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Infrared and fluorescence spectroscopic methods were used to study the kinetics and thermodynamics of the formation of self-assembled films of n-alkanoic acids by adsorption from solutions. The adsorption of stearic acid from hexadecane solutions onto glass and aluminum substrates was shown to lead to monolayer formation. A Langmuir-type transient adsorption model was shown to be applicable to these systems. The stationary fluorescence spectroscopy of a pyrene-labeled alkanolic acid probe was also used to determine the relative values of the kinetic constants of various fatty acids having different number of carbons in the chains. A linear increase of approximately 230 cal/mole in the negative free energy of adsorption with increasing chain length of the fatty acids was found. This is attributed to the energetic contribution of the molecular organization of the aliphatic chains to the self-assembly process.					
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Infrared and Fluorescence Spectroscopic Studies of Self-Assembled
n-Alkanoic Acid Monolayers

by

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Prepared for Publication in Langmuir

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May 30, 1989

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FNT 14
FNT 15

TXT03
PAR24

8 fractions of covalently bound fluorescent probes within the
16 compound of interest can provide molecular-level infor-
22 mation about structure (e.g., configuration and molecular
29 association), microenvironment (e.g., polarity and viscos-
SEN06 34 ity), and dynamics. Useful tools include various stationary
7 fluorescence emission peak intensity ratios, excitation
13 energy-transfer experiments, and transient depolarization
SEN09 18 measurements. The usefulness of the fluorescence probe
8 approach has been demonstrated for a variety of systems,
17 e.g., micellar solutions,¹⁶ polymer adsorption,¹⁷ and
23 Langmuir-Blodgett films.¹⁸

PAR27

SEN03 1 In these two spectroscopic techniques, IR measures
9 directly the presence and orientation of molecules while
SEN06 17 fluorescence indirectly monitors their properties. There-
2 fore, they can be considered as complementary experi-
SEN09 9 mental tools. However, incorporation of the probe mole-
7 cules into the system may actually disturb the structure
16 of the host systems because of the bulkiness of the aro-
SEN12 26 matic fluorophores or the aggregation of them. To min-
3 imize these problems, only the minimum amount of probe
12 molecules should be used.

PAR30

SEN03 1 Allara and co-workers^{1,4,5} and Sagiv and co-workers,^{2,3,7}
9 in their series of extensive studies using a number of
19 characterization techniques have demonstrated that self-
24 assembled films of structure similar to that of the Lang-
33 muir-Blodgett films can be produced under appropriate
SEN06 40 conditions. They also showed that the kinetics of ad-
18 sorption is important in the formation of these organized
26 two-dimensional films, which very few past studies have
yet focused upon.

PAR33

SEN03 1 In this paper, we report the results of our studies of the
SEN06 14 dynamics of the self-assembling adsorption process. We
11 used IR spectroscopy to study the thermodynamic and
22 kinetic aspects of adsorption of fatty acids from nonpolar
SEN09 20 solutions onto polar surfaces. The variation of wettability
6 of the substrate surfaces provides an auxiliary indication
SEN12 14 of monolayer formation. We also report the application
7 of stationary fluorescence spectroscopy of incorporated
13 pyrene probes in adsorbed mixed monolayer films and its
22 use as a simple method for the determination of the re-
SEN15 26 lative adsorption constants. Further studies on the
6 structural aspects of these adsorbed films using fluores-
13 cence probes are currently under way in this laboratory.

TXT06

SEN03 1

PAR36

SEN03 1 2. Experimental Section
SEN09 8 1. Materials. The adsorbates consisted of the homologous
SEN12 18 series of the even n-alkanoic acids, abbreviated as C₁₆ through
4 C₂₂, which were obtained from Sigma Chemical Co. Those samples
SEN15 14 with nominal purities less than 99% were recrystallized twice from
8 ethanol. The pyrene end-tagged palmitic (hexadecanoic) acid
SEN18 18 (Py-C₁₆) was obtained from Molecular Probes, Inc., and used as
9 received. The solvents n-hexadecane (HD), ethanol, acetone, and
SEN21 18 toluene, also from Sigma Chemical Co., were used as received.
SEN24 12 Distilled and deionized water was used for substrate cleaning and
7 contact angle measurements. The microscope glass slides were
SEN27 12 obtained from Becton Dickinson and Co. ("Gold Seal" brand).
1 The ATR crystal (one-pass parallelepiped KRS-5; 45°, 50 × 10
× 3 mm) was obtained from Harrick Scientific Inc.

PAR39

SEN03 1 2. Sample Preparation. Precleaning of the solid substrates
SEN09 7 was found to be vital to the subsequent adsorption process, with
16 the following cleaning procedures found to yield reproducible
SEN12 26 results. The microscope glass slides were first degreased with 120
11 °C H₂SO₄/H₂O₂ (4:1) solution for 20 min, followed by consecutive
21 water, ethanol, and acetone rinses, and finally dried in the (no-
SEN15 31 oxidizing portion of a Bunsen burner flame for ca. 10 s. The
3 aluminum substrates were prepared by evaporating approximately
SEN18 10 1000 Å of ultrapure aluminum onto precleaned Si wafers. (It is
15 well-known that an aluminum surface will develop a thin top layer
SEN21 14 of natural oxide. In this work, no attempt was made to control
11 the surface aluminum oxide thickness after the deposition of
SEN24 20 aluminum.) The aluminum substrates could be reused after
9 cleaned with cold 5% H₂SO₄ solution for ca. 30 s, followed by
21 water, ethanol, and acetone rinses and finally gentle-flame drying.

PAR42

SEN03 1 Adsorbate solutions were prepared by dissolving weighed
6 portions of the fatty acids in HD to desired concentrations covering

FNT 16. FNT 17
FNT 18



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← don't break up this word
non-ox-idiz-ing
→ use these syllables
being

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SEN06 20 the range from 10^{-3} to 10^{-4} M. Precleaned glass vials were used
SEN09 7 as the adsorption cells. During the initial dissolution, it was
SEN12 8 necessary to warm the liquid contents to about 50 °C. The same
4 procedure was also used to redissolve the crystals occasionally
13 formed during solution storage, especially for the more concentrated
SEN18 21 (~0.01 M) solutions of C_{18} and C_{22} . The preparation of
SEN18 8 the monolayer films was carried out at 22 °C. To do this, the
6 substrates were immersed in the solutions for a predetermined
SEN21 18 period of time and then removed. A strong nitrogen gas jet was
8 used to blow off any remaining liquid droplets on the surface or
20 the edges of the substrates.

PAR45

SEN03 1 Pyrene-labeled mixed monolayers were prepared by adsorption
SEN09 9 from solutions of the desired concentration of a particular fatty
SEN06 19 acid, along with a small fraction of the probe Py- C_{18} . Py- C_{18} was
4 first dissolved in HD/toluene (1:1) by warming to about 50 °C.
SEN09 1 The mixed solutions were prepared by diluting more concentrated
21 Py- C_{18} /(HD + toluene) solutions and mixing with a host fatty
SEN12 11 acid solution to the desired molar ratios. The final solutions were
6 of total acid concentration of 0.005 M in solvent mixtures containing
16 about 10% by volume of toluene in HD.

