In Situ FTIR-ATR Analysis and Titration of Carboxylic Acid-Terminated SAMs

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The acid/base properties of surface-confined molecules can differ significantly from those in solution.[1−4] There is significant influence from the polarity of the surface, interfacial electrostatic fields, and the local structure of the solvent.[5,6]

Contact angle titration,[5−7] quartz crystal microbalance measurements,[8,9] amperometry,[10] voltammetry,[4,11−13] laser-induced temperature jump studies,[14] electrochemical titration,[15] double-layer capacitance measurements,[16] and chemical force microscopy measurements[17−22] have all been applied to the study of surface-confined carboxylic acids. While the reported protonation−deprotonation processes typically occur over a broader pH range than what is seen in aqueous solution, in each system there is only a single pK_a reported (between 5.5 and 9).

FTIR spectroscopy has also been applied to the study of COOH-terminated self-assembled monolayers (SAMs). Nuzzo et al.[23] found that SAMs of ω-mercaptohexadecanoic acid (MHDA) on gold exhibit a high degree of molecular orientation and that only a small fraction of the carboxylic acid groups are linked by hydrogen bonds, with an absence of head-to-head dimers. They proposed that ∼50% of neighboring COOH groups are bound by single hydrogen bonds, forming linear oligomers. Smith et al.[24] also reported a highly oriented MHDA SAM, but suggested the existence of slightly distorted head-to-head dimers.

In situ FTIR-ATR titration has been used by Cheng et al.[25] to study siloxane-anchored COOH SAMs. The reported increase of ∼2 pK_a units relative to alkyl carboxylates in solution is similar to that reported by Whitesides et al. for oxidized polyethylene surfaces[26−28] and for SAM systems.[29,30] We report herein an FTIR-ATR analysis of a carboxylic acid-functionalized siloxane-anchored monolayer that for the first time directly measures the balance among differently associated interfacial carboxylic acid groups on the surface and relates their hydrogen bonding with surrounding water molecules and/or among themselves to changes in chain conformation and carboxylate acidity. We also report the direct observation of two different pK_a values within a SAM array.

Using D_2O instead H_2O enhanced the ability to detect C=O signals that would have otherwise been obscured by water signals between $1600−1700$ cm^{-1}. With D_2O, residual water signals are small enough to be handled by background subtraction. Ionic strengths of all solutions were between 0.01 and 0.02 M.[31,32]

We further improved the spectral data by using thin (0.5 mm) two-side polished Si wafers as internal reflection elements (IRE). This increased the number of internal reflections by ∼20 times relative to standard 3 mm thick ATR elements. Using this IRE in a solution cell[25] and using an autotitrator and a peristaltic pump, we achieved excellent sensitivity and reproducibility.

The in situ creation of the carboxylic acid (Scheme 1) was also improved by using AlI₃ to cleave the ester while preserving monolayer integrity (i.e., it did not attack the siloxanes[33]). Both the ester and the acid-terminated SAMs were characterized by ellipsometry, XPS, contact angle, and FTIR measurements.

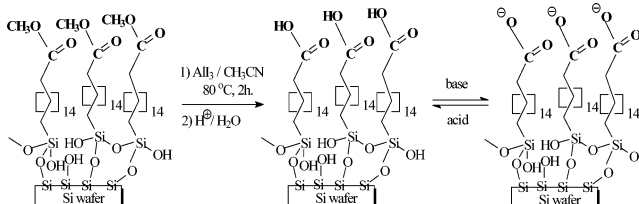**Scheme 1.** Siloxane-Anchored Carboxylate Monolayer

Figure 1 shows a series of FTIR-ATR difference spectra obtained at different pD values, with positive- and negative-pointing peaks at 1556 and 1704 cm^{-1} attributed to carboxylate anion and carboxylic acid moieties, respectively. The absolute intensity of the peaks increases with increasing pD because the reference being subtracted is the spectrum at pD = 2.0. A parallel experiment referenced to spectra at pD = 11.5 showed the same titration behavior. When the areas of the upward pointing peak in either experiment are plotted against pD, titration curves with pK_a values of 4.9 ± 0.4 and 9.3 ± 0.2 are obtained. The value on the y-axis of the observed plateau between the two pK_a values suggests that each represents ∼50% of the overall deprotonation process.[34]
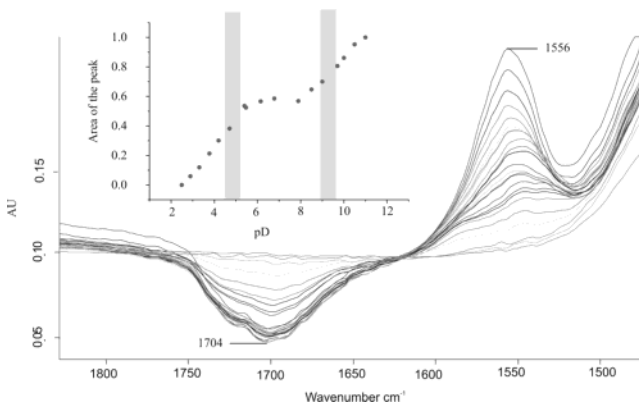

Figure 1. A series of difference FTIR spectra for a carboxylic acid-bearing SAM on a Si substrate. Spectra were taken while the surface was in contact with a D_2O solution (pD from 2.5 to 11.5, in increments of 0.2−0.5 pD units). In this experiment, the single beam spectrum of the monolayer under a pD = 2 solution was used as reference. The inset window plots the amount of carboxylate anion as a function of pD. The gray strips indicate the pK_a values (4.9 ± 0.4 and 9.3 ± 0.2) determined by second derivative analysis of four independent titrations.

