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THE DIRECT DETERMINATION OF THE MEAN SEPARATION OF A TETHERED CHAIN FROM ITS ANCHOR

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ABSTRACT

Neutron reflectivity with isotopic substitution has been used to determine the mean separation between a tethered chain and its anchoring point. The method is described and applied to the study of the structure of a layer of the surfactant tetradecyl trimethylammonium bromide adsorbed at the air-solution interface. At a concentration just below the critical micelle concentration the area per molecule in the adsorbed layer is $48 \pm 2 \text{ \AA}^2$ and the midpoint of the distribution of the tetradecyl chains is found to be $7 \pm 0.5 \text{ \AA}$ from the centre of the trimethylammonium headgroup distribution. This result is independent of the widths of the two individual distributions, the only assumption being that both distributions are even functions about their centres.

INTRODUCTION

Reflection techniques offer the most direct method for determining the distribution normal to a flat surface of a chain tethered to some part of the interface. What is determined from the specular reflection experiment is the scattering length density profile along the direction normal to the interface. There may be uncertainty both about the uniqueness of the scattering length density profile obtained from the experiment and in the conversion of the scattering length density profile into an actual density profile. Here we show that it is possible, with only minor assumptions, to overcome both these difficulties and to obtain information about certain features of the interfacial structure directly. In particular, isotopic labelling can be used in neutron reflection to obtain the mean distance of separation between two distributions without knowing the two distributions themselves. We apply the method to the determination of the separation of a chain from the point at which it is tethered, using as illustration the surfactant tetradecyl trimethylammonium bromide ($C_{14}TAB$) adsorbed at the air-water interface.

THEORY

For weak elastic scattering in the kinematical approximation the specular reflectivity, $R(\kappa)$, from a macroscopically flat surface is [1,2,3]

$$R(\kappa) = \frac{16\pi^2}{\kappa^2} |\rho(\kappa)|^2 \quad (1)$$

where κ is the momentum transfer normal to the interface ($= 4\pi\sin\theta/\lambda$) and $\rho(\kappa)$ is the one dimensional Fourier transform of $\rho(z)$, the average scattering length density profile in the direction normal to the interface,

$$\rho(\kappa) = \int \exp(-i\kappa z) \rho(z) dz \quad (2)$$

The scattering length density is related to the composition by

$$\rho(z) = \sum b_i n_i(z) \quad (3)$$

where $n_i(z)$ is the distribution of the number density of species i . An alternative expression, equivalent to (1), but written in terms of $d\rho/dz = \rho^{(1)}$ is also often used [3]. It is possible to Fourier transform $|\rho(\kappa)|^2$ to obtain the "Patterson" function for the scattering length density,

$$P(z) = \int \rho(z) \rho(u-z) du \quad (4)$$

where $P(z)$ represents the correlation of the scattering length density with itself. In principle there is a phase problem involved in going from $P(z)$ to $\rho(z)$, but a knowledge of $P(z)$ is often sufficient to determine $\rho(z)$ unambiguously if the range of κ used for the experiment is large enough to avoid errors in the Fourier transform [3]. The main source of error is that the range of the reflectivity measurement is limited by the level of the background scattering. This is larger for neutrons than for x-rays and, coupled with the lower incident flux, limits κ_{\max} to about 0.3 \AA^{-1} for neutrons. This is usually an inadequate limit for performing a satisfactory Fourier transform.

We have only outlined the problem of resolution above and there are fine details which would merit a longer discussion. Our main concern here is to show that even when the scattering length density profile has been accurately determined, there remains the difficulty of the unscrambling the scattering length density profile into the individual parts of the structure. That this is not trivial is demonstrated by the scattering length density profile of a block copolymer adsorbed at the air/water interface. Such a layer might be obtained by spreading a styrene-ethylene diblock copolymer on the surface of water and a possible scattering length density profile is shown in Figure 1. What is usually wanted from such an experiment is the mean width of the EO distribution and its separation from the hydrophobic polystyrene moiety. Such information cannot be derived without making unjustified assumptions about the distributions, for example, that the styrene is completely out of the water and the EO entirely immersed. A high accuracy in the determination of the scattering length density profile does not help to solve this problem. Cases may occur where either the scattering length density is dominated by one part of the distribution or the accuracy of the distribution is such that it can be combined with simple assumptions to extract the information of interest. However, the more tenuous the layer, the more serious will be the problem.

