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A Study by Contact Angle of the Acid–Base Behavior of Monolayers Containing ω-Mercaptocarboxylic Acids Adsorbed on Gold: An Example of Reactive Spreading[1]

Colin D. Bain[2] and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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Mixtures of $HS(CH_2)_{10}CO_2H$ and $HS(CH_2)_{10}CH_3$ adsorb onto gold from solution in ethanol and form densely packed, oriented monolayers. These monolayers expose a combination of polar carboxylic acid groups and nonpolar methyl groups at the surface. Varying the concentrations of the two thiols in solution allows the density of carboxylic acids at the surface and the polarity of the monolayer–liquid interface to be controlled. The technique of contact angle titration was used to study the acid–base properties of these mixed monolayers as a function of the composition of the monolayer. The contact angles of water were constant at low pH (<6) and decreased at higher values of pH. Similar behavior has been observed for polyethylene carboxylic acid ($PE-CO_2H$). Unlike $PE-CO_2H$, the contact angles on the monolayers on gold did not level out at high pH: θ continued to decrease. Carboxylic acids at the monolayer–water interface were less acidic than carboxylic acids in solution. The pH at which carboxylic acids in the monolayer were first ionized increased as the concentration of carboxylic acids in the monolayer decreased. The extent to which the free energy of ionization of the carboxylic acids is reflected in the advancing contact angle appears to be different for $PE-CO_2H$ and for monolayers of acid-terminated thiols on gold. The general problem of reactive spreading is discussed.

Introduction

Monolayers formed by the spontaneous assembly of organic thiols from solution onto gold provide a high degree of control over the chemistry and structure of an organic surface.[3-6] In this paper, we exploit the flexibility of these self-assembled monolayers to study the influence of the polarity of an interface on the acidity of carboxylic acids. Methyl-terminated thiols, such as $HS(CH_2)_{10}CH_3$, adsorb from solution onto gold and form nonwettable, hydrophobic surfaces composed predominantly of nonpolar methyl groups. Thiols terminated by carboxylic acid groups form hydrophilic monolayers that are wetted by water.[3] By coadsorbing mixtures of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$ in various mole fractions, we can synthesize surfaces in which the carboxylic acid groups are surrounded largely by nonpolar methyl groups, by other polar acid groups, or by mixtures of the two.[5] This system also allows us to examine the effect on the advancing contact angle of a chemical reaction occurring at the interface between a drop and a surface—in this case, neutralization of a carboxylic acid by aqueous base. Reactive spreading appears to be complex and may lead to different wetting behavior for the same chemical reaction on different substrates.

A knowledge of the acid–base properties of carboxylic acids and other organic acids and bases at solid–liquid interfaces is important for understanding phenomena as diverse as the stability of colloids, the folding of proteins, and the mechanisms of catalysis by enzymes. The considerable interest in these phenomena has led others to study the acidity of carboxylic acids at interfaces and to prepare surfaces composed of carboxylic acids.[7] Surfaces containing at least some carboxylic acids have been created by cutting stearic acid crystals,[8] by oxidizing the surfaces of polymers,[9-11] by functionalizing monolayers of siloxanes adsorbed on silicon,[12,13] and by adsorbing carboxylic acid terminated dialkyl disulfides[14] or dialkyl sulfides[15] onto gold. Some of these systems are poorly characterized[8] or unstable,[12,15] or expose functional groups other than carboxylic acids at the surface.[9-11] None[16] offers the control over the structure of the solid–liquid interface that is possible in monolayers of thiols on gold.

The degree of ionization of carboxylic acids as a function of pH has been studied at the interface between aqueous solutions and organic solvents or air,[17-19] in micelles[20,21] and vesicles,[22] and in Langmuir–Blodgett

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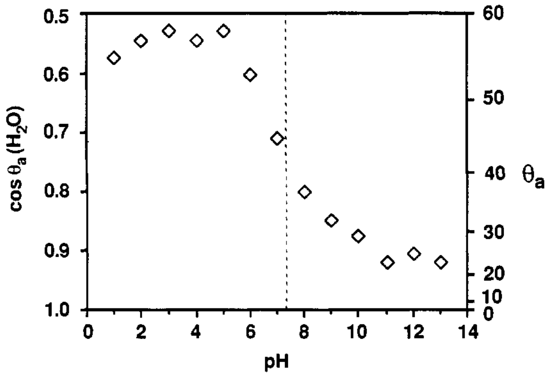

Figure 1. Advancing contact angles measured with sessile drops under air on PE–CO_2H as a function of the pH of buffered aqueous drops (after ref 11). The dashed line indicates the value of $pK_{1/2}$, the value of the pH at the midway point in cos θ between the plateaus at low and high pH.

monolayers[23] spread on water.[24-28] Experimental approaches have been both direct, such as chemical[18,25] or infrared[26] analysis of skimmed films or foams, or direct potentiometric titration[20-22] of large surface area systems, and indirect, by inference from changes in surface potential,[20,24] interfacial tension,[17,18] or the collapse pressure[24,29] and desorption kinetics[28] of Langmuir–Blodgett monolayers. Of all these techniques, only direct titration can easily be applied to the solid–liquid interface and then only to highly dispersed systems, which are harder to characterize than smooth, flat surfaces.[30]

In this work, we examine the contact angle of water on the monolayers as a function of the pH of the water, a technique known as contact angle titration.[11,31,32] Holmes-Farley et al.[11] have shown previously that the contact angle of buffered drops of water is sensitive to the state of ionization of functional groups covalently bound at the surface of functionalized polyethylene. For example, low-density polyethylene film can be oxidized with chromic acid to produce a functionalized interphase which contains a high density of carboxylic acids and ketones and/or aldehydes (PE–CO_2H). The contact angle on PE–CO_2H is independent of pH at low pH, decreases between pH 5 and 11, and levels out at higher pH (Figure 1).[11] Surfaces containing basic groups may also show titration curves. On some derivatives of polyethylene containing surface amines, the contact angle increased with increasing pH due to deprotonation of ammonium salts.[31] Holmes-Farley et al. made three key observations in their study of PE–CO_2H that are relevant here. First, the apparent $pK_{1/2}$—the solution pH at which cos θ is midway between its plateau at high and low pH—of carboxylic acids at the polyethylene–water interface was higher (by approximately 3 pH units) than the pK_a of carboxylic acids in aqueous solution. The initial pH at which ionization was detectable by contact angle was also ~3 pH units higher than we would expect from the pK_a of carboxylic acids in solution. Second, the titration curve was broader than is observed for monocarboxylic acids in solution. Third, the extent of ionization, calculated on the assumption that cos θ varied linearly with the degree of ionization, agreed with infrared analysis of dry samples after equilibration with buffered solutions. Here we extend the technique of contact angle titration to monolayer systems.