The FTIR data also showed variation in the order of the alkyl chains. For pD = 2−5, the degree of order of the chains does not change (as seen in the consistent value of 2919 cm^{-1} for the CH_{2anti} stretch). However, this order increases for pD ≥ 9, as seen by the shift of CH_{2anti} to 2916 cm^{-1}.[35−37]

A deeper understanding of the structural details of the carboxylic acid species was obtained by curve-fitting the signal at $1760−1610$ cm^{-1}. This was possible for experiments using a reference spectrum of pD = 11.5 so that the IR peaks are in the positive direction. Figure 2 shows one such spectrum. At pD = 2.2−5.1, three
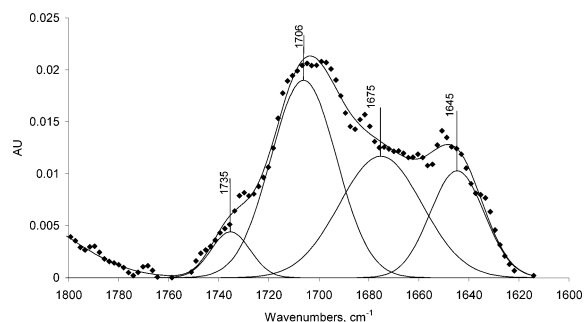
Figure 2. Curve-fitting of the COOD band at pD = 4.2. Dotted line is the experimental spectrum. Solid lines are the resolved components (Gaussian peaks, fixed peak widths, positions fixed as per values in Table 1) based on the second derivative method of deconvolution and the fitted sum of the resolved peaks ($R^2 = 0.991$). The peak at 1645 cm^{-1} is from water.

Table 1. Distribution of COOD Forms (Each Deconvolution $R^2 \geq$ 0.99; Data Are the Average of Four Independent Replicate Experiments)

pD ± 0.3	normalized relative intensities COOD species		
	1734 ± 3 cm^{-1}	1703 ± 3 cm^{-1}	1676 ± 2 cm^{-1}
2.2	21 ± 3	44 ± 3	35 ± 1
2.6	17 ± 2	50 ± 3	33 ± 1
3.2	13 ± 2	54 ± 3	33 ± 3
3.8	11 ± 1	58 ± 2	31 ± 1
4.2	7	52 ± 3	39 ± 1
5.1	5	59 ± 2	36 ± 2
6.1	0	58 ± 2	42 ± 2

components (1734 ± 3, 1703 ± 3, and 1676 ± 2 cm^{-1}) can be resolved, in addition to the residual water at 1645 cm^{-1}. The three bands are assigned[38] to the monomeric, dimeric, and oligomeric COOD species, respectively. At pD = 6.1, only two bands remain. The monomeric form (1734 cm^{-1}) is relatively less stable (Table 1) as the pD increases.[38,39] The relative amounts of the two different bridged species stay at a dimer:oligomer ratio of 1.5 ± 0.3. That 50 ± 10% of the COOD groups deprotonate at the first pK_a while monomeric COOD accounts for only 20% of the fully protonated COOD groups is due to equilibration of the monomer and the aggregates during the titration. The carboxylate anion peak (1556 cm^{-1}) also evidences pD-dependent changes in shape/position; however, these have been attributed to changes in the relative intensity of the antisymmetric stretching vibrations at 1542 and 1562 cm^{-1}.[39,40]

Lacking relative molar absorptivities for the different acid forms, these numbers cannot be translated into the actual abundance of the various forms. However, their coexistence within the monolayer and the more rapid disappearance of the monomer are clear. Regrettably, as deprotonation in base proceeds, the ratio of aggregated forms cannot be determined because the acid peaks are too small to be reliably deconvoluted.

The geometrically constrained diacid described by Rebek[41] is a useful analogue. Deprotonation of one carboxylic acid influences its intramolecular complexation to the other. The remaining hydrogen bond is strengthened, yielding pK_a values of 4.8 and 11.1.

Aggregates of acids also provide important precedent. The pK_a values of micellized fatty acids are reported between 8.6 and 9.7 (similar to our value of 9.3). Crystallization/precipitation occurs at pH 4−5.[42] Langmuir films of fatty acids show pK_a values at both 3.9 and 10.5,[37] again resembling the carboxylate SAMs.

Our results show that a carboxylic acid-bearing SAM is comprised of multiple bridged/unbridged forms at a water interface. Their protonation/deprotonation can be directly monitored. The intermolecular bridging influences SAM structure and chemistry.

Supporting Information Available: Preparation and characterization of the trichlorosilane and the SAMs, equilibria calculations supporting our model, and IR spectra (3000−2800 cm^{-1}) as a function of pD (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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