Interaction of mineral surfaces with simple organic molecules by diffuse reflectance IR spectroscopy (DRIFT) [☆]

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Received 19 December 2007; accepted 4 March 2008

Available online 19 March 2008

Abstract

The adsorption of simple organic molecules to mineral surfaces was investigated by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and by solution chemical analysis. Salicylic acid, myristic acid or octacosane were deposited from water or hexane onto γ -alumina and kaolinite, and examined without evacuation or blending with KBr. The DRIFTS results replicated those from ATR-IR, where available, supporting the validity of DRIFTS as a versatile and convenient alternative to ATR. Results were obtained for coverage as low as 0.02 molecules/nm². Monolayer coverage on γ -alumina was determined from spectra as 0.7 molecules/nm² for salicylic acid, confirmed by solution analysis, and 2 molecules/nm² for myristic acid. Spectral features of salicylic acid deposited on γ -alumina from hexane were not distinguishable from those deposited from water. In almost all cases, spectral features associated with the carboxyl moiety were substantially altered, indicating a significant role in the adsorption mechanism. Adsorption of salicylic acid from hexane onto kaolinite was also as carboxylate, but myristic acid showed both carboxylate and carbonyl. The results from using hexane as solvent compared to water suggest that surface-adsorbed hydroxyl and molecular water, present on mineral oxides under ambient conditions, may be a key determinant of the adsorbate architecture. © 2008 Elsevier Inc. All rights reserved.

Keywords: Infrared spectroscopy; DRIFTS; Oxide minerals; Adsorption; Carboxylic acids; Surface water

1. Introduction

The adsorption of organic molecules onto mineral oxides is of fundamental importance for the understanding of environmental processes [1–3], catalytic processes on oxides such as alumina [4] and the creation of bio-compatible materials [5–7, and the references therein]. An important approach to studying such complex systems is the selection of a carefully-constructed hierarchy of model systems [3,5–15] comprised of pure-phase organic compounds with polar functional groups, interacting with well characterized mineral forms.

Infrared spectroscopy is an important tool in studying organics on minerals. Researchers typically have examined thin films

of treated, deposited mineral in transmission [14,15] or have coated the mineral onto an ATR internal reflectance element immersed in water containing the organic [5–7,9–14]. These latter experiments require collecting spectra from the complete mineral, from the supernatant solution and from the solid phase prepared in a controlled “blank” (no organic present) [9,10,12,13]. Yost et al. [9] noted that the technique worked best if the sample cell was kept in place for each corresponding reference and sample spectrum, to ensure constant transmittance of the empty cell and average angle of incidence of the IR beam. An exact matching of background concentration in solution is needed for the spectra used for subtraction, to isolate the data from organic adsorbed to the mineral surface. In addition, in situ ATR-FTIR, the need to distinguish between organic present both on the mineral and in solution needs to be considered. The solution concentration, the surface concentration and the solution path length must be in a proper relationship.

We were therefore motivated to explore the potential of an alternative IR spectroscopy, diffuse reflectance infrared Fourier

[☆] Authored by Jefferson Science Associates, LLC under U.S. DOE Contract No. DE-AC05-06OR23177. The U.S. Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce this manuscript for U.S. Government purposes.

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transform spectroscopy, DRIFTS [16,17] for use as a complement or alternative to ATR-FTIR. The DRIFTS technique has had limited use in this manner, although it was used, together with ATR-FTIR, in a study of the adsorption of carbonate to goethite and aided in the eliciting a mechanism involving mono-dentate coordination of carbonate and concurrent adsorption of H^+ to surface sites [18].

The DRIFTS technique is particularly suited to fine powdered mineral samples which can be subsequently retrieved for further study. IR light is directed onto the surface of the powder filling the sample cup, where it may be reflected directly or partially adsorbed and then re-emitted with transformation both by the surface and the bulk. The large number of randomly oriented surfaces produces a diffuse scatter of light having undergone a single or multiple scatterings. This wide angled scatter of radiation is collected onto the detector for analysis. The technique gives surface sensitive information and detail from adsorbed species, such as an organic, can be further concentrated by computing the difference spectrum between a sample with the adsorbed species and without it.

Two particular DRIFTS issues merit attention. First, the features of interest for the organic desirably should occur in a spectral region where absorption by the mineral itself is low enough that reflectivity-enhancing additives (e.g., KBr) are not needed. Second, the effective equivalence of the surface molecular environments needs to be established for the nominally “dry” powder in DRIFTS compared to liquid immersion for ATR-IR. The atmosphere at 295 K contains a water vapor pressure of between 2–20 Torr at all times and thus oxide surfaces (such as minerals) are typically terminated by hydroxyl groups and/or coated with one or more layers of adsorbed water [1,2,4,19–21]. The aqueous surface layer affects reactivity, particularly in comparison with materials under ultra high vacuum conditions or otherwise deliberately dried. It follows that DRIFTS studies using finely dispersed minerals which have been treated in solution and then “dried” by exposed to the atmosphere, have adsorbed water molecules with which to interact, and thus should give results, with respect to adsorbed surface species, which are comparable to in-situ solution ATR-IR studies.

In this study organic molecules of different shapes, with or without polar functional groups, have been selected and dissolved using either water or hexane. Each of the molecules selected forms a simple model of components of more complex systems, such as decayed vegetable matter (humic acids) or protein materials from animal sources [6,7,9]. Salicylic acid has an aromatic ring with both carboxylic acid and phenol functional groups and displays limited solubility in both water and hexane. Myristic acid (a long chain mono carboxylic acid, $C_{13}H_{27}COOH$) has a polar carboxylic acid functional group, but the length of the hydrocarbon chain renders it insoluble in water but soluble in hexane. Octacosane, a long chain (C_{28}) alkane, soluble only in non-polar solvents, was included in the investigations, using the deuterated form ($C_{28}D_{58}$) so that the presence of this molecule could be distinguished from the shorter chain hydrocarbon of the solvent.