Although the experimental observations on PE–CO_2H seemed to fit a simple model involving a change in the hydrophilicity of the surface accompanying the conversion of carboxylic acids to carboxylate ions, three subsequent observations have hinted that the situation may be more complex. First, an examination of the wetting of a series of polyethylene samples containing surface functional groups with a wide range of polarity has established that there seems to be a limit to the hydrophilicity of the surface that is observed. Beyond a certain point, no matter how hydrophilic the functional group, the advancing contact angle of water was constant at $\theta_a(H_2O)$ = 20–25°; lower values were virtually never observed.[31] Thus, it is possible that the leveling of $\theta_a(H_2O)$ observed on PE–CO_2H at high pH represents an intrinsic limit to the contact angles on this material (imposed, we believe, by the heterogeneous nature of the surface). The contact angles on some other polyethylene derivatives did, however, level out at high pH at values above this apparent lower limit (e.g., 50° for PE–$CONH(CH_2)_2PO(OH)_2$).[31] Second, samples of polyethylene containing acyl anthranilates at the surface (PE–$CONH$–C_6H_4-*o*-CO_2H) exhibited a very much larger total change in contact angle with pH ($\theta_a(H_2O, \text{pH } 1) = 110°$; $\theta_a(H_2O, \text{pH } 13) = 30°$) than does PE–$CO_2H$ itself,[33] even though the densities of carboxylic acid groups at the surface are comparable. This observation suggests that the contact angles on polyethylene functionalized with carboxylic acids may be determined by factors other than the density of carboxylic acids at the surface; for example, the conformational mobility of the functional groups. Third, the hysteresis in the contact angle of water on PE–CO_2H is very large: $\theta_r(H_2O) \approx 0°$ at all values of pH. PE–CO_2H is, at best, a very nonideal system.

The contact angles of water on monolayers (adsorbed on gold) that contained carboxylic acids at the monolayer–water interface were especially interesting because the shape of the titration curves of the monolayers appeared to be qualitatively different from that of PE–CO_2H. These differences raise the question of how to describe acid–base reactions occurring at interfaces and, more generally, of how to model reactive spreading theoretically. We present a simple model that incorporates the energy of reaction into the calculation of contact angles and discuss the extent to which our data fit the model.

Nomenclature. We use terms such as "monolayer of an alkanethiol" to refer to monolayers formed from a solution of an alkanethiol, although the actual species on the

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surface is probably a thiolate, RS^-.[3,34] We apply the term "reactive spreading" to situations in which the drop of liquid reacts chemically with the surface upon which it is placed. We also include under this term the adsorption of monolayer films on the surface from components in the drop. We use terms such as "acid surface" as shorthand for the cumbersome phrase "surface of a monolayer that exposes predominantly carboxylic acid groups at the monolayer–air or monolayer–liquid interface". The contact angle, θ, is described according to the following convention.[3] The subscript a or r after θ designates whether the edge of the drop was advancing or receding across the surface before the measurement was made. The superscript after θ designates the medium in which the measurements of the contact angles were conducted. The probe liquid used is expressed in parentheses after θ. Thus, $\theta_a^{C_8}(H_2O)$ refers to advancing contact angles of water measured on a substrate immersed in cyclooctane (C_8). Interfacial tensions are designated γ_{ab}, where we use the subscripts s, v, l, and l′ to refer to the solid, vapor, liquid in the drop, and liquid in the surrounding medium, respectively.

Theory. To rationalize the variation in $\theta_a^{air}(H_2O)$ with pH on surfaces of $PE-CO_2H$ (Figure 1), Holmes-Farley et al.[11] started from Young's equation[35]

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \qquad (1)$$

and then made two assumptions. First, γ_{lv} and γ_{sv} are independent of pH. Second, the change in the solid–liquid interfacial free energy, $\delta\gamma_{sl}$, with changes in pH depends linearly on the fraction of carboxylic acids, α_i,converted to carboxylate ions. The second assumption is the same as that employed in early studies by Peters and Danielli of the variation of interfacial tension with pH at the interface between aqueous solutions and organic solutions of carboxylic acid and amine surfactants.[17] The titration of functionalized polyethylene surfaces could apparently be rationalized satisfactorily with this empirical model. Below pH 5 and above pH 11 there was no change in the extent of ionization with pH and hence no change in the contact angle. Between pH 5 and 11, the contact angle decreased as the degree of ionization, and hence the hydrophilicity increased. The essence of this model is that changes in the contact angle are determined by differences in the hydrophilicities of carboxylic acids and carboxylate ions. The free energy of ionization affects the contact angle only to the extent that it influences the difference in hydrophilicity between the ionized and unionized carboxylic acid groups.

If we are to apply this model generally to other surfaces and other systems, we encounter two conceptual problems. First, the model is essentially static: no explicit account is taken of the free energy of reaction (in this case, the ionization of a carboxylic acid) as the drop advances over the surface. Intuitively, we might expect a negative free energy of reaction to drive the advance of the drop edge even if the surface after reaction were less wettable than the surface before reaction. For cases in which the spreading coefficient[36] is positive, Hoffman has shown that excess free energy can be dissipated by viscous processes in a precursor film extending beyond the macroscopic drop edge.[37] The case of finite contact angles and entropically driven reactions is less clear. Second, it is difficult to choose a reference state for γ_{sl} that is consistent with the assumption made in the model. The solid–liquid interfacial free energy, γ_{sl}, is defined by[38]

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - W_{adhesion} \qquad (2)$$

where $W_{adhesion}$ is the work of adhesion of the aqueous solution to the polyethylene surface. The model proposed to rationalize the behavior of $PE-CO_2H$ assumes that γ_{sl} is independent of pH at high pH. If we choose the reference state for γ_{sv} in (2) to be $PE-CO_2H$, then $W_{adhesion}$, and hence γ_{sl}, are dependent on the pH of the drop if the surface is ionized. If we choose $PE-CO_2^-M^+$ as the reference state for γ_{sv}, then $W_{adhesion}$, and hence γ_{sl}, are dependent on the concentration of the counterion, M^+, in solution. With the latter choice of reference state, the contact angle at low pH would be dependent both on pH and the concentration of the counterion.[39]

Contrary to the behavior observed on $PE-CO_2H$ at high pH, the contact angles of buffered drops on mixed monolayers of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$ on gold did not level out at values of pH accessible with aqueous drops (see Figure 3). To try to understand the titration curves of the monolayers, we attempted to incorporate the energy of reaction explicitly in Young's equation.

