# Title

Infrared and Fluorescence Spectroscopic Studies of Self-Assembled n-Alkanoic Acid Monolayers

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## Abstract

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 alkanoic 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.
Infrared and Fluorescence Spectroscopic Studies of Self-Assembled n-Alkanoic Acid Monolayers

by

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Infrared and Fluorescence Spectroscopic Studies of Self-Assembled n-Alkanic Acid Monolayers

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1. Introduction

Organized organic molecular monolayers formed by spontaneous adsorption from solution, known as self-assembled films, have been the subject of a number of studies reported in recent years. As an increasing number of improved physical measurements have been used to study these compact, well-organized structures, which closely resemble Langmuir-Blodgett monolayers, the potential, but yet to be demonstrated, application of this technique in various areas has made it even more promising.

(a) Surfactants solvated in hydrophilic, polar solvents or in the form of micelles above the critical micelle concentration adsorb onto a hydrophobic adsorbent such that the hydrophobic tails of the surfactant molecules attach to the surface. The molecules line up with one another to form a monolayer, leaving the hydrophilic head groups at the surface exposed to the hydrophilic solvent.

(b) Surfactants in hydrophilic, polar solvents adsorb onto a hydrophilic adsorbent in two steps. At first, surfactant molecules adsorb to form a layer with the hydrophilic head groups anchored to the surface and the tails lined up with one another. On top of this first layer, a second layer of surfactant molecules can then adsorb with the tails down to form a hemimicelle or bilayer structure.

(c) Surfactants in hydrophobic, nonpolar solvents adsorb onto a hydrophobic polar surface such that the hydrophobic head groups are bound to the surface while the hydrophobic tails line up with one another, forming a monolayer.

In all systems, the van der Waals interaction among the hydrophobic aliphatic portions of the adsorbate molecules contributes to their alignment. The tendency of these molecules to form organized monolayers increases with increasing length of the aliphatic chain. Cleavage, both by the substrate-head group binding and the van der Waals attraction among the hydrocarbon chains will control the adsorption kinetics. In general, the well-known Langmuir isotherm is applicable for monolayer adsorption, but very little kinetic data have been reported for these types of systems.

Infrared spectroscopy, either in the transmission mode or the grazing incidence reflection-absorption (GIR) mode, has been used for the characterization and structure determination of the self-assembled monolayers. GIR-IR is especially useful in determining the molecular orientation in the film structures because it detects only the vibrational components perpendicular to the substrate surface. Polared ATR-IR can also be used for orientation determination. McKague and Guler have used ATR-IR to quantitatively study the adsorption of the surfactant Aerosol-OT.

Fluorescence spectroscopy of systems containing small
In these two spectroscopic techniques, IR measures directly the presence and orientation of molecules while fluorescence indirectly monitors their properties. Therefore, they can be considered as complementary experimental tools. However, incorporation of the probe molecules into the system may actually disturb the structure of the host systems because of the bulkiness of the aromatic molecules or the aggregation of them. To minimize these problems, only the minimum amount of probe molecules should be used.

2. Experimental Section

1. Materials. The adsorbates consisted of the homologous series of the even n-alkanoic acids, abbreviated as Cn through C24, which were obtained from Sigma Chemical Co. These samples, with nominal purities less than 99%, were recrystallized twice from ethanol. The pyrene end-tagged palmitic (hexadecanoic) acid (Py-C6) was obtained from Molecular Probes, Inc., and used as received. The solvents n-hexadecane (HD), ethanol, acetone, and toluene, also from Sigma Chemical Co., were used as received.

2. Sample Preparation. Precleaning of the solid substrates was found to be vital to the subsequent adsorption process, with the following cleaning procedures found to yield reproducible results. The microscope glass slides were first degreased with 120 °C H2SO4/H2O2 (4:1) solution for 20 min, followed by consecutive water, ethanol, and acetone rinses, and finally dried in a heating bulb. Precleaning of a thin film was achieved in a clean, water-tight container. Two 8 × 10 × 3 mm glasses were obtained from Becton Dickinson and Co. ("Gold Seal" brand). The ATR crystal (one-pass parallelepiped KRS-5: 46°, 50 × 10 × 3 mm) was obtained from Harrick Scientific Inc.