A key goal of the study was to gain new insight into the molecular architecture of adsorbed species, especially at sub-

monolayer coverage and to investigate the role of the solvent on the adsorption. All samples examined in this study were prepared at the ambient solution pH. Thus the salicylic acid samples were prepared at acid pH, with no manipulation of pH during treatment. It should be noted that the observed changes in pH were always in the range where the surface charge of alumina surfaces was positive and siloxane type surfaces possessed no net charge or were negatively charged (with only one exception, which forms an important point of discussion).

ATR-FTIR studies of the interaction of short chain aliphatic carboxylic acids with clays and metal oxides have been reported [6,11–13], but these were all done with aqueous solution. We found no reports of adsorption studies of long chain fatty acids, or salicylic acid, from solution in a non-polar solvent such as hexane.

Tables of the samples are presented in the supporting material, Table S-1 for the aqueous samples (the observed pH conditions are noted) and Table S-2 for the samples prepared in hexane.

Clays occur widely in nature and alumina is of key importance industrially. The materials selected, kaolinite and γ -alumina, have been used extensively in reported IR studies of adsorbed organics [5–7,9,10,12,13,15] principally by in situ ATR-FTIR. Kaolinite, rather than montmorillonite, was selected for study since this class of clays is a simpler starting model than the ‘swelling’ montmorillonite type clays which have interstitial layers of water which must be considered. In these studies γ -alumina was used. As well as this material being widely used in industry, the structure of γ -alumina (which has cations (Al^{3+}) in octahedral and tetrahedral positions) has similarities with that of kaolinite ($Al_2Si_2O_5(OH)_4$) a layered aluminosilicate with octahedral and tetrahedral coordination of cations (Al^{3+} and Si^{4+} , respectively).

Both kaolinite and γ -alumina have surface hydroxyl groups and surface water, bonded to multiple surface site types. The surface of γ -alumina has up to 5 possible OH configurations, the balance depending on the type and distribution of the exposed crystal faces. Each of the OH type groups has a different level of coordination to other surface atoms and bears slightly differing charge (and thus acidity/basicity) [26]. Kaolinite has three types of surface hydroxyl groups, aluminol (AlOH), silanol (SiOH) and water adsorbed to Lewis acid sites [20,21].

Kaolinite particles formed from cleavage are disc shaped with a disc radius 5–10 times that of the disc thickness. The edges of the discs make up approximately 10% of the available surface but contain the greatest concentration of disrupted and broken bonds [26]. Thus in estimating the number of active sites, values obtained from estimates and experimental site density measurements, must be interpreted with the understanding, particularly for clays, that the sites may not be evenly distributed over the whole surface [23]. In understanding the behavior of kaolinite, account must be taken of experimental evidence which supports the larger faces of kaolinite particles being predominantly siloxane surfaces, due to leaching of aluminum by acidic conditions during weathering or kaolinite processing [1,24,25].

The surface charge of a mineral has a vital influence in determining the interaction between the surface and solution species. Experimentally observed values of the iso-electric (iep) point for alumina are in the region of pH 9, with no distinction as to alumina type [27]. The value of the iep for kaolinite depends somewhat on the material (and its previous history). If kaolinite is considered as a structure with one tetrahedral (siloxane) side and one octahedral (gibbsite) side, values for the iep would be midway between those of the siloxane and gibbsite surfaces (in the region of 5.5). Ma and Eggleton [25] reviewed values for the iep for kaolinite samples, finding them to be in the range 3–5. A kaolinite used in a detailed study by Alkan et al. [22] had an iso-electric point of 2.35. Such values indicate the dominant influence on the iep point of kaolinite is the siloxane type surface. Under all but very acidic conditions ($\text{pH} < \text{pH } 2.5 \pm 0.5$) the siloxane surface itself would be negatively charged [27].

2. Materials

2.1. Minerals

The γ -alumina used was supplied by Scientific Minerals Corporation (Bozeman Montana, USA). Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), from Edgar Florida, USA, was supplied by Ward's Natural Science.

2.2. Organics

High purity analytical reagent grade organics were supplied by Sigma–Aldrich, except for the deuterated *n*-octacosane, $\text{C}_{28}\text{D}_{58}$ (GMW 394.8) which was supplied by C/D/N Isotopes Inc. (Pointe-Claire, Quebec, Canada). Hexane was selected as the non-polar solvent since it introduced no functional groups and the shorter chain length of the molecules allowed evaporation of the solvent from the mineral under ambient conditions.

Salicylic acid ($\text{HOC}_6\text{H}_4\text{COOH}$; GMW 138.12) has an aromatic ring with both a carboxylic acid and a phenol functional group and at room temperature is soluble in water up to concentrations in the region of 0.015–0.02 M. The $\text{p}K_1$ of salicylic acid is 2.98, due to the carboxylic acid group, the phenol group has a $\text{p}K_2 = 13.7$ and thus can be considered to generate no acidity [9,10]. For studies of adsorption from solution in hexane, myristic acid ($\text{C}_{14}\text{H}_{28}\text{O}_2$; GMW 228.38) was selected as an example of a long chain fatty acid. Salicylic acid was sufficiently soluble in hexane to allow study for comparison with the adsorption from aqueous systems. Deuterated *n*-octacosane was used to probe the interaction of non-polar alkane with the surface of each of the minerals.