We assume that (1) the aqueous drop and the surface are in thermodynamic equilibrium; (2) the surface is flat and homogeneous; (3) the drop is bounded by a well-defined three-phase line, and ionization is confined to the region within this boundary; (4) the carboxylic acid groups at the surface are characterized by a unique, intrinsic[40] pK_a that is independent of the degree of ionization; and (5) the effective pH at the solid–aqueous interface is the same as the bulk pH. Assumptions 4 and 5 can be relaxed to allow for double-layer effects and for specific interactions between carboxylic acids and carboxylate ions without changing the slope of cos θ against pH at high pH.

The ionization constant, K_a, is defined by

$$K_a = \frac{[RCO_2^-][H^+]}{[RCO_2H]} \qquad (3)$$

where a complete monolayer is defined to be at unit concentration. In terms of the degree of ionization, α

$$K_a = \frac{\alpha[H^+]}{1-\alpha} \qquad (4)$$

$$\log\left(\frac{\alpha}{1-\alpha}\right) = pH - pK_a \qquad (5)$$

$$1-\alpha = \frac{[H^+]}{[H^+] + K_a} \qquad (6)$$

The difference between the two interfacial tensions that occurs in the right-hand side of Young's equation can be broken down into two components, $\Delta G_1 + \Delta G_2$

$$\gamma_{sl} - \gamma_{sv} = \Delta G_1 + \Delta G_2 \qquad (7)$$

Here ΔG_1 is the free energy of immersion of a carboxy-

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[34] See also ref 16.

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[39] Choosing $PE-CO_2H$ as the reference state but allowing γ_{sl} to vary with pH according to (2) is another way of including the energy of reaction in Young's equation.

[40] We use *intrinsic* to refer to the pK_a expressed in terms of the pH at the surface of the monolayer and *apparent* to refer to the pK_a expressed in terms of the bulk pH.

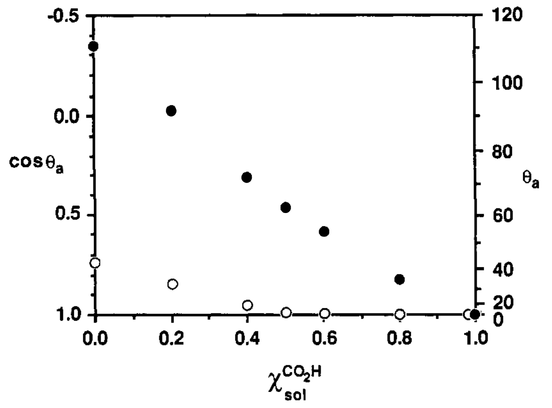

Figure 2. Advancing contact angles of unbuffered, distilled water (pH 5.3, solid circles) and hexadecane (open circles) measured with sessile drops under air on monolayers adsorbed onto gold from solutions containing mixtures of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$. The abscissa represents the mole fraction of $HS(CH_2)_{10}CO_2H$ in solution.

lic acid surface into water without any ionization of the acid groups. If this quantity is assumed to be independent of pH, then

$$\Delta G_1 = -\gamma_{lv} \cos \theta(\text{pH } 1) \tag{8}$$

ΔG_2 is the change in free energy arising from the ionization of a fraction α of the carboxylic acid groups at the surface. If there are n carboxylic acid groups per unit area of the surface, ΔG_2 is equal to n times the free energy change for

$$RCO_2H \rightarrow (1-\alpha)RCO_2H + \alpha RCO_2^- + \alpha H^+ \tag{9}$$

ΔG_2 can be evaluated by integrating the free energy change for (9) from the extent of reaction $x = 0$ to $x = \alpha$.[41] For solutions buffered at a fixed value of pH

$$\Delta G_2 = \int_0^\alpha -nkT \ln K_a + nkT \ln \frac{x[H^+]}{1-x}\,dx \tag{10}$$

$$= \int_0^\alpha 2.3nkT(pK_a - pH) + nkT \ln \frac{x}{1-x}\,dx \tag{11}$$

$$= 2.3\alpha nkT(pK_a - pH) + nkT\left[\alpha \ln \frac{\alpha}{1-\alpha} + \ln (1-\alpha)\right] \tag{12}$$

Using (5) yields

$$\Delta G_2 = nkT \ln (1-\alpha) \tag{13}$$

Substituting (6), (7), (8), and (13) in (1) yields

$$\cos \theta = \cos \theta(\text{pH } 1) - \frac{nkT}{\gamma_{lv}} \ln \left(\frac{[H^+]}{[H^+] + K_a}\right) \tag{14a}$$

$$\cos \theta = \cos \theta(\text{pH } 1) + \frac{2.3nkT}{\gamma_{lv}} \log (1 + 10^{pH-pK_a}) \tag{14b}$$

At low pH, $[H^+] \gg K_a$

$$\cos \theta = \cos \theta(\text{pH } 1) \tag{15}$$

At high pH, $[H^+] \ll K_a$

$$\cos \theta = \cos \theta(\text{pH } 1) + \frac{2.3nkT}{\gamma_{lv}}(pH - pK_a) \tag{16}$$

A graph of cos θ against pH is predicted to be constant well below the pK_a of the carboxylic acid and to increase linearly with a slope of $2.3nkT/\gamma_{lv}$ well above the pK_a. Thus, if we take the energy of ionization into account, the predicted form of the dependence of the contact angles on pH is very different from that observed for PE-CO_2H or from that predicted solely on the basis of the hydrophilicities of the functional groups.

Physically, the increase in cos θ predicted by (16) at high pH (that is, when $\alpha \rightarrow 1$) arises purely from the entropy of dilution of the protons released by ionization of the carboxylic acids. Specific interactions between carboxylic acids and carboxylate anions would increase the acidity of the carboxylic acids at low α and decrease the acidity at high α.[42] The effect of specific interactions would be to broaden the transitional region between the low and high pH behavior, but the contact angles at high pH (i.e., sufficiently basic that essentially all the carboxylic acids are ionized: $\alpha \rightarrow 1$) would be the same as on a monolayer in which the pK_a was independent of α and equal to the mean value of the pK_a in the presence of specific interactions. Field effects would also broaden the transitional regime. The slope of a plot of cos θ against pH would be the same as that in the absence of field effects, but the curve would be translated to higher values of pH.

Hydrophilicity appears in this model indirectly through its relationship to the pK_a: the more hydrophilic the carboxylate anion, the lower the pK_a. Surfaces with different values of pK_a would give rise to a family of curves of cos θ against pH that were parallel at high pH.

