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Surfactant adsorption by total internal reflection Raman spectroscopy. Part III: Adsorption onto cellulose

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ABSTRACT

TIR Raman spectroscopy has been used to study the adsorption of surfactants onto cellulose. The cellulose was prepared by Langmuir–Blodgett deposition of trimethylsilylcellulose onto silica followed by removal of the trimethylsilyl groups with acid to generate a hydrophilic surface. The reaction was followed *in situ* with Raman spectroscopy, revealing a two-step hydrolysis. Adsorption isotherms of hexadecyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100) on hydrophilic cellulose were obtained by TIR Raman scattering under quasi-equilibrium conditions where the bulk concentration was slowly but continuously varied. The isotherms of both surfactants are almost linear, in contrast to the isotherms on hydrophilic silica. The CTAB isotherm shows hysteresis depending on whether the concentration of the surfactant is increasing or decreasing due to a slow adsorption region. A mixture of TX-100 and CTAB shows ideal adsorption, in contrast to adsorption of the same mixture on silica where there is a strong cooperative interaction at low CTAB surface coverage.

1. Introduction

Cellulose is the core component of cotton and paper. The adsorption of surfactants onto cellulose is a key step in the cleaning of cotton textiles and in the deinking of paper during recycling. Optimisation of formulations is assisted by an understanding of the thermodynamics and kinetics of adsorption of surfactants onto cellulose, both as pure compounds and as mixtures. Here we use total internal reflection (TIR) Raman spectroscopy to study the adsorption of surfactants onto cellulose both as binary solutions in water and as a ternary mixture. TIR Raman spectroscopy was invented in the 1970s [1,2] but it is only recently that it has been developed into a powerful, surface-sensitive technique for quantitative studies of adsorption at the solid–liquid interface [3–7]. In Parts 1 and 2 of this series [4,5], we demonstrated the use of TIR Raman spectroscopy in the study of the adsorption of pure and mixed surfactants on a silica substrate. While the technique is at its most straightforward when the substrate is transparent and has vibrational bands that do not overlap with those of the adsorbates, TIR-Raman spectroscopy can also be applied successfully to thin films deposited on transparent substrates even when, as is the case with cellulose, the vibrational spectrum of the thin film strongly overlaps the spectra of the adsorbates of interest.

TIR-Raman exploits the properties of evanescent waves to achieve surface sensitivity and therefore requires the use of surfaces that are flat on the length scale of the wavelength of light. TIR-Raman can be used to study fibrous materials if the material is pressed up against an internal reflection element composed of a high-index material [8], but quantification is difficult and kinetic studies impractical. Fortunately, there are well-established techniques for preparing thin, flat transparent films of cellulose that are suitable for study by optical and neutron scattering techniques [9–11]. In the work reported here, we first use TIR-Raman spectroscopy to characterise the preparation of a model cellulose surface by hydrolysis of the trimethylsilyl groups in a Langmuir–Blodgett film of hydrophobically modified cellulose. Next we look at the adsorption onto cellulose of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB), which is a commonly used model system. The speed of acquisition of TIR Raman spectra allows us to map the adsorption isotherm much more thoroughly than has been done before. Third, we look at the adsorption of the non-ionic surfactant Triton X-100 (TX-100) onto cellulose. TX-100 is challenging to study because it removes some of the cellulose layer, however the chemical specificity of Raman allows the two different processes—adsorption of surfactant and degradation of the layer—to be followed independently. Finally, we look briefly at a mixed surfactant system, demonstrating the ability of TIR-Raman spectroscopy to distinguish two surfactants in the presence of a strong cellulose signal.

Previous work on cellulose has taken two different approaches to sample preparation. Fibrous cellulose [12,13]—for example filter

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paper—has the advantage of replicating real cellulose substrates closely, but the disadvantages that the cellulose surface contains a wide variety of different environments, that *in situ* characterisation of molecules adsorbed to the cellulose is difficult and that adsorption kinetics are likely to be controlled by transport through the fibres rather than by adsorption onto the surface itself. These drawbacks are overcome with thin, flat cellulose substrates. Such surfaces have allowed the use of a wide range of different experimental methods, including X-ray photoelectron spectroscopy [14,15], surface force apparatus [16], atomic force microscopy [17], quartz crystal microbalance [18], ellipsometry [9] and neutron reflectometry [10,11] as well as the TIR Raman spectroscopy we use here. They are also amenable to quantitative studies of adsorption kinetics under well-defined mass transport conditions [9].

Two different approaches exist for the preparation of thin cellulose films [19]: Langmuir–Blodgett (LB) deposition and spin coating. The most common approach to LB deposition, developed by Schaub et al. [20], involves the use of the functionalised cellulose derivative trimethylsilyl cellulose (TMSC). The principal advantage of working with TMSC rather than plain cellulose is that—unlike plain cellulose—TMSC can be dissolved in common non-polar solvents such as chloroform, toluene or *n*-hexane. Thin layers of TMSC can then be formed at the air–water interface and transferred onto hydrophobic surfaces such as hydrophobised gold, glass, silicon or mica. Unfunctionalised cellulose can be regenerated by exposure to HCl vapour. The properties of the deposited surface have been characterised extensively by IR spectroscopy, surface plasmon resonance, ellipsometry, surface force measurements and photoelectron spectroscopy [16,20,21], providing thicknesses of 10 Å per layer for TMSC and 4 Å per layer for the regenerated cellulose, showing that the charge on the cellulose chains is minimal (based on the absence of a double-layer force) and that the removal of the TMS groups is essentially complete.