3. Experimental methods

3.1. Surface area

The surface area per gram of mineral was measured (by the BET method) on a Gemini 2365 from Micromeritics Instrument Corp. The samples were pretreated to remove adsorbed water by heating to 125 °C for 2 h and then cooled (with dry N_2

purging) for at least 30 min. The surface area determination was made at 77.3 K (using liquid N_2 cooling), the adsorbing gas was N_2 and the free space measurement was made using He. Each result was calculated from a 5 point plot. The γ -alumina was determined to have a surface area of 51 m^2/g and the kaolinite, a surface area of 27 m^2/g .

3.2. Samples preparation with aqueous solutions

Samples were prepared with purified water (treated to a resistivity ≥ 18.0 megohm/cm). A summary list of prepared samples is given in Table S-1. The experiments were run at the natural pH generated by the system. Sodium perchlorate, 0.1 M was used to prepare aqueous solutions and to treat the “blanks.” This solution provided an approximately uniform, high background ionic strength for all of the studies. The pH of the solution used for each blank was adjusted, to match that of the corresponding sample treated with organic, by the addition of perchloric acid or sodium perchlorate. Samples were mixed for 30 s by shaking and inverting the tube, the samples were then placed on a slow rotor for 18–24 h. A washing procedure was used to remove pore water containing dissolved organic. The initial solution was decanted, then 5 ml of background solution added and the tube shaken to allow mixing of solid and solution and then the solid allowed to settle. The washing was repeated 3 times. The washed solid was separated from the solution by centrifugation, spread onto a dish and allowed to dry over night, before a spectrum was taken. Salicylic acid samples were protected from light during drying and samples were stored in the dark. Periodic repeat spectra show the samples to be stable over a period of months, under those storage conditions.

A set of aqueous samples with a range of salicylic acid available per gram of mineral, was prepared (Table 1). The concentration of salicylic acid remaining in solution, after treating the mineral, was determined by UV–vis spectroscopy by monitoring absorption at 304 nm. Solutions were passed through a 0.2 μm filter to exclude colloidal material.

3.3. Sample preparation with hexane solutions

The non-aqueous solutions were prepared with reagent grade hexane, a summary list is given in Table S-2. The solvent was used as supplied. Mixing, washing and drying were as for the aqueous samples with hexane substituted for water. A ratio of 1 g of mineral to 20 ml of solution was used for samples and blanks. A concentration series of myristic acid in hexane was prepared by dilution of a 0.02 M stock solution (0.01; 0.005; 0.001 and 0.001 M). The solid to solution ratio was used together with the surface area per gram of mineral and the solution concentration, to calculate a maximum possible myristic acid coverage on the γ -alumina samples of 5, 2, 1, 0.2 and 0.02 molecules per nm^2 (assuming all available myristic acid was adsorbed from solution, values are given to 1 significant figure). Similarly, 1 g samples of kaolinite were treated with 20 ml each of 0.02; 0.01; 0.005; 0.001 and 0.001 M solution of myristic acid in hexane (maximum possible coverage is ~ 2

times that for the γ -alumina samples due to the surface area per g of kaolinite being approximately half that of the γ -alumina).

A solution of salicylic acid in hexane was prepared using; 0.003 g in 20 ml hexane. The solution was mixed overnight on a rotating mixer. No visible solid remained but the solution was filtered as a precaution (using a 0.2 μm cellulose acetate filter). A saturated solution of salicylic acid in hexane was also prepared (0.03 g in 20 ml), solid remained after overnight mixing and this was removed by filtration. Blanks were prepared using hexane passed through a filter. Solutions and solids containing salicylic acid were protected from light during sample preparation and storage.

Hexane solutions of deuterated octacosane, with concentrations of 0.02, 0.01, and 0.001 M were prepared. The treated samples were either subjected to a decantation—washing cycle or, in a limited number of cases, were left such that the treating solution evaporated depositing the solute onto the mineral.

3.4. Spectroscopy

Spectra were collected using a Nicolet NEXUS 670 spectrometer fitted with a SPECTRA-TECH ‘COLLECTOR II,’ DRIFTS unit. The number of scans was set at 100 with a resolution of 4 cm^{-1} , over the range 4000–600 cm^{-1} . The aperture setting was 100 and the scan velocity 0.158 min per scan. These settings maximize the collection of the IR radiation but allow for a spectral resolution of 4 cm^{-1} . There was no use of automatic corrections. Kubelka–Munk units were used in the final format [17]. The system was purged with air passed through a “BALSTON” air drier or (in the earlier experiments) with N_2 .

The sample cup was filled to the top (and lightly leveled using the straight edge of a spatula). Only treated mineral was added to the cup. There was no dilution of the sample with powdered KBr and thus the concentration and distribution of the sample was not an issue. Care was taken to fill the cup in a consistent manner for each sample.

Spectra of the mineral treated with organic and the prepared blank were both collected against a KBr background spectrum. Changes to the surface due to the organic were highlighted by computing a “difference spectrum,” the spectrum of the organic treated mineral minus the spectrum of the mineral blank. The spectra shown in the figures and discussed in the results are all difference spectra, except for those in Fig. 5, (A) and (B), below.

4. Results

4.1. Materials prepared from aqueous solution

4.1.1. Salicylic acid on γ -alumina

The mineral, γ -alumina, was treated with salicylic acid solutions with no further adjustment of pH, thus all solutions were acidic. Under these conditions the surface charge of γ -alumina in the solution would be positive since this mineral has an isoelectric point in the region of pH 8.8.

A spectral window showing peaks due to salicylic acid can be observed in the 1800–1200 cm^{-1} region. In this region the

Fig. 1. Difference spectra for γ -alumina treated with salicylic acid (spectra both shown full scale and with displacement). Upper (displaced, scale -1.0–2.2 KM) sample treated with excess salicylic acid and unwashed. Lower (scale 0–6 KM) washed sample.

only feature not related to the salicylic acid is a broad peak at 1638 cm^{-1} due to adsorbed molecular water on the mineral. This peak will not contribute to the difference spectrum if the moisture content of the samples is perfectly matched, but this is not always the case, particularly with kaolinite, and either a positive or negative peak may be observed.