Results

We immersed gold slides overnight in mixtures of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$ in ethanol at room temperature to form monolayers containing a mixture of carboxylic acid groups and methyl groups at the surface. In Figure 2, we plot the advancing contact angles of water and hexadecane on the mixed monolayers as a function of the composition of the solution.[43] In general, the composition of a monolayer adsorbed from a solution containing two thiols does not mirror the relative concentrations of the two components in solution.[44] The two components in the monolayer do not phase segregate into macroscopic, single-component domains—any clusters of carboxylic acids that do form are at most a few tens of angstroms across.[44] On the other hand, analogy with the behavior of solutions suggests that the distribution within the monolayer is unlikely to be entirely random. In a previous study,[5] we used X-ray photoelectron spectroscopy to determine the relationship between the advancing contact angle of water and the composition of mixed monolayers of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$. Using

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[41] We assume that the components in the monolayer act ideally, so we can write $\Delta G = \Delta G^0 + nkT \ln ([RCO_2^-][H^+]/[RCO_2H])$. The result of the integration, eq 13, may also be obtained more simply by substituting the initial concentration of RCO_2H and the final concentration of RCO_2^- into this expression for ΔG.

[42] We can estimate the effect of specific interactions between head groups by comparing the acidities of maleic acid (*cis*-butenedioic acid), in which the monoanion is stabilized by intramolecular H-bonding, and fumaric acid (*trans*-butenedioic acid), in which the same through-bond electronic effects are present but intramolecular H-bonds are not possible. The $pK_{a,1}$ and $pK_{a,2}$ of maleic acid are 1.83 and 6.07 and of fumaric acid are 3.03 and 4.44 (ref 54, p 210). If intramonolayer H-bonds between carboxylic acids and carboxylate anions have similar strengths to the H-bonds in the monoanion of maleic acid, these specific interactions could broaden the titration curves by up to 3 pH units.

[43] The use of distilled water (pH 5.3) does not result in ionization of the carboxylic acids in the monolayer. Only the 100% acid surface, which is wet by water at all pH, is significantly ionized by a buffered solution at pH 6. With unbuffered solutions there is insufficient base present in the drop to ionize any significant proportion of the carboxylic acids at pH 6.[5]

[44] Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155–7164. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164–7175.

this relationship, we can derive the compositions of the monolayers from the contact angles in Figure 2.

Under air as the ambient medium, it is impossible to obtain a contact angle titration for the pure acid surface because the monolayer is wet by water at all values of pH. A well-established technique for increasing the contact angles of water is to perform the measurements under an inert, immiscible solvent.[45] Cyclooctane (C_8) was a suitable solvent for this purpose: the contact angles measured under cyclooctane were higher than under other liquids surveyed[46] and varied little with temperature. Cyclooctane is relatively nonvolatile and can be obtained in high purity at low cost. An incidental advantage of measuring contact angles under cyclooctane was a reduction in the rate of contamination of the acid surfaces, which is rapid in the laboratory atmosphere. Under cyclooctane, the contact angle of water at low pH on a pure carboxylic acid surface was 30–40°, permitting at least a partial titration curve on all the monolayers (Figure 3).[47]

Figure 3 plots $\theta_a^{C_8}(H_2O)$ against pH for the monolayers adsorbed from solutions containing mixtures of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$. Each titration curve is labeled with the percentage of the chains in the monolayer that were terminated by carboxylic acid groups. The contact angles on the pure monolayer of $HS(CH_2)_{10}CH_3$, which contains no ionizable groups, provided a useful control. Since the contact angles on the pure methyl-terminated monolayer were independent of pH, we are confident that changes in θ with pH on the other monolayers reflect ionization of the carboxylic acids and are not artifacts arising from changes in $\gamma_{ll'}$ or from degradation or reconstruction of the monolayer.[48] We note a number of features of these titration curves. First, the contact angle on all the monolayers containing carboxylic acids was constant at low pH and decreased linearly at high pH. The titration curves did not level out at high pH on any of the monolayers for which we could obtain complete titration curves, in contrast to the contact angles of water on PE–CO_2H (Figure 1). Second, the break point in the titration curve of the 100% acid surface occurred at pH 6, the same pH as was observed on PE–CO_2H. If the changes in θ result from ionization of carboxylic acids, as we believe they do, then the most ionizable groups may be in similar environments in PE–CO_2H and in a monolayer of $HS(CH_2)_{10}CO_2H$ on gold. Third, the onset of ionization appeared to move to higher values of pH as the proportion of carboxylic acids in the monolayer decreased. The break point in the titration curves moved from pH 6 to pH 9 as the proportion of the components of the monolayer that were terminated by carboxylic acid groups decreased from 100% to 14%.

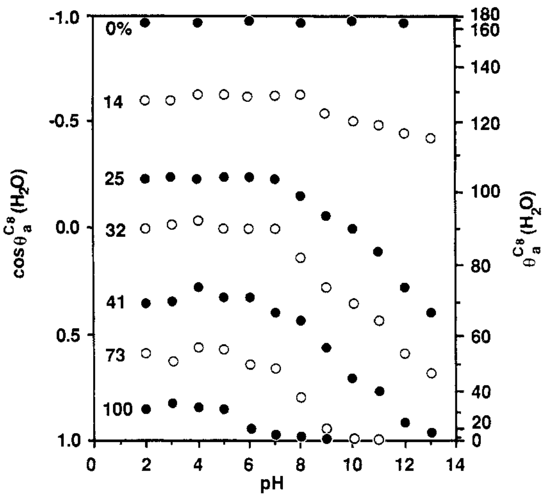

Figure 3. Advancing contact angles of buffered, aqueous solutions measured with sessile drops under cyclooctane on mixed monolayers of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$, plotted as a function of pH. The curves are labeled by the proportion of the chains in the monolayer that were terminated by a carboxylic acid group. The composition of the monolayer was determined by comparing the contact angle of water under air with monolayers whose compositions had been established by XPS (ref 5).

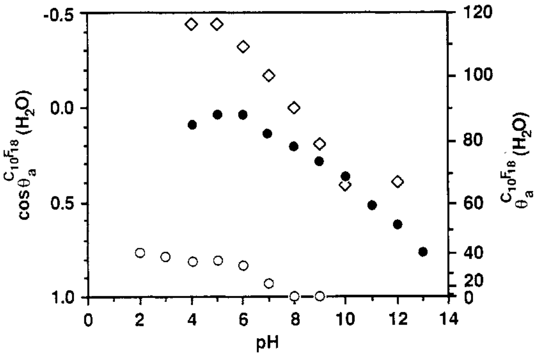

Figure 4. Advancing contact angles of buffered, aqueous solutions measured with captive drops under perfluorodecalin as a function of pH: PE–CO_2H (diamonds); monolayer of $HS(CH_2)_{10}CO_2H$ (open circles); monolayer adsorbed from a 1:1 mixture of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$ (solid circles).

