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THERMAL ANALYSIS OF COMPOUNDS ADSORBED ON LOW-SURFACE-AREA SOLIDS
PART 2. CALORIMETRIC INVESTIGATIONS OF FATTY ACIDS ON CALCITE

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ABSTRACT

Differential scanning calorimetry (DSC) was performed on samples of calcite powder with a monolayer of adsorbed oleic acid. In an air atmosphere, a large exothermic heat was observed (68% of the heat of total combustion), which indicated that substantial combustion of the fatty acid occurred while it was still chemisorbed to the calcite surface. Enthalpies of displacement were measured by flow microcalorimetry (FMC) for the adsorption of stearic and octanoic acids on calcite powder from three solvents (dry heptane, dry isopropanol and a mixture of 1% water in isopropanol). The adsorption was reversible from the isopropanol solvents, but not from heptane; this is discussed as it relates to the nature of the adsorbate–adsorbent bond. Exotherms were observed for the adsorption and endotherms for the desorption in all cases. The magnitudes of the heats (8–30 kJ mol^{-1}) and the reversibility data are consistent with the displacment of a carbonate, bicarbonate or hydroxide ion by a fatty acid anion at the calcite surface.

INTRODUCTION

In this investigation of the adsorption of organic compounds on carbonate minerals, quantitative information is sought on the strength of the adsorbate–surface bond. Differential scanning calorimetry (DSC) was used to interpret the reaction underlying the adsorbate weight loss in a flowing gas stream that had been previously observed in our thermogravimetric investigations of the adsorption [1]. Flow microcalorimetry (FMC) was used to measure the heats of the adsorption and desorption processes in a solid–liquid system; this is more relevant to the geochemical environment to which our work applies.

Measured heats of adsorption processes in solid–liquid systems are not isolated enthalpies of adsorption; they represent the net enthalpy change for the displacement of solvent by adsorbate. This point has been recognized recently [2–6], and the heats are generally referred to as enthalpies of

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displacement. The enthalpies of displacement for surfactant adsorption from aqueous or organic solutions typically fall in the range -5 to -30 kJ mol^{-1} (the process is exothermic), and the adsorption is considered to be physical [2–4].

There are few accounts of experimental work concerning adsorption calorimetry on low-surface-area solids, probably because of the extreme sensitivity required for these measurements. Most of the investigations apply to the adsorption of surfactants on minerals during enhanced oil recovery. Rouquerol [2] measured displacement enthalpies of -10 to -15 kJ mol^{-1} for the adsorption of surfactants from aqueous solution onto ground sand (4 $\mathrm{m}^2\ \mathrm{g}^{-1}$) and kaolin (19 $\mathrm{m}^2\ \mathrm{g}^{-1}$). Van Os and Haandrikman [3] reported displacement enthalpies of -4.8 to -6.5 kJ mol^{-1} for the adsorption of a sulfonate surfactant from aqueous solution onto crushed sandstone (0.35 $\mathrm{m}^2\ \mathrm{g}^{-1}$). Bocquenet and Siffert [7] did not report enthalpies per mole of adsorbate, but they recorded enthalpies of -52 to -100 mJ m^{-2} for the adsorption of sulfonates from aqueous solution onto a clayey sandstone (2.6 $\mathrm{m}^2\ \mathrm{g}^{-1}$) and α-alumina (3.5 $\mathrm{m}^2\ \mathrm{g}^{-1}$). These results are comparable with the others cited here. Rahman [8] measured heats of 170–550 kJ mol^{-1} for the adsorption of some pyridines and stearic acid from benzene onto ferric oxide (9.2 $\mathrm{m}^2\ \mathrm{g}^{-1}$); he detected no heats for similar adsorption on cuprous oxide (2.7 $\mathrm{m}^2\ \mathrm{g}^{-1}$). The large magnitudes of these heats and the dissimilarity between the results of the ferric and cuprous oxides may indicate that there is a concomitant chemical reaction at the ferric oxide surface. Von Rybinski and Schwuger [9] reported heats of adsorption of 27–57 kJ mol^{-1} for the adsorption of sodium oleate and sodium hexadecylsulfate from aqueous solution onto scheelite (4.0 $\mathrm{m}^2\ \mathrm{g}^{-1}$) and calcite (4.5 $\mathrm{m}^2\ \mathrm{g}^{-1}$). Their results for calcite agree well with ours, and the results are compared later.

