Adsorption and desorption of nonionic surfactants on silica from toluene studied by ATR-FTIR - Supporting Information

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Experimental setup

A schematic diagram showing the experiment flow setup used for ATR-FTIR experiments is shown in Figure S1.

Calculation of adsorbed amounts

In order to generate quantitative adsorption data from ATR-FTIR spectroscopy, an understanding of the propogation of the evanescent wave at the interface is neccessary. The electric field amplitudes depend on the refractive properties of the crystal and the adjacent medium or media. For a simple two phase system, Harrick showed that the field amplitudes in the x, y and z directions (E_x, E_y and E_z) can be calculated from the refractive indices of the crystal and adjacent phase,[1] n_1 and n_2 by using the relative refractive index ratio for a wave passing from one to the other, $n_{21} = n_2/n_1$, and the incident angle of radiation, θ:
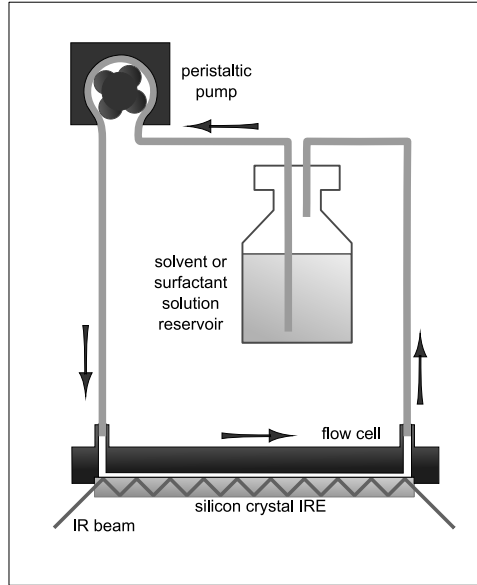
Figure S1: Schematic of the flow setup used for ATR-FTIR experiments.

$$E_x = \frac{2(cos\theta)\left[sin^2\theta - n_{21}^2\right]^{1/2}}{(1 - n_{21}^2)^{1/2}\left[(1 + n_{21}^2)sin^2\theta - n_{21}^2\right]^{1/2}} \tag{S1}$$

$$E_y = \frac{2(cos\theta)}{(1 - n_{21}^2)^{1/2}} \tag{S2}$$

$$E_z = \frac{2cos\theta sin\theta}{(1 - n_{21}^2)^{1/2}\left[(1 + n_{21}^2)sin^2\theta - n_{21}^2\right]^{1/2}} \tag{S3}$$

An alternative set of equations which account for the refractive properties of a thin film at the interface between the crystal and bulk solution is also available. However, based on the previous work of Nievandt *et al.* and others,[2,3] it was decided that the two-phase approximation would be most appropriate in this work. Because this study is concerned with kinetics of adsorption and desorption, and hence varying surface coverages, modeling a constant thin film of organic material is unrealistic. Additionally, due to the organic solvent used,

and considering the potential effect of solvent penetration into the surfactant layer, it is likely that the refractive indices of the surfactant 'film' and bulk solution/solvent may be very similar.

Interaction of the evanescent radiation with the less dense medium results in its attenuation by absorbance, and to effectively describe this, several other quantities must be calculated. Harrick defined two important variables - the depth of penetration, d_p, defined as the distance in the less dense medium taken for the evanescent wave to fall to e^{-1} of its original energy, and the effective thickness, d_e, defined as the thickness of material which would give the same signal in transmission as is obtained via ATR:[1]

$$d_p = \frac{\lambda}{2\pi n_1 (sin^2\theta - n_{21}^2)^{1/2}} \tag{S4}$$

$$d_e = \frac{n_{21} E_0^2 d}{cos\theta} \tag{S5}$$

Here, E_0 represents the electric field amplitude, which is dependent on the polarisation of the incident IR radiation, and can be calculated from Equations S1 to S3. For perpendicular polarization, the field amplitude is equal to E_y, and for parallel polarization, $E_0 = \sqrt{E_x^2 + E_y^2}$. If unpolarized IR radiation is used, as was employed here (or if the ATR instrument scrambles the polarization of the radiation) then an average value can be used,[4] calculated as $d_{e(av)} = (d_{e(perp)} + d_{e(para)})/2$.

Using Equations S4 and S5, the Sperline equation can be used to calculate the adsorbed amount (surface excess, Γ) of surfactant at the crystal interface:[5]

$$\Gamma = \frac{(A/N) - \epsilon C_b d_e}{1000\epsilon(2d_e/d_p)} \tag{S6}$$

In Equation S6, A is the integrated absorbance of the chosen band in the ATR spectrum, N is the number of solution-sensing internal reflections and ϵ is the molar absorption coefficient of the band determined from transmission measurements and the Beer-Lambert law.
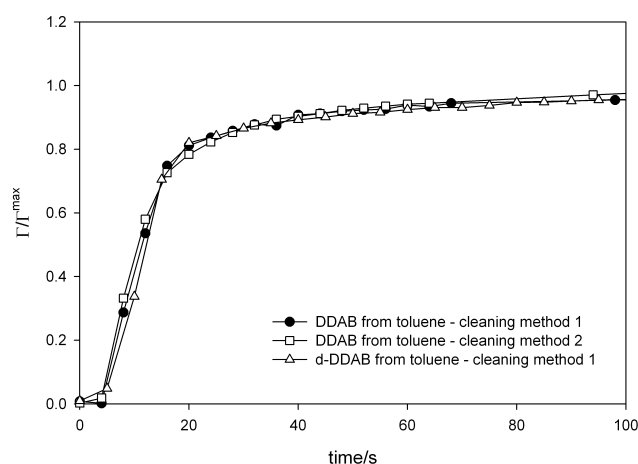
Reproducibility

Figure S2: Reproducibility of adsorption using a test surfactant, DDAB. Note that results have been scaled by dividing by the maximum adsorbed amount.