PAR48

SEN03 1 3. Characterization. A telescope-goniometer was used to
SEN09 7 measure the static contact angles of HD and water on substrates
SEN12 18 before and after adsorption of the fatty acids. Measurements were
SEN15 4 made under atmospheric conditions. A ~~static film~~ ellipsometer
5 with a He-Ne laser source was used to measure the film thickness.

PAR51

SEN03 1 Infrared spectra of the adsorbed films were obtained with a
SEN09 12 Perkin Elmer 1710 FTIR spectrometer, equipped with a DTGS
SEN06 20 detector and a nitrogen-purged sample chamber. The transmission
4 IR spectra of the adsorbed species were directly measured on the
SEN09 15 glass slides. The ATR-IR spectra were taken on the same
10 spectrometer, using a multiple internal reflection attachment
SEN12 17 obtained from Harrick Scientific Inc. The ATR-IR spectra of
6 adsorbed species were obtained by pressing two film-covered
14 substrates against the internal reflection surfaces of the ATR
SEN15 23 crystal. All spectra were taken with 4-cm⁻¹ resolution. In practice,
SEN18 4 it was usually necessary to average 1000-2000 scans in order to
SEN21 15 obtain spectra of acceptable signal-to-noise ratio. The reference
4 spectra, taken with clean substrates prior to adsorption, were
13 subtracted from the sample spectra during data processing.

PAR54

SEN03 1 Fluorescence emission spectra of the pyrene-doped monolayers
SEN09 9 were obtained with a Spex Fluorolog 212 spectrofluorometer with
SEN06 18 a 450-W Xenon arc lamp. The excitation wavelength was set at
6 343 nm, and the spectra were taken in the front-face mode.
SEN09 1 Because of the low signal intensity from these monolayer samples,
12 wide slit widths were used (2 mm), and multiple scans (two to
24 five) were averaged.

TXT09

SEN03 1

PAR57

3. Results

SEN03 1

SEN09 1

SEN12 12

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SEN18 18

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SEN21 5

SEN24 21

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SEN30 23

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1. Surface Wettability and Monolayer Formation.
It is well-known that the change in surface wettability of the substrate can reflect the adsorption of the amphiphilic molecules.¹⁻⁶ In this work, it was used as a qualitative indicator. Clean glass and aluminum substrates were wetted by both water and hexadecane; i.e., they are both hydrophilic and oleophilic. The measured contact angles were small, approximately 5° (±4°). After the adsorption of the amphiphilic fatty acid molecules, the surface wettability was drastically altered, as indicated by the sheeting-off of the oil solutions. Contact angle measurements of equilibrated samples indicated that the fatty acid/Al films were both hydrophobic and oleophobic, as has been reported previously.^{3,4} The static water contact angle on equilibrated fatty acid/Al samples obtained was about 97° (±2°), and the static hexadecane contact angle was about 47° (±2°). For fatty acid/glass samples, the hexadecane contact angle was close to that of fatty acid/Al. However, the water contact angle was small (5-10°), and the fatty acid monolayers were apparently lifted off by water,³ as indicated by subsequent hexadecane contact angle and IR measurements.

To confirm the formation of monolayers, the thickness of equilibrated fatty acid films C_{18} - C_{22} /Al was measured by ellipsometry. The results, which are given in Table I, are very similar to those previously reported by Allara and Nuzzo⁴ and show that the film thicknesses correspond to the extended zig-zag molecular lengths of the film-forming molecules. This suggests that they are indeed monolayers.

Gaertner

subtracted

TXT09
PAR60

9 with the fatty acid chains organized approximately per-
16 pendicular to the substrates.

PAR63

SEN03 1 The chemical composition of the substrate has been
10 known to play a vital role in the formation of adsorbed
SEN06 21 films.³ We have also attempted the same immersion-re-
8 moval procedure of film preparation with Si (having a thin
SEN09 18 top layer of native oxide) and quartz substrates. No
3 oleophobic films of fatty acid were formed by adsorption,
SEN12 12 consistent with that previously reported. A possible ex-
4 planation of this observation involves the metal oxide
SEN15 12 composition of the substrate. According to data from the
7 manufacturer, the glass slides used in the present work
16 contain approximately 72.6% silica, along with several
23 other metal oxides, the major ones being Na₂O (14.1%),
SEN18 32 CaO (7.1%), MgO (3.6%), and Al₂O₃ (1.8%). These metal
4 atoms present on the surface could promote the anchoring
13 of the acid head group, perhaps by chemical bonding (salt
23 formation indicated by infrared spectra), while the van der
32 Waals interaction among the aliphatic tails of the mole-
40 cules stabilizes the molecules within the adsorbed layer,
SEN21 48 perhaps by crystallization. The lack of these additional
7 metal ions in pure silica may lead to poor anchoring.

PAR66

SEN03 1 The hindering strength of the fatty acid monolayers to the
12 glass substrate is lower than those to the (oxidized) alu-
21 minum substrates, as indicated by the poor resistance of
30 fatty acid/glass to water compared to the total stability
SEN06 39 of fatty acid/Al. This could also be attributed to the
9 smaller extent of metal-acid interaction in films on glass
SEN09 18 than those on aluminum. When in contact with water, the
8 adsorbed fatty acid molecules on the nonmetal (i.e., SiO₂)
17 sites of the surface may be replaced by water molecules
27 since the physical binding of the acid head group to SiO₂
35 is weaker than the site-water interaction.

PAR69

SEN03 1 2. Infrared Spectra of Adsorbed Films. Transmis-
SEN09 2 sion infrared spectra of the adsorbed species were obtained
11 for the IR transparent range of glass (wavenumber > 2500
21 cm⁻¹), which contains the CH₂ and CH₃ stretch peaks of
SEN12 31 the aliphatic tails of the fatty acid molecules. A typical
4 unpolarized transmission-IR spectrum of two stearic acid
11 monolayers (one monolayer on each side of the glass slide)
21 adsorbed from 0.01 M hexadecane solution at equilibrium
SEN15 29 is shown in Figure 1. This spectrum is similar to the
8 high-frequency portion of the bulk spectrum of stearic acid
17 obtained from a dispersion in a KBr pellet (not shown),
27 with peaks assignable to the CH₂ symmetric and asym-
35 metric stretches (2850 and 2920 cm⁻¹, respectively) and the
44 CH₃ symmetric and asymmetric stretches (2890 and 2962
52 cm⁻¹, respectively).

FIG 1 (012,33-34)

PAR72

SEN03 1 To obtain the full-range IR spectrum of the adsorbed
SEN06 3 species, unpolarized ATR measurements were made. Two
3 substrates with adsorbed films prepared in the same way
12 were pressed against the two ATR crystal surfaces so that
22 the adsorbate was sampled by the internally reflected IR
SEN09 31 beam. A moderate pressure was necessary in order to
10 "push" the substrate surface into the penetration range of
19 the IR beam, which is on the order of several thousand
SEN12 30 angstroms. After some experimentation, a suitable
7 pressing condition was determined, and reproducible
SEN15 13 spectra could be obtained. However, the detailed effect
8 of the pressure exerted by the plates on the molecular
16 organization in the fatty acid films may be rather com-
SEN18 26 plicated and will not be discussed here. Shown in parts
3 a and b of Figure 2 are the typical ATR-IR spectra of
17 adsorbed stearic acid adsorbed at equilibrium on glass and
SEN21 26 Al substrates, respectively. One significant difference
3 between spectra on these two substrates is that only the
13 1420/1470- and 1580-cm⁻¹ peaks, assigned to the symme-
22 tric and asymmetric COO⁻ stretches, were observed for
30 C₁₈/Al, while the 1730-cm⁻¹ peak, assigned to the free acid
40 C=O stretch, was seen in addition to the carboxylate
SEN24 49 stretches for C₁₈/glass. This implies that on the Al sub-
8 strate the anchoring acid head groups were totally de-
16 protonated into salt (COO⁻),⁴ but on the glass substrate

FIG 2 (018,10-11)

TXT09
PAR72

25 only a portion of them were deprotonated on adsorption,
34 the remainder remaining as free acid. This is also con-
5 sistent with the discussion of the previous section in that
15 the metal atoms on the surface can cause deprotonation
74 of the adsorbed acid head group and the Si portions can-
34 not.