EXPERIMENTAL

The calcite substrate used was calcium carbonate reagent-grade primary standard from Mallinckrodt. X-ray diffraction analysis showed pure calcite, and scanning electron microscopy revealed well-crystallized particles with dimensions of approximately 3 μm. The BET surface area measured by nitrogen adsorption was 0.60 $\mathrm{m}^2\ \mathrm{g}^{-1}$. The powder was used as received for DSC measurements.

Adsorption studies using FMC required calcite with a somewhat higher surface area. This was prepared from the Mallinckrodt calcite powder described above. The sample was ground for 1 h with a Fritsch automatic mortar and pestle. It was then heated at 450°C for 16 h in a CO_2 atmosphere to anneal the surfaces and to remove surface water. Pellets 31 mm in diameter were prepared in a Spex Industries model 3623 die; they were pressed to 1172 bar. The pellets were crushed, and the 170–270 mesh fraction was collected; the sample was wet sieved with deionized water over the 270 mesh sieve to remove fine particles. Analysis by X-ray diffraction showed only calcite. Surface areas measured by nitrogen adsorption were 3.1 and 2.3 m^2 g^{-1} for the two batches prepared. Scanning electron microscopy revealed agglomerates (50–100 μm) of subhedral calcite particles (0.1–5 μm).

Three adsorbates are discussed in this paper. The octanoic acid was obtained from Sigma (better than 99%). Oleic acid (NF/FCC, clear grade) and stearic acid (reagent grade) were obtained from Fisher. Esterification and gas chromatographic analysis of the oleic acid indicated that it contained substantial quantities (20%) of other fatty acids with similar chain lengths, but these impurities did not affect our findings because the combustion behavior of these acids was essentially similar to that of oleic acid.

The solvents used were heptane (Fisher reagent grade or Baker resi-analyzed grade) and isopropanol (Baker reagent grade). For adsorption prior to DSC analysis, the heptane was used as received. However, the FMC studies showed extreme sensitivity to water in the solvents, so pure solvents were dried and subsequently handled in a glove bag with a dry nitrogen atmosphere. The heptane was purified and dried by dropwise passage through a column of alumina (Fisher adsorption, 80–200 mesh), silica gel (Fisher reagent A.C.S., 100–200 mesh) and calcite (Mallinckrodt, as received). The isopropanol was dried by dropwise passage through a column of molecular sieves (Baker activated, type 4A, 8–12 mesh). For the water–isopropanol mixed solvent, water was purified by passage through an activated carbon cartridge, two mixed-bed ion-exchange cartridges and a 0.2 μm filter (Nanopure System by Barnstead). The isopropanol was used as received in the mixed solvent.

Differential scanning calorimetry was carried out using a Perkin–Elmer model DSC-2C. The sample chamber was purged at 40 cm^3 min^{-1} with building air that had been filtered to remove particulates and oil, or with ultrahigh purity nitrogen (99.999%). Optimal results were obtained when the sample and reference compartments each contained a pan with no lid (to improve contact with the purge gas). Each compartment was covered with its perforated platinum cover. The scan rate was 80 °C min^{-1}.

