Chemical instability of octadecylammonium monolayers

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Octadecylammonium in monolayers transforms into a carbamate derivative, as observed by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

Primary alkylammoniums, such as octadecylammonium (ODA), and alkylamines are compounds frequently used for monolayer studies on water[1–7] and for the preparation of hydrophobic clay minerals.[7–10] It is implicitly assumed that these compounds remain chemically stable during the experiment. In this communication we show that octadecylammonium undergoes, at least partially, a chemical reaction to carbamate esters. This is in line with the results obtained by Gaines[1] in 1982. The change in headgroup of alkylammonium could have important consequences e.g. in the case of cation-exchange experiments as the surfactant changes to a non-ionic moiety.

Octadecylammonium chloride (ODA, 99%, Acros) was used as received and was dissolved in a 9 : 1 mixture of HPLC grade chloroform (Fluka, stabilized with 1% ethanol) and HPLC grade methanol (Fisher Chemicals) to prepare a spreading solution of 2×10^{-3} mol dm^{-3}. The cosolvent methanol was needed to make ODA soluble. Langmuir–Blodgett (LB) films were prepared on a NIMA Technology model 611 LB trough at a temperature of 23 ± 1 °C. A microsyringe was used to spread 200 µl of ODA solution over Milli-Q water. After 15 minutes, the film was compressed at a rate of 30 cm^2 min^{-1}. Films were deposited in upstroke (lifting speed of 5 mm min^{-1}) on ZnSe internal reflection elements (IREs) at surface pressures ranging from 2 to 25 mN m^{-1}. The substrates were cleaned prior to each deposition by gently rubbing with a paper tissue soaked in methanol. The IREs were ZnSe trapezoidal-shaped crystals (Spectroscopy Central, UK) (50 mm × 20 mm × 2 mm) with 25 internal reflections and were measured in a vertical ATR cell using a Bruker IFS 66/S FTIR spectrometer. Polarized ATR-FTIR spectra were obtained using a wire-grid polarizer. The FTIR spectrometer was equipped with a liquid nitrogen cooled MCT detector and a KBr beam splitter. A total of 512 individual scans were signal averaged using a spectral resolution of 2 cm^{-1}. Spectra were analyzed with Grams/32 AI version 6.00 software. Film material was sampled by skimming a collapsed ODA film. ^{13}C NMR spectra of this skimmed material were measured with a Bruker AMX300 spectrometer with a magnetic field strength of 7 T. The carbon chemical shifts were referenced to tetramethylsilane. The ^{13}C spectrum was measured without decoupling and 100 scans were accumulated. The pulse length was set at 4.5 ms, and a recycle delay time of 60 s was used.

The surface pressure versus molecular area isotherm of an ODA monolayer on water is shown in Fig. 1. The lift-off area, as determined by extrapolation of the linear section of the isotherm above 10 mN m^{-1}, is 12.6 Å^2 molecule^{-1}. The lift-off area is significantly lower than the area occupied by densely packed alkyl chains (about 20 Å^2). In the literature, various values have been reported for the lift-off area of alkylammonium/alkylamine and some of those papers have proposed this discrepancy to originate from partial dissolution of the monolayer material in the aqueous subphase.[2–4]

Not only the lift-off area, but also the apparent compressibility shows discrepancy. Octadecylamine monolayers are related to ODA monolayers because they follow the same acid–base equilibrium, having a pK_a near 10. The apparent compressibility C' of the ODA monolayer on water ($C' = 1.5$ m N^{-1}), is slightly lower than C' reported for the octadecylamine monolayer on aqueous NaOH solution[6] ($C' = 2.5$ m N^{-1}), but significantly lower than the value reported by Umemura et al.[7] for ODA on water ($C' = 14.7$ m N^{-1}).

We suggest that the chemical instability of the surfactant headgroup, possibly leading to a change in solubility, can account for the inconsistency in the results.

