## Acid-base interactions in wetting

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Abstract-The study of the ionization of carboxylic acid groups at the interface between organic solids and water demonstrates broad similarities to the ionizations of these groups in homogeneous aqueous solution, but with important systematic differences. Creation of a charged group from a neutral one by protonation or deprotonation (whether -NH<sub>3</sub><sup>+</sup> from -NH<sub>2</sub> or -CO<sub>2</sub><sup>-</sup> from -CO<sub>2</sub>H) at the interface between surface-functionalized polyethylene and water is more difficult than that in homogeneous aqueous solution. This difference is probably related to the low effective dielectric constant of the interface ( $\varepsilon \approx 9$ ) relative to water ( $\varepsilon \approx 80$ ). It is not known to what extent this difference in  $\varepsilon$  (and in other properties of the interphase, considered as a thin solvent phase) is reflected in the stability of the organic ions relative to their neutral forms in the interphase and in solution, and to what extent in differences in the concentration of  $H^+$  and  $OH^-$  in the interphase and in solution. Self-assembled monolayers (SAMs)-especially of terminally functionalized alkanethiols (HS(CH<sub>3</sub>)<sub>"</sub>X) adsorbed on gold-provide model systems with relatively well-ordered structures that are useful in establishing the fundamentals of ionization of protic acids and bases at the interface between organic solids and water. These systems, coupled with new analytical methods such as photoacoustic calorimetry (PAC) and contact angle titration, may make it possible to disentangle some of the complex puzzles presented by proton-transfer reactions in the environment of the organic solid-water interphase.

*Keywords:* Contact angle titration; photoacoustic calorimetry; polyethylene carboxylic acid; contact angle; polymer surfaces; wetting; self-assembled monolayers.

#### 1. INTRODUCTION

Interaction of two condensed phases across an interface or interphase (the latter is usually a more appropriate word for organic solids) depends on the details of chemical interactions at/within that interphase. In exploring the details of the influence of the chemistry of the interphase on its properties, it is particularly useful to examine functional groups capable of undergoing acid-base reactions. Proton transfer between acids and bases in solution is the best understood class of organic reactions [1]. These reactions are usually fast: Systems consisting of acids and bases are often at thermodynamic equilibrium, and their energies can thus be analyzed in believable detail. Manipulation of the properties of the solidwater interphase through proton transfer to and from suitable functional groups in the interphase thus offers the opportunity to use simple, well-understood chemistry to influence, cleanly and selectively, one aspect of the molecular composition of the interphase, while leaving others—morphology, many interfacial mechanical properties, the character of non-acidic and non-basic species largely or entirely unchanged.

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Understanding the acidity of organic functional groups at interfaces is important in surface science in at least two contexts. First, it can help to rationalize and control the properties of materials: wetting, adhesion, surface electrical conductivity, tribology, and others of more purely technological interest. Second, it can help to define the fundamental physical properties and 'character' of the interphase—as distinct from any bulk phases present—by using equilibrium proton-transfer reactions as probes. The most relevant properties of an interphase from the vantage of controlling the ionization of groups contained in it would be the capacity of the interphase to support charge (either on an ionizable functional group or as a diffusible species, especially  $H^+$  or  $OH^-$ ), the accessibility of acids and bases in the interphase to potential proton donors and acceptors, and the stability of the interphase to changes in its state of protonation.

In this paper, we will show how the titration of acidic functional groups in the interphase yields useful information about the properties of the interphase: we will focus on the use of contact angle titration and photoacoustic calorimetry (PAC) to study polyethylene carboxylic acid and its derivatives. We will also illustrate the effects of titratable groups in the interphase upon interfacial reconstruction.