Flow microcalorimetry was carried out by the saturation method with an FMC model Mark 2V (Microscal, Ltd.). The instrument had a small sample cell that contained approximately 0.1 cm^3 (0.17 g) of adsorbent. Solvents or solutions were pumped through the cell at 0.21 ml min^{-1} by Braun Perfusor VI syringe pumps from 50 ml Glenco glass syringes with Teflon adjustable plunger seals. All tubing was Teflon, and the stream flowing to the cell was switched with an Altex rotary valve in which the solution contacted only fluorocarbons. Measurements were carried out at the ambient temperature of approximately 20 °C. Adsorption or desorption occurred as the adsorbate concentration in solution was changed in a stepwise manner; the heats were measured by a pair of thermistors embedded in the adsorbent. Each load of adsorbent in the cell was calibrated by a known electrical input to a resistor embedded in the adsorbent. The analog voltage output of the FMC was amplified and digitized by either a Hewlett-Packard model 3054A data acquisition system or a Keithley model 181 nanovoltmeter. Data were collected and stored on a Hewlett-Packard 9845B microcomputer. The voltage vs. time curve was integrated to yield the heats for each stepwise change in concentration. These heats were summed to obtain the cumulative heat change for the overall adsorption or desorption.

DIFFERENTIAL SCANNING CALORIMETRY

DSC was performed on calcite samples with a monolayer coating of oleic acid. The samples were prepared from heptane solutions by the adsorption and washing techniques described by Thomas and Clouse [1]. Thermogravimetric analysis (TGA) confirmed the monolayer coverage. Figure 1 shows the large DSC exotherm and the TGA weight loss curve for one of these samples with air as the purge gas. The exotherm occurs in the same temperature range as the adsorbed organic weight loss in the TGA curve. The area of the peak is 35 J g^{-1} of sample. With the calcite surface area of 0.60 m^2 g^{-1} and the oleic acid monolayer coverage of 7.7 μmol m^{-2} determined by TGA, this heat is equivalent to 7.6 MJ (mol oleic acid)$^{-1}$. The heat for total combustion of oleic acid is 11.1 MJ mol^{-1}. The magnitude of our experimental exotherm indicates that, to a large extent, combustion of

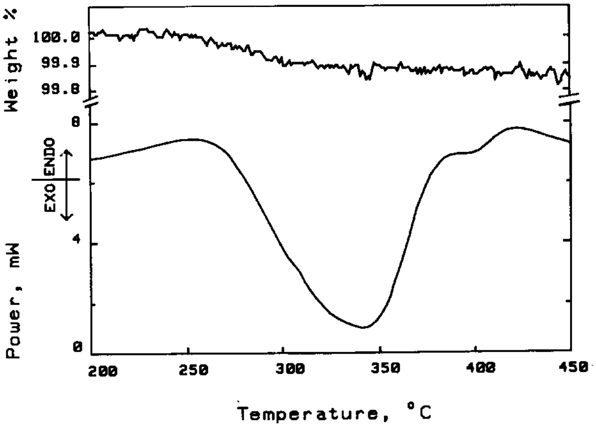


Fig. 1. Thermogravimetric analysis and differential scanning calorimetry curves for an oleic acid monolayer on calcite. The sample was run in air at 10 ° C min^{-1} (TGA) or 80 ° C min^{-1} (DSC).

the oleic acid takes place within the sample chamber. The experimental heat is smaller than the heat of total combustion probably because the DSC combustion does not proceed completely to carbon dioxide and water. (The supply of oxygen to the sample may have been limited, and combustion of oleic acid to carbon monoxide and water yields just 6.0 kJ mol^{-1}.)

It is important to recognize that the exotherm discussed above represents a chemical reaction between the sample and the purge gas, not merely a thermal transition of the sample. When the sample was run in a nitrogen atmosphere, no heat effect was observed by DSC even though an equivalent organic weight loss was observed by TGA. This probably indicates that fewer bonds are broken in the nitrogen atmosphere, and the fatty acid or its volatile fragments are swept away by the purge gas.

