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Adsorption of oleic acid and triolein onto various minerals and surface treated minerals

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Abstract: A systematic investigation of the adsorption of oleic acid was undertaken with various minerals and surface treated minerals, viz., kaolinite, treated kaolinites, montmorillonites, talcs, gibbsites, calcites and a treated calcite. Adsorption onto kaolinite, two of the treated kaolinites (amine and $MgSiO_3$ treated), talcs and gibbsites was well correlated by the Langmuir model, while adsorption on the treated calcite was well correlated by the Freundlich model. Adsorption on a cationic polymer-treated kaolinite was explained in terms of a cooperative mechanism. Adsorption onto montmorillonites was explained in terms of a penetrative mechanism involving exchangeable cations.

Oleic acid adsorption was compared with triolein adsorption on one of the montmorillonites, two adsorbents produced by the surface treatment of this montmorillonite, and one of the talcs. The triolein adsorption of the montmorillonite was considerably less than its oleic acid adsorption, and was explained in terms of a cooperative mechanism. Triolein adsorption of the treated montmorillonites, and the talc was well correlated by the Langmuir model. Larger amounts of triolein were taken up by the treated montmorillonites than by the untreated montmorillonite. The triolein adsorption of the talc was greater than its oleic acid adsorption.

Key words: Adsorption – oleic acid – triolein – minerals – pitch

Introduction

The adsorption of oleic acid and triolein onto minerals and surface treated minerals is of particular importance in the adsorptive control of pulp and paper mill pitch. Pitch is the name given by paper manufacturers to the troublesome substance, derived from colloidally dispersed components of wood resin, which accumulates on pulp handling equipment and paper making machinery [1, 2].

In essence, the components of wood resin are released into pulp and paper mill circulating waters at the pulping stage of the papermaking process [1]. In these waters they have a transitory existence as an unstable oil-in-water emulsion [3] in the concentration range 10 to 10^3 μmol dm^{-3} [1, 4–6]. In a short time coalescence occurs followed by the deposition of the components onto various pulp and paper mill surfaces. These deposits are sticky and inevitably accumulate other material, such as fibres and inorganic compounds [7]. Such an accumulation is the papermakers pitch.

The sticky deposits cause a variety of problems throughout pulp and paper mills [1, 8]. The root of many of these problems lies in the hydrophobic nature of the deposits.

The major components of wood resin, from trees such as pine, spruce, birch and aspen, are organic acids, for example oleic acid, and neutral organics, for example triolein [2, 9–12].

Pitch problems are often alleviated, i.e., controlled, by the use of minerals, and surface treated minerals [1, 13–15]. Minerals operate by, firstly, adsorbing the colloidally dispersed components and, secondly, transporting them out of the pulp and paper mill environment by inclusion in the final paper product. The time scale over which the mineral adsorbents operate is very short, ca. < 1 h, and they are usually added as near as possible to the stage in the papermaking process at which the components are entering the circulating waters. Commonly used pitch-controlling minerals are montmorillonite and talc, while more recent developments have seen the use of other minerals and surface treated minerals for the control of pitch.

Since the efficient control of pulp and paper mill pitch involves the adsorption of organic species, such as oleic acid and triolein, onto minerals (and surface treated minerals), such as montmorillonite and talc, it is essential to understand both qualitatively and quantitatively the adsorption behaviour in these systems, particularly over a short time scale and in the 10 to 10^3 μmol dm^{-3} concentration range. Furthermore, pulp and paper mills invariably contain other minerals, such as kaolinite and calcite, in their circulating waters; kaolinite and calcite are commonly used as an integral part of most grades of paper [1]. Since such minerals may also adsorb wood resin components, it is necessary also to understand the adsorption behaviour in these systems.

In a broader context, a systematic study of the adsorption of simple organic molecules, originally in the form of emulsion droplets, onto a range of well characterized solid surfaces will provide a fundamental understanding of sorption processes at the emulsion/solid interface.

Experimental

Materials

All reagents were of the highest purity and supplied by Merck Ltd., England except for triolein which was supplied by Sigma Chemical Co., England. The purity of the adsorbates was checked by HPLC and Inductively Coupled Plasma Spectrometry. Both adsorbates were found to contain trace amounts of sulphur (possibly in the form of SO_4^{2-}), while the oleic acid was also found to contain trace amounts of another 18 carbon fatty acid which had the same retention time as linoleic acid. In view of the nature and levels of these impurities it was considered reasonable to assume that they did not perturb the adsorption measurements to any significant degree. The water used was distilled once in an all glass apparatus. The minerals and surface treated minerals were supplied as follows (see Tables 1 and 2 for abbreviations): Kao I to III, Mont I to VII, Cal I and III, Talc V were supplied by ECC International Ltd., England. Talc I was supplied by Luzenac, France. Talc II was supplied by Naintsch, Austria. Talc III was supplied by Finnminerals, Finland. Talc IV was supplied by Cyprus Industrial Minerals Co., USA. Gibb I was supplied by Reynolds Metals Co., USA. Gibb II was supplied by Bayer, England. Cal II was supplied by Paper Chemistry Laboratories Inc., USA. Kao IV was prepared in this laboratory by J.M. Adams according to the method of Hodgkin and Solomon [16]. Mont IVb was prepared in this laboratory by A.R. Fugler according to the method of Thompson et al. [17]. Kao V and Mont IVa were prepared in this laboratory by the author as follows: – Kao V was prepared according to the method of Rogan and Adams [18]. Mont IVa was prepared 30 min prior to triolein adsorption by the addition of 78 mg of fatty acid (dissolved in 5 cm^3 of ethanol) to 1 g of Mont IV dispersed in 99 g of water.

Apparatus

Centrifuges: a) MSE operating at 300 revs·s^{-1} for 1 hour, sedimentation coefficient $(B) = 3.2 \times 10^2$ Svedbergs; B is a useful measure of centrifugation conditions and is related to radial geometry (r) and angular velocity (w) of the centrifuge rotor head [19, 20] ($B = \ln(r)/w^2t$); b) IEC operating at 66.7 revs·s^{-1} for 8 h ($B = 4.8 \times 10^2$ Svedbergs); c) MSE operating at 41.7 revs·s^{-1} for 30 min ($B = 6.2 \times 10^4$ Svedbergs). Solvent Concentrator: Techne, operating at 60 °C with a jet of air. Vacuum Oven: Gallenkamp, operating at 60 to 80 °C and 600 to 1000 mbar. Reversed phase HPLC system: LDC/Milton Roy pump, stainless steel tubing (0.254 mm bore), LDC/Milton Roy autosampler incorporating a Rheodyne Inc. injection valve with 200 mm^3 sample loop, Jones Chromatography column heating block and controller, LDC/Milton Roy high sensitivity refractive index detector, LDC/Milton Roy computing integrator, Chessell Ltd. single pen chart recorder. Mobile and stationary phases for oleic acid detection were 0.2 mol dm^{-3} $NaClO_4 \cdot H_2O$ in methanol and two Hichrom 25 cm spherisorb S5ODS2 columns, respectively. Mobile and stationary phases for triolein detection were 0.2 mol dm^{-3} $NaClO_4 \cdot H_2O$ in a 1:1 mixture of methanol/isopropyl alcohol and a Hichrom 25 cm Spherisorb S5ODS2-5104 column, respectively. Operational Settings of the HPLC System: a) Pump flow rate 23.3 mm^3 s^{-1} (oleic acid detection) and 16.7 mm^3 s^{-1} (triolein detection); b) Integrator settings: input voltage 10 V, peak width 15 s, slope sensitivity 50; c) Chart recorder speed 33.3 μm s^{-1}; d) Column temperature 40 °C.