We now address the problem more formally using a procedure similar to that used for determining partial structure factors in liquid mixtures [4]. Substitution of equation (3) into (1) gives

$$R(\kappa) = \frac{16\pi^2}{\kappa^2} \sum b_i b_j h_{ij}(\kappa) \quad (5)$$

where

$$h_{ii}(\kappa) = |n_i(\kappa)|^2$$

and

$$h_{ji} = h_{ij}(\kappa) = \text{Re}\{n_i(\kappa)n_j^*(\kappa)\} \quad (6)$$

$n_i(\kappa)$ are the Fourier transforms of the number density distributions of each species and $h_{ij}(\kappa)$ are the partial structure factors. The n_i could refer to each

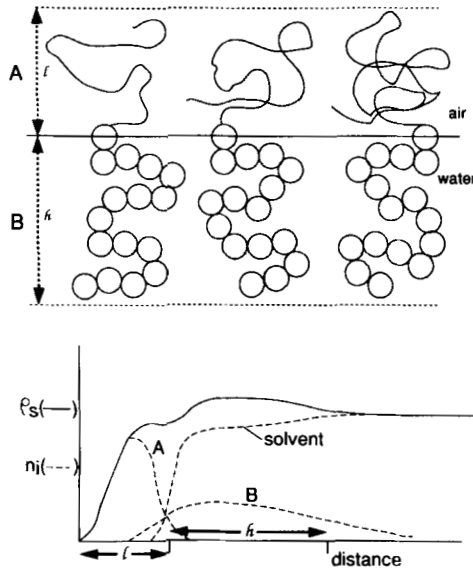


Figure 1 A schematic sketch of a diblock copolymer at the air–water interface with possible number density (n_i) profiles across the interface and the total scattering length density (ρ_s) profile.

atom in the system if the labelling were feasible, but the resolution of the experiment is too low for an exploration of such fine detail and isotopic labelling will generally be confined to groups of atoms. For a surfactant at a surface there are three main features of interest, the extension of the hydrophobic chain, the relation between chains and heads, and the position of the chains and heads in relation to the aqueous solution. A simple description of the structure of the air/solution interface is then in terms of the distributions of the head group, h , of the surfactant, its chain, c , and the solvent, s . In terms of these three labels equations (3) and (5) become

$$\rho(z) = b_c n_c(z) + b_h n_h(z) + b_s n_s(z) \tag{7}$$

and $R(\kappa) = \frac{16\pi^2}{\kappa^2} \{b_c^2 h_{cc} + b_h^2 h_{hh} + b_s^2 h_{ss} + b_c b_h h_{ch} + 2b_c b_s h_{cs} + 2b_h b_s h_{hs}\}$ (8)

An equivalent expression, in terms of $h_{ij}^{(1)}(\kappa)$, can be obtained in terms of the derivative of (7) and it can be shown [3] that

$$\kappa^2 h_{ij}^{(1)}(\kappa) = \dot{h}_{ij}(\kappa) \tag{9}$$

A possible procedure for determining the structure of the interface is then to measure six reflectivity profiles using isotopic substitution to give different values of b_c , b_h and b_s , from which the six different h_{ij} in (8) can be obtained. Each one of the structure factors may be Fourier transformed directly to give $P_{ii}(z)$ and $P_{ij}(z)$ where

$$P_{ii}(z) = \int n_i(u) n_i(u-z) du \tag{10}$$

These functions correspond to functions of the type shown in equation (2) except that they are in terms of the number densities rather than the scattering length density. They therefore give a more direct picture of the structure across the interface. The above procedure can only define the structure in terms of the labelled groups. For example, to determine the distribution of methylene groups at either end of a surfactant alkyl chain it would be necessary to make additional isotopic substitutions.