PAR75

SEN03 1 3. Transient Adsorption Behavior. Unpolarized
SEN06 3 transmission-IR or ATR-IR was used to follow the varia-
11 tion of the peak intensities of C_{18} adsorbed films prepared
21 for various times of immersion from solutions of various
SEN12 30 adsorbate concentrations. Contact angle measurement was
6 used to follow the surface wettability change with time.
SEN15 1 With solutions of relatively low concentrations (10^{-2} - 10^{-4}
9 M for glass substrate and 10^{-4} - 10^{-6} M for aluminum sub-
18 strate), the initial variation of IR peak intensities and
27 contact angles with the time of immersion could be ob-
36 served. Both the IR adsorption peak intensities and the
46 contact angles increased initially with increasing time of
54 immersion as well as increasing adsorbate concentration,
61 and they asymptotically reached plateau values at long
SEN18 69 immersion times and high solution concentrations. The
3 time required to reach the maximum nonwettability in-
10 creases with decreasing concentration of adsorbate solu-
18 tion.

PAR78

SEN03 1 Parts a and b of Figure 3 show the 2920-cm^{-1} trans-
12 mission IR peak intensity and the HD contact angle varia-
21 tion for C_{18} /glass, and parts c and d of Figure 3 show the
34 2920-cm^{-1} ATR-IR peak intensity and the water and HD
SEN06 43 contact angle variation for C_{18} /Al, respectively. The in-
3 tensity of the peaks other than the 2920-cm^{-1} one also
SEN09 13 increased proportionately. The plateau intensities of the
7 high-frequency peaks (CH_2 and CH_3 stretches) were quite
15 reproducible, up to about $\pm 5\%$, which is essentially the
SEN12 24 error of IR measurement at this intensity level. However,
3 the reproducibility of the carbonyl and carboxylate stretch
11 peaks in the lower frequency range was somewhat worse
20 ($\pm 20\%$).

PAR81

SEN03 1 4. Fluorescence of Monolayers Containing Pyrene-
SEN06 6 Labeled Probes. In order to utilize the fluorescence
16 probe method to study the self-assembled films, mea-
18 surements were performed on alkanic acid monolayers
SEN12 22 containing a pyrene-labeled probe. They were prepared
5 on the Al substrates instead of the glass slides because an
16 impurity fluorescence of the glass slides caused difficulties
SEN15 24 in the analysis of the spectra. With fluorescence probes
5 positioned very close to a metal surface, the fluorescence
SEN18 14 intensity is strongly quenched by the metal.¹⁹ In this case,
14 considering that the pyrene groups are located within 100
25 Å of the aluminum surface (the native oxide layer on Al
33 was approximately 50 Å thick), the estimated pyrene
SEN21 43 fluorescence lifetime is about 1 order of magnitude less
5 than the solution values. Nevertheless, good fluorescence
5 spectra can still be obtained.

PAR84

SEN03 1 Mixed monolayers containing the fluorescence probe
8 pyrene hexadecanoic acid, Py-C_{16} , in host fatty acids of
17 even-numbered carbons from C_{10} to C_{22} were prepared by
20 adsorption from solutions containing mostly the host fatty
SEN06 34 acid and 1-5 mol % of Py-C_{16} . All monolayers were
5 prepared under equilibrium adsorption conditions.

PAR87

SEN03 1 A typical fluorescence emission spectrum of a Py-
9 C_{16}/C_{18} mixed monolayer prepared from an HD solution
17 of 0.005 M total acid in which 2% was Py-C_{16} is shown
SEN06 29 in Figure 4. Although the spectrum of pyrene and its
9 derivatives has appeared in many places in the literature,
18 we reproduce a typical spectrum here to demonstrate the
27 quality of data obtainable for these low concentration
SEN09 35 doped monolayers. The shape of this spectrum is similar
9 to the usual pyrene emission, with peaks between 370 and
19 430 nm.

PAR90

SEN03 1 There is no significant excimer formation, as demon-
SEN06 9 strated by the lack of a peak at about 470 nm. In all cases
5 studied here (host length = 14-22 carbons; 1-5% guest in

absorption

FIG 3 (003, 8-9)

FNT 19

FNT 20

FIG 4 (003,31-32)

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PAR90

15 adsorbate solution), the I_E/I_M values of the emission
SEN09 23 ranged between 0.01 and 0.05. This shows that the Py-C₁₈
7 molecules did not aggregate within the adsorbed mono-
14 layers, and thus we can assume the chromophores were
SEN12 23 randomly distributed in the mixed monolayers. It should
4 be noted that the concentration of the probe molecules in
14 the adsorbed monolayers may not be identical with the
23 fraction of the probe within the total adsorbate concen-
SEN15 31 tration. Judging from the excimer fluorescence content,
8 the fraction of probe in the adsorbed films is likely less
19 than that in the adsorbate solutions.

PAR93

SEN03 1 Since the fluorescence observed for the mixed mono-
9 layers was predominantly from isolated pyrene chromo-
15 phores, the monomer emission intensity should correspond
SEN06 22 to the amount of Py-C₁₈ adsorbed on the substrate. With
3 host fatty acids of carbon number greater than about 14,
13 the pyrene monomer emission intensity was found to in-
SEN09 21 deed vary with the preparation conditions. Figure 5 shows
8 the 377-nm peak intensity of mixed monolayers prepared
13 at equilibrium from solutions of 1-4.8% tagged acids in
SEN12 22 0.005 M total concentration. The intensity increased ap-
5 proximately linearly with the molar fraction of Py-C₁₈ in
14 solution and decreased by about half as the carbon number
SEN16 24 of the host fatty acid increased by 2. With host fatty acids
SEN18 6 C₁₄ and lower, however, this trend was not followed. For
3 these short chains, a different adsorption mechanism may
11 be dominant or the adsorbed film may be disordered.

TXT12

SEN03 1
PAR96

4. Discussion

SEN03 1 1. Adsorption Kinetics and Transient Langmuir
SEN09 7 Kinetic Model. The IR and contact angle data, shown
9 in Figure 3a-d, show almost identical trends, as previously
SEN12 10 discussed. The change in water and HD contact angles
10 indicates the change in surface chemical composition of
SEN16 15 the substrates. Clean glass and aluminum surfaces have
8 contact angles close to zero, while at long immersion times
18 and with high enough solution concentrations the contact
26 angles of the adsorbed films approach plateau maximum
SEN18 24 values. The parallelism of the increase in the contact
10 angles and the IR absorbance suggests that these two
19 measurements monitor the same quantity—the surface
SEN21 25 coverage of the adsorbate. Intermediate values of contact
6 angles and adsorbance between the initial and the maxi-
14 mum values correspond to intermediate surface coverages.
SEN24 1 At these intermediate coverages, the adsorbate molecules
9 are perhaps organized in a patchlike fashion, and the
18 contact angle measurement, which takes a macroscopic
25 average over a certain surface area, picks up some
34 "average" value between that of the clean surface and the
44 fully covered one.