Measurement of adsorption (general)

Oleic acid and triolein adsorptions on various minerals and surface treated minerals were measured over the concentration range ca. 10 to 10^3 μmol dm^{-3} using reversed phase HPLC. The experimental set-up was static and maintained in a constant temperature room at 20 °C. 1.00 ± 0.01 g (equivalent dry weight) of adsorbent was shaken with 99.00 ± 0.02 g of water for 4 h. 10 cm^3 of a dilute solution of adsorbate in ethanol, of known concentration, was added and the resulting adsorbate/ethanol/water/adsorbent dispersion (sample), in which the adsorbate was in the form of emulsion droplets, was shaken. The quantity apparently adsorbed was evaluated from measurement of the concentration of adsorbate remaining suspended after the centrifugal separation of the adsorbent. This separation was achieved by the subjection of the dispersion to the appropriate set of centrifugal conditions required to sediment the adsorbent, i.e., B in the range 6.2×10^4 to 3.2×10^2 Svedbergs.

The pH of the various mineral and surface treated mineral dispersions lay within the neutral to slightly alkaline pH range, and the zeta potentials of the oleic acid and triolein emulsion droplets were ca. − 53 mV and close to zero, respectively.

Oleic acid and triolein adsorptions were measured slightly differently. The method used for each adsorbate is detailed below.

Measurement of oleic acid adsorption

40 cm^3 of the sample dispersion (prepared as above) was centrifuged and 20 cm^3 of the supernatant was pipetted into a vial. A control dispersion was prepared by adding 10.00 ± 0.02 cm^3 of the dilute, ethanolic oleic acid solution to 99.00 ± 0.02 g of water. 20 cm^3 of this dispersion was also pipetted into a vial. The water and ethanol were removed from these vials (vacuum oven or solvent concentrator) and a known volume (between 1.5 to 20 cm^3) of the mobile phase of the HPLC system pipetted into each vial. After dissolution of the oleic acid into the mobile phase, 1.4 cm^3 of this solution was filtered into an Autosampler vial. Three injections of both sample and control were made by the Autosampler into the HPLC system. The concentration of oleic acid present in the sample and the quantity of oleic acid adsorbed were determined from a knowledge of the oleic acid concentration of the control and the peak areas generated by both sample and control.

Measurement of triolein adsorption

A magnetic follower was added to the sample dispersion (prepared as above) and the dispersion stirred vigorously. 37.0 ± 0.1 g of the dispersion was centrifuged. In the centrifugation of talc-containing dispersions the process was stopped momentarily, at least twice, and the sides of the centrifuge tube tapped in order to dislodge mineral held at the meniscus.

The centrifuge tube was placed in a vertical position in a test tube rack. About 5 cm^3 of hexane was carefully pipetted onto the meniscus of the supernatant. After several minutes most of this hexane layer was carefully transferred by pipette into a glass vial. This procedure was repeated twice and the removed hexane layers were combined. In this way any triolein present at the meniscus was extracted into a suitable volatile solvent.

The supernatant was poured into a 100 cm^3 separating funnel. 20 cm^3 of an aqueous solution of aluminium sulphate (2% wt./vol.) and 10 cm^3 of chloroform were pipetted into the funnel which was then shaken vigorously for 5 min, with the occasional careful release of pressure. Most of the lower chloroform layer was drained off and added to the hexane extract obtained earlier. A further two 20 cm^3 aliquots of chloroform were pipetted into the funnel, with shaking and draining procedures carried out between each aliquot addition, as described above. In this way any triolein present in the supernatant was extracted into a suitable volatile solvent.

The volatile solvents (ethanol, hexane and chloroform) and any traces of water were removed from the vial by evaporation over a period of 4 h (solvent concentrator). $20.0 \pm 0.1\ \mathrm{cm}^3$ of HPLC mobile phase was pipetted into the previously cooled vial. After dissolution of the triolein into the mobile phase, $1.4\ \mathrm{cm}^3$ of this solution was filtered into an Autosampler vial. Three injections were made by the Autosampler into the HPLC system and an average response (peak area) of this system to the triolein obtained.

The quantity of triolein apparently adsorbed was evaluated from a knowledge of the triolein originally added to the adsorbent dispersion and the quantity of triolein detected by the HPLC system. This latter quantity was determined from the average HPLC system response to the injected triolein by means of a triolein-HPLC system response curve.

Precision and overall errors

The oleic acid and triolein detection limits of the appropriate HPLC systems were 10.8 and 3.0 nmol, respectively. These relate to detectable concentration limits in the experimental set-up employed of 2.69 and $0.14\ \mu\mathrm{mol\,dm}^{-3}$ for oleic acid and triolein, respectively. The precision in the responses (i.e., peak area) of each HPLC system to oleic acid and triolein, expressed as the average of the coefficient of variation (V, equal to the standard deviation as a percentage of mean), were 1.59 and 0.31%, respectively. This variation along with errors incurred in the experimental procedure gave a precision in oleic acid and triolein concentrations of 4.29 and 2.24%, respectively. Overall, the errors in the quantity adsorbed and the equilibrium (or residual) concentration for both adsorbates were ca. $1\ \mu\mathrm{mol\,g}^{-1}$ and $10\ \mu\mathrm{mol\,dm}^{-3}$, respectively.

Measurements of exchangeable cation composition (D) and specific surface area (S)

The D of each montmorillonite adsorbent was determined conventionally at neutral pH by exchange with NH_4^+ ion [21]. The principal exchangeable cations were found to be Ca^{2+}, Mg^{2+} and Na^+. The results are given in Table 3.

For most of the adsorbents S was taken to be that given by the BET (N_2) method. However, for the montmorillonite adsorbents (Mont I to VII) S was taken to be the summation of the specific surface area of the intercrystalline pores plus the specific surface area of the external surface, and to be given by the ratio

$$S = \frac{(S_{\mathrm{MONT}})_{\mathrm{MAX}}}{n}, \qquad (1)$$

where $(S_{\mathrm{MONT}})_{\mathrm{MAX}}$ is the theoretical maximum-specific surface area of montmorillonite (here taken to be $752\ \mathrm{m}^2\,\mathrm{g}^{-1}$, assuming a montmorillonite unit cell weight of $734\ \mathrm{g\,mol}^{-1}$ [22]) and n is the montmorillonite average tactoid size. The value of n depends on the nature of the exchangeable cations present in the montmorillonite, and ranges from 1.0 for a Li-montmorillonite to 7.0 for a Ca-montmorillonite. In the case of the montmorillonite adsorbents, which each contain the exchangeable cations Na^+, Ca^{2+} and Mg^{2+}, the value of n will almost certainly lie between these two extremes. Indeed, by reference to the work of Schramm and Kwak [23] it is possible to estimate a value of n for each montmorillonite from a knowledge of its D. The n and S of Mont I to VII are given in Tables 1 and 3.

For the surface treated montmorillonite adsorbents (Mont IVa and IVb) S was taken to be the total molecular area of the protruding long chain moieties of the treatment agents. Thus, in the case of Mont IVa S was taken to be the total molecular area of the fatty acid treatment agent (less the molecular area of the fatty acid head groups), while the S of Mont IVb was taken to be the total molecular area of the two long chain moieties of the quaternary ammonium compound treatment agent.

Ethanol as adsorbate carrier solvent

Ethanol was chosen as the solvent for the adsorbates for two reasons: a) to act as a water soluble solvent for the adsorbates and so bring about their spontaneous emulsification in water by the condensation method of Davies and Rideal [24], and b) to act as a solvent in which the adsorbates had a limited solubility. Thus, the addition of $10\ \mathrm{cm}^3$ of ethanolic adsorbate solution to 99 g of water (i.e., ca. 9% vol./vol. ethanol) produced: a) emulsion droplets (of size ca. 250 nm), and b) a medium containing less than 50% (vol./vol.) ethanol having virtually the same inability to dissolve oleic acid and triolein as that of water alone [25]. Hence, the adsorption experiment was conducted such that oleic acid and triolein were adsorbed from a medium that was not significantly different from water.

