic acid on the glass surface will be given for oleic acid coated on the soda lime–silicate glass later.

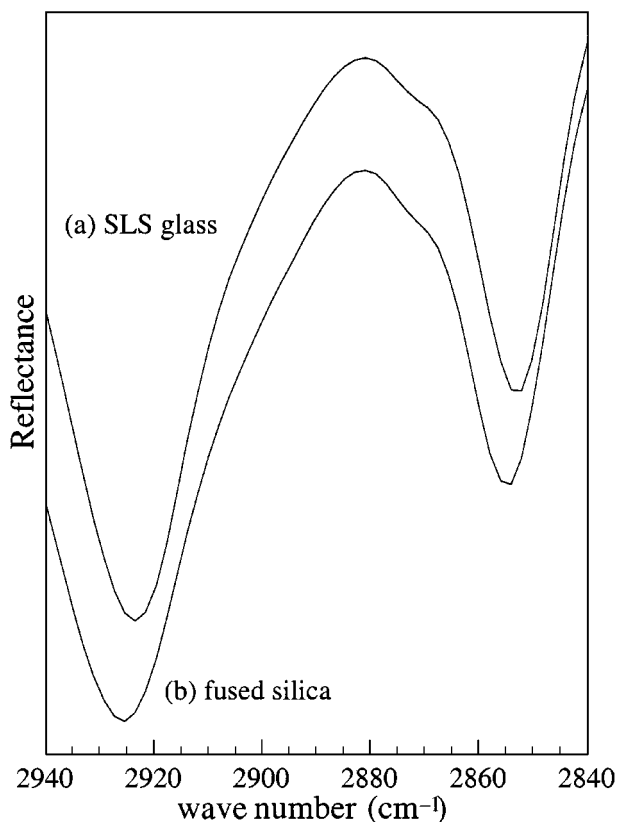
Fig. 6 illustrates the C–H stretching vibration region for the coated oleic acid on both soda lime–silicate glass and fused silica. The spectrum of oleic acid coated on the soda lime–silicate glass possesses a band at 3006 cm^{-1} assigned to the asymmetric stretching mode for $-\text{CH}=\text{}$ groups (Fig. 6A). Bands at 2956 and 2923 cm^{-1} arise from the asymmetric stretching modes for $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively; bands at 2873 and 2852 cm^{-1} arise from the symmetric stretching modes, respectively. The spectrum for the oleic acid coated on the fused silica possesses an asymmetric stretching mode for $-\text{CH}=\text{}$ groups at 3006 cm^{-1} , asymmetric stretching modes for $-\text{CH}_3$ and $-\text{CH}_2-$ groups at 2958 and 2925 cm^{-1} , respectively, and symmetric stretching modes for the latter groups at 2873 and 2854 cm^{-1} , respectively. The stretching modes of $-\text{CH}_2-$ groups for the oleate groups and the oleic acid molecules appear at lower wave numbers for the soda lime–silicate glass than for the fused silica. The band location for the vibrational mode is affected by the lateral interaction of the hydrocarbon chains mostly due to van der Waals forces. In general, this reflects the change in the *gauche/trans* conformer ratio or packing density of the hydrocarbon chains [39–43]. The band locations for the asymmetric CH stretching modes shift to lower wave numbers, when the lateral interaction of the alkyl chains becomes stronger. Therefore, a shift of the band to a low wave number is caused by the change from a flexible state to a more rigid (more ordered and solid-like) state of alkyl chains with respect to each other. Therefore, this observation indicates that the organic molecules coated on the soda lime–silicate glass have a more ordered structure than on the fused silica.

In the case of the fused silica, the protonated carboxylate (COOH) groups of oleic acid bond with Si–OH groups on the glass surface through only hydrogen bonds. Because the hydrogen bonds between COOH groups of oleic acid molecules and the surface hydroxyl groups are relatively weak on the fused silica (see Fig. 5b), the molecular chains possess somewhat more flexibility than on soda lime–silicate glass. The molecular chains of hydrogen-bonded oleic acid molecules possess a wider range of angles of orientation with respect to the glass surface. It thus makes the coated oleic acid less ordered and compact on the surface of fused silica. The conformation of the coated oleic acid molecules that are present above the first hydrogen-bonded molecular layer cannot be much different than that for pure oleic acid. The collection of oleic acid molecules in the pure liquid state shows isotropic properties.

