A study of competitive adsorption of organic molecules onto mineral oxides using
DRIFTS

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ABSTRACT

Analysis of DRIFTS spectra was used for a quantitative study of competitive adsorption of myristic and salicylic acids onto kaolinite or γ -alumina. Peaks unique to the ring or the chain were selected and single molecule studies used as calibration. Samples were exposed to hexane solution containing equal molecular quantities of each acid. The surface loading of salicylic acid was not influenced by the presence of myristic acid on either mineral but the maximum loading of myristic acid was decreased (46 - 50 %) by salicylic acid. Displacement of myristic acid from γ -alumina, but not kaolinite, was observed when excess salicylic acid remained in solution. A 25 % increase in the maximum loading was observed for kaolinite, but not for γ -alumina. On γ -alumina, after a loading of 1 molecule per nm^2 , increased exposure resulted in salicylic acid adsorption only, this value is approximately the same for salicylic acid adsorption from aqueous solution or for water washed hexane treated samples [1, 2]. Thus a set of sites for adsorption of either acid is indicated together with other energetically less favorable sites, which can be occupied by salicylic, but not by myristic, acid.

GRAPHICAL ABSTRACT

Analysis of DRIFTS spectra was used for a quantitative study of competitive adsorption of myristic and salicylic acids onto kaolinite or γ -alumina. The graph shows adsorption of myristic acid onto kaolinite via the height of the peak at 2926 cm^{-1} (arising from the alkyl chain).

1. Introduction

This paper is the third in a three part series concerning the use of diffuse reflectance infrared Fourier transform spectroscopy, DRIFTS, to study the adsorption of simple organic molecules onto γ -alumina and kaolinite with both qualitative and quantitative analysis. This paper reports a study of competitive adsorption of salicylic and myristic acids, from solution in hexane, onto γ -alumina and kaolinite, done with quantitative analysis of the DRIFT spectra obtained, using single molecule studies as a calibration. Both of the selected organic acids were found in previous associated studies [1, 2] to adsorb from solution in hexane as carboxylate onto γ -alumina and kaolinite. The results suggest that the surface associated water, present on mineral oxides under ambient conditions, mediates the organic uptake. The nature of this water layer was discussed earlier [1, 2]. The spectra obtained from sample sets prepared to determine the minimum detection level and maximum surface loading were used as a calibration tool in this present study of competitive adsorption together with the calibrated adsorption of myristic acid onto γ -alumina and kaolinite presented in this paper.

The inorganic and organic materials were selected to form a model system using well studied and characterized components. Salicylic acid has an aromatic ring with both carboxylic acid and phenol functional groups and myristic acid is a long chain mono-carboxylic acid. Both of these molecules are soluble in hexane. Kaolinite was selected for study since this clay is widely distributed in the environment and has only surface water molecules to consider and no interstitial water, as is the case for swelling montmorillonite type clays [3]. The other inorganic material studied was γ -alumina, widely used in industry, particularly in the field of catalysis. The metal oxides selected

have similarities in structure, in that both have cations in octahedral and tetrahedral positions, Al^{3+} in each for γ -alumina, and in the case of kaolinite, Al^{3+} in octahedral and Si^{4+} in tetrahedral positions [3, 4].

The finely divided powder form of the selected metal oxides was particularly suited to examination using DRIFTS. The limitation of the DRIFTS technique in obtaining quantitative information has been a vexing problem, especially in the field of studying environmental materials such as soil humic acid [5]. The determination of the relative distribution of components of humic acid obtained in a variety of soils has been reported [6] and techniques developed for soils to determine parameters such as moisture content and total organic carbon [7].