The difference spectra for samples of γ -alumina treated with sufficient 0.015 M salicylic acid such that only 20% of the salicylic acid was removed from solution are shown in Fig. 1 (the spectra from both a treated and washed sample and a treated and unwashed sample are shown). The initial pH of the treating solution was 1.8 and the final pH of the suspension 3.8. Features can be seen resulting from each of the organic functional groups (carboxyl and phenolic OH) and the carbon structure. The spectrum of the unwashed sample shows evidence of multiple layers with broader peaks and shifted peak positions compared with a sample which was treated and then washed such that the salicylic acid present was sufficient only for monolayer coverage. In comparing the spectra of the washed and unwashed samples, it can be seen that multiple layers formed from dry-down have different bonding environments compared with molecules bonded to the mineral surface. A small broad band just above 1700 cm^{-1} suggests the presence of the carbonyl group ($-\text{C}=\text{O}$) on the unwashed sample but is absent on the washed sample. The spectrum for the washed sample corresponds closely to those obtained by ATR/IR for alumina and salicylic acid in pH 5 solution [10]. No new peaks were observed and no peaks were missing. A summary of the peaks positions is given in the supporting information (Table S-3). Peaks resulting from C–C vibrations of the benzene ring were observed consistently 8–10 cm^{-1} higher using the DRIFTS method than those observed using ATR-FTIRS, indicating some difference in the π -electron density of the ring. A shift of 8–10 cm^{-1} was also observed for the asymmetric vibration of the carboxylate group (but not in the position of the symmetric vibration).

Table 1
Concentration series for salicylic acid (SAL) on γ -alumina (1 g in 20 ml)

SAL conc. (mM)	Molecules/nm ² available	Initial pH	Final pH	Molecules/nm ² used	% SAL used	% coverage ^a	Curve code in Fig. 2
15	3.5	1.8	3.8	0.72	20	100	Not shown
10	2.3	2.0	4.5	0.74	32	100	A
5.0	1.2	2.3	5.2	0.75	64	100	B
1.0	0.2	3.0	6.1	0.2	95	30	C
0.25	0.05	3.6	6.3	0.06	91	8	D
0.10	0.02	4.0	6.3	0.02	94	3	E

^a 100% = monolayer.

The peak positions of the carboxylate peaks in the DRIFTS spectrum support a direct binding of salicylate to the γ -alumina surface which is positively charged at pH values below its iep, in the region of pH 8.8 [27]. The observation of carboxylate rather than a carbonyl group is consistent with the deprotonation of the carboxyl group at pH > 3 (the final pH of the treating suspension was 3.8). The observed separation, between the asymmetric vibration and symmetric vibration of the carboxylate peaks of 163 cm⁻¹ is within the range observed for bridging bidentate bonding [6]. The position of peaks due to the phenolic OH obtained by the DRIFTS and the in situ ATR-FTIR methods, corresponded (both for the major peak at 1263 cm⁻¹ and a minor peak at 1326 cm⁻¹). The position of the phenolic peak at 1262 cm⁻¹ gives information about the bonding of this group [9,10]. The shift in peak position from that observed for salicylate in solution at pH 5 (1252 cm⁻¹) supported hydrogen bonding of the phenol group with sites on the γ -alumina surface, stronger than the hydrogen bonding observed in the solution species. Thus the spectra support the interaction of both the carboxyl and phenol groups to the surface.

4.1.2. Correlation of spectra with coverage for salicylic acid on γ -alumina

A series of 1 g samples of γ -alumina were treated with 20 ml of solution, of differing concentrations, as summarized in Table 1. The DRIFT difference spectra obtained from these materials are shown in Fig. 2 (and in Figure S-1 in the supporting information). The amount of salicylic acid removed from solution by addition of γ -alumina was calculated from the difference in concentration between a filtered sample of the mineral suspension (determined by adsorption of light at 304 nm) and the initial solution concentration. The results in Table 1 and in Fig. 2 indicate that salicylic acid is adsorbing onto the surface of the γ -alumina. The number of molecules of salicylic acid per nm² was calculated using a measured surface area of 51.4 m²/g. For samples with an excess of organic molecules available, compared with available surface sites, the amount of salicylic acid removed from solution was constant (within experimental error), corresponding to 0.7–0.8 molecules/nm². This is significantly lower than estimates of the number of hydroxyl groups on the surface, suggesting limitation of adsorption to preferred surface sites and/or steric interference between the adsorbed molecules. The spectra from these samples (which were washed to prevent deposition of organic from dry down of residual solution) show a consistent peak intensity for samples

Fig. 2. A comparison of adsorption of salicylic onto γ -alumina with increasing coverage of salicylic acid: All difference spectra have been baseline corrected and are shown on a common offset scale. The spectra are for coverage (% monolayer) of: (A) 100% large excess, (B) 100%, (C) 30%, (D) 8%, (E) 3%.

treated with available organic in excess of monolayer surface coverage (Fig. 3).

For suspensions where the availability of suitable adsorption sites is in excess of the salicylic acid, >90% of the salicylic acid is adsorbed, but not 100%, an equilibrium being established between the adsorbed and solution species. The DRIFT spectra for these materials (Fig. 2) show sensitivity of the peak height to surface coverage, for each of the functional groups and the ring peaks.

At coverage of 0.02 molecules/nm² spectral peaks from salicylic acid can be distinguished but a larger number of scans (increased from 100 to 1600) were required for this sample to achieve an adequate signal to noise ratio (see Figure S-1 in the supporting information). Thus the limit of detection for this system is of the order of 0.02 molecules/nm² (3% of monolayer coverage).