The experiments were performed on adsorbed oleate, but we expect that the results would be much the same for other fatty acids adsorbed on calcite. The large exotherm in air implies that the calcite–oleate surface bond is as stable in this atmosphere as the chemical bonds within the oleate itself; otherwise, the oleate would have desorbed and been purged from the sample chamber before combustion. This provides further evidence (in addition to our results on reversibility [1]) that fatty acids (actually fatty acid anions) chemisorb on carbonates.

FLOW MICROCALORIMETRY

Adsorption studies carried out using FMC yield information on the mechanism, reversibility and strength of adsorption of fatty acids on calcite. These experiments were performed for two adsorbates (stearic acid and octanoic acid) from three solvents (dry heptane, dry isopropanol and a mixture of 1% water in isopropanol (by volume)). Solution concentrations were changed in a stepwise manner. The adsorbent bed was allowed to equilibrate with each new solution concentration; the heat change for each step was measured and summed with the previous heats from zero adsorbate concentration. The data are presented in Figs. 2–5 as the cumulative enthalpies of displacement for the adsorption and desorption processes as a function of concentration of adsorbate in the solvent stream. The cumulative nature of the data results in increasing error bars as the run progresses. The non-zero enthalpies at zero concentration following the adsorption–desorption cycles in Figs. 4 and 5 serve as a good indication of the maximum error in the data. Because the abscissa is solution concentration, the reader should bear in mind that, while the plateau value of the enthalpy of displacement corresponds to the average at monolayer coverage, intermediate values do not correspond directly to surface coverage. The enthalpy for the first molecule adsorbed and for the last molecule adsorbed are probably different. All systems exhibit exotherms on adsorption and endotherms on de-

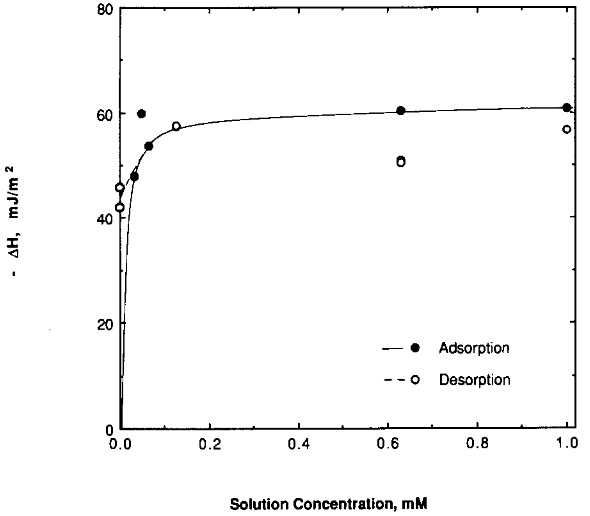


Fig. 2. Enthalpy of displacement for adsorption and desorption of octanoic acid on calcite from dry heptane.

sorption. For each system, with the exception of octanoic acid from dry isopropanol, duplicate experimental runs were performed, and all data points are shown on the figures.

Figures 2 and 3 show the results for adsorption and desorption from dry heptane. The curves for octanoic acid in Fig. 2 and the curves for stearic acid in Fig. 3 are very similar. Both chemicals begin to adsorb at very low concentrations and level off at monolayer coverage at a solution concentra-

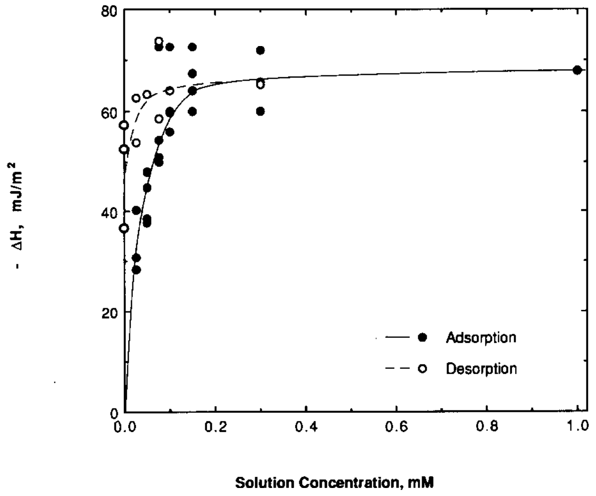


Fig. 3. Enthalpy of displacement for adsorption and desorption of stearic acid on calcite from dry heptane.