The technique used here and in our previous studies [1, 2] added samples to the cup with no dilution with KBr and the spectra were recorded at ambient temperature under a flow of purified dry air. Spectra of γ -alumina and kaolinite samples treated with organic were collected together with that of a prepared blank for each. A “difference spectrum” for each sample treated with the organic under study was generated by the simple subtraction of the spectrum of the relevant prepared blank. This “difference spectrum” highlighted the changes to the surface due to the adsorption of the organic. The use of samples without dilution with KBr allowed greater sensitivity as to the presence of adsorbed organic and eliminated the problem of a consistent distribution of sample in the KBr mix in achieving quantitative analysis. Studies with salicylic acid adsorption onto γ -alumina and kaolinite showed that consistent handling of the samples (so as to maintain the same particle size distribution) allowed selection of a peak and analysis of peak height (or area under the peak) to determine the surface loading of the

organic up to the maximum possible with the washing step used. The quantitative spectral analysis was verified by analysis of the spent solution to determine the quantity of remaining salicylic acid [1, 2]. The results of the quantitative studies using hexane as the solvent, as reported in our previous papers, are used as a calibration in this present study of competitive adsorption; the adsorption of salicylic acid onto γ -alumina and kaolinite [2] and myristic acid onto γ -alumina [1]. The results of the calibration of the adsorption behavior of myristic acid onto kaolinite are presented in this paper.

2. Materials and Method

The materials used here were as described in the first phase of this work [1]. To achieve approximately equal surface areas for each, 1.0 g of γ -alumina and 2.0 g of kaolinite were used giving an area of $53 \pm 1 \text{ m}^2$. Reagent grade *n*-hexane was used as the solvent. In addition to the preparation of samples exposed to both salicylic and myristic acid, a study was made of the quantitative adsorption of myristic acid alone onto kaolinite and the spectra obtained used as a calibration for the competitive study.

Weighed samples of organic were dissolved in either 15 ml of hexane or sufficient to dissolve the allotted quantity. The samples were placed in glass vials or flasks and covered with foil to exclude light. Samples were mixed by shaking for 30 seconds and then placed on a slow rotor platform and left overnight. Samples were decanted and washed 3 times with 5ml of fresh hexane and then left to dry ("hexane-rinsed"). Selected samples treated with a high loading of myristic acid were set aside and the hexane was permitted to evaporate ("dried-down"). The samples were stored under ambient atmospheric conditions, protected from light. Blanks were prepared with

hexane. The blanks were checked for residual solvent after a 24 h drying period, by examining the 3000 – 2700 cm^{-1} region for peaks due to aliphatic carbon.

Samples for the study of the competitive adsorption of salicylic and myristic acid were prepared such that for each sample the solution contained the same molar quantity of each (details are given in Table S1 in the supporting material). The mineral samples were exposed to quantities in the range of 0.025 to 3.5 molecules per nm^2 each of salicylic acid and myristic acid.

3. Spectroscopy

All samples were examined without the addition of KBr. Spectra were collected using a Nicolet NEXUS 670 spectrometer fitted with a SPECTRA-TECH “COLLECTOR II”, DRIFTS unit. The system was purged with air passed through a “BALSTON” air purifier and drier. 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 minutes 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. Quantitative analysis of DRIFT spectra required the use of Kubelka-Munk (KM) units in the graphical format (calculated by instrument software from the recorded % transmission) [8]. Spectra of the materials 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 a “difference spectrum”, the spectrum of the organic treated mineral minus the spectrum of the mineral blank, computed by simple subtraction. When displaying multiple spectra baseline correction may have been

performed and this is noted in the caption. Selected peaks were baseline corrected for determination of the peak height.