The variation of peak height with surface coverage is given in Fig. 3 with part (top) showing a rapid increase in peak height, for the symmetric carboxylate stretch at 1382 cm⁻¹, and for the phenolic –OH stretch at 1263 cm⁻¹, with increasing availability of salicylic acid per unit surface area, and a leveling of peak height at availability greater than 1 molecule/nm². This evidence supports the findings from the solution studies of monolayer coverage of 0.7 molecules/nm², with subsequent layers being removed by the washing step. Peak height as a function

Fig. 3. Correlation of carboxylate (1382 cm^{-1}) and phenol group (1263 cm^{-1}) peak height with available molecules of salicylic acid in solution (upper) and adsorbed (lower) as determined by changes in solution concentration: (x) phenolic $\text{-OH } 1263\text{ cm}^{-1}$, (◆) $\text{-COO } 1381\text{ cm}^{-1}$.

Fig. 4. Samples of γ -alumina with monolayer coverage of salicylic acid, prepared with different solution pH conditions: curve (A) pH 1.8–3.8; curve (B) pH 2.0–4.5; curve (C) pH 2.3–5.2. The spectra are shown on a common scale (0–15 KM) with displacement for ease of viewing.

of surface coverage is shown in Fig. 3 (bottom), with a linear increase up to monolayer coverage being observed for both functional groups.

The three samples of γ -alumina which were shown to have monolayer coverage were prepared using different concentrations of salicylic acid in solution and thus the solution pH conditions for each differed, the pH of the final suspension varied from 3.8 to 5.2 (see Table 1). The spectra of these three samples are identical within the limits of technique (see Fig. 4) and thus the form of the adsorbed salicylic acid is not being influenced by pH differences observed for sample preparation.

Examination of observed solution pH, consistently show a rise over the treatment period for each of the samples prepared (see Table 1). The results are consistent with the removal of salicylic acid from solution, onto the γ -alumina surface. Since the organic molecule is adsorbed as carboxylate, an associated removal of hydrogen ions from solution is also occurring. The mechanism for this could be adsorption to a surface site or removal of hydroxyl ions from the surface (displacement by the adsorbing carboxylate).

Examination of the spectra shown in Fig. 2 shows that differences in the bonding environment of functional groups associated with salicylic acid occurs with increasing surface coverage. The observed changes are in the form of new peaks at higher surface coverage, rather than a shifting of peak positions observed at lower coverage. The symmetric stretch of the carboxylate group is at 1374 cm^{-1} for the sample with coverage of 30% of a monolayer (curve C), but a second contribution at 1400 cm^{-1} is evident with monolayer coverage (curves A and B). Changes are also observed in the phenol peak, with increasing surface coverage. A peak at 1262 cm^{-1} is observed with both monolayer and sub-monolayer coverage, but, samples with monolayer coverage show contribution from an additional peak at 1250 cm^{-1} . The peak position at 1250 cm^{-1} is close to that observed for salicylic acid in pH 5 solution [5] and would suggest less interaction with the mineral surface. The observed changes are the same for each of the samples with monolayer coverage (see Table 1 and Fig. 2, curves A and B) even though there was variation in the pH at which the samples were prepared. Since the spectral features seen at low coverage persist to high coverage as other spectral features arise, this argues against steric interference between the organic molecules as a source of the changes. Thus a strong hypothesis for the observed changes is that as coverage increases, sites with the most preferred surface coordination fill first. For the sample treated with the most concentrated salicylic acid solution (0.015 M) and left unwashed, features which appear with increasing surface coverage, become dominant for the symmetric carboxylate stretch and the phenol group. This further supports the coordination of a surface layer of salicylic acid to the mineral, which differs from that of subsequent layers of salicylic acid deposited onto the surface by dry-down.

4.1.3. Salicylic acid on kaolinite

Spectra from kaolinite and kaolinite treated with salicylic acid were used to determine if a window existed for the observation of the organic on the clay surface. The spectral window observed for salicylic acid (and other organics) is more limited compared with that on γ -alumina. A very strong peak in the clay spectrum in the region of $1200\text{--}1240\text{ cm}^{-1}$ limits observations to above 1350 cm^{-1} . A further limitation to observation within the range is a peak due to surface molecular water on clay at 1638 cm^{-1} . The drying of clay samples to matched water content is a greater problem for kaolinite than with γ -alumina. If the water content of a sample and its corresponding blank are not closely matched, a positive or negative peak in this region peak may interfere with the observation of peaks due to organics.

Fig. 5. Minerals treated with 0.015 M salicylic acid (initial pH ≤ 2). Spectra are full scale; (A) kaolinite (scale 0–0.3 KM); (B) γ -alumina (scale 0–8 KM).

In the investigations using kaolinite, evidence of salicylic acid adsorption onto this mineral was limited to samples prepared with solutions close to saturation, with an initial pH of 2.0 or less and the final pH of the suspension < 3 as shown in Fig. 4. No salicylic acid could be detected on samples prepared at higher (but still acidic) pH (see Table S-1). At pH values below 2.5 all of the surface types of kaolinite will positively charged or be close to neutral and salicylic acid in solution predominantly un-ionized ($pK_{a1} = 2.98$). It should be noted that the washing of the samples would removed complexes of salicylate with aluminum ions in solution. For kaolinite in a pH 2 suspension, the half life of an aluminum cation surface site is of the order of 135 days [1, chap. 5] and thus there would be limited loss during the duration of the present experiments and aluminum adsorption sites would remain available on the kaolinite surfaces, particularly the disc edges. Thus the salicylate observed in the spectra are molecules adsorbed to the surface of the minerals.