The most intriguing feature of the data in Figures 1 and 3 is the different behavior at high pH of the contact angles of water on PE–CO_2H and on the monolayers on gold. To ensure that the difference between the two substrates is not an artifact of the different techniques used to measure the contact angles, we compared the contact angles on PE–CO_2H and on monolayers on gold under a common inert solvent. Unfortunately, we were not able to use cyclooctane: hydrocarbons swell polyethylene. Perfluorocarbons do not. Figure 4 plots the contact angles of water on three samples immersed in perfluorodecalin: PE–CO_2H, a pure monolayer of $HS(CH_2)_{10}CO_2H$, and a monolayer adsorbed from a 1:1 mixture of $HS(CH_2)_{10}CO_2H$ and $HS(CH_2)_{10}CH_3$. Since perfluoro-

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(46) Other liquids surveyed included hexadecane, hexane, isooctane, cyclohexane, *cis/trans*-decalin, bicyclohexyl, toluene, benzonitrile, nitrobenzene, butyl acetate, butyl ether, and *o*-dichlorobenzene.

(47) Even when measured under cyclooctane, the titration curves of the 100% and 73% acid surfaces were cut off by $\cos\theta = 1$.

(48) The contact angle on a pure monolayer of $HS(CH_2)_{10}CH_3$ was also independent of pH when measured under air. We have titrated mixed monolayers of $HS(CH_2)_{15}CH_3$ and $HS(CH_2)_{15}CO_2H$ (ref 31) and of $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{10}CO_2H$, under air: we did not observe plateaus at high pH with these systems, in contrast to PE–CO_2H. We also titrated a monolayer of $HS(CH_2)_{11}OH$ on gold. Under air, water wets this monolayer at all values of pH. The contact angles under cyclooctane declined slightly at high pH (from 43° at pH 2 to 39° at pH 13 on one sample), even though we do not expect the alcohol groups to ionize. The contact angle of the drop with pH 13 declined slowly with time, reaching 20° after 2 h. The most probable cause of this change is the ionization of trace, surface-active impurities in the cyclooctane.

Our experimental procedure did not readily lend itself to the measurement of receding contact angles under cyclooctane. We have previously reported advancing and receding contact angles on mixed monolayers of $HS(CH_2)_{15}CO_2H$ and $HS(CH_2)_{15}CH_3$ under air.[31] Compared to PE–CO_2H ($\theta_r = 0°$), the hysteresis in the contact angle of acidic water on the mixed monolayers was small ($\cos\theta_r - \cos\theta_a < 0.2$) and independent of the composition of the monolayer. The origin of this hysteresis is unclear: the monolayers are not heterogeneous on a length scale capable of producing metastable states in which an advancing drop could be kinetically trapped. The hysteresis in the contact angle of water at pH 13 increased rapidly as the proportion of carboxylic acid groups at the surface of the monolayer increased. For $\chi_{CO_2H} > 0.3$, $\theta_r^{air}(H_2O$, pH 13) was zero.

decalin is denser than water, we employed the captive drop rather than the sessile drop technique for these measurements.[49] Although perfluorodecalin does not cause bulk swelling of polyethylene, it does induce a reconstruction of the polyethylene–liquid interphase.[50] The initial contact angle of water on PE–CO_2H increased as the time of immersion of the PE–CO_2H in perfluorodecalin before the drop of water was placed on the surface increased. The contact angle of a drop of water resting on the surface slowly decreased. We found that stable contact angles could be obtained with acidic or basic drops, provided that the sample of PE–CO_2H was immersed in the perfluorodecalin for at least 10 min before a drop of water was placed on the surface and a further 10 min was allowed to elapse before the contact angle was measured. We presume that the surface reconstructs in contact with perfluorodecalin to bury the polar carboxylic groups but reexposes them when a water droplet is applied. The contact angles on the monolayer samples did not vary with time. Figure 4 shows that, at high pH, the titration curve of PE–CO_2H leveled out, as it does under air, but the contact angles on the mixed monolayer still declined linearly. The difference in shape between the titration curves of polyethylene and the monolayers on gold at high pH thus appears to be real.

Discussion

Acidity of Carboxylic Acids at the Surface of Monolayers on Gold. Ideally, we would like to extract thermodynamic quantities, such as the pK_a or p$K_{1/2}$, from the titration curves. In practice, the titration curve of the pure acid surface is cut off by $\theta_a = 0°$, and the relationship between α and $\cos\theta$ is unclear, preventing the determination of either of these quantities. A value that we can extract from these data is the pH at which significant ionization (in the sense that it causes a measurable change in the contact angle) first occurs.

Most of the previous studies[17,24,26–28] on carboxylic acids at interfaces yielded estimates of the pK_a in the range 7–10. The apparent pK_a is not, in general, a unique quantity. Even if the intrinsic pK_a is a constant, field effects can cause the apparent pK_a to increase with the degree of ionization, α. The values of pK_a quoted have generally been taken to be the pH of half-ionization, p$K_{1/2}$, which is a well-defined quantity. In addition to double-layer effects, the pK_a may vary with α due to a range of local environments of the carboxylic acid groups or from specific effects such as ion pairing or H-bonding. Some authors[24,26] have attempted to use the Gouy–Chapman theory to correct for the effects of the electrostatic double layer and hence to obtain an intrinsic pK_a for the carboxylic acids. The values of pK_a that they obtained were generally 1–2 pH units higher than the solution value. Other authors have criticized this approach[51] and have obtained results incompatible with Gouy–Chapman theory.[18,22] Whatever the details of the dependence of the pK_a on α may be, field effects do not change the pH of the onset of ionization. This pH is clearly higher on the monolayer of $HS(CH_2)_{10}CO_2H$ ($\sim$6) than for carboxylic acids in aqueous solution ($\sim$3). The onset of ionization occurred at the same pH on the monolayer of $HS(CH_2)_{10}CO_2H$ and on PE–CO_2H, which suggests that the most ionizable groups are in similar environments in these two surfaces.