3. Adsorbate solutions were prepared by dissolving weighed portions of the fatty acids in HD to desired concentrations covering fractions of covalently bound fluorescent probes within the compound of interest can provide molecular-level information about structure (e.g., configuration and molecular association), microenvironment (e.g., polarity and viscosity), and dynamics. Useful tools include various stationary fluorescence emission peak intensity ratios, excitation energy-transfer experiments, and transient depolarization measurements. The usefulness of the fluorescence probe approach has been demonstrated for a variety of systems, e.g., micellar solutions, polymer adsorption, and Langmuir-Blodgett films.
the range from $10^{-4}$ to $10^{-8}$ M. Precleaned glass vials were used as the adsorption cells. During the initial dissolution, it was necessary to warm the liquid contents to about 50°C. The same procedure was also used to redissolve the crystals occasionally formed during solution storage, especially for the more concentrated (e.g., 0.1 M) solutions of C16 and C18. The preparation of the monolayer films was carried out at 22°C. To do this, the substrates were immersed in the solutions for a predetermined period of time and then removed. A strong nitrogen gas jet was used to blow off any remaining liquid droplets on the surface or the edges of the substrates.

Pyrene-labeled mixed monolayers were prepared by adsorption from solutions of the desired concentration of a particular fatty acid, along with a small fraction of the probe Py-C16, Py-C18, which was first dissolved in HD/toluene (1:1) by warming to about 50°C. The mixed solutions were prepared by diluting more concentrated Py-C16 (HD + toluene) solutions and mixing with a host fatty acid solution to the desired molar ratios. The final solutions were of total acid concentration of 0.008 M in solvent mixtures containing about 10% by volume of toluene in HD.

Py-C16, Py-C18 were obtained with a Perkin-Elmer 1110 FTIR spectrometer, equipped with a DTGS detector and a nitrogen-purged sample chamber. The transmission IR spectra of the adsorbed species were directly measured on the glass slides. The ATR-IR spectra were taken on the same spectrometer, using a multiple internal reflection attachment obtained from Harrick Scientific Inc. The ATR-IR spectra of adsorbed species were obtained by pressing two film-covered substrates against the internal reflection surfaces of the ATR crystal. All spectra were taken with 4-cm⁻¹ resolution. In practice, it was usually necessary to average 1000–2000 scans in order to obtain spectra of acceptable signal-to-noise ratio. The reference spectra, taken with clean substrates prior to adsorption, were subtracted from the sample spectra during data processing.

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

3. Results

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. 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. 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, as indicated by subsequent hexadecane contact angle and IR measurements.

To confirm the formation of monolayers, the thickness of equilibrated fatty acid films C16-C18/Al was measured by ellipsometry. The results, which are given in Table I, are very similar to those previously reported by Almar and Nuzzo, 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.
with the fatty acid chains organized approximately per-
 pendicular to the substrates.

The chemical composition of the substrate has been
 known to play a vital role in the formation of adsorbed
 films. We have also attempted the same immersion-re-
 moval procedure of film preparation with Si (having a thin
 top layer of native oxide) and quartz substrates. No
 oleophobic films of fatty acid were formed by adsorption.

consistent with that previously reported. A possible ex-
 planation of this observation involves the metal oxide
 composition of the substrate. According to data from the
 manufactur er, the glass slides used in the present work
 contain approximately 72.5% silica, along with several
 other metal oxides, the major ones being Na2O (14.1%),
 CaO (7.1%), MgO (3.6%), and Al2O3 (1.3%). These metal
 atoms present on the surface could promote the anchoring
 of the acid head group, perhaps by chemical bonding (salt
 formation indicated by infrared spectra), while the van der
 Waals interaction among the aliphatic tails of the mole-
 cules stabilizes the molecules within the adsorbed layer,
 perhaps by crystallization. The lack of these additional
 metal ions in pure silica may lead to poor anchoring.