Fig. 5 shows the spectrum obtained from a kaolinite sample exposed to 0.015 M salicylic acid (of sufficient quantity for multiple layers) and then washed before drying. The initial pH of the solution was 1.8 and the final pH 2.6. By comparing the spectrum with one obtained for γ -alumina treated with 0.015 M salicylic acid (and then washed) the presence of salicylic acid on the kaolinite is more easily seen. The strongest peak at 1477 cm^{-1} , due to the benzene ring, is clearly identifiable and coincides with the equivalent peak for adsorption onto γ -alumina. No peak due to carbonyl is evident (in the region of 1700 cm^{-1}). The bonding of the carboxyl group to kaolinite is as carboxylate, with peaks observed in the region of 1550 and 1415 cm^{-1} . The bonding of the carboxyl group of salicylic acid is as carboxylate for both minerals but differences are observed. On γ -alumina, there is a strong peak at 1382 cm^{-1} which shows a shoulder at 1400 cm^{-1} . For kaolinite, a peak centered at 1414 cm^{-1} can be considered to comprise components at 1421 and 1406 cm^{-1} . The carboxylate asymmetric vibration observed at 1544 cm^{-1} on γ -alumina is shifted from 10 to 1554 cm^{-1} on kaolinite. No comparison can be made be-

Fig. 6. (a) The DRIFT spectra (both full scale) of minerals treated with hexane and dried. Grey: kaolinite (scale 0–16 KM); Black: γ -alumina (scale 0–7 KM). (b) The adsorbed water peak region of the DRIFT spectra (both full scale) of minerals treated with hexane and dried. Grey: kaolinite (scale 0–0.5 KM); Black: γ -alumina (scale 0–0.8 KM).

tween the interactions of the phenol group with the minerals since observation are limited to above 1350 cm^{-1} for kaolinite.

4.2. Materials prepared from hexane solution

4.2.1. Minerals treated with solvent only

Samples were treated with *n*-hexane and dried to be used as “blanks” for the analysis of the adsorption behavior of other molecules dissolved in this solvent. The $-\text{CH}_3$ and $-\text{CH}_2$ groups of alkanes have strong adsorption in the 3000 – 2800 cm^{-1} region and this region was monitored for evidence of residual hexane on the blanks. The γ -alumina and kaolinite treated with hexane and allowed to dry, showed no presence of residual hexane. The hexane treated kaolinite and γ -alumina show a small broad peak (at 1640 – 1635 cm^{-1}) due to the presence of adsorbed water (Fig. 6a). The spectral region for the adsorbed water is shown on an expanded scale in Fig. 6b.

Fig. 7. Adsorption of salicylic acid onto γ -alumina after exposure to 0.2–0.3 molecules of salicylic acid per nm^2 of mineral. The difference spectra are shown full scale with displacement. Black: adsorption from a hexane solution (scale 0–1.5 KM). Grey: adsorption from aqueous solution (scale 0–2.8 KM).

4.2.2. γ -alumina treated with salicylic acid in hexane

The presence of salicylic acid on the treated γ -alumina was observed in the 1750–1200 cm^{-1} region of the DRIFTS spectrum and highlighted in the difference spectrum (Fig. 6 black curve). Peaks in this region result from each of the organic functional groups (carboxyl and phenolic OH) and the carbon-ring structure. The observed peak positions and their assignments are listed in Table S-1 in the supporting information. Neither sample shows the presence of carbonyl, the bonding of the carboxyl group is as carboxylate, for adsorption from each of the aqueous and hexane solution. The spectra shown in Fig. 7 are from samples exposed to 0.02 milli-moles of salicylic acid per gram of mineral, but, for one sample hexane was the solvent (black curve) and for the other (grey curve) water was the solvent. In comparing the spectra, the two spectra are closely matched, as to peak positions and relative intensities, no new peaks are observed and no peaks are missing. The aqueous study with the equivalent availability of salicylic acid per unit surface area, showed the surface to have sub monolayer coverage of ~ 0.2 molecules/ nm^2 .

4.2.3. Kaolinite treated with salicylic acid in hexane

For studies involving the adsorption of organics onto kaolinite, the spectral window for observing salicylic acid (and other organics) was more limited compared with that on γ -alumina. The spectrum shown in Fig. 8 was obtained from kaolinite treated with a saturated solution of salicylic acid in hexane (and then washed with hexane before drying). The peak positions and the assignments are summarized in Table S-1 in the supporting information. The clearest peaks are due to the aromatic ring but peaks due to the functional groups can be identified. In the studies of kaolinite treated with aqueous solution, if the water content of a sample and its corresponding blank are not closely matched, a positive or negative peak due to adsorbed water is observed (at 1638 cm^{-1}). This effect is not observed for the sample treated with hexane. The positions of peaks in

Fig. 8. Difference spectrum of salicylic acid adsorbed onto kaolinite from a saturated solution of salicylic acid in hexane.

Fig. 9. DRIFT subtraction spectra of myristic acid adsorbed onto: kaolinite (grey: displaced, scale 0–1.0 KM); γ -alumina (black: scale 0–12 KM).

Fig. 8 which arise due to the aromatic ring are close matched with those observed in the aqueous studies (see Table S-1 in the supporting information). There is no evidence of the presence of the carbonyl group (no peak is observed in the region of 1700 cm^{-1}) but peaks correlated with carboxylate can be resolved. The carboxylate peaks each show a shoulder inferring contribution from differing binding environments (cleanly cleaved surfaces, edges and corner sites are all present on naturally sourced materials). Evidence of phenolic, C–O–H, bending is observed at 1330 cm^{-1} . Information due to phenolic –OH stretch occurs below 1300 cm^{-1} and difficult to interpret, due to a strong broad peak in the clay spectrum with a maximum at 1250 cm^{-1} .