PAR99

SEN03 1 If we assume that the plateau adsorption at the highest
12 solution concentrations corresponds to the full coverage
19 of the surface "sites" of the substrate, as for the monolayer
30 adsorption, the fractional coverages of the substrate surface
38 can then be calculated from the normalized IR peak in-
SEN06 47 tensities. From theoretical considerations, monolayer
6 adsorption can be thought of as a surface site filling pro-
18 cedure, with the adsorption and desorption steps coun-
23 teracting each other.

PAR102

SEN03 1 Here, we also neglect the diffusional mass-transfer re-
3 sistance, as has previously been validated by Grow and
18 Shaeiwitz²¹ for adsorption of several surfactants from
SEN06 25 aqueous solutions. In general, for the adsorption of sur-
8 factants onto planar surfaces, the surface concentration
15 of the adsorbate is so small that the adsorption step is
SEN09 26 always rate-controlling. In this manner,²¹⁻²³ a transient
7 Langmuir adsorption kinetic model can be written as

$$\frac{d\theta}{dt} = \frac{k_a}{N_0}c(1 - \theta) - \frac{k_d}{N_0}\theta \quad (1)$$

15 where θ is the fractional surface coverage calculated from
24 the normalized IR peak intensity, t is the adsorption time.
34 k_a and k_d are the adsorption and desorption rate constants.

FIG 5 (009. 3- 4)

absorbance

FNT 21-23

REQU 1 (009.14-15)

TXT12
PAR102

44 N_0 is the surface adsorbate concentration at full coverage,
53 and c is the solution concentration of adsorbate.

PAR105

SEN03 1 Integration with the initial condition $\theta = 0$ at $t = 0$ gives

$$\theta = \frac{k_a c}{k_a c + k_d} \left(1 - \exp \left[-\frac{k_a}{N_0} \left(c + \frac{k_d}{k_a} \right) t \right] \right) \quad (2)$$

REQU 2 (003,14-15)

SEN06 1 This equation reduces to the Langmuir adsorption iso-
9 therm at equilibrium, i.e., as $t \rightarrow \infty$

$$\theta_{eq} = \frac{k_a c}{k_a c + k_d} = \frac{c}{c + \kappa} \quad (3)$$

REQU 3 (006,16-17)

17 where

$$\kappa = k_d/k_a \propto \exp(\Delta G_a^\circ/RT)$$

REQU a (006,17-18)

16 and ΔG_a° is the free energy of adsorption at infinite di-
28 lution.

PAR108

SEN03 1 For the adsorption of C_{18} from solutions of concentra-
10 tions between 10^{-2} and 10^{-4} M onto glass slides, the tran-
sient absorbance data obtained in section 3.3. can be used
SEN06 30 for kinetic calculations. Figure 6a shows the transient
7 surface coverage obtained by normalizing the 2920-cm^{-1}
14 IR absorption peak intensities, such as those shown in
23 Figure 3a, to the plateau value at higher solution concentra-
32 tions ($c \geq 5 \times 10^{-4}$ M) and long enough immersion times
SEN09 44 ($t \geq 5$ min). For solutions of concentration on the order
9 of 10^{-2} M, full coverage ($\theta = 1$) was reached in a couple of
SEN12 23 minutes. On the other hand, for very dilute solutions, it
11 took hours to reach the equilibrium coverages, θ_{eq} , which
SEN16 20 were less than unity. The equilibrated coverage data,
4 obtained with glass slides immersed in solutions for 24 h,
were also reasonably well fitted with eq 3, as shown in
SEN18 27 Figure 6b. Using the value of κ obtained, we used the
11 functional form of eq 2 to fit the data (as shown by the
24 curves in Figure 6a) with an exponential constant, which
SEN21 33 should equal $(-k_a/N_0)(c + k_d/k_a)$. As a check for fitting,
7 the exponential constants obtained were plotted against
SEN24 14 c , as shown in Figure 6c. As can be seen, the fitting of the
10 model was reasonably good.

FIG 6 (006, 3-4)

PAR111

SEN03 1 From the above data fitting, the numerical value $\kappa = (1.5$
13 $\pm 0.1) \times 10^{-6}$ mol/cm² was obtained, which in turn gives
the free energy of adsorption $\Delta G_a^\circ = -7.3 \pm 0.1$ Kcal/mol
SEN06 35 for C_{18} /glass. The numerical values of the adsorption and
9 desorption rate constants k_a and k_d can be obtained from
the fitting, if the surface concentration at full coverage,
SEN09 28 N_0 , is known. If we assume $N_0 = 8.3 \times 10^{-10}$ mol/cm²,
11 which corresponds to an area of ≈ 20 Å² per fatty acid
22 molecule (the area projected in the transverse direction
30 taken up by a closely packed carbon chain),⁹ we find that
41 $k_a = (1.0 \pm 0.1) \times 10^{-5}$ cm/s and $k_d = (1.5 \pm 0.1) \times 10^{-14}$
57 mol/(cm²·s).

FNT 24-27

PAR114

SEN03 1 Parts a and b of Figure 7 show similar results for the
14 adsorption of stearic acid from solutions of concentrations
22 between 10^{-4} and 10^{-6} M onto aluminum substrates, again
31 obtained by monitoring the normalized 2920-cm^{-1} ATR-IR
SEN06 38 absorption peak intensity. The trends observed in this
7 system are the same as those of the C_{18} /glass case, but the
19 range of solution concentration over which significant
SEN09 26 coverage variation can be seen is quite different. For so-
lution concentrations greater than about 0.001 M, the
11 adsorption was very rapid, much faster than in the C_{18} /
SEN12 20 glass case. Again, the fits were reasonably good, and we
obtain $\kappa = (5.0 \pm 0.4) \times 10^{-10}$ mol/cm² and $\Delta G_a^\circ = -9.2$
SEN16 13 ± 0.1 kcal/mol for C_{18} /aluminum. If we again assume N_0
7 $= 8.3 \times 10^{-10}$ mol/cm², we estimated that $k_a = (5.2 \pm 0.4)$
23 $\times 10^{-4}$ cm/s and $k_d = (2.6 \pm 0.3) \times 10^{-11}$ mol/(cm²·s).

FIG 7 (003, 9-10)

PAR117

SEN03 1 These kinetic constants may be underestimations be-
5 cause the actual N_0 may be greater than the ideal value
SEN06 19 as a result of surface roughness.⁷ In this work, no attempt
7 was made to control the surface roughness of either type
SEN09 17 of substrate. The glass slides received from the manu-
8 facturer were not microscopically smooth, and the ther-

TXT12
PAR117

15 mally grown aluminum oxide on the evaporated aluminum
23 substrate will also lead to a considerable degree of surface
33 roughness.