#### 2. THE PHYSICAL-ORGANIC CHEMISTRY OF INTERFACIAL ACIDITY

Measurement of the acidity of functional groups at the interphase between an organic solid and water is substantially more complicated than the corresponding measurement in homogeneous aqueous solution. We list below, without greatly detailed elaboration, some of the factors that contribute to this complexity (Fig. 1). For specificity, we will illustrate points using 'polyethylene carboxylic acid' (PE-CO<sub>2</sub>H), a material about which we have accumulated a substantial body of background information [2-10]. PE-CO<sub>2</sub>H is prepared by oxidation of low-density polyethylene film with chromic acid solution under specified conditions.



Figure 1. Schematic examples of different types of environments for an ionizable acidic functional group (O) in the interphase between an organic solid and water.

It has carboxylic acid and ketone or aldehyde groups as the only functionality in the oxidatively transformed interphase [2, 4].

(1) The interphase is a finite, heterogeneous region. The concept of a homogeneous, well-defined 'surface' (in the sense of the gold (111) crystal face) is not a good description of the functionalized region between the bulk polymer and homogeneous solution. This interfacial region is rough and heterogeneous on many scales [4].

(2) Local dielectric constant. The dielectric constant at any point in the interphase will be intermediate between that of the bulk polyethylene ( $\sim 2$ ) and bulk water (80). The local dielectric constant in the interphase may, of course, vary substantially from point to point, depending on the local structure in the interphase.\*

(3) Local polyacidic interactions. If the local volumetric density (the equivalent of the concentration in homogeneous solution) of carboxylic acid groups in the interphase is high, hydrogen bonding between them may serve to stabilize the protonated form of the system, and thus to increase the concentration of base required at equilibrium to remove protons [12, 13]. Similarly, if this density is high, charge-charge interactions between carboxylate anions (especially when poorly screened in a medium of low dielectric constant) will be unfavorable and may substantially hinder the introduction of further negative charges into the interphase, once ionization has started [14].

(4) Local dipole arrays. Ordered regions of the polymer could align dipoles originating in individual functional groups in ways that would be energetically favorable or unfavorable. The ability of the functional groups to relax to conformations having a lower energy would depend on the local viscosity. The mobility of functional groups within the interphase is another parameter that is not clearly understood in these systems, although movement of groups between the interphase and the bulk is well documented [7, 15].

(5) Interfacial water. Water close to interfaces appears, in some circumstances, to have properties sufficiently different from water in the bulk homogeneous liquid phase that 'interfacial water' can be considered to be a distinct liquid [16]. The extent to which water in, for example, a pore in polyethylene lined with carboxylic acid groups would have the same dielectric constant as water in the bulk solution is hard to judge.

(6) Local concentrations of hydronium and hydroxide ions. The  $pK_a$  of an acid in solution is defined in terms of concentrations [equation (1)].

<sup>\*</sup>The low interfacial dielectric constant of the interphase arises from the chemical heterogeneity in the interphase, which can be seen as a mixed 'solution' of functionalized and unfunctionalized polyethylene and water. Thus, this effect will be observed irrespective of the actual dielectric constant of the interfacial water. For experimental evidence pertaining to the dielectric constant of the interphase between  $PE-CO_2H$  and water, see ref. [4]. For a discussion of the properties of interfacial liquids, see ref. [11].

$$K_{a} = \frac{[H^{+}][A^{-}]}{[HA]}.$$
 (1)

The concentration of hydronium and hydroxide ions in homogeneous aqueous solution is a reasonably well-defined quantity over a wide range of concentrations. The corresponding 'concentration' in the vicinity of a functional group in an interphase is presently impossible to measure. Any measurement of  $[H^+]$  or  $[OH^-]$  in this type of environment can probably only be an estimate based on a relative scale. One can, in principle, assume the behavior of a reference acid in the interphase and measure the proton donor ability of another acid of interest relative to that reference. Assuming that the group being examined and the reference group experience the same local environment—an assumption that is probably incorrect in most cases—it is at least possible using this procedure to order acidities in the interphase.