4.2.4. Minerals treated with myristic acid in hexane

After treatment and washing, γ -alumina and kaolinite showed the presence myristic acid (Fig. 9). Two key spectral regions contain information relating to the organic; the 3000–2800 cm^{-1} region has peaks due to the aliphatic carbon chain and the 1800–1300 cm^{-1} region has peaks related to the func-

Table 2
DRIFTS absorbance peaks for myristic acid adsorbed onto minerals

γ -alumina (cm^{-1})	kWSc (cm^{-1})	Peak source
2958	2963	S _{asym} $-\text{CH}_3$
2922	2919	S _{asym} $-\text{CH}_2$
2853	2853	S _{sym} $-\text{CH}_2$
–	1699	C=O
1566	1597	COO [–] stretch
(1575; 1560; 1540)		High conc.; broad peak
1470; 1465; 1457	1470; 1465; 1457	Lower conc.; multiple peaks
		CH ₂ def (~ 1465) and
		CH ₃ asym def
1414	1411	$-\text{COO}^-$
1307	1307	C–O

tional group. Fig. 9 shows subtraction spectra for adsorbed myristic acid on γ -alumina and on kaolinite. Myristic acid is evident on both minerals. A summary of the observed peaks is given in Table 2. Strong bands due to the aliphatic chain are observed in the $3000\text{--}2800\text{ cm}^{-1}$ region. There is also a major peak due to $-\text{CH}_2$ at 1468 cm^{-1} . Myristic acid has peaks related to the carboxylic acid group in the region $1800\text{--}1300\text{ cm}^{-1}$. On both γ -alumina and on kaolinite, strong peaks are observed related to the dissociated carboxylate form ($-\text{COO}^-$) of the functional group (with two equal C–O bonds). This differs significantly from the un-dissociated form of the acidic functional group in the organic solvent. The presence of the acid carboxyl group is observed only on kaolinite (the grey curve in Fig. 9) with a peak at 1670 cm^{-1} arising from carbonyl, $-\text{C}=\text{O}$. This peak is less intense than those observed for the carboxylate or the aliphatic chain. The γ -alumina showed the presence of carbonyl only on a sample treated and left unwashed. Thus the evidence indicates a special interaction between the organic and the mineral surface, compared with subsequent dried down layers (which can be removed by the washing cycle).

The peaks on γ -alumina due to carboxylate, are at 1562 and 1411 cm^{-1} , the separation (151 cm^{-1}) suggests bridging bi-dentate bonding [6] of the carboxylate to the mineral surface. On kaolinite, the carboxylate peaks show some differences in position from those on γ -alumina but the separation of the peaks still suggests bi-dentate bridging of the carboxylate to the surface. The presence of both carbonyl ($-\text{C}=\text{O}$) and carboxylate on the surface of kaolinite supports two distinct types of sites for the bonding of the myristic acid to the surface. The relative strength of the carboxylate peaks, compared with the carbonyl peak, and the similarities between the carboxylate peaks on kaolinite and γ -alumina, suggests that the dominant binding sites on kaolinite are alumina type faces. The second type of binding could be interaction of the aliphatic chain with siloxane type surfaces, leaving a protonated carboxyl group with minimal interaction with the surface.

4.2.5. A study of the sensitivity of DRIFTS to the quantitative adsorption of myristic acid onto γ -alumina from hexane

A series of γ -alumina samples was prepared with a maximum possible coverage of myristic acid of 5, 2, 1, 0.2 and $0.02\text{ molecules/nm}^2$ (assuming 100% removal of myristic acid from solution). The full set of subtraction spectra for vary-

Fig. 10. Myristic acid on the surface of γ -alumina after treatment and washing (common scale). Maximum possible coverage: (A) 5; (B) 2; (C) 1; (D) 0.2; (E) $0.02\text{ molecules/nm}^2$.

Fig. 11. The sensitivity of DRIFT spectra of myristic acid adsorbed to γ -alumina; for peaks related to the functional group and the aliphatic chain. (■) $-\text{CH}_2$; 1465 cm^{-1} , (▲) $-\text{COO}^-$; 1410 cm^{-1} .

ing coverage of myristic acid on γ -alumina are shown in Fig. 10. Analysis of the change in peak height with available myristic acid (Fig. 11) shows that for major peaks associated with the functional group (carboxylate peak at 1410 cm^{-1}) and the aliphatic chain ($-\text{CH}_2$ deformation, 1465 cm^{-1}) there is a linear increase with availability, up to 2 molecules/nm^2 and then no further increase (within experimental error) at 5 molecules/nm^2 . This would indicate that monolayer coverage is in the region of 2 molecules/nm^2 , which is 2–3 times that observed for the adsorption of salicylic acid onto the same material.

At a maximum possible coverage of $0.2\text{ molecules/nm}^2$, 100 scans are sufficient to clearly distinguish myristic acid peaks (Fig. 10, curve D) but an increased number of scans would be required to confirm detection at $0.02\text{ molecules/nm}^2$.

In the case of kaolinite the intensity of peaks attributable to myristic acid varied with the availability per unit surface area (as observed for γ -alumina). With the disc-like structure of kaolinite and the significant differences between the edge surface and the face, a single value for surface coverage is not applicable. Using 100 scans, myristic acid was clearly detected on kaolinite (with peaks for both carboxylate and the aliphatic chain) when there was an availability of $0.1\text{ molecules/nm}^2$.

Fig. 12. Deuterated octacosane ($C_{28}D_{58}$) C–H stretch region. Each spectrum is full scale. Curve K is $C_{28}D_{58}$ adsorbed to kaolinite (baseline corrected; scale 0–0.035 KM). Curve A is a mix of $C_{28}D_{58}$ and KBr (displaced; scale –1.5–3.5 KM).

but no carboxyl peak was observed with this level of availability.