A particularly simple example of this method is when the isotopic composition of the water is adjusted so that its ρ matches that of air (null reflecting water). If ρ of the head group is also matched to air (approximately achieved by using the protonated head group) but ρ of the chain is not (achieved by deuteration) all terms except the first one in equation (8) vanish. Multiplication of this reflectivity profile by $\kappa^2/16\pi^2b_c^2$ gives h_{cc} which may be transformed to give $P_{cc}(z)$, from which it is often straightforward to determine the chain distribution. $P_{hh}(z)$ and $P_{ss}(z)$ can similarly be determined directly in separate experiments.

The limitation of this method of analysis is that data can only be obtained over a limited range of κ and the practical problems of Fourier transformation are such that it may seldom be worth doing. However, important structural information can often be obtained *without* doing the Fourier transform. The self partial structure factors, h_{ii} , contain information about the distribution of each labelled component but not about the relative positions of the components. The information about the relative positions is contained in the cross partial structure factors, h_{ij} .

A property of Fourier transforms is that when a distribution is moved a distance δ from the origin its Fourier transform is changed by a phase factor [5], i.e. if

$$n^\dagger(z) = n(z - \delta) \\ n^\dagger(\kappa) = n(\kappa)\exp(-i\kappa\delta) \quad (11)$$

then and the cross term between two shifted distributions is

$$h_{ij}(\kappa) = \text{Re}\{n_1^\dagger(\kappa)n_2^{\dagger*}(\kappa)\exp[-i\kappa(\delta_1 - \delta_2)]\} \quad (12)$$

where $\delta (= \delta_1 - \delta_2)$ is the separation of the two distributions. It may often be the case that the distributions are perfectly even about their centres. For example both chain and head distributions are zero at large positive and negative values of z and are therefore predominantly even functions. When $n_c(z)$ and $n_h(z)$ are exactly even about their centres, equation (12) shows that

$$h_{ch} = (h_{cc}h_{hh})^{1/2}\cos\kappa\delta \quad (13)$$

APPLICATION OF THE THEORY

Simister et al.[6] have examined the structure of C_{14} TAB at the air/water interface using isotopic species with the C_{14} chain deuterated or protonated, the TAB head group deuterated or protonated, and the solvent at various contrasts between D_2O and n.r.w. Thus two labels have been used within the same molecule so as to determine the relative configuration of the two parts within the interfacial region. In this case the contribution of the Br^- counterion is insignificant and can be neglected. Furthermore, separate surface tension experiments have shown that there is negligible thermodynamic difference between the isotopes so it can safely be assumed that the structure is unchanged by isotopic substitution. There are six $h_{ij}(\kappa)$ functions to be determined from the data, h_{cc} , h_{hh} , h_{ss} , h_{cs} , h_{hs} , and h_{ch} , which were determined from eleven isotopic measurements. To retain the

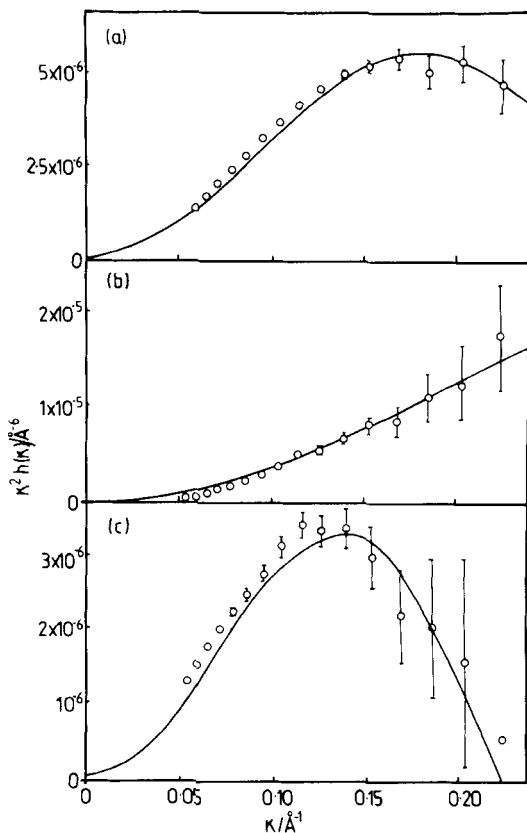


Figure 2 Experimental partial structure factors for $C_{14}TAB$, (a) chain/chain, (b) head/head, and (c) chain/head [6].