As the carboxylic acids at the surface of the pure acid monolayers were progressively diluted with methyl groups, the onset of ionization moved to higher pH: from pH 6 for the 100% acid surface to pH 9 for the 14% acid surface. In part, this shift is only apparent, arising because a higher proportion of the carboxylic acids in the dilute surfaces must be ionized before a measurable change in the contact angle occurs. In part, a real shift arises from the changing environment of the carboxylic acids. The effects of structure and environment on acidity in solution are well-known[52] and suggest at least two factors that might contribute to the decrease in the intrinsic acidity of carboxylic acids at the interface, relative to carboxylic acids in solution, and to the decrease in acidity with decreasing polarity of the interface. First, the ions formed by dissociation of the carboxylic acid are strongly stabilized by "electrostatic solvation",[53] the strength of which is dependent on the dielectric constant of the medium. For example, the pK_a of acetic acid increases from 4.7 in pure water to 10.1 in 82% dioxane/18% water.[54] Replacing carboxylic acids at the monolayer–water interface by methyl groups decreases the local dielectric constant and might thus decrease the acidity of the carboxylic acids. Second, the steric bulk of adjacent chains at the surface of the monolayer might hinder the formation of hydrogen bonds between the carboxylic acids and water. An analogy from solution chemistry is the difference between the pK_a of *tert*-butylmethylneopentylacetic acid (6.97) and acetic acid (5.55) in 1:1 methanol/water.[55]

The flexibility of the technique of self-assembly will allow several natural extensions of the work presented in this paper. For example, by employing a methyl-terminated chain that is slightly longer than the carboxylic acid terminated chain, the acidity of the carboxylic acids could be monitored as a function of the depth that they are buried below the monolayer–solution interface. Alternatively, other functional groups could be introduced into the surface of the monolayer in order to stabilize or destabilize the carboxylate anions.[18,56]

Effect of the Energy of Reaction on the Contact Angle. One of the most puzzling, and potentially most interesting, aspects of this work is the apparent difference in the titration behavior of the monolayers containing CO_2H groups and of PE–CO_2H at high pH.[57] It is possible that the titration curves of the monolayers do

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(57) "When one's experimental findings are not quite those anticipated, the proper course is not to minimize, but to maximize the discrepancies, because by doing so new discoveries are made": the philosophy of N. K. Adam (Danielli, J. F. In *Monolayers*; Goddard, E. D., Ed.; Advances in Chemistry 144; American Chemical Society: Washington, DC, 1975; pp 1–8).

(58) The electrolyte concentration is too high for Gouy–Chapman theory to apply at all distances from the surface, and some form of Stern layer probably exists. The Gouy–Chapman theory does, however, provide us with a simple, order of magnitude calculation of the broadening of the titration curve due to field effects.

(59) It should be possible to resolve this question with monolayers incorporating a more acidic carboxylic acid, such as an α,α-difluoro acid. With mixed monolayers of this compound with the methyl-terminated thiol of the same chain length, a greater range of pH above the pK_a could be probed.

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Table I. Measured and Predicted Values of $\gamma_{\mathrm{ll'}}$ × Slope of cos θ against pH for Various Mole Fractions of Carboxylic Acid in Mixed Monolayers of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$

χ_{CO_2H}	expt, mN/m[a]	theory, mN/m[b]
0.14	1.7	6
0.25	5.3	11
0.32	5.8	14
0.41	6.2	18
0.73	7.3	32
1.00		44

[a] Derived from the linear portions at high pH of the curves in Figure 3. [b] Calculated from (16) with $n = 4.7 \times 10^{14}$ cm^{-2} for the 100% acid surface, $\gamma_{\mathrm{ll'}} = 50$ mN/m.

actually level out but not at basicities accessible with aqueous drops. The titration curve would have to be much broader for the monolayers than for PE–CO_2H. Within Gouy–Chapman theory, the maximum broadening of the titration curve due to double-layer effects would be 3 pH units under our experimental conditions and less on the monolayers containing fewer carboxylic acids.[58] Even after adding this broadening to the width of a titration curve of a monocarboxylic acid in solution (~2 pH units), we would expect to see the titration curves level out in the accessible range of pH. If, in addition, the intrinsic pK_a varied with α (that is, the monolayers behaved as polyacids), it is possible that a sigmoidal titration curve might extend beyond pH 14. We note, however, that none of the previous studies on carboxylic acids at aqueous interfaces suggested that carboxylic acids remained unionized at pH 14. Furthermore, it is not clear why the titration curve should be much broader for monolayers than for PE–CO_2H. In PE–CO_2H, the intrinsic pK_a of the carboxylic acids may, in principle, be influenced by electronic and steric effects, by variations in the dielectric constant of the local environment, and by H-bonding between carboxylic acids and carboxylate anions. In monolayers, only the last of these effects is likely to be significant. Further experiments will be necessary to determine incontrovertibly the form of the titration curves of the monolayers at high pH.[59]

If, in fact, the titration curves do not level out at high pH, then it is likely that the free energy of ionization is instrumental in determining the contact angle. The form of the contact angles agrees qualitatively with the theoretical prediction of (16), but refinement of the theory (or a better understanding of the data) will be necessary for quantitative agreement. The observed slopes are less (by a factor of 2–4) than those predicted from (16) and vary little with the composition of the surface, contrary to the linear dependence on n predicted theoretically (Table I).

Reactive Spreading: General Comments. The contact angle titrations of the carboxylic acid surfaces raise the general question of how best to incorporate the energy of reaction into the theory of wetting. Reactive spreading is a complex topic that has not been extensively studied theoretically. The models presented by Holmes-Farley et al.[11] and in this paper are by no means the only ones for reactive spreading. The early study by Hare and Zisman[60] of the spreading of *n*-alcohols and *n*-alkanoic acids on high-energy surfaces, such as silica, alumina, and platinum, was consistent with neither of these models. The liquids in that study adsorb onto silica, alumina, or platinum and form oriented monolayers that expose nonpolar methyl groups at the monolayer–liquid interface. The model of Holmes-Farley et al. would predict spreading of these liquids due to the high value of γ_{sv}. The model presented here would predict spreading because of the large negative free energy of adsorption of the alcohols and acids on the substrates. The liquids did not spread, however, and exhibited sharp three-phase lines and contact angles typical of substrates coated with a preadsorbed monolayer of the liquid. In the experiment of Hare and Zisman, the vapor pressures of the liquids were sufficiently high that monolayers might have adsorbed from the gas phase in advance of the drop edge. We have observed the same result, however, for less volatile liquids, such as hexadecanethiol on gold or octadecyltrichlorosilane on glass.[61] Recent advances in the theory of spreading[62] suggest that a thin precursor film extends in front of an advancing drop edge. A monolayer film, which would not be wetted by the liquid, could adsorb onto the substrate from the precursor film. The free energy of formation of the monolayer would be dissipated in the precursor film. The drop of liquid would only spread until the contact angle reached the value of the advancing contact angle on the monolayer-coated substrate. We note that if ionization of PE–CO_2H were to occur beyond the drop edge,[63] so that aqueous drops spread over a surface with the same degree of ionization as the surface beneath the drop, an approach based on relative hydrophilicities of functional groups, such as that developed by Holmes-Farley et al.,[11] may well be correct. If the monolayer-forming material is present as a dilute solution (~1%) in a solvent that does not wet a monolayer-coated surface, a range of interesting behavior may occur.[61] For example, the drop may first spread and then retract, or it may travel across the surface.[64] A detailed discussion of these phenomena is beyond the scope of this paper.