PAR120

SEN03 1 The adsorption and desorption constants k_a and k_d can
11 be mathematically described by a one-dimensional inter-
SEN06 17 action energy profile model.^{20,21} This is illustrated sche-
5 matically in Figure 8, where ϕ is the adsorbate-surface
14 interaction energy and x is the distance between the ad-
SEN09 23 sorbate and the surface. On the basis of an order-of-
7 magnitude analysis assuming a square-well-type profile,
13 Grow and Shaeiwitz²¹ determined k_a as a function of the
23 adsorption barrier $\phi_{\max}$ and k_d as a function of the de-
SEN12 23 sorption barrier ($\phi_{\max} - \phi_{\min}$). According to their calcula-
5 tions, the k_a and k_d values obtained in this study corre-
15 spond to adsorption and desorption barriers on the order
24 of $12kT$ and $28kT$, respectively, for C_{18}/Al and $18kT$ and
SEN15 34 $31kT$, respectively, for $C_{18}/glass$. The $\phi_{\max}$ value of C_{18}/Al
7 is smaller than that of $C_{18}/glass$, but the $-\phi_{\min}$ value of
SEN18 18 C_{18}/Al is greater than that of $C_{18}/glass$. The high ad-
4 sorption barrier, $\phi_{\max}$, is mostly from the negative entropy
13 of adsorption due to the loss of configurations of the hy-
SEN21 23 drocarbon chains.²⁰ However, the $\phi_{\min}$ values obtained here
8 show that there is still a difference due to the substrate,
19 perhaps not only resulting from the adsorbate-surface
26 interaction but also the difference in surface roughness.

PAR123

SEN03 1 For adsorption of surfactants from aqueous solutions on
10 polar surfaces, although the mechanism is bilayer forma-
17 tion, the Langmuir kinetics has been applied to the ad-
SEN06 26 sorption of the first monolayer. Tabulated in Table II is
7 an order-of-magnitude comparison of our results with the
15 kinetic constants reported for adsorption of a number of
24 surfactants from solutions obtained by using the Lang-
31 muir-type model.

PAR126

SEN03 1 A detailed comparison between different systems is not
10 possible because of factors such as the pore diffusion mass
20 transfer resistance for particulate adsorbents, the effect
27 of different adsorbents, the preparation or cleaning con-
34 ditions, and the ionic strength effect for aqueous solutions.
SEN06 1 However, the comparison shows that the parameters k_a ,
10 k_d , and κ obtained for stearic acid $\rightarrow$ glass in this work were
23 roughly of the same order of magnitude as those obtained
33 in most other studies for surfactants of comparable chain
42 length adsorbed onto glass, alumina, or similar adsorbents.
SEN09 1 The two cases that showed the most discrepancy were as
12 follows: (1) κ and k_d were notably high for the cetyl-
23 pyridinium chloride $\rightarrow$ TiO_2 system,²² in which there is
32 possibly a different head group orientation; (2) k_a was
41 particularly low for the Aerosol-OT $\rightarrow$ Ge system,¹⁵ in
50 which the surfactant has rather short chains and the ad-
SEN12 59 sorbent Ge is a rather inactive substance. The most sig-
4 nificant observation of these results is that the values of
14 $1/\kappa$ and k_a for stearic acid $\rightarrow$ Al are significantly greater
25 than those for any other system with particulate mineral
SEN15 34 adsorbent studied. This indicates that the adsorbing
7 ability of metallic aluminum (even oxidized) is considerably
15 higher relative to the mineral oxides.

PAR129

SEN03 1 For practical purposes, the adsorption kinetic model can
10 be used to calculate the necessary concentration and time
19 of immersion needed to prepare a compact monolayer on
SEN06 28 a particular solid substrate surface. The dependence of
5 κ on the hydrocarbon chain length will be discussed in the
16 next section.

PAR132

SEN03 1 2. Determination of Relative Adsorption Constants.
SEN06 9 If we use a Langmuir-type, two-component, competitive
9 adsorption model, the fractional coverage of the guest
17 molecule, θ_g , can be expressed as

$$\theta_g = \frac{c_g/\kappa_g}{c_g/\kappa_g + c_h/\kappa_h + 1} \propto I \quad (4)$$

23 where κ_g and κ_h are the equilibrium constants, as defined
33 in eq 3, for the guest molecule Py- C_{18} and the host fatty
SEN12 46 acid, respectively. I is the monomer fluorescence (377 nm)

FIG 8 (006, 8- 9)

TBL II (006, 5- 6)

REQU 4 (009,22-23)

TXT12
PAR132

SEN16 9 intensity. Under the experimental conditions used, $c_s \ll$
9 c_h , $\theta_h \approx 1$, and eq 4 reduces to

$$\theta_s/h = \frac{c_s}{c_s + \kappa_s/\kappa_h} \quad (5)$$

REQU 5 (015,17-18)

PAR135

SEN03 1 The constant κ_s for the guest molecule is unknown,
11 leading to unknown probe concentration in the films, as
SEN06 20 mentioned in section 3.4. However, this problem can be
7 eliminated by taking the ratio of the slopes of any two lines
19 in Figure 5, which equals the ratio of the constants κ_s
30 between host fatty acids (such as $\kappa_h(C_{22})/\kappa_h(C_{20})$, $\kappa_h(C_{20})/\kappa_h(C_{18})$, etc.). These ratios, in turn, give the difference
SEN09 37 of the free energy of adsorption between various host fatty
9 acids. With the value for C_{18}/A_1 obtained in section 4.1.
SEN12 19 as the starting point, the $-\Delta G_s^\circ$ values for other fatty acids
11 can then be calculated, as shown in Figure 9.
22

don't split up $\kappa_h(C_{20})$

FIG 9 (012,30-31)

PAR138

SEN03 1 As previously discussed, the Langmuir adsorption model
9 does not apply for systems with fatty acids shorter than
SEN06 19 C_{12} . It is possible that for these systems there is a different
13 and complicated adsorption mechanism, such as multilayer
20 formation, as Allara and Nuzzo have suggested on the basis
30 of their ellipsometry measurements.⁴

PAR141

SEN03 1 For fatty acids long enough to achieve the Langmuir
11 adsorption behavior, based on the energy additivity, the
19 contribution made by the head group, $-\Delta G_s^{\text{ch}}$, and that
28 of the N_c methylene groups to the free energy of adsorption
39 of a surfactant may be separated as

$$-\Delta G_s^\circ = -\Delta G_s^{\text{ch}} + N_c W \quad (6)$$

REQU 6 (003,45-46)

48 where W is the energetic contribution of the carbon chain
SEN06 56 per unit methylene group. As shown in Figure 9, there is
9 a linear increase in the negative free energy of adsorption,
19 and from eq 2 we obtained $W = 230 \pm 20$ cal/mol per CH_2
SEN06 33 in the aliphatic tail. This can be interpreted as the con-
8 tribution of the van der Waals interaction among the al-
17 iphatic chains to the stabilization of the adsorbed am-
25 phiphilic molecules.

PAR144

SEN03 1 Bigelow, Glass, and Zisman²⁴ used a temperature of
10 wetting method to obtain the energy of adsorption of a
SEN06 20 series of amphiphiles on platinum. They also observed an
14 increase in the (negative) energy of adsorption with in-
SEN06 16 creasing hydrocarbon chain length. In several other studies
6 on the adsorption of surfactants to air/water or oil/water
15 interfaces, such a trend has also been observed, but usually
SEN12 25 with a higher value of W . A comparison of these experi-
6 mental values is given in Table III.

