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**Quantifying Acid–Base Properties of Organic  
Functional Groups at a Polyethylene–Water Interface  
by Photoacoustic Calorimetry**

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This paper describes the use of photoacoustic calorimetry (PAC)<sup>1</sup> to characterize acid–base equilibria involving organic chromophores covalently attached at the interphase between surface-functionalized polyethylene (PE) film<sup>2,3</sup> and water. We use proton transfer reactions to define the polarity and solvating capability of the interphase between organic surfaces and water.<sup>4</sup> Characterizing these physical–organic properties of interphases is difficult: light scattering at interfaces (especially *rough* interfaces) complicates many UV–vis absorption and fluorescence methods; infrared spectroscopy cannot be applied routinely to systems involving water; thermometric and conductometric methods are insensitive for solids having low surface areas. The measurement of the contact angle of buffered water on surfaces as a function of pH—“contact angle titration”—yields valuable information about acid–base equilibria,<sup>3</sup> but depends on unverified assumptions.<sup>5</sup>

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**Table I.** Experimental Values of  $pK_{1/2}$  and  $pK_a$  for Organic Functional Groups in Aqueous Solution and at a Polyethylene-Water Interface<sup>a</sup>

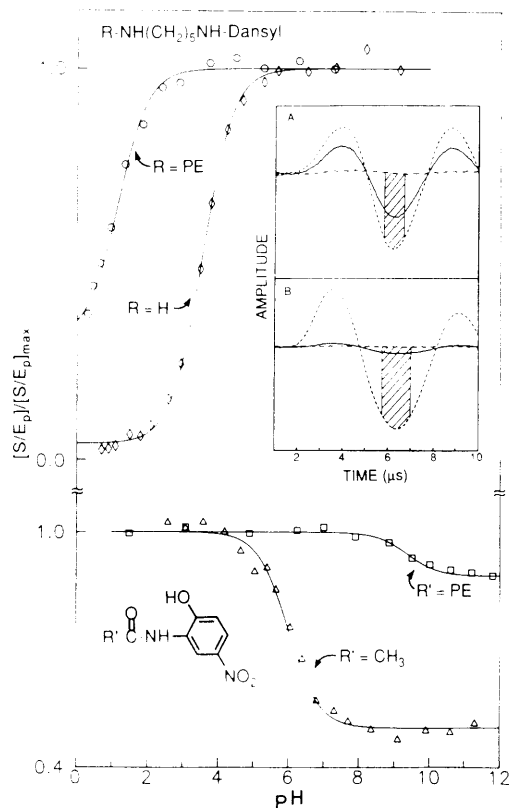
	R = PE-CO <sup>b</sup>		R = H	
	$pK_{1/2}$	<i>n</i>	$pK_a$	<i>n</i>
RNH(CH <sub>2</sub> ) <sub>2</sub> NH-dansyl	0.56 ± 0.11	3	3.52 ± 0.03 <sup>c</sup>	2
RNH(CH <sub>2</sub> ) <sub>5</sub> NH-dansyl	1.2 ± 0.2 <sup>c</sup>	3	3.57 ± 0.09 <sup>c</sup>	2
RNHC <sub>6</sub> H <sub>3</sub> -3-NO <sub>2</sub> -6-OH	9.3 ± 0.1	3	7.00 ± 0.10 <sup>d</sup>	2
RNHNHCOC <sub>6</sub> H <sub>4</sub> -4-OH	12.4 ± 0.2	3	8.29 ± 0.30	3

<sup>a</sup> Aqueous solutions of HCl and NaOH were used to vary the pH during these acid-base titrations. The addition of these trace amounts of acid or base themselves cause no change in the PAC signal other than that due to degree of protonation of the substrate. The errors listed are 1 standard deviation of the number of independent experiments indicated by *n*. <sup>b</sup> All films were prepared from PE-CO-Cl as described in ref 8. A fresh film was prepared for each measurement. Any acid chloride functionality that was not converted to the appropriate amide is hydrolyzed during the synthetic workup. <sup>c</sup> See refs 8 and 13 for previous estimates of these values. <sup>d</sup> The  $pK_a$  of R = COCH<sub>3</sub>, as determined by PAC, is 6.02 ± 0.03 (*n* = 2).