Note that this procedure for comparing acidities is substantially less certain than that used in constructing acidity functions [1, 17] or in estimating acidities in non-aqueous or mixed aqueous-organic solvents [1, 18]. In both of these problems in measuring acidities in non-aqueous but still homogeneous solution, it is possible to extend the relative scales of acidity so that they are referenced directly to measurements of aqueous solutions in which 'p $K_a$ ' and 'pH' have their normal meanings. The strategies of using series of overlapping reference indicators (when constructing acidity functions) and of using the glass membrane electrode as a reproducible, if thermodynamically ill-defined, reference (as one technique for measuring acidity in non-aqueous solutions) have no direct counterpart in surface chemistry. It is thus not possible to measure the concentration or thermodynamic activity of hydronium ion or hydroxide ion in an interphase. Since both the medium in which the interfacial proton-transfer reactions occur-the interphase-and the concentrations of ions in the interphase are undefined, it is not possible to define a value of ' $pK_a$ ' for a functional group in an interphase using currently available techniques (Fig. 2). It may, however, be possible to define the value of the solution pH at which the functional group in the interphase is half-protonated [4, 6, 8, 9]. This value-which we call the  $pK_{1,2}$ —is a reproducible and useful number, but is less interpretable than the  $pK_{a}$ .



Figure 2. The estimation of a value of acidity in an interphase requires knowing both the concentrations of  $H^+$  and  $OH^-$  in the interphase and the concentrations of unionized and ionized functional groups. In the absence of complete information concerning all the species involved in ionization, it is only possible to talk about the *solution* pH at which *interfacial* ionization occurs.

(7) Surface reconstruction: changes in interfacial structure on ionization. The mobility of functional groups in polymers varies with (inter alia) the temperature, the molecular weight and molecular weight distribution of the polymer chains, and the extent to which the system is plasticized by low-molecular-weight components including the solvent [15]. Parameters such as local interfacial viscosity for PE-CO<sub>2</sub>H and its derivatives would be expected to be different in protonated and unprotonated forms [19]. Although, in principle, these parameters can be measured experimentally, only limited measurements have been made [3]. The extent to which the gross morphology of the interphase changes, and the influence of these changes on the ionization and swelling of functional groups during acid-base reactions remain to be established.

### 3. MEASUREMENT OF SURFACE ACIDITY

A wide range of experimental techniques have been applied with varying degrees of success to the measurement of the extent of ionization of groups at surfaces [4-6, 8-10, 20-23]. These measurements are often technically difficult, as well as difficult to interpret. Any method requiring the equivalent of a 'pH electrode' is probably not practical for measuring acidity in the microscopic volume of the interphase. Other electrochemical measurements are similarly limited, although techniques such as the measurement of electrophoretic mobility can provide some information about the density of fixed charge on the surface as a function of the pH [24]. As a result, most measurements of surface acidity have relied on spectroscopic examination of chromophoric groups [4-6, 23]. Infrared (IR) spectroscopy is, in general, difficult to apply in aqueous solutions, and Raman spectroscopy (aside from surface-enhanced Raman) does not have the sensitivity required for most studies of interfaces. Ultraviolet, visible, and fluorescence measurements are complicated by scattering from the interphase, and often by absorption by the bulk phases. The difficulty in identifying and introducing an appropriate chromophore for each spectroscopic technique often limits the usefulness of that technique.

We, and others, have experimented with protocols to avoid some of these problems. The experiments were sometimes practical, but the results were often ambiguous. For example, in an effort to apply IR spectroscopy in studying the ionization of interfacial acids, we equilibrated PE-CO<sub>2</sub>H film against aqueous solutions having known values of pH, removed the film from the water, blotted it until the majority of the superficial water had been removed, and measured the IR spectrum of the CO<sub>2</sub>H and CO<sub>2</sub><sup>-</sup> groups [4]. How closely the ratio of CO<sub>2</sub>H to CO<sub>2</sub><sup>-</sup> measured spectroscopically using this technique at any value of pH (and especially at high and low values of the pH) corresponds to that obtained when the film is in contact with the solution is difficult to establish absolutely, although the results were in surprisingly good agreement with those obtained using other methods, when comparisons were possible.