TBL III (012,12-13)

PAR147

SEN03 1 It can be noted that except for one drastically different
12 result ($W = 1200$ cal/mol for alkanolic acids/oil $\rightarrow$ Pt), the
23 W values obtained for various surfactants adsorbed onto
31 metal surfaces from either oil solutions or melt generally
SEN06 40 fell in the range 200-400 cal/mol. This is quite reasonable
6 since the melt of the surfactants has, in principle, very
16 similar properties to the hydrocarbon (e.g., HD) solutions.
SEN06 1 For surfactants/water $\rightarrow$ water interface systems, the value
10 of W fell in the range 700-800 cal/mol, significantly higher
SEN12 20 than that for oil, melt, or vapor systems. This is perhaps
3 due to the strong repulsion of water against the aliphatic
15 chains.

PAR150

SEN03 1 The trend of a linear increase in $-\Delta G_s^\circ$ with N_c also
11 explains the inability of shorter fatty acids (e.g., $N_c < 10$)
SEN06 24 to self-assemble. As N_c decreases, the energy of adsorption
9 decreases correspondingly, and at some point either the
17 required concentration becomes greater than the available
24 solubility or the rate of adsorption becomes too slow for
34 any detectable adsorption to occur.

TXT15

SEN03 1

PAR153

SEN03 1

11 In summary, we have presented results of infrared and
18 fluorescence studies of the kinetics and thermodynamics
SEN06 28 of the self-assembly of fatty acid on planar solid substrates
from oil solutions. We obtained the Langmuir-type rate

5. Summary



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PAR153

7 constants of adsorption (related to the mechanism of ad-
15 sorption) and the variation of the free energy of adsorption
25 (related to the thermodynamics of adsorption). These
3 results can indeed help shed light on the understanding
SEN12 12 of this type of systems. For further understanding of the
7 self-assembly process, detailed studies on such important
14 aspects as the substrate-adsorbate interaction and the
21 effect of surface roughness remain to be done.

TXT15
PAR156

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UNIT NO. 241
Gal. 11 LA4M19 LA880224E V005 1004 890421

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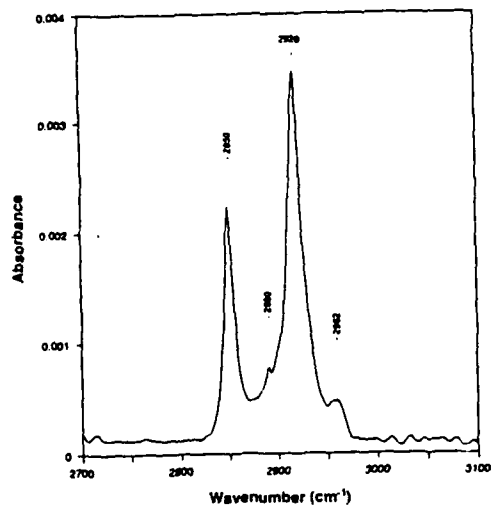


Figure 1. High-frequency-range transmission IR spectrum of two stearic acid (C_{18}) monolayers (one monolayer on each side) adsorbed on a glass slide from 0.01 M solution in HD; immersion time = 30 min.

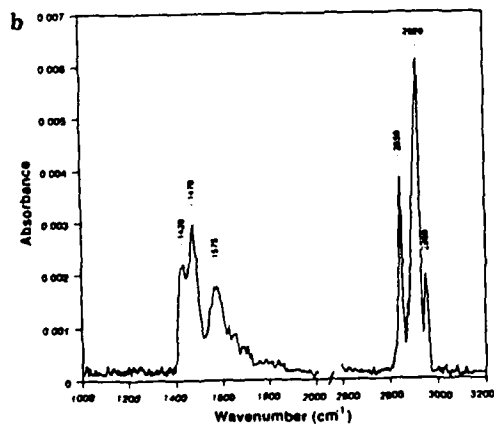
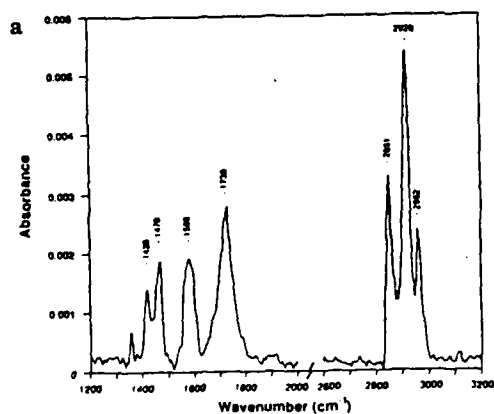


Figure 2. Unpolarized ATR-IR spectrum of one stearic acid (C_{18}) monolayer adsorbed on a (a) glass slide and (b) evaporated aluminum substrate (with an oxide layer on top) from 0.01 M solution in HD; immersion time = 30 min.

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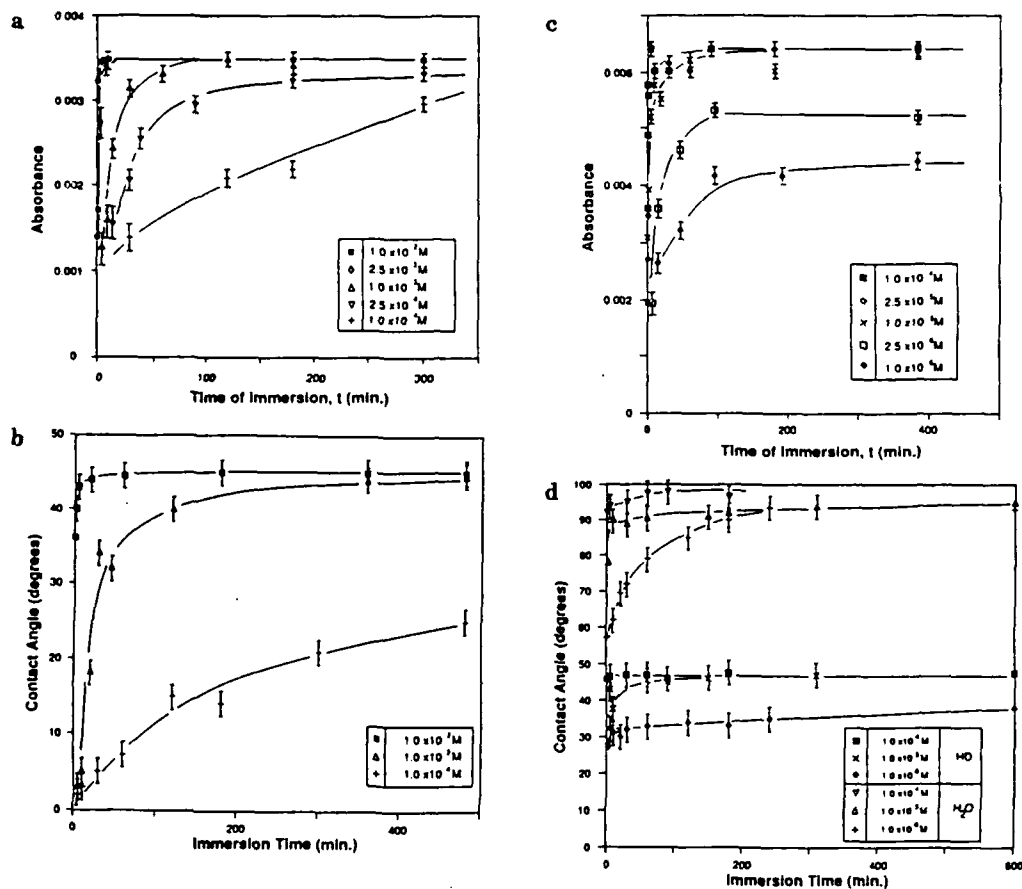


Figure 3. Transient adsorption behavior of C_{18} from HD solutions monitored by infrared spectroscopy and contact angle: (a) glass slides, 2920-cm^{-1} transmission IR peak intensity; (b) glass slides, HD contact angle; (c) aluminum substrates, 2920-cm^{-1} peak intensity; (d) aluminum substrates, H_2O and HD contact angles.