Results and discussion

The majority of adsorbents were virtually insoluble in the dispersing medium and the adsorbates were physically adsorbed [26]. Therefore, the adsorbate/adsorbent equilibrium was attained rapidly: Allingham et al. [27] have shown that the adsorption in similar systems was complete within 10 min. However, for those oleic acid/adsorbent dispersions where the adsorbent had a finite solubility in the dispersing medium (i.e., Cal I and II), a proportion of the oleic acid was chemically adsorbed [28–30], and, therefore, such systems did not attain a state of equilibrium in the time scale of the experiment [26]. Thus, the concentration of oleic acid remaining suspended was considered as an equilibrium concentration (C, in units of μmol dm^{-3}) for the majority of adsorbent dispersions, but considered only as a residual concentration, at the time of sampling, for those dispersions containing soluble adsorbents.

The measured triolein adsorptions were corrected for the loss of triolein from the continuous phase at equilibrium by processes other than adsorption onto minerals (or surface treated minerals). A brief outline of this correction is given in the Appendix; there was no significant loss of oleic acid from solution by such processes.

The (apparent[1]) adsorption of each mineral and surface treated mineral is reported in Tables 1 and 2, initially, as the quantity adsorbed at the (first) plateau in the adsorption isotherm (X_P, in units of μmol g^{-1}). In many cases, X_P was the maximum adsorption, and was attained within C ca. 300 μmol dm^{-3}. The adsorption is also reported as the adsorption density at the plateau in the adsorption isotherm (A_P, in units of μmol m^{-2}). A_P was derived from X_P by means of the relation

$$A_P = \frac{X_P}{S} \,. \tag{2}$$

In the case of Cal III the quantity adsorbed and the adsorption density are reported as the values at $C = 300\ \mu$mol dm^{-3} (X_{300} and A_{300}, respectively) for ease of comparison with the rest of the adsorption data.

The value of X_P for a particular adsorbent is compared, wherever possible, with that expected ($(X_P)_{\mathrm{THE}}$) on the basis of theoretical considerations by assuming a particular orientation of the adsorbate molecule. For example, oleic acid may be assumed to have an orientation that is either flat on, or perpendicular to, a surface. Then, $(X_P)_{\mathrm{THE}}$ is given by

$$(X_P)_{\mathrm{THE}} = \frac{S}{S_{\mathrm{OL}} \times N} \,, \tag{3}$$

where S_{OL} is the molecular area of oleic acid on a surface; for a flat orientation S_{OL} is taken to have the value of 1.14 nm^2 [31], whereas for a perpendicular orientation with the carboxylate group pointing towards the surface S_{OL} is taken to have the value of 0.21 nm^2 [31]. N is Avogadro's constant. The $(X_P)_{\mathrm{THE}}$ value of each adsorbent, except Cal I to III, is also given in Tables 1 and 2; values of $(X_P)_{\mathrm{THE}}$ are designated with either F ($S_{\mathrm{OL}} = 1.14$ nm^2) or E ($S_{\mathrm{OL}} = 0.21$ nm^2) to indicate the oleic acid molecular area used in their calculation.

Oleic acid adsorption onto Kao I to IV [32], Talc I to V and Gibb I and II [33]

The adsorption isotherms (typical ones are shown in Fig. 1) have a common rectangular hyperbolic shape which obeys the Langmuir model, and the adsorption data can be fitted to the linear equation

$$\frac{C}{X} = \frac{K_L}{X_P} + \frac{C}{X_P} \,, \tag{4}$$

where K_L is a constant and X is the quantity adsorbed (in units of μmol g^{-1}); for the adsorbents here, X_P was the maximum adsorption. Thus, a plot of C/X vs. C should yield a straight

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[1] In view of the concentrations of adsorbate used, and with the generally large proportion of adsorbate taken up, the differences between apparent and true adsorptions are not important

Table 1. Oleic acid adsorption data

Adsorbent (abbreviation)	S $\mathrm{m^2\,g^{-1}}$	X_P $\mu\mathrm{mol\,g^{-1}}$	A_P $\mu\mathrm{mol\,m^{-2}}$	$(X_P)_{THE}$ $\mu\mathrm{mol\,g^{-1}}$	Adsorption isotherm shape class
Kaolinite (Kao I)	9.9	13	1.3	14 (F)	H2
Kaolinite heated to 1000 °C (Kao II)	17.1	13	0.8	25 (F)	L2
Kaolinite treated with primary amine (Kao III)	6.5	26	4.0	51 (E)	H2
Kaolinite treated with $MgSiO_3$ (Kao IV)	25.2	65	2.6	199 (E)	L2
Kao II treated with cationic polymer (Kao V)	14.1	37	2.6	111 (E)	S3
Montmorillonite: moderately high Na^+ (Mont I)	234	169	0.7	183	C2
Montmorillonite: low Na^+ (Mont II)	203	181	0.9	168	C2
Montmorillonite: high Ca^{2+} (Mont III)	160	197	1.2	215	C2
Montmorillonite: high Na^+ (Mont IV)	246	212	0.9	197	C2
Montmorillonite: very high Ca^{2+} (Mont V)	158	214	1.4	232	C2
Montmorillonite: very high Na^+ (Mont VI)	257	219	0.9	227	C2
Montmorillonite: moderately high Na^+ and Mg^{2+} (Mont VII)	200	257	1.3	231	C2
Talc: Very coarse, average particle size ca. 6 µm (Talc I)	3.2	22	6.9	25 (E)	H2
Talc: Coarse, average particle size ca. 3.5 µm (Talc II)	8.3	57	6.9	66 (E)	H2
Talc: Medium, average particle size ca. 1.9 µm (Talc III)	8.8	92	10.5	70 (E)	H2
Talc: Fine, average particle size 1.65 µm (Talc IV)	13.6	101	7.4	108 (E)	H2
Talc: Ultra-fine, average particle size < 1.5 µm (Talc V)	14.1	115	8.2	111 (E)	H2
Gibbsite: Fine, average particle size < 1.5 µm (Gibb I)	12.7	99	7.8	100 (E)	H2
Gibbsite: Ultra-fine, average particle size < 1.0 µm (Gibb II)	15.4	163	10.6	122 (E)	H2

Table 1a. Oleic acid adsorption data

Adsorbent (abbreviation)	S $\mathrm{m^2\,g^{-1}}$	X_{300} $\mu\mathrm{mol\,g^{-1}}$	A_{300} $\mu\mathrm{mol\,m^{-2}}$	Adsorption isotherm shape class
Calcite: Marble flour (Cal I)	5.5			Abstraction
Calcite treated with sodium silicate (Cal II)	3.7			Abstraction
Calcite treated with stearic acid (Cal III)	5.0	28	5.6	Freundlich

Table 2. Triolein adsorption data

Adsorbent (abbreviation)	S $\mathrm{m^2\,g^{-1}}$	X_P $\mu\mathrm{mol\,g^{-1}}$	A_P $\mu\mathrm{mol\,m^{-2}}$	$(X_P)_{THE}$ $\mu\mathrm{mol\,g^{-1}}$	Adsorption isotherm shape class
Mont IV	246	25	0.1	197	S3
Mont IV treated with fatty acid (Mont IVa)	119	57	0.5	197	L3
Mont IV treated with quaternary ammonium compound (Mont IVb)	118	120	1.0	196	H3
Talc IV	13.6	393	28.9	75	H1

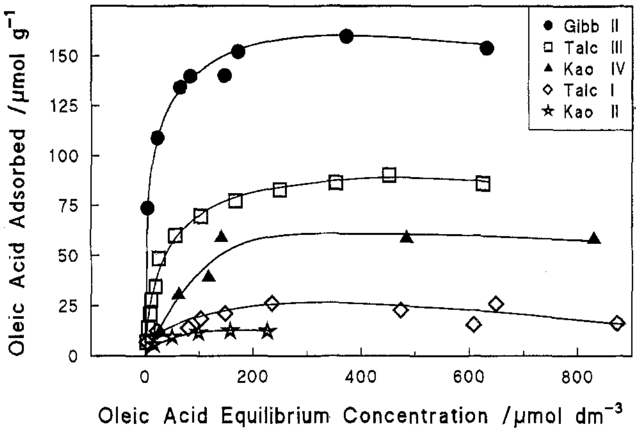

Fig. 1. Adsorption isotherms of oleic acid on Kao II and IV, Talc I and III, and Gibb II