We have recently explored two new methods to try to provide procedures for measuring acidity that complement the existing methods. *Contact angle titration* measures the contact angle of drops of buffered aqueous solution on surfaces containing an ionizable functionality as a function of the pH of these drops [4–6,

8-10, 20-22]. *Photoacoustic calorimetry* (PAC) measures the photoacoustic signal from a surface as a function of the pH [23, 25]. Neither technique is a panacea, but each provides valuable information. Contact angle titration is amenable to a wide variety of surfaces, and is independent of the optical properties of these surfaces. PAC circumvents many of the optical problems associated with light scattering at rough surfaces.

The origin of contact angle titration was the elementary hypothesis that when functional groups ionize at a solid-water interface, their hydrophilicity (and the hydrophilicity of the interphase) increases. This change would be reflected in a change in the solid-liquid interfacial free energy,  $\gamma_{SL}$ , and thus, via the familiar Young's equation, in a change in cos  $\theta$  [equation (2);  $\gamma_{SV}$  and  $\gamma_{LV}$  are, respectively, the interfacial free energies of the solid-vapor and solid-liquid interfaces].

$$\cos \theta = \frac{\gamma_{\rm SV} - \gamma_{\rm SL}}{\gamma_{\rm LV}}.$$
 (2)

A plot of  $\theta$  (or of cos  $\theta$ ) vs. pH does, in fact, show an inflection resembling that expected for the titration of a functional group in solution (Fig. 3). This value of the solution pH at which the inflection is centered has, in several instances, been correlated with ionization of the interfacial functional group [4-6, 8, 20]. Thus, contact angle titration is, at least, a useful *qualitative* technique for examining certain types of ionizations.

The most important generalization to emerge from application of contact angle titration to derivatives of PE-CO<sub>2</sub>H is that the apparent acidities of functional groups in these interphases differ markedly from those in solution [4-6, 8]. This difference is uniformly in the sense expected if transformation of a neutral to a charged group were more difficult in the interphase than in solution. For most of the systems examined, the absolute value of the difference between  $pK_{1/2}$  and  $pK_a$  is 2-4 units, although in related studies of self-assembled monolayers, it



Figure 3. Contact angle titrations of three organic solids having interfacial CO<sub>2</sub>H groups: ( $\bullet$ ) = PE-CO<sub>2</sub>H; ( $\odot$ ) = Si/O<sub>2</sub>Si(CH<sub>2</sub>)<sub>15</sub>CO<sub>2</sub>H; (O) = AuS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H. The 'pH' in this plot is the pH of the buffered aqueous solution in contact with the sample, and the ' $\theta_a$ ' is the advancing contact angle. Although it is not possible to titrate a SAM of HS(CH<sub>2</sub>)<sub>10</sub>CO<sub>2</sub>H on gold under air, it is possible when the sample is immersed in a non-polar solvent, e.g. cyclo-octane.

appears that carboxylic acids present in relatively low 'concentration' in a nonpolar surface may not ionize until the pH of the aqueous solution is greater than 10 [21, 22].

As our exploration of the phenomena contributing to contact angle titration has continued, the subject has become more complex. It appears, for example, that the plateau in the titration curve observed for polyethylene carboxylic acid may be due to a limit in the hydrophilicity of the material (Fig. 4) [8]. This limit, in turn, is probably dependent on the procedure used for derivatization. We still have not resolved the relative contributions of thermodynamic and kinetic factors to the observed contact angle. For example, is the value of the advancing contact angle set, at least in part, by reactive spreading? That is, does the edge of a drop of alkaline water expanding on PE-CO<sub>2</sub>H (or a carboxylic acidterminated SAM) continue beyond some hypothetical 'equilibrium' value, driven by reaction of hydroxide ion with the carboxylic groups? The advancing and receding contact angles of water on PE-CO<sub>2</sub>H and its derivatives and on carboxylic acid-terminated SAMs on gold have different values [8, 9, 21]: What is the origin of this hysteresis, and what information can be derived from it? How important is the presence of a condensed water film on that part of the surface not covered by the drop [8]?