4. Results

4.1 The calibration of the adsorption of myristic acid onto kaolinite.

Kaolinite samples were treated with myristic acid dissolved in hexane such that from 0.1 to 5.0 molecules of were available per nm². The height of the peak at $2926 \pm 1 \text{ cm}^{-1}$ arising from asymmetric stretching vibration of the methylene (CH₂) units of the alkyl chain was selected for quantitative analysis (Figure 1). The spectrum obtained from a kaolinite sample treated with hexane solvent only, and allowed to dry (a “blank”) is also shown in Figure1 and it should be noted that no peaks due to the hexane can be seen. A plot of the height of the peak at $2926 \pm 1 \text{ cm}^{-1}$, versus the molecules of myristic acid available per nm² of kaolinite surface (Figure 2) showed an increase in peak height up until an availability of 1.2 molecules per nm², after which no significant increase in peak height was observed with increasing amounts of myristic acid. Comparison of washed samples in Figure 3 gave an estimate of 1.1 – 1.5 molecules per nm² of myristic acid resistant to removal by the washing step. Analysis of the myristic acid remaining in solution confirmed this result. To determine this value, a measured volume of solution decanted from the clay suspension before the washing step, was passed through a 0.2 um filter and allowed to evaporate and the weight of residual myristic acid determined. For samples with an availability of myristic acid per nm² of kaolinite surface > 2 molecules per nm², the measured uptake using solution analysis was 1.1 – 1.3 molecules per nm², supporting the spectral evidence and confirming that the extra

organic present on unwashed samples (with an initial availability of > 2 molecules per nm^2) was from solution dry down.

4.2 The competitive adsorption of myristic and salicylic acids onto γ -alumina

A unique peak of each of the organic molecules was selected for quantitative study. The height of each of the selected peaks was measured and compared with the peak height for a sample with matching exposure to each of the competing components.

In the case of myristic acid, a peak at $2926 \pm 1 \text{ cm}^{-1}$, arising from methylene asymmetric stretch, was selected. A peak arising from the benzyl ring, at $1476 \pm 1 \pm 1 \text{ cm}^{-1}$ region, was selected for salicylic acid. A peak at 1466 cm^{-1} in the myristic acid spectrum arising from the asymmetric bend of the methyl group was observed as a shoulder in the ring peak due to salicylic acid when both of the carboxylic acids were present. Correction was made to the peak height at $1476 \pm 1 \text{ cm}^{-1}$, arising from salicylic acid, to account for contribution due to myristic acid. The peak height at this value for a myristic acid only sample with the same loading of myristic acid. Note was taken that the maximum loading of myristic acid for the samples with co-adsorbed with salicylic acid was 1 molecules per nm^2 , with a decrease to 0.5 molecules per nm^2 with increased availability of salicylic acid.

The variation of the height of the peak at $1476 \pm 1 \text{ cm}^{-1}$ with exposure of γ -alumina samples to salicylic acid in hexane, either as the sole component or in combination with an equal number of molecules of myristic acid is shown in Figure 4. It can be seen that the presence of myristic acid did not influence the loading of salicylic acid on the surface of γ -alumina. Figure 5 shows the variation in the peak at 2926 cm^{-1} (arising from the

alkyl chain) with exposure to hexane solutions of myristic acid or myristic acid with an equal component of salicylic acid. For an availability of ≤ 1 molecules per nm^2 the data points for myristic acid only and myristic acid in the presence of salicylic acid are the same within the experimental error of $\pm 10\%$ (indicated on the graph). A maximum loading of ~ 1 molecules per nm^2 was achieved for myristic acid in the presence of salicylic acid, half that observed when only myristic acid was present in the solution. For increasing availability above 1 molecule per nm^2 of each of myristic and salicylic acids, there was a decrease in myristic acid on the surface, with the implication of displacement by salicylic acid. For a sample with a full loading of salicylic acid (of 3.5 molecules per nm^2) there are still 0.5 molecules per nm^2 of myristic acid, giving a total loading 14 % higher than for salicylic acid alone.

In the 3000 – 2800 cm^{-1} region (Figure 6) no new peaks were observed when salicylic acid was co-adsorbed with myristic acid or with increasing surface loading of myristic acid either with or without the presence of salicylic acid. No changes were observed in the position of the peak due to methyl asymmetric stretch (2926 cm^{-1}) either for increasing loading or the presence of salicylic acid. In the case of both the asymmetric and symmetric methylene stretch, no change was observed due to the presence of salicylic acid, but a 3-5 cm^{-1} shift to lower wave number was observed (for samples treated with myristic acid only) when the surface loading increased from 1 to 2 molecules per nm^2 . This loading level was not achievable when myristic acid was competing with an equal molecular quantity of salicylic acid. No unique features or changes in peak position were observed in relation to salicylic acid when myristic acid

was co-adsorbed. A new peak at 1486 cm^{-1} was observed for samples with > 1 molecule per nm^2 of salicylic acid, with or without myristic acid present (not shown).