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

Infrared Spectra of Adsorbed Films. Transmission
 infrared spectra of the adsorbed species were obtained
 for the IR transparent range of glass (wavenumber > 2500
 cm\(^{-1}\)), which contains the CH\(_3\) and CH\(_2\) stretch peaks of
 the aliphatic tails of the fatty acid molecules. A typical
 unpolarized transmission-IR spectrum of two stearic acid
 monolayers (one monolayer on each side of the glass slide)
 adsorbed from 0.01 M hexadecane solution at equilibrium
 is shown in Figure 1. This spectrum is similar to the
 high-frequency portion of the bulk spectrum of stearic acid
 obtained from a dispersion in a KBr pellet (not shown),
 with peaks assignable to the CH\(_2\) symmetric and asym-
 metric stretches (2850 and 2920 cm\(^{-1}\), respectively) and the
 CH\(_3\) symmetric and asymmetric stretches (2890 and 2962
 cm\(^{-1}\), respectively).

To obtain the full-range IR spectrum of the adsorbed
 species, unpolarized ATR measurements were made. Two
 substrates with adsorbed films prepared in the same way
 were pressed against the two ATR crystal surfaces so that
 the adsorbate was sampled by the internally reflected IR
 beam. A moderate pressure was necessary in order to
 "push" the substrate surface into the penetration range of
 the IR beam, which is on the order of several thousand
 angstroms. After some experimentation, a suitable
 pressing condition was determined, and reproducible
 spectra could be obtained. However, the detailed effect
 of the pressure exerted by the plates on the molecular
 organization in the fatty acid films may be rather com-
 plicated and will not be discussed here. Shown in parts
 a and b of Figure 2 are the typical ATR-IR spectra of
 stearic acid adsorbed at equilibrium on glass and
 Al substrates, respectively. One significant differ-
 ence between spectra on these two substrates is that only the
 1420/1470- and 1580-cm\(^{-1}\) peaks, assigned to the symmet-
 ric and asymmetric COO\(^{-}\) stretches, were observed for
 C\(_{18}\)/Al, while the 1730-cm\(^{-1}\) peak, assigned to the free acid
 C=O stretch, was seen in addition to the carboxylate
 stretches for C\(_{18}/\)glass. This implies that on the Al sub-
 strate the anchoring acid head groups were totally de-
 protonated into salt (COO\(^{-}\)), but on the glass substrate
only a portion of them were deprotonated on adsorption, the remainder remaining as free acid. This is also consistent with the discussion of the previous section in that the metal atoms on the surface can cause deprotonation of the adsorbed acid head group and the Si portions cannot.

3. Transient Adsorption Behavior. Unpolarized transmission-IR or ATR-IR was used to follow the variation of the peak intensities of C≡O adsorbed films prepared for various times of immersion from solutions of various adsorbate concentrations. Contact angle measurement was used to follow the surface wettability change with time.

With solutions of relatively low concentrations (10⁻⁴ to 10⁻¹ M for glass substrate and 10⁻⁴ to 10⁻² M for aluminum substrate), the initial variation of IR peak intensities and contact angles with the time of immersion could be observed. Both the IR adsorption peak intensities and the contact angles increased initially with increasing time of immersion as well as increasing adsorbate concentration, and they asymptotically reached plateau values at long immersion times and high solution concentrations. The time required to reach the maximum nonwettability increases with decreasing concentration of adsorbate solution.

4. Fluorescence of Monolayers Containing Pyrene-Labeled Probes. In order to utilize the fluorescence probe method to study the self-assembled films, measurements were performed on alkane acids monolayers containing a pyrene-labeled probe. They were prepared on the Al substrates instead of the glass slides because an impurity fluorescence of the glass slides caused difficulties in the analysis of the spectra. With fluorescence probes positioned very close to a metal surface, the fluorescence intensity is strongly quenched by the metal. In this case, considering that the pyrene groups are located within 10 Å of the aluminum surface (the native oxide layer on Al was approximately 50 Å thick), the estimated pyrene fluorescence lifetime is about 1 order of magnitude less than the solution values. Nevertheless, good fluorescence spectra can still be obtained.

Mixed monolayers containing the fluorescence probe pyrene hexadecanoic acid, Py-C₁₆, in host fatty acids of even-numbered carbon from C₁₂ to C₂₂ were prepared by adsorption from solutions containing mostly the host fatty acid and 1–5 mol % of Py-C₁₆. All monolayers were prepared under equilibrium adsorption conditions.