It is unlikely that any single model applies to all cases of reactive spreading. The actual behavior may depend on the rate and free energy of reaction, the viscosity and surface tension of the drop, the wettability of the substrate before and after reaction, and the heterogeneity of the surface.

Conclusions

The environment of carboxylic acids at the solid–liquid interface can be controlled by using mixed monolayers of thiols adsorbed from solution onto gold. The contact angle of water on monolayers formed by coadsorption of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}CO_2H$ was constant at low pH and decreased at high pH. The shape of the titration curve was qualitatively different from that on oxidized polyethylene (PE–CO_2H). The free energy of ionization may have a greater influence on the contact angle of water on the monolayers than on PE–CO_2H. On PE–CO_2H, consideration of the different hydrophilicities of the carboxylic acids and carboxylate ions leads to a plausible model for the interpretation of the titration curves.[11] The titration curves of the monolayers agree qualitatively with the predictions of a simple model in which changes in θ are due to the free energy of ionization. A better theoretical understanding of reactive wetting will be necessary to obtain quantitative agreement

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(63) This possibility was also raised by the authors.[11] When a drop of sulfuric acid was placed on a surface of polyethylene containing covalently bound, fluorescent dansyl groups, fluorescence was extinguished by protonation of the dansyl groups outside the region confined by the observed drop boundary, in addition to the surface beneath the drop (Holmes-Farley, S. R., unpublished results).

(64) In a dilute solution, there is insufficient adsorbate in the precursor film to form a densely packed monolayer. Even at high concentration, if formation of a monolayer were sufficiently slow, a drop could advance over the surface before a monolayer had time to adsorb from the precursor film.

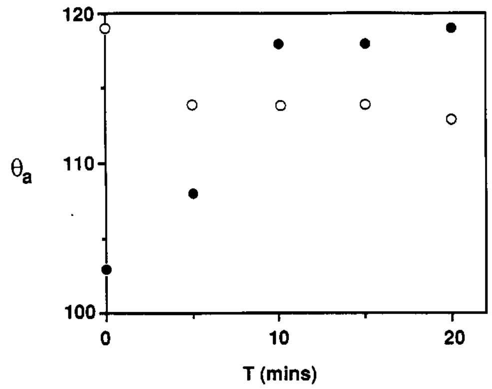

Figure 5. Contact angles of water at pH 4 on PE–CO$_2$H immersed in perfluorodecalin. Solid circles: initial contact angles of drops of water placed on the surface after the sample had been immersed in perfluorodecalin for *T* min. Open circles: contact angles of a drop of water placed on the surface 15 min after the sample had been immersed in perfluorodecalin; the abscissa represents the time after the drop was placed on the surface.

with the experimental data and to derive thermodynamic quantities such as the pK_a or p$K_{1/2}$ of the carboxylic acids at the monolayer–aqueous interface.

Reactive spreading is clearly a complex topic in which a number of different types of interesting behavior are possible. A full understanding will require not only consideration of the equilibrium thermodynamics of the three-phase line but also the dynamics of the spreading drop.

The acidity of the carboxylic acids at the surface of an organic monolayer on gold was lower than the acidity of carboxylic acids in solution and decreased as the interface was made progressively less polar. The changes in acidity can be understood by comparison with parallels in solution. At biological pH (~7), only the pure carboxylic acid surface was significantly ionized.

The modifications we made in the environment of the carboxylic acids at the surface of the monolayer were of a simple type—changes in the polarity of a planar interface. With self-assembled monolayers, it is easy to introduce disorder in the surface, include other functional groups at the surface, or vary the depth of carboxylic acids beneath the monolayer–liquid interface.[5,6,44] Such monolayers could yield valuable information on the effect of environment or specific interactions on acidity at interfaces. To use contact angles as an accurate probe of the acidity of such monolayers, however, we must first improve our understanding of contact angle titrations in particular and reactive spreading in general.

Experimental Section

Materials. The gold substrates for these experiments were prepared by either thermal or electron-beam evaporation of 1000–2000 Å of gold onto 3-in. silicon(111) wafers (Monsanto), which had been precoated with 50 Å of chromium to improve adhesion. These procedures produce polycrystalline films with a strong (111) texture.[14,65] The wafers were stored in polypropylene containers (Fluoroware) until use, which was generally within 1 day of evaporation. Ethanol (US Industrials Co.) was deoxygenated with bubbling nitrogen. Hexadecane (Aldrich, 99%) and cyclooctane (Aldrich, gold label) were percolated twice through neutral, Grade 1 alumina, after which they passed the Bigelow test.[66] Perfluorodecalin (PCR) was distilled and percolated through neutral, Grade 1 alumina. Water was deionized and then distilled in a glass and Teflon still. Undecanethiol and 11-mercaptoundecanoic acid were available from previous studies.[3,15] Polyethylene carboxylic acid (PE–CO$_2$H) was provided by S. R. Holmes-Farley and was prepared by chromic acid oxidation of LDPE film according to established procedures.[11]

Preparation of Monolayers.[67] The gold-coated wafers were cut into slides (ca. 1 cm × 3 cm), rinsed with ethanol, and blown dry with a stream of argon before being immersed in solutions of thiols overnight at room temperature. These solutions were freshly prepared in deoxygenated, absolute ethanol. The mole fractions of undecanethiol and 11-mercaptoundecanoic acid were varied while keeping the total concentration of thiols in the solutions constant at 1 mM.

Contact Angles. All measurements of contact angles were advancing angles and were performed with a Rame-Hart Model 100 goniometer.

1. **Measurements under Air.** Slides were removed from the solutions from which the monolayer had been adsorbed, rinsed with ethanol, blown dry with argon and placed in an environmentally controlled chamber near 100% relative humidity. A 1-μL drop of distilled water (2 μL for contact angles over ~80° to improve accuracy) was formed at the end of a PTFE-coated, blunt-ended needle. The needle was lowered until the drop touched the surface and then removed. As the drops detached themselves from the needle, they advanced over the surface.