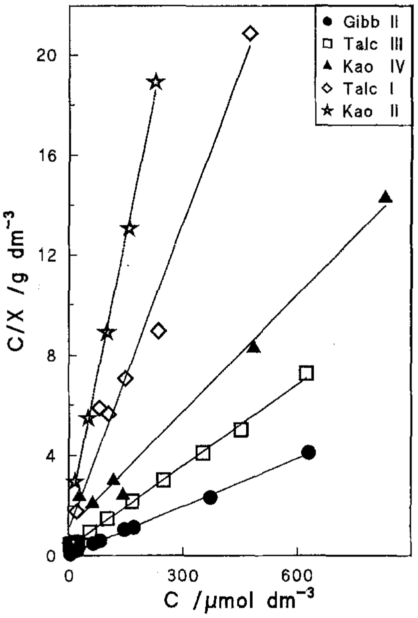

Fig. 2. Langmuir adsorption isotherms of oleic acid on Kao II and IV, Talc I and III, and Gibb II

line having a slope of $1/X_P$ from which the value of X_P may be readily obtained. Typical plots of C/X vs. C are shown in Fig. 2. In all cases there was a good correlation between C/X and C, with correlation coefficients (r^2) of 0.98 or better.

The isotherms are of the type L2 or H2 in the Giles et al. [34] system of isotherm classification. It may be inferred, therefore, that the adsorption was governed by the amount of available surface and the molecular area of the oleic acid molecule. Such adsorption will, after a rapid increase in X over a small increase in C, reach the plateau value X_P.

The initial regions of the isotherms for the hydrophobic adsorbents, viz., Kao III, Talc I to V, and the hydroxylated adsorbents, viz., Gibb I and II, lie very near to the y-axis, and thus there was a high affinity of oleic acid for these types of adsorbent [35]. In quantitative terms, oleic acid had a high affinity for the adsorbents in that more than 90% of the added oleic acid was adsorbed in the initial region of the isotherm; in the present work this level of adsorption is used as the criterion for high affinity. Accordingly, the A_P values for these adsorbents are high (4.0 to 10.6 μmol m^{-2}) compared to those of the remaining adsorbents.

The X_P values for Kao III and Talc I to V are much greater than would be expected on the basis of a flat orientation of the oleic acid molecule. This disparity, which has a magnitude much larger than that which could be accounted for by any errors in S, is commonly observed in the adsorption of large organic molecules with a low solubility in water [27]. It is usually attributed [34] to the clustering of such molecules at the moment of adsorption or the adsorption of micelles in droplet form. In either case the inference is the same: the magnitude of the X_P values for Kao III and Talc I to V, would infer that the oleic acid was adsorbed in an associated form. This inference is substantiated by the long plateaus of the isotherms, which mean that the unadsorbed oleic acid had a very low affinity for the layer of molecules already adsorbed [34]. Thus, if oleic acid molecules were adsorbed in an associated form with their hydrophobic frameworks directed towards the hydrophobic surface and a density of negative charge pointing towards the bulk solution, then the approach of further oleic acid molecules would have been prohibited. Associated, i.e., globular or hemi-spheroidal, adsorption has been invoked elsewhere [36] to explain the uptake of unexpectedly large amounts of amphipathic materials from the aqueous phase onto a hydrophobic surface.

Gaudin and Fuerstenau [37] have referred to associations of adsorbed surfactant, orientated with their ionic head groups directed towards a surface, as hemimicelles. Since the expected orientation of the adsorbed associations in the present study are such that their ionic head groups are pointing in the opposite direction, i.e., away from the surface, they are probably best described as inverse-hemimicelles.

The actual molecular area of oleic acid on Kao III and Talc I to V, may be obtained from the reciprocal of the slope of a plot of X_P vs. S. A linear regression analysis of such a plot, shown in Fig. 3, gave a slope of 8.22 μmol m^{-2} which equates to a molecular area of oleic acid on these adsorbents of 0.20 nm^2. This particularly small value represents the area of the methyl end group of oleic acid. It would appear, therefore, that the reason for the adsorption of unexpectedly large amounts of oleic acid on Kao III and Talc I to V lies with the very small footprint of each oleic acid molecule on such adsorbents. Apparently, the oleic acid molecules were able to pack together closely in an orientation that was, presumably, perpendicular to the adsorbent's surface, with the methyl ends of their carbon skeletons directed towards the surface. According to Tanford [38] the driving force for such adsorption would be the replacement of unfavourable hydrophobic/water interactions (at the adsorbent/water interface) with favourable hydrophilic/water interactions (at the coated adsorbent/water interface). In this case the hydrophilic/water interactions are presumably hydrogen bonding interactions between carboxylate groupings of the adsorbed oleic acid and the surrounding water.

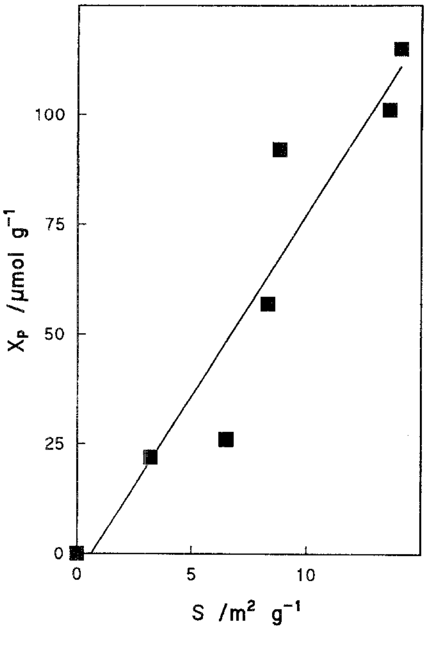

Fig. 3. Plateau adsorbed amounts of oleic acid as a function of hydrophobic, specific surface area

The X_P values for Gibb I and II are very similar to the corresponding $(X_P)_{THE}$ values, calculated using $S_{OL} = 0.21$ nm^2. The use of this value for S_{OL} here is based on the work of Parfitt et al. [39] who have shown that the principal mode of interaction between organic acids and gibbsites is a ligand exchange between carboxylate groups of the organic acids and surface hydroxyls of the mineral. Thus, it would appear that the gibbsites adsorbed about a monolayer of oleic acid.

The initial region of the isotherm for the hydrophilic adsorbent, Kao I, lies very near to the y-axis and, in a similar fashion to the oleic acid/adsorbent interactions described above, there was a high affinity of oleic acid for this adsorbent. However, in contrast to the adsorption of the hydrophobic adsorbents the A_P for Kao I is low (1.3 μmol m^{-2}) and the X_P value is similar to $(X_P)_{THE}$, with S_{OL} set to 1.14 nm^2. The X_P value, in this case, can be considered as a monolayer value.

The initial regions of the isotherms for Kao II and IV lie away from the y-axis, and, thus, there was a low affinity of oleic acid for these types of adsorbent. In quantitative terms, oleic acid had a low affinity for the adsorbents in that (always) less than 90% of the added oleic acid was adsorbed; in the present work this level of adsorption is used as the criterion for low affinity. Accordingly, the A_P for Kao II is lower than that for a similar adsorbent, Kao I, and the X_P value is about half of that expected theoretically, using $S_{OL} = 1.14$ nm^2. Thus, the adsorption of oleic acid here must have occurred only onto highly active sites of the calcined surface. Similarly, the A_P for Kao IV is about a third less than that for an analogous adsorbent, Kao III.

For simplicity, the molecular area of either end of the oleic acid molecule is taken to be 0.21 nm^2.