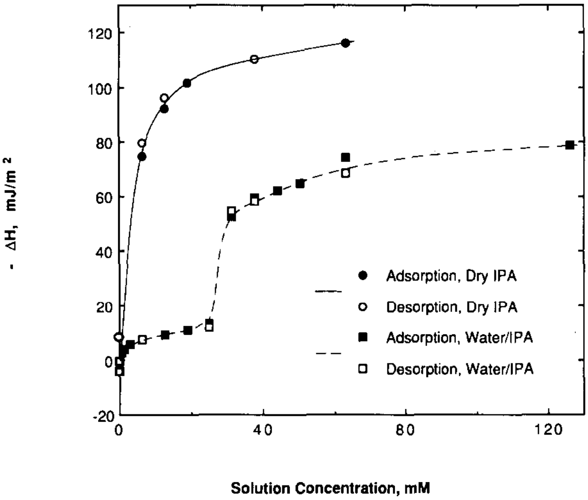


Fig. 4. Enthalpy of displacement for adsorption and desorption of octanoic acid on calcite from dry isopropanol and from 1% water in isopropanol.

tion of approximately 0.2 mM. With decreasing adsorbate concentration, most of the adsorption appears to be irreversible. TGA analyses of the samples after FMC confirm that the plateau corresponds to monolayer coverage and that the adsorption is partially (30%) reversible. The immediate rise in the adsorption curve can be attributed to the fact that the heptane solvent does not compete for surface sites. The shape of these curves is similar to the typical Langmuir isotherm that is commonly used to describe the adsorption of gases (where there is no solvent to compete). The

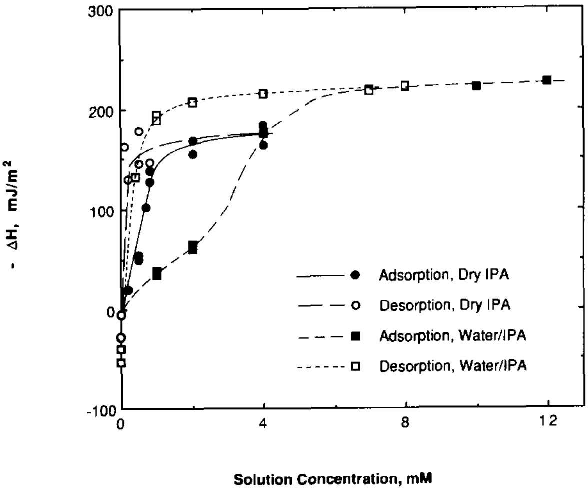


Fig. 5. Enthalpy of displacement for adsorption and desorption of stearic acid on calcite from dry isopropanol and from 1% water in isopropanol.

irreversibility of these heptane systems corroborates our TGA studies of adsorbate reversibility [1]. Heptane is not capable of ionizing and replacing the acid anion at the surface. It has no means of satisfying the surface charge. The 30% reversibility observed here can be interpreted as an equilibrium with the trace water contamination (not removed by our drying procedure) in the flowing heptane stream.

Figure 4 shows the adsorption of octanoic acid on calcite from dry isopropanol and 1% water in isopropanol. The monolayer plateau for dry isopropanol requires a higher solution concentration than does the adsorption from heptane shown in Fig. 2; the wet isopropanol requires an even higher solution concentration. This reflects the activity of the solvent as a competitor for surface sites. Water is the most active, then isopropanol and, finally, heptane. The S-shaped curve for the wet system is typical of an adsorption isotherm for an ionic surfactant onto an oppositely charged solid from aqueous solution [10,11]. The steep rise in adsorption is attributed to an additional stabilization which arises when the hydrocarbon chains begin to interact with one another. This hydrophobic association at the surface is often visualized as hemimicelle formation. Both of the systems shown in Fig. 4 are completely reversible, and desorption retraces the adsorption curve.