2. **Measurements under Cyclooctane and Perfluorodecalin.** To measure contact angles under cyclooctane and perfluorodecalin, we replaced the environment chamber with a glass tank containing two supports upon which a slide could be placed. Both perfluorodecalin and cyclooctane were saturated with distilled water before being placed in the tank. In cyclooctane, a drop of water was formed at the end of a needle, as above, and lowered through the cyclooctane to the surface of the gold slide, and the needle was then removed. For contact angles over about 140°, the drop of water adhered better to the needle than to the surface: for these surfaces, drops of water were allowed to sink through the cyclooctane onto the slide. In perfluorodecalin, the samples were placed upside down on the supports, and drops of water were raised until they touched the lower surface of the sample (captive drop technique). The contact angles on samples of PE–CO$_2$H immersed in perfluorodecalin changed with time (Figure 5). Stable contact angles were obtained by immersing the polyethylene in the perfluorodecalin for at least 10 min before placing a drop of water on the surface and waiting a further 10 min before measuring the contact angles.

Titrations. Each titration of a monolayer on gold was performed on a single sample. Due to the reconstruction of polyethylene, we used a fresh sample for each pH for the titration of PE–CO$_2$H under perfluorodecalin. The gold slides were rinsed successively with ethanol, 0.1 N HCl, distilled water, and ethanol and then blown dry with argon between each set of measurements. This cleaning procedure was necessary to keep contamination to acceptable levels. Each set of measurements comprised, where possible, eight drops at two different values of pH, placed alternately along the slide. For contact angles near zero, fewer drops than this could be placed on the slide at one time (a minimum of six measurements—both sides of three drops—were made for all the aqueous solutions that did not wet the surface). The contact angles were measured in the following order: 5, 8, 7, 2, 9, 4, 10, 6, 3, 12, 11, and 13. On the 41% acid surface, the contact angles at four values of pH were remeasured after the titration: the maximum difference between measurements at the same pH was 4°. The range of contact angles measured for a series of drops on a slide was normally less than 5°, with the exception of some samples with contact angles near 0° or 180°. The qualitative agreement between the contact angles on the two independently prepared sets of slides was excellent. Quantitatively, the contact angles in the two experiments varied by less than 5° in most cases, the principal exception being the slides adsorbed from a 3:2 solution of HS(CH$_2$)$_{10}$CO$_2$H/HS(CH$_2$)$_{10}$$_3$. In this case, the two curves were offset by about 8°, presumably due to errors in the preparation of one of the

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[67] Full experimental details may be found in ref 3 and 15.

Langmuir **1989,** *5,* 1378–1383

adsorption solutions. All the buffers were 0.05 M, with the exception of the pH 11 buffer, which was 0.1 M. The following buffers were used for the titrations under cyclooctane:malonic acid (pH = 2, 3), sodium phosphate (4, 12), acetic acid (5), maleic acid (6), HEPES (7, 8), boric acid (9,10) 1,3-diamino-2-propanol (11), and KCl (13). The pH of the buffers was within 0.1 unit of the values stated.

Acknowledgment. We thank S. R. Holmes-Farley and Ernest B. Troughton (Lord Corporation) and H. Biebuyck for valuable discussions during the course of this work.

Registry No. $HS(CH_2)_{10}CO_2H$, 71310-21-9; $HS(CH_2)_{10}CH_3$, 5332-52-5; Au, 7440-57-5.

UV Absorption Spectra of Azobenzene-Containing Long-Chain Fatty Acids and Their Barium Salts in Spread Monolayers and Langmuir–Blodgett Films

Takeshi Kawai, Junzo Umemura, and Tohru Takenaka*

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

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Surface pressures and UV absorption spectra of spread monolayers of azobenzene-containing long-chain fatty acids and their barium salts on the water surface have been simultaneously recorded as a function of surface area. The observed spectral changes upon compression have been discussed in connection with phase transitions and changes in the aggregation state of the azobenzene chromophores. Acids and their barium salts with an 8-carbon alkyl chain exhibit the phase transition from the liquid crystalline (fluid) to gel (two-dimensional-crystalline) phases with decreasing surface area. The compounds with a 12-carbon alkyl chain, however, are in the gel phase throughout the whole surface area examined. In the gel phase, all compounds form an H-aggregate. In addition, UV absorption spectra of Langmuir–Blodgett films deposited on quartz plates have been measured and compared with those of the spread monolayers on the water surface.

Introduction

In recent years, a great deal of interest has been devoted to the Langmuir–Blodgett (LB) films consisting of organized molecular assemblies in the form of ultrathin films. The molecular aggregation and orientation in LB films inherently depend upon those molecular states in spread monolayers on the water surface. Therefore, studies of characterizations of spread monolayers are essential to understand the molecular aggregation and orientation in LB films. Monolayers on the water surface have been studied in situ by means of surface potential,[1] resonance Raman spectroscopy,[2] and UV-vis absorption spectroscopy.[3,4] Recently, new techniques for studying monolayers on the water surface have been developed including synchrotron X-ray diffraction,[5,6] sum-frequency vibrational spectroscopy,[7] and infrared external reflection spectroscopy.[8] UV–vis absorption measurements on the water surface have also been facilitated by the use of a newly developed spectrophotometer with optical fibers and a multichannel detector.[9,10]

In this paper, we applied this technique to simultaneous measurements of UV absorption spectra and surface pressure of spread monolayers of azobenzene-containing long-chain fatty acids (Figure 1, abbreviated as mAnH, m = 8 or 12 and n = 3 or 5) and their barium salts (mAnBa) on the water surface. Changes in molecular aggregations in the spread monolayers upon compression were studied on the basis of wavelength shifts of the π–π^* transition band. Features of the surface pressure (π)–area (A) isotherms of these monolayers were discussed in connection with the molecular aggregation and orientation. Further, the molecular states of LB films transferred onto quartz plates were studied by recording polarized and unpolarized UV absorption spectra and compared with the results for the spread monolayers prior to the transfer.

Experimental Section

Four kinds of azobenzene-containing long-chain fatty acids used in this study were the high-purity products of Dojindo Laboratories which give respective single spots in thin-layer chromatograms. Water was purified with a modified Mitamura Riken Model PLS-DFR automatic lab still consisting of a reverse osmosis module, an ion-exchange column, and a double distiller. A Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough with a Wilhelmy balance was used for the π–A isotherm measurements as well as LB film preparations. Temperature of the aqueous subphase was controlled within an accuracy of ±0.3 °C by a Neslab Model Coolflow-25 water bath with a circulating pump. Monolayers of the acids were spread from dilute chloroform solutions (0.7 mg/mL, 100 μL) on the 900-cm^2 surface of pure water at pH 6.2 or on that at pH 7.7 containing 2

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