

QUANTIFYING ACID-BASE PROPERTIES OF ORGANIC FUNCTIONAL GROUPS AT
A POLYETHYLENE-WATER INTERFACE BY PHOTOACOUSTIC CALORIMETRY

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Supplementary Material

For homogeneous solutions; the expression used was: $S/(KE_p) = \{(1-10^{-A})/(A[K_a + 10^{-pH}])\} \{S_{ini}10^{-pH} + S_{fin}K_a\}$, where S is the amplitude of the observed photoacoustic wave (taken as the integrated areas shown in Figure 1), K is the instrumental sensitivity parameter, E_p is the irradiation energy, A is the total absorbance of the solution at that pH, K_a is the acidity constant, S_{ini} is the limiting value of S at low pH and S_{fin} is the limiting value of S at high pH. For the films, we derived an approximate solution to the equations relating photoacoustic signal to the acidity constant: $S/(KE_p) = \{S_{fin}10^{-pH}\} + \{S_{fin}K_{1/2}/(K_{1/2} + 10^{-pH})\}$. The approximation used -- that the photoacoustic signal observed for a two component system is a summation of the individual PAC signals, which are themselves assumed to be linear with respect to concentrations for each component -- is expected to affect the values of pK_a (Table I) by

<0.1 pK_a units. For both equations, the observed data are fit to the equation and S_{ini}, S_{fin} and pK are allowed to vary to determine the bestfit. These fitting methods were tested against "synthesized" data which showed that for data of the type described in this manuscript, even where the plateau regions at high or low pH are not fully experimentally accessed, the uncertainty on this fitted pK value is ≤0.1 pK units. The simplex method was used for all fittings: Routh, M. W.; Swartz, P. A.; Denton, M. B. Anal. Chem. 1977, 49, 1422-1428. We used pK_{1/2} rather than pK_a to characterize the acidity of interfacial groups to emphasize that the meaning of pK_a for an interfacial group is ambiguous: the concentration and thermodynamic activity of protons in the interphase is not easily related to the pH of the bulk solution.