Oleic acid adsorption on Kao V [18]

The adsorption isotherm, shown in Fig. 4, has an S shape and is of type S3 [34]. In particular, the isotherm has an initial region that is convex to the concentration axis and which rises to a short plateau ($X_P = 37$ μmol g^{-1}). At higher values of C a steep, second rise in adsorption occurs. It may

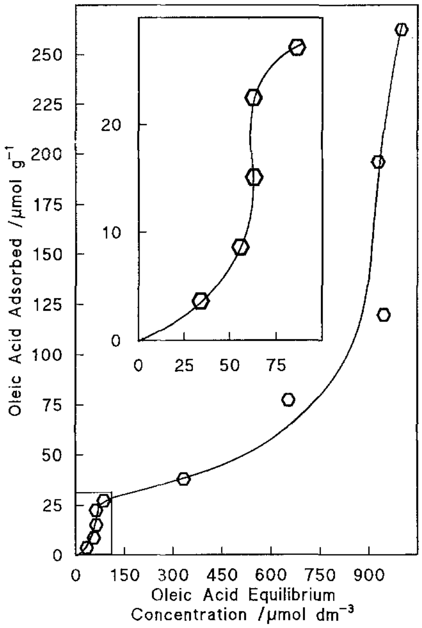

Fig. 4. Adsorption isotherm of oleic acid on Kao V

be inferred from the shape of the initial region that the more oleic acid there is adsorbed the easier it is for additional oleic acid to become fixed [34]. This implies that a side-by-side association occurs between adsorbed oleic acid molecules presumably positioned with their anionic head groups directed towards the cationic surface and their longest axis situated in a perpendicular orientation away from the surface [34]. Such adsorption, termed co-operative, is commonly observed [40] for the adsorption onto charged (and insoluble) substrates of amphipathic molecules like oleic acid which have a fairly large hydrophobic residue, i.e. more than five carbon atoms, and a marked location of charge, i.e. a polar headgroup.

The plateau at 37 µmol g^{-1} indicates the completion of an adsorbed layer, while the shortness of this plateau means that the layer exposed a surface to the bulk solution which had nearly the same affinity for oleic acid as that of the original surface. The quantity adsorbed at the completion of this layer is only one-third of $(X_P)_{THE}$, with S_{OL} set to 0.21 nm^2. Accordingly, the A_P value here is smaller than the A_P values of the high affinity, hydrophobic adsorbents. However, it is recognized [34] that solvent is present in those monolayers which are normally bound to adsorbents having the same degree of polarity as that of the solvent: this is the case for the Kao V/water system. Thus, on the basis of the value of 0.1 nm^2 [41] for the area occupied by a water molecule, it would appear that for every adsorbed oleic acid molecule there is, on average, four molecules of water additionally adsorbed.

The second rise, beginning at C ca. 500 µmol dm^{-3} can be readily attributed to further adsorption onto the layer of molecules already adsorbed. The sharpness of this second rise and the expected orientation of the molecules in the initial layer suggests that this further adsorption occurred onto an homogeneous, hydrophobic layer. However, the quantity of oleic acid further adsorbed was far greater than that in the initial layer, and indicates that adsorption was occurring in a similar fashion to that observed onto the hydrophobic adsorbents, as discussed above.

Oleic acid adsorption on Mont I to VII

The adsorption isotherm for Mont IV is typical of those obtained for these adsorbents and is shown in Fig. 5. It has an initial region which lies very close to the y-axis and where X varies linearly with C up to ca. 100 µmol dm^{-3}. Above this concentration the isotherm becomes, almost abruptly, horizontal and the adsorption data can be fitted to Eq. (4).

In view of the closeness of the isotherm to the y-axis it may be inferred that there was a high

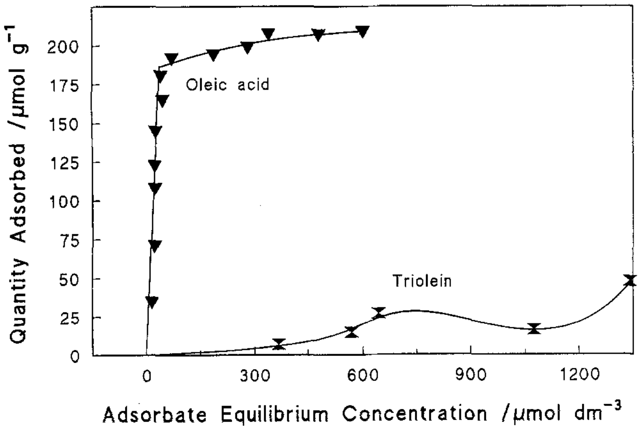

Fig. 5. Adsorption isotherms of oleic acid and triolein on Mont IV

affinity of oleic acid for this type of adsorbent. This high affinity is readily explained in terms of the occurrence of hydrogen bonding interactions between oleic acid and the exchangeable cations on the montmorillonite surface. Mortland [42] and Theng [43] have described this interaction more fully as hydrogen bond formation between the carboxylate group of an organic acid molecule and a water molecule in the primary hydration shell of an exchangeable, polyvalent cation on the montmorillonite surface. The mode of bonding here is referred to as cation-water bridge formation, while the organic acid-water-cation-montmorillonite complex is known as an outer coordination complex [44]. In contrast to polyvalent ions, monovalent ions have only a very limited ability to act as bridging agents in such complexes [44]. For example, Edwards and Bremner [45] concluded that the dispersion of natural soil aggregates by treatment with monovalent cations was due to the displacement, by the monovalent ions, of the polyvalent cations of the clay-cation-organic acid complex of the aggregates, while Theng and Scharpenseel [46] have shown that the amount of an organic acid adsorbed by a montmorillonite saturated with monovalent cations was an order of magnitude less than that of a montmorillonite saturated with divalent ions.

The interaction of organic acid with polyvalent rather than monovalent cations is understandable in view of the greater charge density (i.e., the greater polarizability) of the higher charged ions. This is manifest as a strong interaction between such ions and water molecules both in bulk solution [47] and at the montmorillonite surface [48], resulting in the polarization of electron density away from the water molecules towards the cation. Thus, it would be expected that the interaction of oleic acid carboxylate groups would occur most predominantly with the electron deficient water molecules present in the primary hydration shell of polyvalent cations, rather than with water molecules associated with less polarizing (monovalent) cations.

This selective interaction of organic acid with some exchangeable cations of montmorillonite is supported by the present work in that no simple correlation was found between X_P and S for the montmorillonite adsorbents. The great diversity in D of these adsorbents is apparent from Table 3. It is evident that the X_P for montmorillonites will be influenced by D, and in particular the amounts of polyvalent cations.

The linearity of the initial region of the isotherm implies that as more oleic acid was adsorbed more sites for adsorption were created i.e., the number of sites for adsorption remained constant. This constant partition of oleic acid between the aqueous phase and the adsorbent, almost up to the maximum adsorption possible, indicates that the oleic acid penetrated regions of the adsorbent that were inaccessible to the solvent, water [34]. In the case of the adsorption of a molecule possessing a large hydrophobic residue, such as oleic acid, onto a porous mineral, such as montmorillonite, it would be expected that an initial adsorption into a solvent free region would lead to repulsion between the hydrophobic residue of the oleic acid and the hydrophilic montmorillonite

Table 3. Montmorillonite data: D values and derived parameters

Adsorbent	D			n	Accessible, bridging cations		$(X_P)_{THE}$
	Na^+	Ca^{2+}	Mg^{2+}		Ca^{2+}	Mg^{2+}	
	$\mu mol\,g^{-1}$	$\mu mol\,g^{-1}$	$\mu mol\,g^{-1}$		$\mu mol\,g^{-1}$	$\mu mol\,g^{-1}$	$\mu mol\,g^{-1}$
Mont I	356	158	137	3.22	49.1	42.5	183
Mont II	251	155	155	3.70	41.9	41.9	168
Mont III	146	373	132	4.69	79.5	28.1	215
Mont IV	411	170	131	3.06	55.6	42.8	197
Mont V	123	472	81	4.77	99.0	17.0	232
Mont VI	579	150	182	2.93	51.2	62.1	227
Mont VII	339	186	248	3.76	49.5	66.0	231

surface resulting in the expansion of this region with the consequential exposure of more sites for adsorption.