A typical fluorescence emission spectrum of a Py-C₁₆/C₁₂ mixed monolayer prepared from a HD solution of 0.005 M total acid in which 2% was Py-C₁₆ is shown in Figure 3. Although the spectrum of pyrene and its derivatives has appeared in many places in the literature, we reproduce a typical spectrum here to demonstrate the quality of data obtainable for low concentration doped monolayers. The shape of this spectrum is similar to the usual pyrene emission, with peaks between 370 and 430 nm.

There is no significant excimer formation, as demonstrated by the lack of a peak at about 470 nm. In all cases studied here short length = 14–22 carbons; 1–5% guest in...
Since the fluorescence observed for the mixed monolayers was predominantly from isolated pyrene chromophores, the monomer emission intensity should correspond to the amount of Py-C_{16} adsorbed on the substrate. With host fatty acids of carbon number greater than about 14, the pyrene monomer emission intensity was found to indeed vary with the preparation conditions. Figure 5 shows the 377-nm peak intensity of mixed monolayers prepared at equilibrium from solutions of 1-4.8% tagged acids in 0.005 M total concentration. The intensity increased approximately linearly with the molar fraction of Py-C_{16} in solution and decreased by about half as the carbon number of the host fatty acid increased by 2. With host fatty acids C_{14} and lower, however, this trend was not followed. For these short chains, a different adsorption mechanism may be dominant or the adsorbed film may be disordered.

4. Discussion

1. Adsorption Kinetics and Transient Langmuir Kinetic Model. The IR and contact angle data, shown in Figure 3a-d, show almost identical trends, as previously discussed. The change in water and HD contact angles indicates the change in surface chemical composition of the substrates. Clean glass and aluminum surfaces have contact angles close to zero, while at long immersion times and with high enough solution concentrations the contact angles of the adsorbed films approach plateau maximum values. The parallelism of the increase in the contact angles and the IR absorbance suggests that these two measurements monitor the same quantity—the surface coverage of the adsorbate. Intermediate values of contact angles and absorbance between the initial and the maximum values correspond to intermediate surface coverages. At these intermediate coverages, the adsorbate molecules are perhaps organized in a patchlike fashion, and the contact angle measurement, which takes a macroscopic average over a certain surface area, picks up some “average” value between that of the clean surface and the fully covered one.

If we assume that the plateau adsorption at the highest solution concentrations corresponds to the full coverage of the surface “sites” of the substrate, as for the monolayer adsorption, the fractional coverages of the substrate surface can then be calculated from the normalized IR peak intensities. From theoretical considerations, monolayer adsorption can be thought of as a surface site filling procedure, with the adsorption and desorption steps counteraacting each other.

Here, we also neglect the diffusional mass-transfer resistance, as has previously been validated by Grow and Shaeiwitz for adsorption of several surfactants from aqueous solutions. In general, for the adsorption of surfactants onto planar surfaces, the surface concentration of the adsorbate is so small that the adsorption step is always rate-controlling. In this manner, a transient Langmuir adsorption kinetic model can be written as

$$\frac{d\theta}{dt} = \frac{k_a(1 - \theta)}{N_s} - \frac{h_a}{N_s} \delta$$

where $\theta$ is the fractional surface coverage calculated from the normalized IR peak intensity, $t$ is the adsorption time, $k_a$ and $h_a$ are the adsorption and desorption rate constants.
$N_o$ is the surface adsorbate concentration at full coverage, and $c$ is the solution concentration of adsorbate.

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

$$\theta = \frac{k_c}{k_c + k_1} \left(1 - \exp \left[-\frac{k_1}{N_o} \left(c + k_2 \right) t\right]\right)$$

This equation reduces to the Langmuir adsorption isotherm at equilibrium, i.e., as $t \to \infty$

$$\theta_m = \frac{k_c}{k_c + k_1} = \frac{c}{c + x}$$

where

$$x = k_2 / k_1 = \exp(\Delta G^a_{ad}/RT)$$

and $\Delta G^a_{ad}$ is the free energy of adsorption at infinite dilution.