PAC is a spectroscopic technique that has characteristics of potentially great value in surface chemistry. In this technique, the sample is irradiated with a short pulse of light, and the dissipation of the energy absorbed by a chromophore into the solution as heat is detected in the form of an acoustic wave in the liquid film using a pressure transducer (Fig. 5) [25]. PAC is very sensitive, especially for systems showing weak absorbances due to sample against a very weakly



Figure 4. A plot of the advancing contact angle,  $\theta_a$ , of water on various functional derivatives of PE-CO<sub>2</sub>H against the hydrophilicity of the functional groups shows a limit at high values of hydrophilicity. The hydrophilicity is given by the Hansch parameter,  $\pi$ . This parameter is defined as  $\pi_x = \log P_x - \log P_H$ , where  $P_H$  is the partition coefficient of the parent compound, R-H, between two solvents, and  $P_x$  is the partition coefficient of the substituted compound, R-X. The values shown here were derived using benzene as the parent compound, and water and 1-octanol as the solvents (see ref. [27]).



Figure 5. Representative titration curves for chromophoric acids and bases at a polyethylene-water interphase, and comparison with curves for the same groups in water. The vertical axis is the normalized intensity of the photoacoustic signal. The inset shows representative photoacoustic waves arising from dansyl groups at low (-----) and high (-----) values of pH, and from the background (----). The upper inset shows signals arising from dansyl groups attached to polyethylene; the lower inset shows signals arising from dansyl groups in aqueous solution. The value of pH is the pH of the buffered aqueous solution in which the derivatized polyethylene is immersed or in which the dansyl derivative is dissolved. S is the integrated intensity of the observed pressure wave (shown as the cross-hatched region in the inset);  $E_p$  is the power of the laser pulse.

absorbing backgroud. PAC is thus ideal for examining a strongly absorbing functional group located in the interphase between optically transparent polyethylene and water, because the technique has an intrinsically low background in this system and is also insensitive to scattering of light at the solid-liquid interface or by crystalline heterogeneity in the polyethylene.

We believe that PAC, when applicable, provides the best spectroscopic technique now available for analyzing the acidity of interfacial functional groups. Application of PAC to acidic and basic derivatives of PE-CO<sub>2</sub>H has given values of  $pK_{1/2}$  in agreement with those from contact angle titration [23].

PAC has, so far, been applied to a limited range of problems in surface acidity.

Nonetheless, in several cases, the normalized dependence of the PAC signal on the pH for similar functional groups in the interphase between polyethylene and water and in homogeneous aqueous solution has also suggested two additional, important facts. First, the titratable groups seem to comprise a single population: they fit a single titration curve with a single value of  $pK_{1/2}$  [23]. Second, a significant, non-zero PAC signal is observed for values of pH where no signal is expected, based on our previous observations [5]. The origin of this background is not presently understood.

# 4. THE INFLUENCE OF FUNCTIONAL GROUP ACIDITY ON SURFACE RECONSTRUCTION

One of the interesting characteristics of PE-CO<sub>2</sub>H and its derivatives is that the surface of these materials reconstructs on heating (and probably also reconstructs on mechanical deformation or on swelling with organic solvents) [7]. When the temperature of PE-CO<sub>2</sub>H is raised to a value close to the melting point of the polymer ( $T \approx 100^{\circ}$ C), functional groups migrate from the region of the interphase that determines the contact angle into deeper regions of the polymer [7, 15]. In these regions, the functional groups may still be observed by penetrating forms of spectroscopy (IR [4, 6], fluorescence [5], and to some extent XPS [4]), but they no longer influence wetting by water.

This reconstrution of the surface involves migration of a functional group from a near-surface region to the interior of the polymer. Particularly when the functional group is polar and in contact with water, this movement might be anticipated to be energetically unfavorable, mainly owing to the loss of solvation energy when the functional group moves from water to hydrocarbon. As expected, using this argument, the rate of thermal reconstruction of PE-CO<sub>2</sub>H is much slower when the sample is in contact with aqueous alkaline solution and the carboxylic acid groups are present in ionized form than when the carboxylic acids are protonated and the sample is dry [7, 15].