There are two regions of a montmorillonite, termed the interlayer spacings and intercrystalline pores [49], into which penetration of organic acids like oleic acid can occur giving rise to constant partition (or linear) isotherms. However, organic acid penetration into interlayer spacings is sensitive to ambient solution pH and only occurs below pH 4 [44]. This is because interlayer complexes only form between organic acids and montmorillonites when the acids are in the uncharged state [44] which for most organic acids, with pK_a values between 4.5 and 5.5 [50], is in the low pH region. This pH dependency of interlayer penetration is generally observed. For example, Theng and Scharpenseel [46], Theng [49] and Law [51] have not detected interlayer penetration of montmorillonites by organic acids at neutral pH, whereas Schnitzer and Khan [52] measured interlayer expansion of montmorillonites on the uptake of organic acids at pH 2.5. Furthermore, organic acid penetration into interlayer spacings only occurs at high adsorbate concentrations (i.e., about an order of magnitude greater than in the present work) [44] and with relatively long adsorbate/montmorillonite contact times (i.e., > 5 h) [53–56]. This absence of interlayer penetration is bourne out in the present work: x-ray diffraction analysis of the montmorillonite-oleic acid complexes did not show any measurable increase in basal spacing over and above the original montmorillonites. Thus, the constant partition isotherms observed for the montmorillonites can be rationalized in terms of the penetration of oleic acid into intercrystalline pores.

In contrast to the high affinity isotherms registered by oleic acid, the A_P values for these adsorbents are low, with an average value of ca. 1.03 μmol m^{-2}, and comparable with the A_P values for similar surfaces, viz., Kao I and Kao II. Thus, it would appear that oleic acid has a high affinity only for certain active sites of the accessible montmorillonite surface (i.e., intercrystalline pores and external surface). In view of the foregoing discussion it is likely that these sites were exchangeable polyvalent cations and that these cations occupy only a fraction of this montmorillonite surface. Indeed, the average A_P value equates to a value of 1.61 nm^2 for the quantity of accessible montmorillonite surface per oleic acid molecule. This value is almost eight times larger than the area of that part of the oleic acid molecule (the carboxylate group) that was interacting with the montmorillonite. Thus, it would appear that the reason for the low A_P values for the montmorillonites is that only about one-eighth of the accessible montmorillonite surface was actually interacting with the oleic acid, via its polyvalent cations.

In the present work the principal, exchangeable, polyvalent cations of the montmorillonites were the divalent ions Ca^{2+} and Mg^{2+}. Thus, in order to simplify the calculations of $(X_P)_{THE}$, it was assumed that oleic acid interacted strongly only with these cations. The neglect of the interaction of other polyvalent cations, such as trivalent ions, with oleic acid is not unreasonable since it has been shown by Scharpenseel [57] that the higher the cation valency the less stable is the organic acid-montmorillonite complex.

Accepting the interaction of oleic acid with exchangeable Ca^{2+} and Mg^{2+} ions, the quantities of these cations which were accessible to oleic acid (i.e., those cations which are present on the surfaces forming the intercrystalline pores and on the external surfaces of the adsorbent) are obtained by scaling the measured Ca^{2+} and Mg^{2+} exchange capacities of each montmorillonite by the ratio

$$\frac{S}{(S_{MONT})_{MAX}}, \tag{5}$$

which, on inserting the earlier expression for S (Eq. (1)), becomes equal to n^{-1}. The quantities of the accessible (bridging) cations of the adsorbents are included in Table 3. Values of $(X_P)_{THE}$ for the montmorillonites are then obtained by summing these scaled capacities, multiplied by the appropriate stoichiometry (i.e., a stoichiometry of 2:1 for the interaction between oleic acid and exchangeable Ca^{2+} and Mg^{2+} ions). The $(X_P)_{THE}$ values of these adsorbents are included in Tables 1 and 3.

The X_P values for Mont I to VII are very similar to the corresponding $(X_P)_{THE}$ values, with V ca. 7.5%. Such a good agreement would appear to make the assumptions outlined above eminently reasonable.

The isotherm has a long plateau, at high C, that is indicative of a low affinity of free oleic acid for the accessible adsorbent surface. Such a low affinity may be interpreted as the end point in the reaction of oleic acid with accessible divalent cations.

Oleic acid adsorption on Cal III

The adsorption isotherm, shown in Fig. 6, has a gently curving shape that remains concave to the concentration axis and does not exhibit any tendency towards a limiting value. This shape of isotherm obeys the Freundlich model, and the adsorption data can be fitted to the equation

$$\mathrm{Log}(X) = \mathrm{Log}(K_F) + \alpha \mathrm{Log}(C)\,, \qquad (6)$$

where K_F is a constant and α is < 1. A plot of Eq. (6) for Cal III gave a good correlation ($r^2 = 0.98$) between Log(X) and Log(C) and the value of 0.65 for α. It is very likely, therefore, that adsorption occurred onto different overlapping surfaces with a range of affinities for the adsorbate molecule [58].

In view of the very likely heterogeneity [59] of the adsorbents' surface and the amphipathic nature of the adsorbate molecule it would seem reasonable to assume that the observed adsorption occurred onto surfaces with a range of polarities, covering the range from polar to non-polar. This is understandable in terms of a surface model of this stearic acid-coated chalk in which polar sites (carboxylate groups of the stearic acid) are dispersed across a predominantly non-polar coating (carbon skeletons of the stearic acid). In addition, Smith [60] has shown that polar, acid insoluble residues (alumino silicates) can occupy a large proportion of the surface of chalk particles.

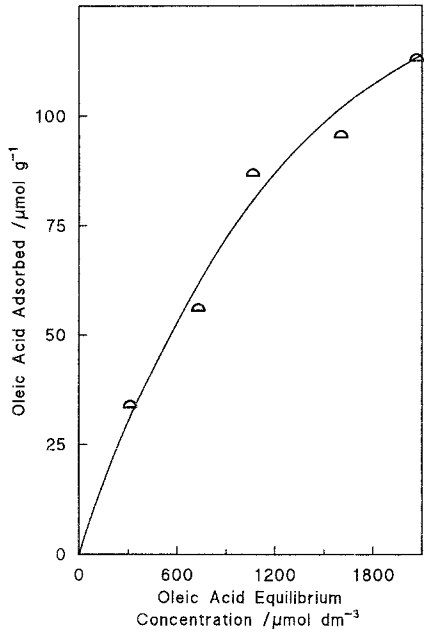

Fig. 6. Adsorption isotherm of oleic acid on Cal III

The X_{300} and A_{300} values are similar to the corresponding X_P and A_P values of the low surface area hydrophobic adsorbents, viz., Kao III and Talc I. However, an important difference in oleic acid adsorption onto a (very likely) heterogenous surface, such as Cal III, compared to that on hydrophobic surfaces, such as Kao III and Talc I, must be stressed. The gently curving, concave shape of the isotherm for Cal III means that there remained, over the concentration range studied, a significant affinity of the free, unbound oleic acid molecules for the layers of molecules already adsorbed. Thus, in comparison with oleic acid adsorption on hydrophobic surfaces, it would appear that such adsorption on a treated calcite surface did not lead to the formation of an adsorption-inhibiting density of negative charge directed towards the bulk solution, but rather the formation of a layer of lower polarity that was conducive to further adsorption.

Oleic acid abstraction by Cal I and II

Data for Cal I and II were only obtained over a narrow, residual concentration range due to the precipitation of much of the added oleic acid, presumably as calcium oleate. For example, in the case of Cal II more than 95% of the added oleic acid was precipitated when its initial concentration was $< 850\,\mu\mathrm{mol\,dm^{-3}}$ (determined from a plot of residual versus initial concentrations); significant, residual concentrations of oleic acid were found when the initial concentration was $> 850\,\mu\mathrm{mol\,dm^{-3}}$. This concentration relates to an initial $\mathrm{Ca^{2+}}$ ion concentration of $425\,\mu\mathrm{mol\,dm^{-3}}$ which is comparable with that measured by Somasundaran [29] for an Iceland Spar calcite suspension in a similar experimental set up. Furthermore, the value of $3.8 \times 10^{-15}\,\mathrm{mol^2\,dm^{-6}}$ for the solubility product of calcium oleate, calculated from the determined oleic acid and $\mathrm{Ca^{2+}}$ ion concentrations, is similar to solubility product values quoted in the literature [61, 62]. Thus, the data for Cal I and II are presented as a plot of the quantity abstracted vs. residual concentration. Such a plot is shown in Fig. 7 for the abstraction of oleic acid by Cal II; this plot is typical of those obtained for Cal I and Cal II.