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For the adsorption of C$_8$H$_{16}$O from solutions of concentrations between $10^{-4}$ and $10^{-3}$ M onto glass slides, the transient absorption data obtained in section 3.3, can be used for kinetic calculations. Figure 6a shows the transient surface coverage obtained by normalizing the 2920-cm$^{-1}$ IR absorption peak intensities, such as those shown in Figure 3a, to the plateau value at higher solution concentrations ($c \geq 5 \times 10^{-4}$ M) and long enough immersion times ($t \geq 5$ min). For solutions of concentration on the order of $10^{-3}$ M, full coverage ($\theta = 1$) was reached in a couple of minutes. On the other hand, for very dilute solutions, it took hours to reach the equilibrated surface coverages, $\theta_m$, which were less than unity. The equilibrium coverage data, obtained with glass slides immersed in solutions for 24 h, were also reasonably well fitted with eq 3, as shown in Figure 6b. Using the value of $x$ obtained, we used the functional form of eq 2 to fit the data (as shown by the curves in Figure 6a) with an exponential constant, which should equal $(-k_2/N_o)(c + k_2/k_1)$. As a check for fitting, the exponential constants obtained were plotted against $c$, as shown in Figure 6c. As can be seen, the fitting of the model was reasonably good.

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From the above data fitting, the numerical value $x = (1.5 \pm 0.1) \times 10^{-3}$ mol/cm$^2$ was obtained, which in turn gives the free energy of adsorption $\Delta G^a_{ad} = -7.3 \pm 0.1$ Kcal/mol for C$_8$/glass. The numerical values of the adsorption and desorption rate constants $k_1$ and $k_2$ can be obtained from the fitting, if the surface concentration at full coverage, $N_o$, is known. If we assume $N_o = 8.3 \times 10^{-10}$ mol/cm$^2$, which corresponds to an area of $=20 \text{ Å}^2$ per fatty acid molecule (the area projected in the transverse direction taken up by a closely packed carbon chain), we find that $k_1 = (1.0 \pm 0.1) \times 10^{-8}$ cm/s and $k_2 = (1.5 \pm 0.1) \times 10^{-14}$ mol/(cm$^2$-s).

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Parts a and b of Figure 7 show similar results for the adsorption of stearic acid from solutions of concentrations between $10^{-4}$ and $10^{-3}$ M onto aluminum substrates, again obtained by monitoring the normalized 2920-cm$^{-1}$ ATR-IR absorption peak intensity. The trends observed in this system are the same as those of the C$_8$/glass case, but the range of solution concentration over which significant coverage variation can be seen is quite different. For solution concentrations greater than about 0.001 M, the adsorption is very rapid, much faster than in the C$_8$/glass case. Again, the fits were reasonably good, and we obtain $x = (5.0 \pm 0.4) \times 10^{-10}$ mol/cm$^2$ and $\Delta G^a_{ad} = -9.2 \pm 0.1$ kcal/mol for C$_8$/aluminum. If we again assume $N_o = 8.3 \times 10^{-10}$ mol/cm$^2$, we estimate that $k_1 = (5.2 \pm 0.4) \times 10^{-8}$ cm/s and $k_2 = (2.6 \pm 0.3) \times 10^{-14}$ mol/(cm$^2$-s).

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These kinetic constants may be underestimations because the actual $N_o$ may be greater than the ideal value as a result of surface roughness. In this work, no attempt was made to control the surface roughness of either type of substrate. The glass slides received from the manufacturer were not microscopically smooth, and the thermal...
The adsorption and desorption constants $k_a$ and $k_d$ can be mathematically described by a one-dimensional interaction energy profile model. This is illustrated schematically in Figure 8, where $w$ is the adsorbate-surface interaction energy and $x$ is the distance between the adsorbate and the surface. On the basis of an order-of-magnitude analysis assuming a square-well-type profile, Grow and Sheehiwiess determined $k_1$ as a function of the adsorption barrier $\psi_{\text{max}}$ and $k_d$ as a function of the desorption barrier $\psi_{\text{max}} - \psi_{\text{min}}$. According to their calculations, the $k_a$ and $k_d$ values obtained in this study correspond to adsorption and desorption barriers on the order of $12\Delta T$ and $28\Delta T$, respectively, for Cu(II)/Al and $19\Delta T$ and $31\Delta T$, respectively, for Cu(II)/glass. The $\psi_{\text{max}}$ value of Cu(II)/Al is smaller than that of Cu(II)/glass, but the $\psi_{\text{max}}$ value of Cu(II)/Al is greater than that of Cu(II)/glass. The high adsorption barrier, $\psi_{\text{max}}$, is mostly from the negative entropy of adsorption due to the loss of configurations of the hydrocarbon chains. However, the $\psi_{\text{max}}$ values obtained here show that there is still a difference due to the substrate, perhaps not only resulting from the adsorbate-surface interaction but also the difference in surface roughness.