A remarkable example of the coupling of wetting to the ionization of functional groups is presented by the amide formed by reaction of PE-COCl with anthranilic acid (PE-anthranilamide) (Fig. 6) [20]. In contact with acid, this material is very hydrophobic; in contact with base, it becomes very hydrophilic. The difference between these two states of the material appears to be a small conformational change in the anthranilamide moiety (Fig. 7). At high pH, the surface arranges the anthranilamide groups to expose  $CO_2^-$  moieties; at low pH, only C-H bonds are exposed.

# 5. ACIDITY OF INTERFACIAL GROUPS. RESULTS FROM STUDIES OF PE-CO<sub>2</sub>H AND DERIVATIVES, AND COMPARISONS WITH SELF-ASSEMBLED MONOLAYERS

Protonation or deprotonation of functional groups at interfaces changes the atomic/molecular properties of these groups, and consequently changes the macroscopic properties of the surfaces. To what extent is it now possible to predict the acidity of functional groups in interphases from their properties in solution? Can one predict the influence of protonation or deprotonation on a macroscopic property such as wetting?



Figure 6. Representative pH titration curves for a number of aminobenzoic acid derivatives of PE-CO<sub>2</sub>H. The vertical axis is proportional to the cosine of the advancing contact angle of water,  $\cos \theta_a(H_2O)$ , on these surfaces. This measure, and not simply the contact angle  $\theta_a$ , is used because, from Young's equation,  $\cos \theta$  is directly proportional to the net free energy of interaction of the contact angle measurements. The horizontal lines represent the contact angles of several analogous but non-titratable derivatives of polyethylene. The solid curve is the contact-angle titration curve obtained from PE-CO<sub>3</sub>H.



Figure 7. Hypothesized change in conformation of 'polyethylene-anthranilamide' on going from low to high pH.

In broad terms, it is possible to predict trends and approximate magnitudes. It is not possible to predict accurate values for  $pK_{1/2}$  or contact angle based on a knowledge of  $pK_a$ , or even to rationalize satisfactorily many of the trends. Deprotonation of a carboxylic acid by aqueous hydroxide ion and protonation of an amine by hydronium ion both require higher concentrations of the base or acid by two to four orders of magnitude when the functional group is present in the interphase between  $PE-CO_2H$  or its derivatives and water than when that functional group is simply dissolved in water [4-6, 8, 20]. This effect could be due to a relatively low local dielectric constant in the interphase, or to a low concentration of hydroxide ion (hydronium ion) in the interphase (both relative to bulk solution), or to a combination of the two. Many of the properties of interfacial groups on  $PE-CO_2H$  suggest an interfacial dielectric constant of approximately 10 [4]. This value would tend to discriminate energetically against any charged species—whether covalently incorporated into the interphase or entering it by diffusion—relative to the bulk solution.

Polyacidity in the interphase could take two forms. First, during ionization of carboxylic acids by base there could be an accumulation of concentrations of weakly screened negative charges sufficiently high that unfavorable coulombic interactions would require increased concentrations of hydroxide to achieve complete ionization. Second, the carboxylic acid groups might be sufficiently close together that hydrogen bonds would stabilize them in protonated form and thus, also, would increase the difficulty of removing protons. Although the majority of carboxylic acid groups in PE-CO<sub>2</sub>H are clearly hydrogen bonded to one another (by infrared analysis) [4], polyacidity probably does not contribute to the apparent low acidity of the carboxylic acid groups in this material. Increasing the ionic strength of the aqueous solution in contact with PE-CO<sub>2</sub>H does not seem to change the curves obtained by contact angle titration [4]. This observation supports the assertion that polyacidity is not a major contributor to the acidity of carboxylic acid groups on PE-CO<sub>2</sub>H. This traditional test is, however, one that has been developed for use in homogeneous solution with soluble ions, and its applicability to the interphase is open to some question for two reasons. First, the solutions used in contact angle titrations are buffered and are already at a relatively high ionic strength (especially at low and high values of pH). Second, added metal halide salts might themselves be excluded from the interface, and might even be excluded preferentially relative to hydronium or hydroxide ion.

