Behaviour of 1-Octadecanethiol Film Spread over Silver Nitrate Solution

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Force-area isotherm of 1-octadecanethiol over aqueous silver nitrate subphase has been studied. A comparison of this isotherm with that obtained over pure water subphase is of interest, since thiols are known to form complexes with Ag^+ in bulk aqueous solutions. As the monolayer over the silver nitrate solution is compressed, at first it behaves as a typically expanded monolayer, and then goes through a less steep region of transition, after which the isotherm becomes identical to that over pure water. This has been interpreted as being caused by the silver part of the complex having been squeezed out of the monolayer into the subphase.

Key Words: 1-Octadecanethiol film, Silver nitrate, Area isotherm.

INTRODUCTION

In a number of previous papers[1-5] Ahmad and co-workers have reported reactions between monolayers and the substrates over which they are spread. The state of the compression of the monolayer can affect the reaction dramatically. Since the reacting molecules are constrained to a plane and the surface pressure determines how they are oriented in space, different states of compression of the reacting monolayer may cause a difference in reactivity and even the nature of the products. Also, as a result of the reaction, the surface-pressure-area isotherm of the system will alter, and the characteristics of the isotherm can give information about the orientation of the reaction products.

One system of interest is the monolayer of 1-octadecanethiol. Studies on the oxidation of the thiol monolayer to disulfide over aqueous solution-air interface have been reported previously[3,5]. Because of the tendency of thiols to form complexes with silver ion[9-11] in bulk aqueous solutions, it is of interest to study the behaviour of a monolayer of 1-octadecanethiol that has been spread over silver nitrate solution. No such study has been reported in literature so far. The surface-pressure isotherm of 1-octadecanethiol over water changes markedly when there are Ag^+ ions present in the substrate, which can form a complex with the monolayer. The monolayer over silver nitrate solution exhibits a relatively flat transition region, which has been interpreted as corresponding to a change in

the orientation of the complex relative to the interfacial plane. Upon continued compression a stage is reached when the monolayer behaves like that over pure water.

EXPERIMENTAL

All water used was doubly distilled using an all-glass still. The subphase was prepared by dissolving the required mass of silver nitrate (supplied by BDH; 99.8% pure) in water to get a solution of the required concentration. 1-Octa-decanethiol was commercially available (Riedel de Haen AG) and recrystallized from ethanol before use. Hexane (99%) and potassium nitrate (99.9%, Merck) were used as such without further purification.

A Nima trough (manufactured by Nima Technology, Coventry, England) was used during the study. This is essentially a modified, computer-controlled, Langmuir trough, made from PTFE, rectangular in shape and with dimensions 36 cm by 20 cm by 0.5 cm. The trough is fixed onto an aluminium base through which water can be circulated from a thermostated bath. There are two movable PTFE barriers, with one of the barriers supporting a pressure sensor, to which a piece of filter paper is attached, that acts as a Wilhelmy plate. The surface tension and the area enclosed by the barriers are digitally displayed on the computer screen. The graph between the surface pressure and the area between the barriers was displayed on the computer screen.

Measurements: A 2.4×10^{-3} M solution of the thiol was prepared in hexane. The trough was filled with water or a 0.1 molar silver nitrate solution at 25°C, and the surface was swept by moving the compression barrier over the entire surface and applying suction to remove any impurities. The barriers were then positioned to get a suitable area between them. The 1-octadecanethiol solution (20 or 50 microlitres) was added dropwise to the surface using a Hamilton microsyringe. After allowing about 10 minutes for the hexane to evaporate, the monolayer was compressed at a speed of 10 cm²/min. The isotherm was also measured over pure water used as the substrate, and over 0.1 molar potassium nitrate as a control.