For adsorption of surfactants from aqueous solutions on polar surfaces, although the mechanism is bilayer formation, the Langmuir kinetics has been applied to the adsorption of the first monolayer. Tabulated in Table II is an order-of-magnitude comparison of our results with the kinetic constants reported for adsorption of a number of surfactants from solutions obtained by using the Langmuir-type model.

A detailed comparison between different systems is not possible because of factors such as the pore diffusion mass transfer resistance for particulate adsorbents, the effect of different adsorbents, the preparation or cleaning conditions, and the ionic strength effect for aqueous solutions. However, the comparison shows that the parameters $k_a$, $k_d$, and $x$ obtained for stearic acid -- glass in this work were roughly of the same order of magnitude as those obtained in most other studies for surfactants of comparable chain length adsorbed onto glass, alumina, or similar adsorbents.

The two cases that showed the most discrepancy were as follows: (1) $x$ and $k_d$ were notably high for the cetylpyridinium chloride -- TiO$_2$ system, in which there is a possible different head group orientation; (2) $k_a$ was particularly low for the Aerosol-OT -- Ge system, in which the surfactant has rather short chains and the adsorbent Ge is a rather inactive substance. The most significant observation of these results is that the values of $1/x$ and $k_d$ for stearic acid -- Al are significantly greater than those for any other system with particulate mineral adsorbent studied. This indicates that the adsorbing ability of metallic aluminum (even oxidized) is considerably higher relative to the mineral oxides.

For practical purposes, the adsorption kinetic model can be used to calculate the necessary concentration and time of immersion needed to prepare a compact monolayer on a particular solid substrate surface. The dependence of $x$ on the hydrocarbon chain length will be discussed in the next section.

If we use a Langmuir-type, two-component, competitive adsorption model, the fractional coverage of the guest molecule, $\theta_g$, can be expressed as

$$\theta_g = \frac{c_g/x_1}{c_g/x_1 + c_s/x_2 + 1} = f$$

where $x_1$ and $x_2$ are the equilibrium constants, as defined in eq 3, for the guest molecule Py-C$_8$ and the host fatty acid, respectively. $f$ is the monomer fluorescence (377 nm).
The constant $c_g$ for the guest molecule is unknown, leading to unknown probe concentration in the films, as mentioned in section 3.4. However, this problem can be eliminated by taking the ratio of the slopes of any two lines in Figure 5, which equals the ratio of the constants $c_g$ between host fatty acids (such as $c_g(C_{12})/c_g(C_{20})$) and fatty acids. With the value for $C_{12}/Al$ obtained in section 4.1, as the starting point, the $-\Delta G^*_{a,b}$ values for other fatty acids can then be calculated, as shown in Figure 9.

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

Bigelow, Glass, and Zisman used a temperature of wetting method to obtain the energy of adsorption of a series of amphiphiles on platinum. They also observed an increase in the negative energy of adsorption with increasing hydrocarbon chain length. In several other studies on the adsorption of surfactants to air/water or oil/water interfaces, such a trend has also been observed, but usually with a higher value of $W$. A comparison of these experimental values is given in Table III.

It can be noted that except for one drastically different result ($W = 1200$ cal/mol for alkanolic acids/oil -- Pohl, the $W$ values obtained for various surfactants adsorbed onto metal surfaces from either oil solutions or melt generally fell in the range 200-400 cal/mol. This is quite reasonable since the melt of the surfactant has, in principle, very similar properties to the hydrocarbon (e.g., HD) solutions.

For surfactants/water -- water interface systems, the value of $W$ fell in the range 700-900 cal/mol, significantly higher than that for oil, melt, or vapor systems. This is perhaps due to the strong repulsion of water against the aliphatic chains.

The trend of a linear increase in $-\Delta G^*_{a,b}$ with $N_c$ also explains the inability of shorter fatty acids (e.g., $N_c < 10$) to self-assemble. As $N_c$ decreases, the energy of adsorption decreases correspondingly, and at some point either the required concentration becomes greater than the available solubility or the rate of adsorption becomes too slow for any detectable adsorption to occur.