Alternatively, TMSC can be spin-coated onto a substrate such as an anchoring polymer attached to silicon [9,22], or directly onto silicon or gold [14], followed by hydrolysis to remove the TMS groups. Kontturi and coworkers showed that partial hydrolysis was possible and could be controlled by changing the vapour pressure of HCl and the exposure time [14]. Neuman et al. showed that it is also possible to spin coat cellulose directly using trifluoroacetic acid as a solvent [23]; the current preferred solvent is N-methylmorpholine-N-oxide (NMMO) [24]. Cellulose has to be deposited onto an anchoring polymer—rather than directly onto silica—with the choice of polymer affecting the thickness of the surface. For all spin-coating processes, a range of experimental parameters can be used to control the film thickness, with typical values being 200–1000 Å.

We used Langmuir–Blodgett deposition of TMSC rather than spin coating, principally because the films produced can be made thinner than those from spin-coating, with much finer control over the thickness of the film. A thin film is important in TIR Raman to minimise the Raman signal from cellulose, which overlaps the surfactant spectra.

The adsorption of CTAB onto cellulose has been studied by both neutron reflectometry [10] and AFM [17]. The two sets of data are not directly comparable since the surfaces were prepared in different ways: the AFM study used unfunctionalised cellulose spin-coated on top of a polymer layer [24] whereas the neutron reflectometry used Langmuir–Blodgett deposition of a hydrophobically modified cellulose to produce hydrophobic and hydrophilic cellulose layers. Measured by neutron reflectometry, levels of adsorption onto hydrophilic cellulose and hydrophilic silica were similar ($5.9\,\mu\text{mol m}^{-2}$), whereas the level of adsorption onto hydrophobic cellulose was roughly a third lower ($3.9\,\mu\text{mol m}^{-2}$). Modelling of the neutron data suggested some intermixing between the hydrophobic cellulose and CTAB, whereas the CTAB self-assembled on top of the hydrophilic cellulose. AFM data revealed the formation of admicelles on a hydrophilic cellulose surface.

The adsorption of nonionic surfactants to cellulose has also been studied. Torn et al. followed the adsorption kinetics of a variety of ethylene glycol alkyl ether (C_nE_m) surfactants using optical reflectometry [9]. Singh and Notley used AFM to show a mixture of spherical and rodlike micelles for $C_{16}E_8$ and $C_{14}E_6$ on cellulose surfaces [25]. Adsorption of $C_{12}E_6$ and mixtures of CTAB and $C_{12}E_6$ have been investigated by neutron reflectometry [11]. $C_{12}E_6$ appeared to change the structure of both TMS-functionalised and plain cellulose while the original structure was largely recovered on rinsing. In mixtures, the composition of the surface layer on plain cellulose was close to ideal. The surface excess was largely independent of composition on both types of cellulose.

Several authors have studied adsorption of surfactants onto cellulose fibres. Paria et al. looked at the adsorption of TX-100, sodium dodecylbenzenesulfonate and CTAB) onto filter paper [12,26]: the kinetics were generally slow, taking between 5 and 50 min to complete. Alila et al. used oxidation of cellulose fibres to control the surface charge and then investigated the adsorption of different chain lengths alkyl trimethylammonium bromide surfactants [13]. The nature of cellulose fibres makes comparison of these results to those obtained on a thin flat cellulose film almost impossible.

2. Experimental

2.1. Materials

Hexadecyltrimethylammonium bromide (Sigma–Aldrich, 99%) was recrystallized three times from acetone/methanol. Triton X-100 (Sigma–Aldrich)—a nonionic surfactant with a branched octylphenyl tail group and a poly(oxyethylene) head group with an average of 9.5 EO units—was used as received. Water was obtained from a Millipore Gradient A-10 filtration unit (18.2 MΩ cm, TOC < 4 ppb). Trimethylsilyl cellulose was synthesised according to the method given in reference [27].

2.2. Raman

The TIR-Raman system has been described in detail elsewhere [4,6]. The Raman light is collected with commercial Raman microscope (Ramascope 1000, Renishaw, Wootton-under-edge, UK). The pump laser is a continuous-wave, frequency-doubled solid-state laser (Opus 532, Laser Quantum, Manchester, UK) with a wavelength of 532 nm, typically operated at 0.7 W yielding ~0.5 W at sample. The beam was gently focused to a diameter of ~10 μm. A silica hemisphere was used as the substrate for the cellulose to minimise optical aberrations. The angle of incidence at the silica–water interface was 73.0° giving an illuminated region of 30 × 10 μm and a sampling depth for Raman scattering of 103nm. The incident laser was S polarised (perpendicular to the plane of incidence), since this polarisation gives the highest signal levels. The Raman scattered radiation was collected through the fused silica prism with a 50× ULWD, 0.55 NA objective (Olympus) and directed into the spectrometer. Typically we collected only the y-polarised light (parallel to the incident S light, designated Sy); x-polarised light could also be selected (designated Sx). Data were acquired over a fixed wavenumber range (from 2600 to 3200 cm^{-1}) encompassing the C–H stretching region of the Stokes scattering.

For measurements on quasi-equilibrium systems—using the continuously stirred mixer described later—a continuous set of 10–30 s spectra were acquired. For measurements on the kinetics of adsorption and desorption (presented in supplementary material)