On the other hand, a large portion of the oleic acid species is dissociatively adsorbed on metal ion sites



(A)



(B)

Figure 6 (A) The DRIFT spectra for C-H stretching modes of oleic acid coated on (a) the soda lime-silicate glass and (b) the fused silica. (B) The DRIFT spectra for C-H stretching mode of oleic acid coated on (a) the soda lime-silicate glass and (b) the fused silica.

on the on the soda lime-silicate glass surface through the formation of metal-carboxylate complex bonds. The COO-M bond linkage strongly coordinates COO⁻ ions

of the molecules on the glass surface. For the Na oleates formed on the glass surface, the main species involves a symmetric ionic bond between a COO⁻ ion and a sodium ion. Thus, the orientation of the alkyl chain of the molecule possesses less flexibility on the surface due to the formation of this type of bond. For the other types of complexes involving metal oleates formed on the glass surface (except the unidentate type), the flexibility of the molecular chain is extremely limited because of the symmetric bond linkage of the chelates (for example, the bidentate type). The oleate molecules with a unidentate type of bond will also possess less flexibility with respect to the alkyl chains, as compared with the hydrogen-bonded oleic acid molecules. Therefore, the oleate molecular chains on soda lime-silicate glass have a significant anisotropy, with COO⁻ ions anchored to metal ion sites on the soda lime-silicate glass, as compared with that on silica glass or in pure oleic acid.

The undissociatively adsorbed oleic acid molecules on the soda lime-silicate glass surface are distributed in the rigid and oriented metal oleate arrangements. Thus, the oleic acid molecules possess a different environment on the soda lime-silicate glass, as compared with the silica glass and pure oleic acid. The arrangement of the coated oleic acid molecules is modified by the oriented structure of the metal oleate. The COOH groups of the oleic acid molecules that form dimeric COOH groups in the coating are forced to approach to a closer distance by the adjacent metal-oleate species, which have more ordered and rigid alkyl chains. Consequently, this causes more perturbation of the C=O stretching mode for dimeric COOH groups on the soda lime-silicate glass, lowering its band location. The compact and ordered aliphatic chains of metal-oleates also possibly limit the hydrogen bonding angle between COOH and Si-OH and reduce its flexibility. As shown in Fig. 5, this can also be related to a shift to a lower wave number of the band due to the C=O stretching modes for the monomeric oleic acid molecules on the soda lime-silicate glass than on the fused silica or in pure oleic acid. Therefore, oleic acid molecules coated on the soda lime-silicate also have a somewhat more ordered (compact) structure and anisotropy, because of the arrangements of the aliphatic chains of the oleic acid molecules with respect to the glass surface.

4. Conclusions

The results obtained from these FTIR spectral studies indicate that the coating mechanism for oleic acid on glass depends on both the composition of the glass surface and its dissolution properties. The composition of the glass also affects the structural nature of the coated organic layers. The following conclusions can be drawn:

1. Oleic acid is coated on the soda lime-silicate glass as metal-oleates (as indicated by the formation of metal-carboxylate complexes) along with oleic acid molecules hydrogen bonded to Si-OH sites. In contrast, coatings on fused silica contain only hydrogen-bonded oleic acid.

2. On the soda-silicate glass surface, COOH groups of oleic acid molecules are completely dissociated and bonded to Na⁺ ions, even if smaller amounts of Na⁺ ions are present in this glass than in soda lime-silicate glass. This result occurs because of higher accumulation of Na⁺ ions on the glass surface in ethyl alcohol, due to the higher diffusion rate of Na⁺ ions in this glass.

3. The location of the band due to the C=O stretching mode for dimeric COOH along with that due to the C-H stretching modes for the coated oleic acid or metal-oleates indicates that the coated layer is more ordered and compact on the soda lime-silicate than it is on the silica surface or in pure liquid oleic acid because of the oriented structure of the metal-chelate complexes on the soda lime-silicate glass. On the surface, COO⁻ ion groups on the alkyl chains of the coated molecules are anchored by metal ions on the glass surface. These coordinate strongly with the COO⁻ ions on the glass surface and make the alkyl chains of the oleate molecules less flexible.

Undissociatively adsorbed oleic acid molecules are distributed among the metal-oleate molecules. The oriented nature of the metal-oleate species makes the alkyl chains of these oleic acid molecules more rigid. It also makes the hydrogen bonds between COOH groups of oleic acid molecules stronger on the soda lime-silicate surface than on the surface of fused silica or in pure liquid oleic acid.

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