In summary, we have presented results of infrared and fluorescence studies of the kinetics and thermodynamics of the self-assembly of fatty acid on planar solid substrates from oil solutions. We obtained the Langmuir-type rate
Acknowledgment. We gratefully acknowledge Dr. R.

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


Figure 1. High-frequency-range transmission IR spectrum of two stearic acid (C17) 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 (C17) monolayer adsorbed on a (a) glass slide and (b) evaporated alumina substrate (with an oxide layer on top) from 0.01 M solution in HD; immersion time = 30 min.
Figure 3. Transient adsorption behavior of $C_6H$ 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-$C_{16}/C_{19}$ mixed monolayer adsorbed on aluminum substrate from solution of 0.005 M total acid concentration containing 2% Py-$C_{16}$ by mole.
Figure 5. Fluorescence emission peak intensity, 377 nm, of Py-C$_{14}$/C$_{m}$ mixed monolayers adsorbed on aluminum substrates from solutions of 0.005 M total acid concentration containing 1-4.8% of Py-C$_{14}$ by mole, with host fatty acid chain length between 14 and 22.
Figure 6. Kinetic model fitting of C₄₅₆₇₈₉₁₀ adsorption on glass slides:
(a) Fractional surface coverage as a function of time and solution concentration. Data points were calculated from 2920-cm⁻¹ transmission IR peak intensities such as shown in Figure 6a. curves were fitted with s values obtained from Figure 6b and an exponential time constant in eq 2. (b) Equilibrium coverage (with immersion times > 24 h) as a function of concentration; curves were fitted with eq 3, the Langmuir isotherm. (c) Check of fitting of eq 2 by the correlation of the exponential constant and concentration, c.
Figure 7. Kinetic model fitting of C_{14} adsorption on aluminum substrates: (a) fractional coverage as a function of time and solution concentration; (b) equilibrium coverage (with immersion times > 24 h); for details see Figure 6.

(c) Check of fitting.
Figure 6. Typical one-dimensional interaction energy profile near \( \text{CAP0} \), 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.
Table I. Film Thickness of Alkanoic Acids Adsorbed from Solutions in HD on (Oxidized) Aluminum Substrate from Ellipsometric Measurements

<table>
<thead>
<tr>
<th>HD840</th>
<th>substance</th>
<th>adsorbate</th>
<th>myristic acid</th>
<th>palmitic acid</th>
<th>stearic acid</th>
<th>arachidic acid</th>
<th>behenic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROW05</td>
<td>no. of carbons</td>
<td>14</td>
<td>16</td>
<td>18</td>
<td>20</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>ROW06</td>
<td>extended molecular length (Å)</td>
<td>19.4</td>
<td>21.9</td>
<td>24.5</td>
<td>27.0</td>
<td>29.5</td>
<td></td>
</tr>
<tr>
<td>ROW70</td>
<td>film thickness (Å)</td>
<td>19.5 ± 1.5</td>
<td>21.0 ± 1.5</td>
<td>23.6 ± 2</td>
<td>27.3 ± 2</td>
<td>29.5 ± 2</td>
<td></td>
</tr>
</tbody>
</table>

*Solution concentration 0.01 M (C_{14}, C_{16}, C_{18}) and 0.005 M (C_{18}, C_{20}); immersion time 30 min.