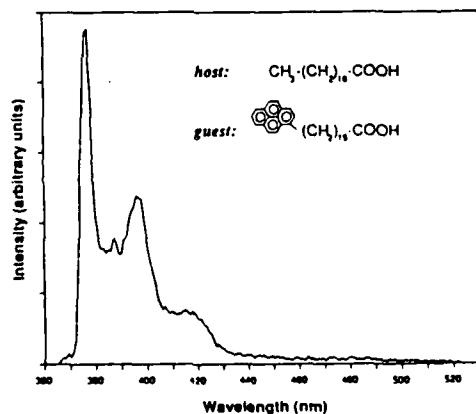


Figure 4. Typical fluorescence emission spectrum of $Py-C_{18}/C_{18}$ mixed monolayer adsorbed on aluminum substrate from solution of $0.005 M$ total acid concentration containing 2% $Py-C_{18}$ by mole.

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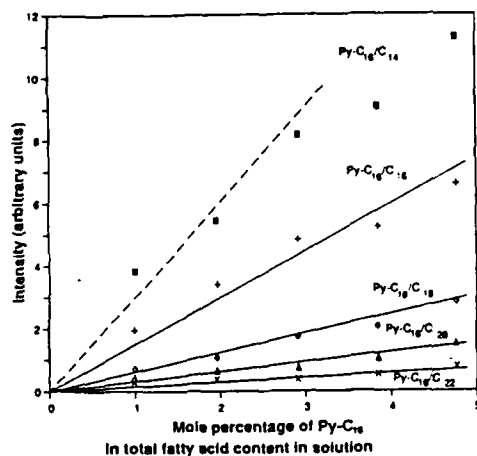
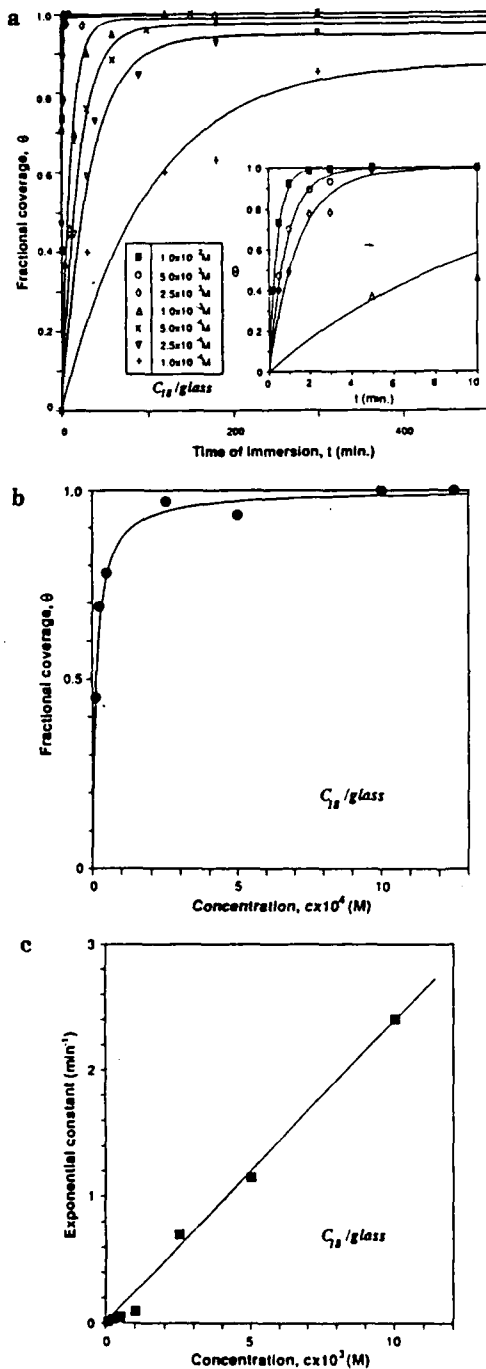


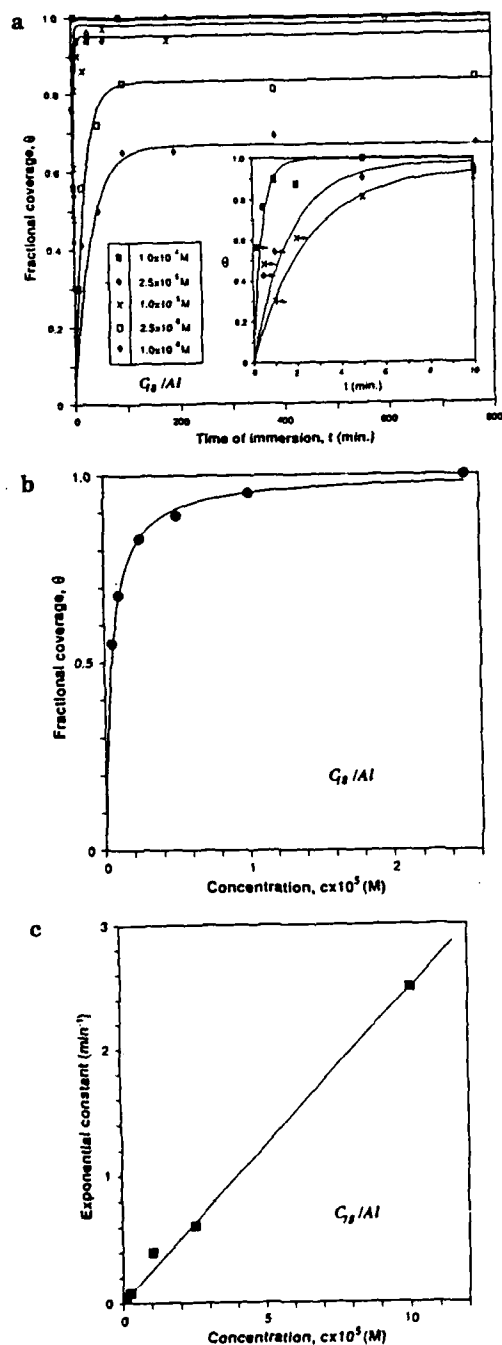
Figure 5. Fluorescence emission peak intensity, 377 nm, of Py-C₁₈/C_n mixed monolayers adsorbed on aluminum substrates from solutions of 0.005 M total acid concentration containing 1-4.8% of Py-C₁₈ by mole, with host fatty acid chain length between 14 and 22.