Fig. 2 gives the FTIR spectrum of ODA in KBr and the ATR-FTIR spectrum of a monolayer of ODA deposited at 2 mN m^{-1}. Spectra of films deposited at higher surface pressures were qualitatively similar. The most intense and diagnostic bands of ODA/KBr are the CH$_2$ rocking vibration at 720 cm^{-1}, the CH$_2$ deformation at 1470 cm^{-1} and the CH$_2$ stretching vibrations at 2917 and 2850 cm^{-1}. In the monolayer one observes the same
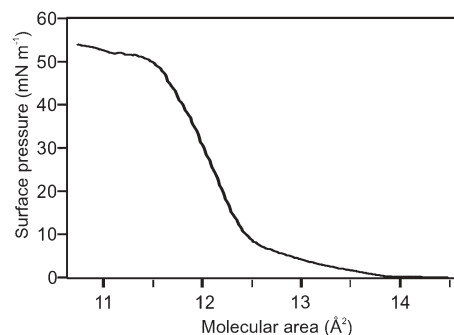
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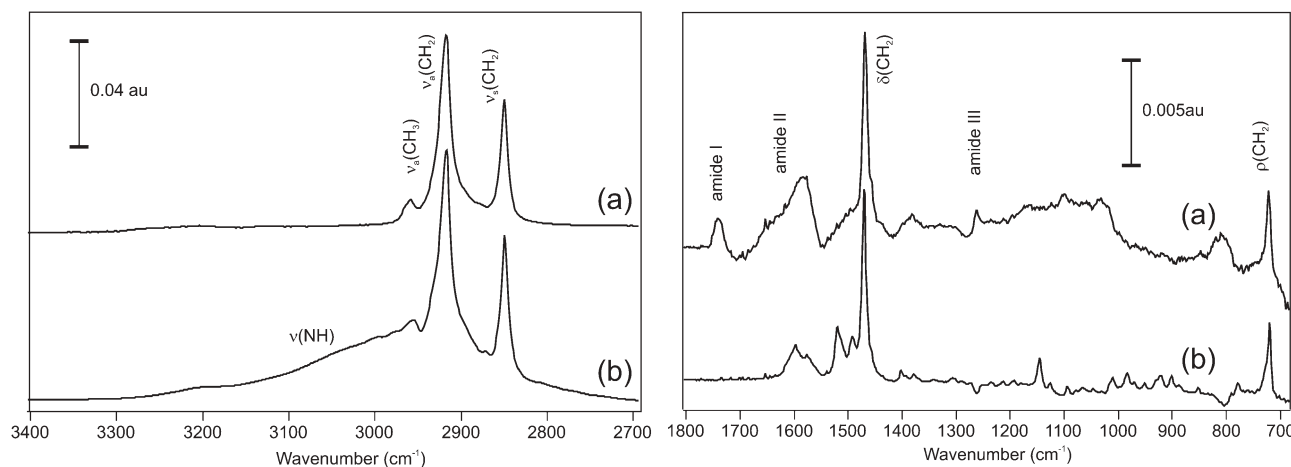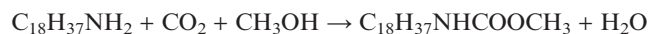

Fig. 1 Surface pressure versus molecular area isotherm of an ODA monolayer on water.

Fig. 2 (trace a) ATR-FTIR spectrum of an ODA monolayer deposited at 2 mN m^{-1} and (trace b) transmission infrared spectrum of ODA in KBr. Spectra are shown in the 3400–2700 cm^{-1} and 1800–700 cm^{-1} regions.

bands and three additional bands at 1740, around 1550–1680, and 1262 cm^{-1}. These bands are indicated as amide I, amide II and amide III. They have C=O and N–H character, similar to the amide bands in urethanes and proteins.[11] They are seen in the spectra of the monolayers, but are absent from the spectrum of ODA/KBr. The presence of these bands indicates that ODA has undergone a chemical reaction. Two additional pieces of evidence support this conclusion. (1) In the 2700–3400 cm^{-1} region of the same spectra (Fig. 2), one remarks—besides the C–H stretching vibrations—a broad band of NH stretchings in the ODA/KBr spectrum, which is nearly absent from the monolayer spectrum. This indicates that the NH groups have disappeared to a large extent in the monolayers due to a chemical reaction. (2) The ^{13}C NMR spectra of skimmed monolayers of ODA give a peak at 168.2 ppm characteristic of a C=O group (Fig. 3).[12]

The infrared and NMR data indicate that a chemical transformation of some, or all, of the ODA has occurred as revealed by the presence of the carbonyl group. Prior studies have suggested that amines react with atmospheric carbon dioxide to form carbamates.[1,13] Here we propose a reaction between ODA, dissolved carbonate species and methanol or between octadecyl-amine, atmospheric CO$_2$ and methanol, to form *n*-octadecyl carbamate methyl ester.

$$C_{18}H_{37}NH_3^+ + HCO_3^- + CH_3OH \rightarrow$$
$$C_{18}H_{37}NHCOOCH_3 + 2\ H_2O$$

$$C_{18}H_{37}NH_2 + CO_2 + CH_3OH \rightarrow C_{18}H_{37}NHCOOCH_3 + H_2O$$

An analogous reaction can be written with ethanol instead of methanol. In HPLC grade chloroform, ∼ 1% ethanol is added as a stabilizer.

These results are significant, because they show that the surfactant is susceptible to a chemical transformation. Furthermore, the apparent ease of formation of the carbamate ester can explain some of the inconsistencies in the literature concerning the monolayer properties (such as lift-off area and the apparent compressibility) of primary amines or primary
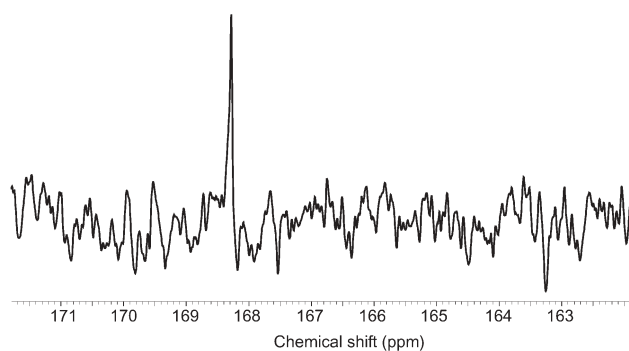

Fig. 3 ^{13}C NMR spectrum of ODA film material skimmed from the water surface.

ammonium cations. Moreover, there are IR studies on alkylamines and alkylammoniums that report a band near 1740 cm^{-1}, with no connection of this band made to carbamates.[5,14] An important implication of these findings is related to the charge of the headgroup. ODA is a positively charged surfactant and carbamate ester is a neutral compound. Reaction to carbamate ester may thus have consequences for the cation-exchange properties with clay minerals and other polyelectrolytes.

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