As surface preparation is so influential in surface adsorption experiments, to demonstrate the reproducibility of the ATR-FTIR measurements, and to verify that the cleaning procedure generated a consistent surface, several test experiments were conducted using different methods of cleaning the silicon crystal. For the first cleaning procedure, copious amounts of ethanol, 0.5 M HCl and deionised water were flowed over the crystal surface. A spectrum was then taken to check no hydrocarbon signal was visible in the region 3000-2800 cm^{-1}. For the second cleaning procedure, the crystal was carefully demounted from the cell, fol-

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lowed by mechanical abrading with a cotton bud in 0.5 M HCl, rinsing with ethanol and then DI water, drying in nitrogen and re-mounting in the cell. Again, a spectrum was taken to ensure no hydrocarbon signal could be seen. To check that desorption kinetics for the non-ionic surfactants were not affected by surface preparation/cleaning, desorption profiles were generated for $C_{12}E_3$ from the crystal when cleaned by each method. Additionally, a further test system for adsorption using the cationic surfactant dodecyldimethylammonium bromide (DDAB) was used. This surfactant was chosen as it adsorbs strongly from toluene, is easy to dry effectively, gives well-resolved, sharp peaks in the alkyl region and was available in deuterated form to check that no signal effects were noted for the bands in the C-H region. Results of these two reproducibility experiments are shown in Figures S2 and S3. The average deviation in reproduced experiments was less than 2%.
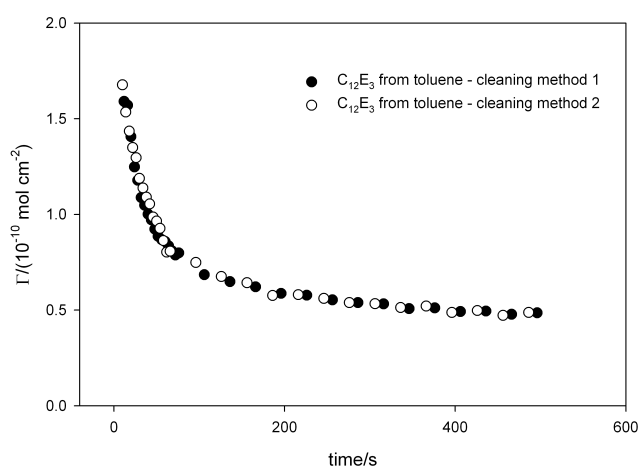

Figure S3: Reproducibility of desorption kinetics from the two methods of crystal cleaning/preparation for $C_{12}E_3$.

Overlapping bands

Because of the volumes of solvent used, it was not possible to run the experiments using deuterated toluene. Equally, the prohibitive cost of deuterated nonionic surfactants ruled out their use. Hence, the problem of overlapping hydrocarbon stretches from the methyl (C-H)s in toluene and those in the surfactants was encountered. As surfactant adsorbs, there is a slight decrease in the signal from toluene, as sensed by the evanescent wave, because some toluene molecules at the surface are displaced by surfactant. Hence, the apparent C-H stretching signal from the surfactant is slightly reduced by the 'missing' toluene. This effect is surprisingly small, as (a) in the integration, the contribution from CH_3 signals tends to be dwarfed by much more intense CH_2 absorbances, and (b) the absolute amount of toluene displaced is small compared to the total amount sensed by the evanescent radiation. As surfactant signals were only integrated between 2960 and 2814 cm^{-1}, the aromatic C-H stretches in toluene were not overlapping.
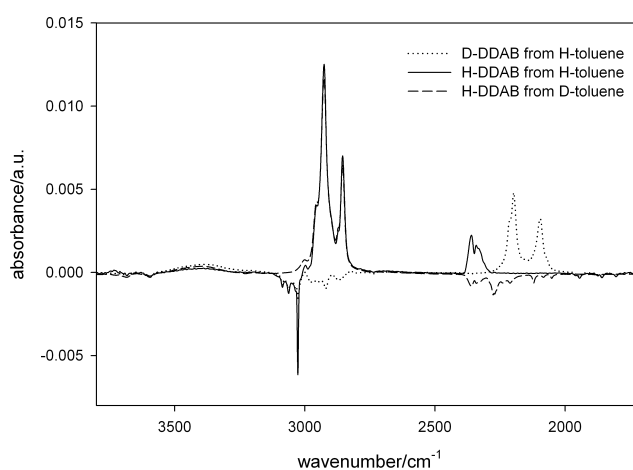

Figure S4: The effect of toluene absorbance on the surfactant signal for DDAB in toluene with varying deuteration. All surfactant solutions were measured at 1.3 mM.

In order to quantify the effect of the toluene CH_3 signals on the surfactant spectra, a series of

test samples using the cationic surfactant DDAB were run in varying deuteration conditions (Figure S4). By integrating the negative H-toluene signal when D-surfactant was adsorbed, it was possible to calculate the approximate impact of the toluene peaks on the integrated H-surfactant signal. This represented around 6% of the total surfactant integral, and assuming an approximately linear relationship between the appearance of surfactant signal and disappearance of toluene signal (molecularly reasonable), this 6% correction was applied to all spectra. It is recognized that this is not "perfect", therefore the error imparted by this correction was assumed to be around 3%, which was accounted for in subsequent analyses of rate constants and adsorbed amounts.

References

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