4.2.6. Minerals treated with deuterated octacosane dissolved in hexane

The results of experiments with myristic acid prompted studies using a long chain alkane (octacosane) with no functional groups to determine the interaction of the alkane chain with alumina and siloxane type surfaces. To enable a clear distinction of the spectral signal for octacosane from that of the hexane solvent a deuterated form of the molecule was used ($C_{28}D_{58}$) was selected. Strong peaks in the C–D stretch region (2300 – 2000 cm^{-1}) were used to monitor the presence of the organic on the surface of the treated minerals (Fig. 12, curve A).

No evidence of $C_{28}D_{58}$ was observed, after washing, in the spectra of treated γ -alumina samples, including that treated with 0.02 M solution (such that 5 molecules of $C_{28}D_{58}$ were available per nm^2 of mineral surface). The limit of detection was not an issue since $C_{28}D_{58}$ was clearly detected in the spectra of samples treated with 0.2 and 0.05 molecules/ nm^2 and left unwashed. In the case of kaolinite, $C_{28}D_{58}$ was clearly detected, after washing, on the surface of samples treated with 9 and with 5 molecules available per nm^2 but not on samples treated with 0.5 or 0.05 molecules/ nm^2 (Fig. 12, curve K shows the spectrum from the sample treated with 9 molecules available per nm^2). In contrast, myristic acid was still detectable on samples of kaolinite treated with availability as low as 0.05 molecules/ nm^2 . Since the interaction of $C_{28}D_{58}$ with γ -alumina and kaolinite was investigated via a hexane solution, the role of the solvent, also a non-polar alkane, as compared to the solute is of relevance. The lower molecular weight of hexane enabled it to be evaporated more readily from the surface as compared with deuterated octacosane. Since none of the deuterated organic was observed on γ -alumina, its presence on the surface of kaolinite infers that the material is adsorbed, but its presence on the sample treated with only the most concentrated of the prepared solutions suggests a competitive adsorption with hexane.

5. Conclusions

DRIFTS studies were successful in gaining surface specific information regarding the interaction of organic molecules with mineral surfaces. It was possible to determine the density of monolayer coverage of molecules adsorbed onto γ -alumina (this being 5–10 times less than estimates of active surface sites) and to reach significantly low detection limits, of the order of 1–10 molecules per 100 nm^2 . The monolayer coverage of myristic acid on γ -alumina was 2–3 times that observed for salicylic acid on the same mineral. For both myristic acid and salicylic acid, surface sites are occupied by the carboxyl functional group, as carboxylate, with spectral support for bridging bidentate coordination, involving 2 surface sites, but, salicylic acid also has interaction of the phenol group with a surface site. This factor would contribute to the lower surface density observed for monolayer coverage, compared with that of myristic acid.

In all cases for uptakes less than one monolayer equivalent, the adsorption of the carboxylic acid functional group onto clay and γ -alumina from acid aqueous solutions was as carboxylate, the spectral features for the carbonyl moiety being missing. This suggests a sorption mechanism of bonding to metal cations on the mineral surface. Adsorption onto a mineral surface also involves reaction of the hydrogen ion, either by reaction in solution with displaced hydroxyl or by adsorption onto oxygen sites on the mineral surface.

New insights were gained as to the molecular architecture of adsorbed species. Changes in the bonding environment were identified with increasing coverage at the sub-monolayer level, with the formation of new peaks at higher surface coverage, rather than a shifting of peak positions observed at lower coverage. This supports certain types of adsorption sites, such as corner or edge sites, being occupied preferentially at lower surface coverage, rather than changes due to inter molecular interaction at higher surface coverage.

Of particular note was the result that when hexane was used as the solvent, that adsorbed water or hydroxyl groups present on the surface of the minerals influenced the adsorption of organic molecules onto the mineral surface, particularly the interaction of polar functional groups with surface sites. The spectra of myristic acid and salicylic acid adsorbed onto kaolinite and onto γ -alumina, from solution in hexane, showed the presence of carboxylate. The results imply the displacement of hydrogen ions from the carboxyl group being accommodated, via the water layer, by a negatively charged surface site (rather than being taken up by the hexane solvent). There was evidence of carbonyl on unwashed surfaces. In the case of γ -alumina, the washing step removed all of the carbonyl species from the surface, supporting the group being present as a physisorbed layer formed by dry down onto this mineral. A comparison of spectra of salicylic acid adsorbed onto γ -alumina from aqueous solution and from solution in hexane (the ratio of mineral to salicylic acid in solution being equal) showed no evidence of differences in the adsorbed salicylic acid.

In the case of myristic acid adsorbed onto kaolinite, from solution in hexane, in addition to carboxylate, carbonyl was

retained after washing, indicating two distinct forms of adsorption. The possibility of the carbonyl group being present due to adsorption of the aliphatic chain to a siloxane type surface was supported by the observation studies with $C_{28}D_{58}$ which showed the adsorption of the non-polar alkane chain to kaolinite but not to γ -alumina. Thus a possible interpretation of the observation of both carboxyl and carbonyl groups for myristic acid adsorbed onto kaolinite, is interaction of the carboxylic acid group with alumina type surface sites (adsorbing as carboxylate) and the interaction of the aliphatic chain with the siloxane type surface, leaving the functional group exposed and unionized in the hexane solvent.

Acknowledgments

We gratefully acknowledge helpful discussions with Dr. Elizabeth A. Canuel of the Virginia Institute of Marine Sciences and Dr. Dennis J. Walls of DuPont. We thank Robert Schmidt for technical assistance and the Commonwealth of Virginia for financial support.

Supporting material

Supporting material for this article may be found on ScienceDirect, in the online version.

Please visit DOI: [10.1016/j.jcis.2008.03.024](https://doi.org/10.1016/j.jcis.2008.03.024).

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