Comparison of the highly disordered solid-water interphase presented by PE-CO<sub>3</sub>H and the more ordered interfaces presented by self-assembled monolayers suggests that the two are governed by similar rules. The carboxylic acid groups in SAMs also require contact with a strongly basic solution to accomplish their ionization [21]. (Corresponding studies with amine-terminated SAMs are complicated by the high reactivity of the amino group, which leads to ready contamination of the surfaces [26].) It is not possible to define a value of  $pK_{1/2}$  for  $CO_2H$  groups incorporated into SAMs, since no plateau in the curve of  $\cos \theta$  vs. pH is observed at high values of pH [21]. The magnitude of the shift in *onset* of ionization can, however, be defined, and can be larger for SAMs than for PE- $CO_2H$ . Since this shift toward high values of pH becomes larger as the carboxylic acid groups become more dilute at the interface [21], the most probable explanation for the low apparent acidity of these groups is a low local dielectric constant at the monolayer-water interface. To what extent the low local dielectric constant influences the energetics of converting CO<sub>2</sub>H to CO<sub>7</sub> groups, and to what extent it influences the partitioning of hydroxide ion or hydronium ion between the interface and the bulk solution, remains to be established.

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The only macroscopic property that correlates well with ionization of interfacial groups is wettability by water. As expected, converting neutral to charged groups at the interface increases the wettability of the interface by water. In very general terms, the contact angle of water on derivatives of PE-CO<sub>2</sub>H correlates with the hydrophilicity of the functional groups (as reflected in their Hansch  $\pi$ values-group additivity parameters related to the free energy of transfer of the group between water and octanol) [27, 28]. The correlation is, however, odd, in the sense that the influence of functional group polarity on wetting seems to 'saturate' at high values of polarity [8]. Although increasing the polarity of the group X in a series of materials having the composition PE-X decreases the contact angle for groups of low and intermediate polarity, a number of highly polar groups give rise to similar, non-zero values of the contact angle [8]. We have offered a hypothesis to explain these data based on the idea that, for highly polar interfacial functional groups and at high relative humidity, the surface will consist mostly of adsorbed water, independent of the polarity of the groups at the interface. We have not, so far, devised a direct test of this hypothesis.

### 6. SUMMARY

The behavior of acidic and basic functional groups at interfaces is an apparently simple subject with many complex features. As with many simple reactions, it is difficult to disguise ignorance. We know that these functional groups follow patterns of reactivity similar to those observed in solution, but that there are important systematic differences between behavior in the interphase and in solution. There is no sound theoretical understanding of these differences, and, at the moment, no experimental method applicable to the measurement of those properties—interfacial thermodynamic activities of hydronium and hydroxide ion, microscopic dielectric constant and solvating capacity of the interphase, structure, properties, and thermodynamic properties of the three-phase solid– liquid-vapor region at the edge of a reactive liquid drop on an acidic or basic surface—that would be most helpful in resolving these issues.

New experimental techniques are, however, now appearing that promise to renew the study of interfacial acid-base reactions. SAMs are structurally well-defined systems that will serve as tractable models for these studies [21, 22]. PAC and contact angle titration offer new approaches to determining the extent of ionization, and to correlations of ionization and wetting. Microfabrication may make possible the construction of microelectrodes, and the study of local concentrations [29]. X-Ray techniques are offering increasing resolution in the study of the structure of interfaces between condensed phases [30, 31].

The simplest subjects may teach the most profound lessons in science. We hope that study of simple acid-base reactions at solid-water interfaces will provide fundamental information concerning these ubiquitous systems.

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