The results for stearic acid from dry isopropanol and 1% water in isopropanol are shown in Fig. 5. The desorption curves indicate a strong hysteresis, but they do reverse completely at zero concentration. The hysteresis is probably due to the strong attractions between these longer hydrocarbon chains. If the adsorption were stopped at half coverage, a fairly random distribution of filled sites would probably be found; however, if the desorption were stopped at half coverage, the adsorbate would probably be found in dense patches on the surface.

The plateau values of the enthalpies of displacement are given in Table 1; they range from -60 to -224 mJ m^{-2}. The monolayer surface coverages of these adsorbates were measured by TGA according to techniques reported

TABLE 1

Enthalpies of displacement for adsorption on calcite (plateau values, 20 ° C)

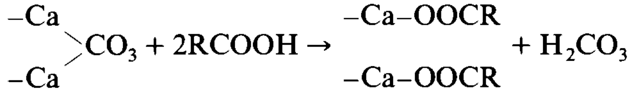
Adsorbate	Solvent	Surface coverage (μmol m^{-2})	$-\Delta H_{\mathrm{dpl}}$ (mJ m^{-2})	$-\Delta H_{\mathrm{dpl}}$ (kJ mol^{-1})
Octanoic acid	Dry heptane	8.1	60	7.5
	Dry IPA		115	14.2
	1% water–IPA		75	9.3
Stearic acid	Dry heptane	7.4	67	9.1
	Dry IPA		174	23.5
	1% water–IPA		224	30.3

IPA, isopropanol.

previously [1], and the results for all the solvents were equal within the experimental error. Average values are given in Table 1. Displacement enthalpies per mole of adsorbate were calculated from the plateau enthalpies and the average monolayer coverages and are reported in Table 1. They range from -8 to -30 kJ mol^{-1}. These values are comparable with plateau enthalpies reported previously in the literature [2–4,6,7,9]. In particular, our work agrees very well with von Rybinski and Schwuger's study of adsorption of oleate on calcite from aqueous solution [9]. They report a heat of adsorption of -27 kJ mol^{-1}. Our result for stearic acid on calcite from the water–isopropanol mixture is -30 kJ mol^{-1}. The agreement is reasonable because the two systems are so similar; both oleic acid and stearic acid have 18 carbons, and water is the dominant surface competitor in each case.

Most investigators [2–4,6,7,9] consider displacement enthalpies of these magnitudes to be representative of physical adsorption. However, displacement enthalpies alone do not give sufficient information to discern physical from chemical adsorption; the enthalpy difference between two physical bonds and between two chemical bonds may be similar even though the absolute magnitudes of the bonds are very different. On the basis of the temperatures observed for the weight losses by TGA [1], the requirement of an ion for reversibility of the adsorption and the large exotherms indicating combustion in the DSC curve, these enthalpies are interpreted as the difference between two chemical (ionic) bonds at the calcite surface.

We believe that the fatty acid anion binds to a calcium ion and displaces a lattice anion from the calcite surface. The surface anion may be carbonate, bicarbonate or hydroxide, so the adsorption may be represented by one or more of the following reactions



$$\begin{matrix}\text{-Ca}\\ \text{-Ca}\end{matrix}\!>\!\mathrm{CO_3} + 2\mathrm{RCOOH} \rightarrow \begin{matrix}\text{-Ca-OOCR}\\ \text{-Ca-OOCR}\end{matrix} + \mathrm{H_2CO_3}$$