The quantities abstracted by Cal I and II were much greater than would be expected on the basis of the limiting S_{OL} value of 0.21 nm^2. Indeed, this was still the case even after the subtraction of the quantity of oleic acid initially precipitated from the quantity of oleic acid abstracted. Thus, it would appear that a finite amount of oleic acid was removed from solution, presumably by precipitation with freshly dissolved Ca^{2+} ions, during the course of the experiment. This is expected thermodynamically: there should be very little residual oleic acid in a calcite suspension in accordance with the small solubility product of calcium oleate.

Triolein adsorption on Mont IV

The adsorption isotherm, shown in Fig. 5, has an S shape and is of the type S3 [34]. In particular, the isotherm has an initial region that is convex to the concentration axis and which rises to a fairly long plateau. The isotherm as a whole lies far from the y-axis, and thus there was little affinity of triolein for this type of adsorbent. Accordingly, the A_P value is particularly low, ca. 0.1 μmol m^{-2}. The X_P value of ca. 25 μmol g^{-1} is about one-eighth of the value, $(X_P)_{THE}$, which would be expected on the basis of a hydrogen bonding interaction between the carbonyl groups of two triolein molecules and an accessible divalent cation on the montmorillonite surface.

It may be inferred from the shape of the initial region that the more triolein there was adsorbed the easier it was for additional triolein to become fixed [34]. This implies that triolein was adsorbed in a cooperative manner in a similar fashion to the adsorption of oleic acid on Kao V.

The plateau indicates the completion of an adsorbed layer, while the length of this plateau (ca. 500 μmol dm^{-3}) means that the adsorbed layer exposed a surface to the bulk solution which had even less affinity for triolein than the original surface.

At high C (ca. 1100 μmol dm^{-3}) a gradual, second rise in adsorption is discernible. The rise is readily attributable to the further adsorption of triolein onto the layer of molecules already adsorbed.

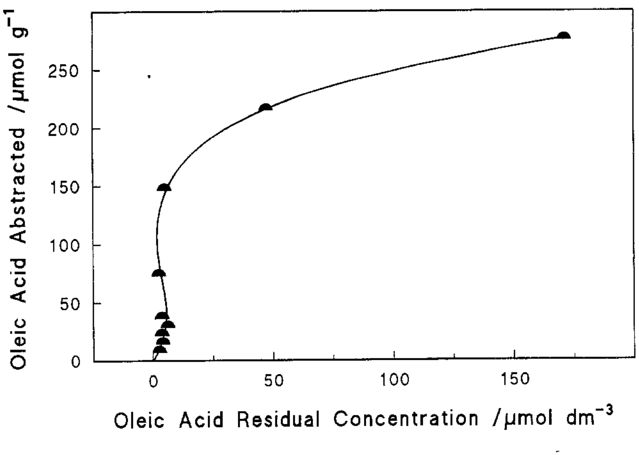

Fig. 7. Abstraction of oleic acid by Cal II

Comparison of triolein adsorption with oleic acid adsorption, on Mont IV

The adsorption isotherms of triolein and oleic acid on Mont IV are compared in Fig. 5. Considerably more oleic acid was adsorbed than triolein, ca. eight times as much on a molar basis and ca. three times as much on a weight basis. This greater adsorption of oleic acid is readily explained in terms of the occurrence of hydrogen bonding interactions between oleic acid and exchangeable divalent cations on the montmorillonite surface (discussed earlier), and, apparently, the near absence of any such interactions in the adsorption of triolein.

Triolein adsorption on Mont IVa and Mont IVb

The adsorption isotherms, shown in Fig. 8, have a rectangular hyperbolic shape at low C (i.e., < 450 μmol dm^{-3}), which obeys the Langmuir model, and the adsorption data can be fitted to the linear equation (Eq. (4)). In the case of Mont IVa the initial region of the isotherm lies slightly away from the y-axis, which indicates that there was only a moderate to low affinity of triolein for this type of adsorbent. In contrast, the initial region of the isotherm for Mont IVb lies very close to the y-axis indicating a high affinity of

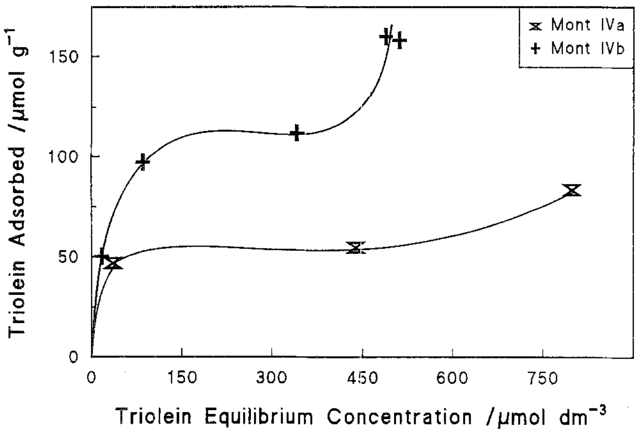

Fig. 8. Adsorption isotherms of triolein on Mont IVa and IVb

triolein for this adsorbent. Accordingly, the A_P value for Mont IVb is twice that for Mont IVa, i.e., 1.0 μmol m^{-2} compared to 0.5 μmol m^{-2}. At higher C values a gradual, second rise in adsorption occurs. The isotherms are of the type L3 and H3 [34] for Mont IVa and Mont IVb, respectively.

The plateau in each isotherm indicates the completion of an adsorbed layer while the long lengths of these plateaus (ca. 300 to 700 μmol dm^{-3}) indicates a low affinity of free triolein for the layer of triolein already adsorbed. The quantities adsorbed at the plateaus ($X_P = 57$ and 120 μmol g^{-1}) are much greater than those taken up on a bare montmorillonite surface (see Mont IV). This is to be expected in view of the hydrophobic treatment agents used in the preparations of these adsorbents; the addition of either fatty acid or quaternary ammonium compound to a montmorillonite will undoubtedly produce an adsorbent that will present a much more hydrophobic surface to its environment than the bare montmorillonite surface.

In the case of adsorption onto Mont IVa the X_P value is about a third of the value, $(X_P)_{THE}$, which would be expected on the basis of a 1:1, side-by-side association between the long chain hydrocarbon moiety of the fatty acid treatment agent and a similar moiety of the triolein molecule. The X_P value for Mont IVb is about two-thirds of that, $(X_P)_{THE}$, which would be expected on the basis of a 1:1, side-by-side association between a long chain hydrocarbon moiety of the quaternary ammonium-compound treatment agent and a similar moiety of the triolein molecule.

The second rise in each isotherm (beginning at ca. 400 to 700 μmol dm^{-3}) is readily attributable to the further adsorption of triolein onto the layer of molecules already adsorbed. In view of the fact that both adsorbents were readily wetted by, and dispersed in, water, it would seem reasonable to assume that their surfaces retained polar regions (presumably bare bentonite surface) in addition to the non-polar regions arising from the hydrocarbon moieties of the treatment agents. Thus, after an initial Langmuir-type interaction between hydrocarbon moieties and triolein molecules, further triolein molecules could then become adsorbed only by entering into interactions of varying intensities with the heterogenously polar surface.

Triolein adsorption on Talc IV

The adsorption isotherm was only obtained over a narrow range of C due to the limited solubility of triolein (i.e., ca. 25 mmol dm^{-3}) in the carrier solvent, ethanol, and the high triolein capacity of Talc IV. This problem did not arise in triolein adsorption on Mont IV, IVa and IVb because of their lower capacity for triolein. Thus, in the case of these adsorbents much more triolein remained unadsorbed in the continuous phase and a wider range of C was covered.