We have used as substrates for this work surface-oxidized polyethylene films ( $\rho = 0.92$  g/mL; 100  $\mu$ m thick; pretreated to remove additives) to which were covalently attached 1-(dimethylamino)naphthalene-5-sulfonyl (dansyl) or phenolic groups (Table I).<sup>6</sup> These functionalized polyethylene films were suspended in water in a standard UV-vis cuvette and irradiated with a low-energy, unfocused light pulse from a nitrogen laser (337.1 nm; ca. 10  $\mu$ J/pulse; 2-mm-diameter spot).<sup>7</sup> The photoacoustic signal generated from each of the four films exhibited an excellent signal-to-noise ratio (Figure 1). Control experiments established that these PAC signals were due to the attached organic functionality and that each system was stable to irradiation: (i) Both unfunctionalized (PE-H) and oxidized (PE-CO<sub>2</sub>H) polyethylene films gave weak, pH-independent PAC signals. (ii) The functionalized polyethylene films that gave strong, pH-dependent signals showed contact angle titration behavior consistent with that reported earlier.<sup>8</sup> (iii) The intensity of the PAC signal from a functionalized film at constant pH was linearly proportional to laser energy.<sup>7,9</sup> (iv) The PAC signal remained invariant over long periods of time at fixed pH, indicating that no solvolytic chemistry occurred. (v) Extended irradiation had no effect on the PAC signal, implying that no beam damage occurred. (vi) Upon removal of the films from the cuvette, no PAC signal was detected in the aqueous solution.

The changes in the PAC signal as a function of the degree of protonation are due to changes both in the heat release quantum yield,  $f_h$ , and in the extinction coefficient of the protonated/deprotonated substrates. For example, the dansyl moiety has an extinction coefficient of  $\sim 4000$  M<sup>-1</sup> cm<sup>-1</sup> at 337.1 nm while the protonated dansyl moiety has a value of  $\sim 200$  M<sup>-1</sup> cm<sup>-1</sup>.<sup>10</sup> In addition, the fluorescence quantum yields of these two species are quite different. The pH titration data generated in these PAC experiments were readily fit by a standard  $pK_a$  titration expression.<sup>11</sup> The similar quality of the fit for the data from the films and from solution suggests that the PAC experiment samples a single population of functional groups in the interphase.

The value of  $pK_{1/2}$ —the solution pH at which the surface ionization of a functional group in the interphase appeared to be half complete—differed from the value of  $pK_a$  for that group in homogeneous solution in the direction predicted if one assumes it is more difficult to create a charge in the interphase than in



**Figure 1.** Acid-base titration curves for the molecules and polyethylene films indicated. The solid lines are the calculated titration curves.<sup>11</sup>  $S/E_p$  refers to the observed PAC signal normalized to laser energy and is based on the basic PAC equation,  $S = KE_p f_h (1 - 10^{-4})$ . Inset A: Photoacoustic waves at pH = 11.5 (---) and pH = 0.3 (—) for the dansyl film shown, and for distilled water (···). Inset B: Photoacoustic waves at pH = 10.0 (---) and pH = 0.8 (—) for the dansyl derivative in homogeneous solution, and for distilled water (···). For both insets, the hatched area indicates the "integration" performed to obtain  $S$ , the experimental value of the photoacoustic signal.

solution.<sup>2,3,5</sup> The magnitude of these shifts (2.3–4.1 pH units) is consistent with a previous characterization of a PE-dansyl-water interphase as having an effective dielectric constant  $\epsilon \approx 9$ .<sup>8</sup> For all functionalized films examined, the fractional change in the amplitude of the PAC signal for the functionalized films on going from low- to high-pH asymptotes was consistently smaller than that for the same chromophore in solution (Figure 1). Experiments are in progress to define the cause of the changes in relative amplitudes.

Our results demonstrate that PAC is a simple and sensitive method to quantify acid-base equilibria at the interface between polyethylene film and water. This photoacoustic technique has the advantages that it is insensitive to scattering of light from the interface and is easily applicable to systems in which water is the liquid phase. For PAC to be useful as a technique for characterization of interphases, the signal due to molecules at the interphase must be large compared to that arising from bulk solid or liquid phases. The chromophore used to label the interphase and to characterize the degree of ionization should therefore have a high extinction coefficient relative to that of the solid and liquid phases. The system used here—with optically transparent polyethylene and water as the two phases and strongly absorbing functional groups attached at the polyethylene-water interphase—takes advantage of one of the strengths of photoacoustic spectroscopy: the ability to detect very weak absorption against a near-zero background.<sup>12</sup>

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(10) Measured in this work.

(11) The procedure used is described in supplementary material in the microfilm edition.

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We believe that PAC has the characteristics to be a highly useful tool for studying interphases between optically transparent solid and liquid phases, provided that an appropriate reporter group with a suitable extinction coefficient can be localized in that environment.

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**Supplementary Material Available:** Methodology for extracting  $pK_a$ 's from the data generated in the PAC studies described in the paper (2 pages). Ordering information is given on any current masthead page.