$$\text{-Ca-}\mathrm{CO_3H} + \mathrm{RCOOH} \rightarrow \text{-Ca-OOCR} + \mathrm{H_2CO_3}$$

$$\text{-Ca-OH} + \mathrm{RCOOH} \rightarrow \text{-Ca-OOCR} + \mathrm{H_2O}$$

These reactions are written as we expect them to take place in organic solvents. The solution species are neutral, and the charge is balanced. The ionization takes place at the calcite surface. In an aqueous environment, the solution species may be anionic (deprotonated), and the charge need not be balanced. Studies of the point of zero charge of calcite [12] indicate that the surface charge shifts in the negative direction on adsorption of oleate. Thus, some adsorption in aqueous solution is not charge balanced, and a fatty acid anion can adsorb without displacing a previously bound inorganic anion.

Desorption in our FMC experiments required an ionizable species in the organic solvent to replace the fatty acid anion at the surface. We model the desorption for water and isopropanol as the displacing species by

$$\text{-Ca-OOCR} + H_2O \rightarrow \text{-Ca-OH} + \text{RCOOH}$$

$$\text{-Ca-OOCR} + C_3H_7OH \rightarrow \text{-Ca-OC}_3H_7 + \text{RCOOH}$$

In the flow microcalorimetry experiments, the overall enthalpy change is observed for the system during adsorption or desorption. It is a function of four processes:

(1) removal of the adsorbate from the solvent;
(2) breaking of the surface–inorganic-ion bond;
(3) formation of the surface–adsorbate bond;
(4) solubilization of the inorganic ion in the solvent.

The net displacement enthalpy can be expressed by the equation

$$\Delta H_{\mathrm{dpl}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$$

where each ΔH parameter is the enthalpy change for the step indicated. The number of variables in this overall process prevents us from performing an exact analysis, but some comparisons can be made.

Plateau enthalpies for octanoic and stearic acids from heptane are -60 and -67 mJ m^{-2} respectively; these values and the shapes of the curves are very similar. Because heptane is such a weak solvent, solvation energies for the two adsorbates are similar, so the ΔH_1 values are similar. Both octanoic and stearic acids bond to the surface via a carboxylate; the different hydrocarbon chain lengths do not yield different stabilizations from lateral interactions because the solvent is also a hydrocarbon chain; therefore the enthalpies of the adsorption bonds (ΔH_3) are similar. Hence, it is reasonable that the net enthalpies of displacement and the shapes of the curves are nearly identical.

The largest difference observed is that of stearic acid from isopropanol (wet or dry) which shows a more negative displacement enthalpy than the others. This can probably be attributed to a large negative ΔH_1 value. Removal of the long hydrophobic chain of stearic acid from isopropanol dramatically lowers the enthalpy of the system because the alkyl chain disrupts the solvent's hydrogen bonding when it is dissolved.

SUMMARY

These calorimetric results substantiate the idea that fatty acid anions bind to the calcite surface with ionic bonds. The nearly complete combustion observed by DSC indicates that the adsorbate–surface bond is a chemical bond, not a physical interaction. The fact that desorption in FMC requires an ionizable solvent confirms that the adsorption involves an ionic bond. These findings, together with the previously reported thermogravimetric results [1] that show a one-to-one correspondence between surface calcium sites and close-packed fatty acid molecules at monolayer coverage, strongly support a calcium–fatty-acid-anion bond as the mechanism of adsorption. A similar conclusion has been reached for calcium fluoride as the adsorbent by Lovell et al. [13], who used IR spectroscopy to identify calcium–oleate bonds when oleic acid or oleate was adsorbed.

The fact that fatty acids adsorb strongly on calcite has been known for many years in the mineral flotation industry [12,14], where oleate is used to float calcite in aqueous solutions. We have probed the mechanism and conditions of this adsorption to allow us to predict where and when such adsorption will take place in the geochemical environment. Forthcoming papers will address geochemical issues in more detail.

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