RESULTS AND DISCUSSION

Fig. 1 shows a typical isotherm of the thiol over silver nitrate solution at 25°C. On comparing this isotherm with the one over pure water (shown in Fig. 2), it becomes apparent that the two isotherms coincide at high surface pressures, and both give the same eventual limiting area per molecule of around 0.22 nm². Other characteristics of the isotherms are different. Over silver nitrate solution, the monolayer behaves like a typical expanded film. As it is compressed, the surface pressure increases, but a stage is reached when the isotherm becomes much less steep. Beyond this region, the surface pressure increases sharply in the manner of a typical condensed film.
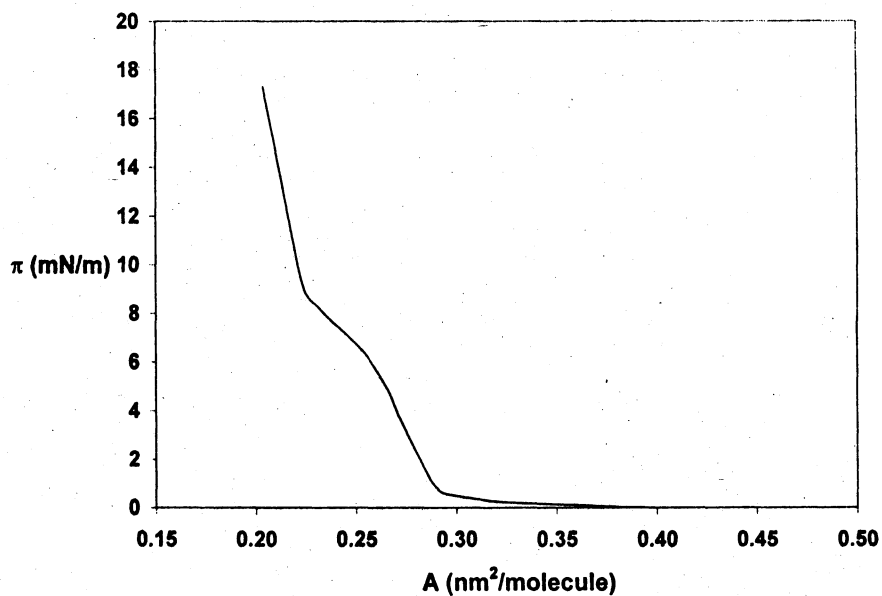
Fig. 1.   π-A isotherm of 1-octadecanethiol over 0.1 M AgNO$_3$ solution at 25°C using a Wilhelmy balance (initial area 200 cm^2, final area 75 cm^2, compression rate 10 cm^2 min^{-1}).
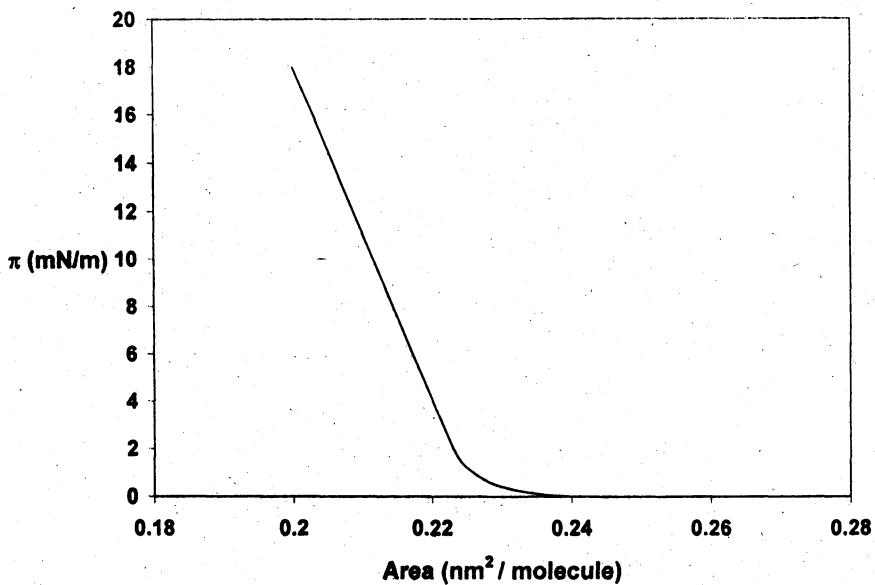

Fig. 2.   π-A isotherm of 1-octadecanethiol over water at 25°C using a Wilhelmy balance (initial area 200 cm^2, final area 75 cm^2, compression rate 10 cm^2 min^{-1}).

Over pure water, on the other hand, the isotherm is like that of a typically condensed monolayer, which shows a region of negligible surface pressure, followed by a steep increase in surface pressure at low areas per molecule. On comparing the two cases, it becomes obvious that at high compressions, the two isotherms are similar. At low surface pressures, however, the isotherms have different characteristics. The limiting area per molecule for both the monolayers is *ca*. 0.22 nm^2. Over potassium nitrate solution, the isotherm is essentially similar to pure water, showing that the effects observed are due to the silver ions and not the nitrate ions.

As the monolayer is spread over the solution, Ag$^+$ reacts with the thiol group forming a complex. On the basis of what is known[6–8] about the thiolato complexes of silver at these relative concentrations of Ag$^+$ and the thiol, the complex formed will have the stoichiomectric formula Ag-S-R, where R is the octadecyl chain. In the monolayer, the Ag-S part of the complex is expected to be in the interfacial region. Thus the expanded nature of the monolayer over the silver nitrate solution at low surface pressures can be explained in terms of this bulky head group (Ag-S).

At the other extreme, when the surface pressures are large, the monolayer over the solution becomes condensed and the two isotherms become similar. The fact that given sufficient compression, the monolayer over the Ag$^+$ behaves similarly to that over pure water, suggests that in the region of high surface pressure, silver atoms do not affect the area per molecule of the thiol. This can happen if Ag atoms are removed from the interfacial layer, which indicates that they are squeezed out and pushed into the underlying subphase. The observed limiting area approximates the cross-sectional area of the hydrocarbon chain, indicating that the Ag atom no longer influences the area/molecule of the monolayer.

At intermediate pressures, as the monolayer over the solution is being compressed, Ag atoms are being progressively pushed away from the interface and into the subphase. This explains the relatively flat region, where the surface pressure increases at a lower rate. When the silver atoms have all been squeezed out, a closed packing of the S-R part of the complex results. The monolayer then shows characteristics identical to that of the thiol monolayer over pure water, and the surface pressure starts increasing steeply as the monolayer is compressed.

While the stoichiometric formula of the thiolate species is Ag-S-R, there is evidence[9] to suggest that in solution there are in fact oligomers with the formula [Ag-S-R]$_n$. No reliable value of n has been obtained for the primary alkyl thiolates because of the problems posed by their insolubility, but for the secondary and tertiary alkyl thiolates, the values of n have been reported as 12 and 8 respectively. In the solid state, the complex exhibits a quasi-hexagonal Ag-S lattice, with geometry around Ag atom being trigonal planar, while that around S is more or less tetrahedral, with each S joined with three Ag atoms and having a vertical alkyl group[11]. The form in which the complex exists at the interface may well be

different from that in solution, because of the constraints imposed on S being in a plane. In any case, our interpretation of the isotherm does not depend critically on whether the complex exists as oligomers on the interface, and how many units the oligomers consist of. The isotherm can be interpreted in terms of the Ag atoms being squeezed out from the interface and into the bulk at high surface pressures.

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