INITIAL TABLE WIDTH IS DOUBLE COLUMN

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

<table>
<thead>
<tr>
<th>HD840</th>
<th>substance</th>
<th>adsorption system</th>
<th>adsorption</th>
<th>k_{a}/N</th>
<th>k_{a}/N</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROW05</td>
<td>n-alkane sulfonates (C_{10}-C_{18})</td>
<td>water -- alumina particles</td>
<td>3 x 10^{-6}</td>
<td>4 x 10^{-7}</td>
<td>7 x 10^{-7}</td>
<td>9 x 10^{-7}</td>
</tr>
<tr>
<td>ROW06</td>
<td>octadecyl sulfonates (C_{18})</td>
<td>water -- glass particles</td>
<td>6 x 10^{-7}</td>
<td>2 x 10^{-7}</td>
<td>1 x 10^{-7}</td>
<td>21</td>
</tr>
<tr>
<td>ROW07</td>
<td>n-alkyl benzenesulfonates (C_{10}-C_{18})</td>
<td>water -- Berea sandstone particles</td>
<td>8 x 10^{-8}</td>
<td>1 x 10^{-8}</td>
<td>2 x 10^{-8}</td>
<td>6 x 10^{-8}</td>
</tr>
<tr>
<td>ROW08</td>
<td>dodecyl benzenesulfonates (C_{18})</td>
<td>water -- alumina particles</td>
<td>3 x 10^{-7}</td>
<td>4 x 10^{-7}</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>ROW09</td>
<td>n-alkyltrimethylammonium bromide (C_{10})</td>
<td>water -- alumina particles</td>
<td>8 x 10^{-7}</td>
<td>8 x 10^{-7}</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>ROW10</td>
<td>cetyltrimethylammonium bromide (C_{18})</td>
<td>water -- glass particles</td>
<td>8 x 10^{-8}</td>
<td>1 x 10^{-8}</td>
<td>2 x 10^{-8}</td>
<td>21</td>
</tr>
<tr>
<td>ROW11</td>
<td>oleylbenzylammonium bromide (C_{18})</td>
<td>water -- Berea sandstone particles</td>
<td>5 x 10^{-8}</td>
<td>2 x 10^{-8}</td>
<td>1 x 10^{-8}</td>
<td>21</td>
</tr>
<tr>
<td>ROW12</td>
<td>cetylpyridine chloride (C_{18})</td>
<td>water -- TiO_{2} particles</td>
<td>4 x 10^{-8}</td>
<td>2 x 10^{-8}</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>ROW13</td>
<td>Aerosol OT (C_{18})</td>
<td>water -- Ge plate</td>
<td>1 x 10^{-8}</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROW14</td>
<td>Aerosol OT (C_{18})</td>
<td>heptane -- Ge plate</td>
<td>2 x 10^{-8}</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ROW15</td>
<td>stearic acid (C_{18})</td>
<td>hexadecane -- glass plate</td>
<td>1.5 x 10^{-8}</td>
<td>1.8 x 10^{-8}</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW16</td>
<td>stearic acid (C_{18})</td>
<td>hexadecane -- Al plate</td>
<td>5 x 10^{-8}</td>
<td>2 x 10^{-8}</td>
<td>24, 25</td>
<td></td>
</tr>
</tbody>
</table>

INITIAL TABLE WIDTH IS DOUBLE COLUMN

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

<table>
<thead>
<tr>
<th>HD840</th>
<th>substance</th>
<th>adsorption system</th>
<th>adsorption</th>
<th>cal/mol</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROW05</td>
<td>n-alkanoic acid</td>
<td>oil -- air interface</td>
<td>1200</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW06</td>
<td>n-alkylamine</td>
<td>oil -- air interface</td>
<td>400</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW07</td>
<td>n-alkanoic acid</td>
<td>oil -- Pt interface</td>
<td>230</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW08</td>
<td>n-alkylalcohol</td>
<td>melt -- melt/Pt interface</td>
<td>188</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW09</td>
<td>n-alkanamide</td>
<td>melt -- melt/Pt interface</td>
<td>212</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW10</td>
<td>n-alkylamine</td>
<td>melt -- melt/Pt interface</td>
<td>338</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW11</td>
<td>n-alkanamide</td>
<td>melt -- melt/Pt interface</td>
<td>103</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>ROW12</td>
<td>n-alkanoic acid</td>
<td>water -- oil/water interface</td>
<td>820</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>ROW13</td>
<td>n-alkylalcohol</td>
<td>water -- air/water interface</td>
<td>750</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>ROW14</td>
<td>n-alkanoic acid</td>
<td>water -- air/water interface</td>
<td>690</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>ROW15</td>
<td>n-alkanoic acid</td>
<td>water -- air/water interface</td>
<td>670</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>ROW16</td>
<td>n-alkylalcohol</td>
<td>vapor -- Hg/air interface</td>
<td>570</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

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The manuscript type is A.

Running Heads

Self-Assembled n-Alkanoic Acid Monolayers

Chen and Frank

Author Index Entries

Chen, S. H.
Frank, C. W.

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