4.3 The competitive adsorption of myristic and salicylic acids onto kaolinite

In studies using kaolinite, spectral features due to the methyl and methylene groups of the alkyl chain were observed in the $3000 - 2800\text{ cm}^{-1}$ region (with no input from adsorbed salicylic acid). The peak at $2926 \pm 1\text{ cm}^{-1}$, arising from methylene asymmetric stretch, was selected for the quantitative analysis for adsorbed myristic acid (Figure 7). The maximum loading for myristic acid on kaolinite was significantly less when an equal molecular quantity of salicylic acid was present compared with adsorption from a solution of myristic acid only (0.5 ± 0.05 compared with 1.3 ± 0.1 molecules per nm^2). For samples exposed to ≤ 0.5 molecules per nm^2 of myristic acid the surface loading was not influenced by the presence of an equal quantity of salicylic acid.

The selection of a peak for quantitative analysis of adsorbed salicylic acid was more limited in the case of kaolinite. The $1500 - 1440\text{ cm}^{-1}$ region shows a broad peak attributed to ring modes of the molecule with the peak maximum at $1476 \pm 1\text{ cm}^{-1}$ (Figure 8). This region also contains a significant peak due to myristic acid, with the peak maximum at $1469 \pm 1\text{ cm}^{-1}$. The peak height at $1476 \pm 1\text{ cm}^{-1}$ was chosen for quantitative analysis (Figure 9) but correction was made for the height of the peak at this value for myristic acid, using a myristic acid only sample with the same loading (with note being taken that the maximum loading of myristic acid for the samples with co-adsorbed with salicylic acid was 0.5 molecules per nm^2). The loading of salicylic acid adsorbed onto kaolinite did not show any changes due to the presence of myristic acid, and thus the

maximum loading was 2 ± 0.2 molecules per nm^2 , equal to that observed with salicylic acid only samples.

5. Conclusions and discussion

The maximum surface loading of myristic acid on the γ -alumina samples was 50 % less in the presence of salicylic acid, than that observed for myristic acid only samples (1 compared with 2 molecules per nm^2). As the exposure of samples to a mix of these organics increased, the total adsorption of salicylic acid increased but a further decrease (from 1 to 0.5 molecules per nm^2) in the adsorption of myristic acid was observed. The maximum loading of salicylic acid was 3.5 molecules per nm^2 , with or without the presence of myristic acid.

In the single acid studies using γ -alumina, the maximum adsorption of salicylic acid was greater than that of myristic acid (3.5 compared with 2.0 molecules per nm^2). Thus it would seem that although there were sufficient sites to accommodate more carboxylate groups, these were not suited to adsorption by myristic acid, possibly since this molecule is significantly larger than salicylic acid. The total organic loading observed at the point after which increased availability of myristic and salicylic acids resulted in the adsorption of salicylic acid only, was 1 molecules per nm^2 , close to the maximum loading of 0.7 molecules per nm^2 observed for salicylic acid remaining after water washing or adsorbed from aqueous solution (see Thomas and Kelley 2009 [2]). Thus a set of sites suited for adsorption of either salicylic or myristic acids was indicated. Another, energetically less favorable, set of adsorption sites exists can be occupied by salicylic acid but not by myristic acid. With increasing amounts of salicylic

acid remaining in solution after maximum adsorption has been achieved, some displacement of myristic acid was observed.