FNN28
FNP81



CAP00 1 Figure 6. Kinetic model fitting of C_{18} adsorption on glass slides:
CAP03 12 (a) Fractional surface coverage as a function of time and solution
CAP06 23 concentration. Data points were calculated from 2920-cm^{-1}
6 transmission IR peak intensities such as shown in Figure 3a; curves
19 were fitted with λ values obtained from Figure 6b and an expo-
CAP08 30 nential time constant in eq 2. (b) Equilibrium coverage (with
6 immersion times > 24 h) as a function of concentration; curves
CAP12 17 were fitted with eq 3, the Langmuir isotherm. (c) Check of fitting
6 of eq 2 by the correlation of the exponential constant and con-
17 centration, c .

FNN28
FNP81



CAPO0 1 Figure 7. Kinetic model fitting of C_{18} adsorption on aluminum
CAPO3 10 substrates: (a) fractional coverage as a function of time and
21 solution concentration; (b) equilibrium coverage (with immersion
28 times > 24 h); for details see Figure 6.

(c) Check of fitting;

FNN28
 FNP81

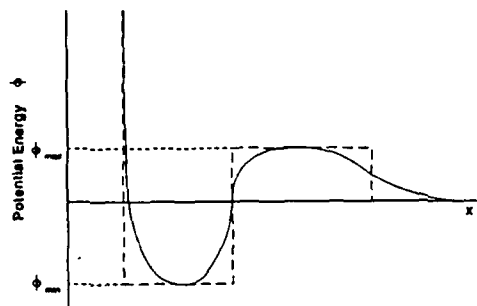


Figure 8. Typical one-dimensional interaction energy profile near a surface.

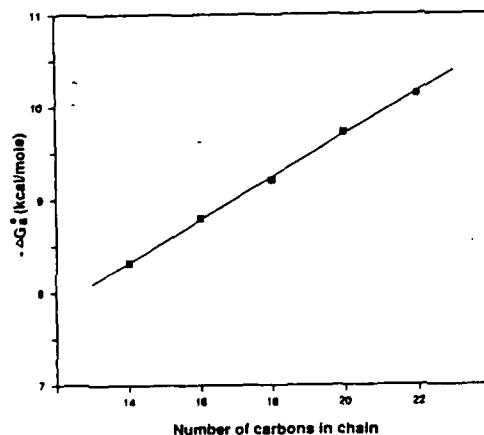


Figure 9. Free energy of adsorption of fatty acids on aluminum at infinite dilution as a function of carbon chain length, calculated from data shown in Figure 7 and eq 5.

TTL20 Table I. Film Thickness of Alkanoic Acids Adsorbed from Solutions in HD on (Oxidized) Aluminum Substrate from Ellipsometric Measurements*

HDB40	adsorbate	myristic acid	palmitic acid	stearic acid	arachidic acid	behenic acid
ROW50	no. of carbons	14	16	18	20	22
ROW60	extended molecular length (Å)	19.4	21.9	24.5	27.0	29.5
ROW70	film thickness (Å)	19.5 ± 1.5	21.0 ± 1.5	23.6 ± 2	27.3 ± 2	29.6 ± 2

FNT80 *Solution concentration 0.01 M (C₁₄, C₁₆, C₁₈) and 0.005 M (C₂₀, C₂₂); immersion time 30 min.

AID00 INITIAL TABLE WIDTH IS DOUBLE COLUMN

TTL20 Table II. Order of Magnitude Comparison of the Adsorption Rate Constants Measured in Different Systems

HDB40	substance	adsorption system	σ , mol/cm ²	k_a/N_0 , cm ³ /(mol·s)	k_d/N_0 , s ⁻¹	ref
ROW50	n-alkane sulfonates (C ₁₀ -C ₁₄)	water → alumina particles	3×10^{-8} - 1×10^{-6}	4×10^4 - 7×10^4	7×10^{-3} - 9×10^{-3}	21
ROW60	sulfonate (C ₁₄)	water → glass particles	6×10^{-7}	2×10^4	1×10^{-3}	21
ROW70	n-alkyl benzenesulfonates (C ₁₀ -C ₁₂)	water → Berea sandstone particles	8×10^{-8} - 1×10^{-7}	2×10^2 - 6×10^2	2×10^{-6} - 6×10^{-6}	22
ROW80	dodecyl benzenesulfonate (C ₁₂)	water → alumina particles	3×10^{-6}	1×10^3	4×10^{-3}	23
ROW90	n-alkyltrimethylammonium bromides (C ₁₀ , C ₁₄)	water → alumina particles	8×10^{-8} - 7×10^{-7}	4×10^4 - 6×10^4	8×10^{-3} - 3×10^{-3}	21
ROW100	cetyltrimethylammonium bromide (C ₁₆)	water → glass particles	8×10^{-8} - 3×10^{-7}	1×10^4	2×10^{-3}	21
ROW110	oxyethylated nonylphenols (C ₉ -C ₁₀)	water → Berea sandstone particles	5×10^{-8} - 1×10^{-7}	2×10^2 - 6×10^2	1×10^{-8} - 8×10^{-8}	22
ROW120	cetylpyridinium chloride (C ₁₆)	water → TiO ₂ particles	4×10^{-8}	6×10^2	2×10^{-1}	23
ROW130	Aerosol-OT (C ₉)	water → Ge plate		1×10^2		15
ROW140	Aerosol-OT (C ₉)	heptane → Ge plate		2×10^2		15
ROW150	stearic acid (C ₁₈)	hexadecane → glass plate	1.5×10^{-8}	1.2×10^3	1.8×10^{-4}	this work
ROW160	stearic acid (C ₁₈)	hexadecane → Al plate	5×10^{-10}	4×10^4	2×10^{-4}	this work

AID00 INITIAL TABLE WIDTH IS DOUBLE COLUMN

TTL20 Table III. Comparison of the Contribution of the Free Energy of Adsorption per Unit Hydrocarbon Chain Length of Surfactant Measured in Different Systems

HDB40	substance	adsorption system	W, cal/mol	ref
ROW50	n-alkanoic acids	oil → oil/Pt interface	1200	24
ROW60	n-alkylamines	oil → oil/Pt interface	400	24
ROW70	n-alkanoic acids	oil → oil/Al interface	230	this work
ROW80	n-alkyl alcohols	melt → melt/Pt interface	188	24
ROW90	n-alkanoic acids	melt → melt/Pt interface	212	24
ROW100	n-alkylamines	melt → melt/Pt interface	336	24
ROW110	n-alkanamides	melt → melt/Pt interface	103	24
ROW120	n-alkanoic acids	water → oil/water interface	830	25
ROW130	n-alkyl alcohols	water → air/water interface	750	26
ROW140	n-alkanoic acids	water → air/water interface	690	26
ROW150	n-alkanoic acids	water → air/water interface	770	27
ROW160	n-alkyl alcohols	vapor → Hg/air interface	570	26

AID00 INITIAL TABLE WIDTH IS SINGLE COLUMN

The number of words in this manuscript is 6313.

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Running Heads

Self-Assembled n-Alkanoic Acid Monolayers

Chen and Frank

Author Index Entries

Chen, S. H.

Frank, C. W.

Text Page Size Estimate = 5.4 Pages

Graphic Page Size Estimate = 3.4 Pages

tetradecone sulfonate #

will look on final

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