The isotherm, shown in Fig. 9, has a shape which obeys the Langmuir model, and the adsorption data can be fitted to the linear equation (Eq. (4)). The isotherm is of the type H1 [34]. It may be inferred, therefore, that the adsorption

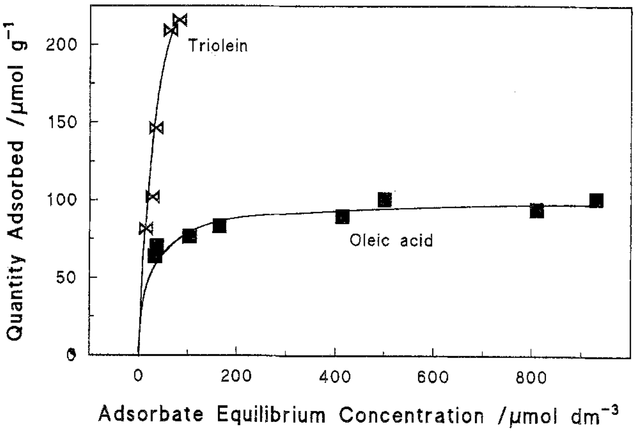

Fig. 9. Adsorption isotherms of oleic acid and triolein on Talc IV

was governed by the amount of available surface and the molecular area of the triolein molecule.

The initial portion of the isotherm lies very near to the *y*-axis. This observation and the level of adsorption indicates that the triolein had a high affinity for the adsorbent. The A_P value is particularly high at 28.9 μmol m^{-2}. In addition, the X_P value is much greater than that which would be expected, $(X_P)_{THE}$, on the basis of the molecular area of the shortest hydrocarbon moiety of the triolein molecule, i.e., ca. 0.3 nm^2. This disparity has been discussed earlier and is usually attributed to the clustering of the adsorbate molecules at the moment of adsorption. Thus, it would appear that triolein was adsorbed in an associated form on Talc IV.

In a similar fashion to the adsorption of oleic acid on the hydrophobic adsorbents, the driving force for the adsorption of appreciable quantities of triolein on Talc IV would be the replacement of unfavourable hydrophobic/water interactions (at the adsorbent/water interface) with favourable hydrophilic/water interactions (at the coated adsorbent/water interface) [38]. In this case, however, the hydrophilic/water interactions are presumably hydrogen bonding interactions between carbonyl groupings of the adsorbed triolein and the surrounding water.

Comparison of triolein adsorption with oleic acid adsorption, on Talc IV

The adsorption isotherms of triolein and oleic acid on Talc IV are compared in Fig. 9. Considerably more triolein was adsorbed than oleic acid, ca. four times as much on a molar basis and ca. 12 times as much on a weight basis. This greater adsorption of triolein is readily explained in terms of the greater, almost total, hydrophobicity of the triolein molecule, compared to that of the amphipathic oleic acid molecule. Thus, more extensive hydrophobic interactions (i.e., triolein-talc and triolein-triolein van der Waals interactions) can occur when triolein is adsorbed on a talc surface than when oleic acid is adsorbed on such a surface.

Conclusions

The adsorption of oleic acid, originally in the form of emulsion droplets, onto minerals and surface treated minerals, viz., kaolinite, treated kaolinites, montmorillonites, talcs, gibbsites, calcites and a treated calcite, has been studied. The adsorption onto kaolinite, two of the treated kaolinites (amine and $MgSiO_3$ treated), talcs and gibbsites was well correlated by the Langmuir model, while the adsorption on the surface treated calcite was well correlated by the Freundlich model. The adsorption on another treated kaolinite (cationic polymer treated) was explained in terms of a cooperative mechanism in which the polar head groups of the oleic acid molecules were directed towards the surface and their longest axis was situated in a perpendicular orientation away from the surface. The adsorption onto the montmorillonites was explained in terms of a penetrative mechanism in which the oleic acid penetrated the intercrystalline pores of the montmorillonites and interacted with some exchangeable cations. Large amounts of oleic acid were precipitated by the calcite adsorbents and the uptake of oleic acid here was best described as abstraction.

In the case of those minerals and treated minerals with a hydrophobic surface (e.g. talcs and treated kaolinites), a good correlation was found between the maximum amount adsorbed and specific surface area. This led to the particularly small value of 0.20 nm^2 for the molecular area of oleic acid on these adsorbents, and explained their considerable adsorption capacity for oleic acid. However, no such correlation was found for the montmorillonite adsorbents. In this case, the maximum amount adsorbed was shown to be influenced by the amounts of polyvalent, exchangeable cations. This influence was the basis of an explanation for the contradiction between the observed high affinity isotherms and the comparatively small amounts adsorbed. Apparently, only about one eighth of the accessible montmorillonite surface interacts strongly, via its polyvalent cations, with oleic acid.

The oleic acid adsorption was compared with the triolein adsorption of one of the montmorillonites, two adsorbents produced by the surface treatment of this montmorillonite, and one of the talcs. As with oleic acid, the triolein was also originally in the form of an emulsion. The triolein adsorption of the montmorillonite was explained in terms of a cooperative mechanism. The quantitative triolein adsorption of this mineral was considerably less than its oleic acid adsorption. The triolein adsorption of the surface treated montmorillonites, and the talc was well correlated by the Langmuir model. Larger amounts of triolein were taken up by the treated montmorillonites than by the untreated, parent montmorillonite. The quantitative triolein adsorption of the talc was considerably greater than its oleic acid adsorption.

The type (and extent) of surface of a mineral (and a surface treated mineral) plays a major role in the adsorption of oleic acid and triolein, originally in the form of emulsion droplets. The observed differences in the oleic acid and triolein adsorption behaviour of a variety of different mineral-based adsorbents are consistent with the known differences in the types (and extents) of surfaces of these adsorbents (see Tables 4, 5).

These adsorption studies will help to elucidate the role of minerals and surface treated minerals in the adsorptive control of paper mill pitch, and will increase our fundamental knowledge of sorption processes at the emulsion/solid interface.

Table 4. Summary of oleic acid adsorption data

Surface type	Adsorbents	A_P (range)
		μmol m^{-2}
Hydroxylated	Gibb I and II	7.8 to 10.6
Hydrophobic	Talc I to V	6.9 to 10.5
	Kao III and IV	2.6 to 4.0
Mixed hydrophobic/ hydrophilic	Cal III	5.6 (A_{300} value)
Hydrophilic positive charge	Kao V	2.6
Hydrophilic negative charge	Kao I and II	0.8 to 1.3
	Mont I to VII	0.7 to 1.4

Table 5. Summary of triolein adsorption data

Surface type	Adsorbents	A_P
		μmol m^{-2}
Hydrophobic	Talc IV	28.9
Mixed hydrophobic/hydrophilic	Mont IVb	1.0
	Mont IVa	0.5
Hydrophilic	Mont IV	0.1

Appendix

Correction to measured, apparent triolein adsorptions: The loss of triolein from the continuous phase at equilibrium by processes other than adsorption onto minerals (or surface treated minerals)

It was found that, in the absence of any mineral-based adsorbent, the quantity of triolein remaining in the water/ethanol continuous phase at equilibrium, as detected and measured by HPLC, was always significantly less than the amount of triolein originally added to the liquid phase. This difference, which increased with the quantity of triolein remaining in the liquid phase, was attributed to the loss of triolein from the liquid phase at equilibrium by processes other than adsorption onto mineral-based adsorbents, for example, sorption onto glassware. A quantitative knowledge, and appropriate compensation, of such an adsorbate depletion was obviously essential for an accurate determination of the adsorption of this particular adsorbate.

The variation of the quantity of triolein lost from the liquid phase (T_L), with the quantity of triolein remaining in the liquid phase at equilibrium (T_E) was determined, in the absence of any mineral-based adsorbent, and the results recorded as a plot of T_L versus T_E. This plot was then used to correct the initial, measured triolein adsorption.

Acknowledgments

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