In the case of the kaolinite samples, the maximum surface loading of the myristic acid was 46 % lower in the presence of salicylic acid; the maximum loading was 0.5 molecules per nm², a decrease from 1.3 molecules per nm². No decrease in this myristic acid loading was observed when excess salicylic acid remained in solution. This would indicate that there is a set of sites are suited for adsorption of either salicylic or myristic acids. Another, energetically less favorable, set of adsorption sites exists which can be occupied by salicylic acid but not by myristic acid. In the case of kaolinite, maximum myristic acid loading was achieved for exposure to 0.5 molecule per nm² of each of myristic and salicylic acid (a total of 1 molecule per nm²), further adsorption of salicylic acid was observed to a loading of 2 molecules per nm². Thus the maximum total loading of organic was 2.5 molecules per nm², a 25 % increase over that observed for salicylic acid alone.

Acknowledgements

We gratefully acknowledge the Commonwealth of Virginia for financial support.

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Figure 1: Myristic acid adsorbed onto kaolinite from solution in hexane, shown on a common scale with base-line correction. Available molecules per nm² (from the top); 0.22; 0.11; and 0.0 (the blank).

Figure 2: Changes in the height of the peak at 2926 cm⁻¹(due to -CH₂ asymmetric stretch) with increasing availability of myristic acid per nm² of kaolinite surface.

Figure 3; Estimation of maximum surface loading for the adsorption of myristic acid onto kaolinite. Available molecules per nm² (from top), 3.3 unwashed (bold black); 3.3 molecules (black); 2.2 (bold dashed); 1.1 (dashed). Spectra have been base-line corrected and are shown on a common scale.

Figure 4; Variation height of the peak at 1476 cm^{-1} with the exposure of γ -alumina samples to salicylic acid in hexane, either as the sole component or in combination with an equal quantity of myristic acid.

Figure 5; Variation height of the peak at 2926 cm^{-1} with the exposure of γ -alumina samples to myristic acid in hexane, either as the sole component or in combination with an equal quantity of salicylic acid.

Figure 6: Signal due to the alkyl chain. Samples with salicylic acid co-adsorbed with myristic acid (bold dashed grey) compared with samples with myristic acid only (black spectra). The bold black spectrum is for a sample with 2 molecules per nm² all other samples have ≤ 1 molecule per nm² of myristic acid.

Figure 7: Variation height of the peak at 2926 cm^{-1} , arising from the alkyl chain, with the exposure of kaolinite samples to myristic acid in hexane either as the sole component or in combination with an equal quantity of salicylic acid.

Figure 8: Kaolinite with adsorbed organic; (A) 1.0 molecules per nm² each of salicylic acid myristic acids; (B) 1.1 molecules per nm² salicylic acid only; (C) 0.55 molecules per nm² myristic acid only.

Figure 9: Variation height of the peak at 1476 cm^{-1} , arising from the aromatic ring, with the exposure of kaolinite samples to salicylic acid in hexane either as the sole component or in combination with an equal quantity of myristic acid. The peak height was corrected for the contribution of myristic acid at this wavenumber.

Supporting Material

Table S1: Competitive adsorption of salicylic acid and myristic acid (dissolved in hexane) onto 1 g samples of γ -alumina or 2g samples of kaolinite (all samples washed)

A γ -alumina K kaolinite	Total available molecules / nm ²	SAL available Molecules / nm ²	MYR available Molecules / nm ²	Moles of each organic	Wt g SAL	Wt g MYR	Vol ml hexane
A(K) C1	7	3.5	3.5	3×10^{-4}	0.0414	0.0685	100
A(K)C 2	5	2.5	2.5	2×10^{-4}	0.0276	0.0457	100
A(K)C3	2	1.0	1.0	1×10^{-4}	0.0138	0.0228	100
A(K)C4	1	0.5	0.5	5×10^{-5}	0.0029	0.0114	50
A(K) C5	0.5	0.25	0.25	2×10^{-5}	0.0028	0.0046	15
A(K) C6	0.2	0.1	0.1	1×10^{-5}	0.0014	0.0023	15
A(K) C7	0.05	0.025	0.025	2×10^{-6}	0.0003	0.0005	15
A(K)- BLK	0	0	0	0	0	0	15