analogy with the block copolymer shown in Figure 1 we consider here only the relation between chain and tethering point (i.e. the head group). For this only three isotopic compositions are required to give h_{cc} , h_{hh} , and h_{ch} . These three partial structure factors at a single concentration (3×10^{-3} M, $0.8 \times$ c.m.c.) are shown in Figure 2. The chain-chain structure factor, h_{cc} , rises more rapidly than h_{hh} and reaches a maximum within the observed κ range. Thus $n_c(z)$ must be a wider distribution than $n_h(z)$, as would be expected from the relatively greater length of the chains, but neither function is determined over a sufficiently wide range of κ to make it possible to do a Fourier transform. However, the mean width of the distribution can be determined with reasonable accuracy from these two curves, although the

shape is not well characterised. For both cases the calculated partial structure factors for a uniform layer or a Gaussian distribution cannot be distinguished with certainty. The best fit of Gaussian profiles to h_{cc} and h_{hh} gives full widths at half height of 16 ± 1 and 5.5 ± 3 Å respectively and the fits are shown as continuous lines in Figure 2(a) and (b). In fitting the profiles we have made use of the stoichiometry of the system which requires that

$$\int n_h(z) dz = \int n_c(z) dz \quad (14)$$

The cross term $h_{ch}(\kappa)$ (Figure 2(c)) could be fitted in the same way as for Figure 2(a) and (b), i.e. by assuming Gaussian distributions for chains and heads. It is, however, possible to use the more direct procedure based on equation (13) by assuming that n_c and n_h are exactly symmetrical about their centres. The observed h_{ch} is then related to the geometric mean of h_{cc} and h_{hh} by the phase factor $\cos \kappa \delta$ and we find that δ has to be 7 ± 0.5 Å to fit the experiment (see Figure 3), values of δ of either 6 or 8 Å giving an inadequate fit to the data. Thus a minor assumption is all that is necessary to derive the separation of the centres of the two distributions, the chains and their tethering points, with great accuracy and without any assumptions about the widths of the two distributions. Moreover, since the tethering points will generally have a finite width, whether they be mobile or fixed on a rough wall, the mean separation of the two distributions may be the most interesting feature of the interface that can be defined by experiment.

DISCUSSION

Although we have shown that direct information can be obtained about the separation of a chain from its tethering point, we have made the assumption that the two distributions are even about their centres. This may not be exact and it is worth examining the effects of deviations from the condition. For a general distribution consisting of both even and odd parts the Fourier transform consists of real(') and imaginary(*) parts

$$n_c(\kappa) = n_c'(\kappa) + i n_c''(\kappa) \quad (15)$$

The cross partial structure factor between the general distribution for component c and an even distribution h is then given by

$$h_{ch} = (h_{hh})^{1/2} (n_c' \cos \kappa \delta + n_c'' \sin \kappa \delta) \quad (16)$$

where $\delta = (\delta_c - \delta_h)$ and is the separation between the centres of the two distributions h and c. If the assumption has been made in analysing the data that both distributions are even, the apparent separation δ' will be given by

$$(h_{cc})^{1/2} \cos \kappa \delta' = n_c' \cos \kappa \delta + n_c'' \sin \kappa \delta \quad (17)$$

where $(h_{cc})^{1/2}$ is determined by experiment. Thus the approximation consists in putting n_c'' to zero on the right hand side of equation (17), although it is correctly included in the experimental $(h_{cc})^{1/2}$.

We use the simple distribution shown in Figure 4 to test the approximation. Figure 4(a) and (b) show the even and odd parts of the distribution respectively and Figure 4(c) the total. The distribution is totally even about its centre when n_{c2} is either 0 or n_{c1} . The Fourier transforms of the two components of the distribution of Figure 4 are

$$\begin{aligned} \kappa n_c'(\kappa) &= 2n_{c1} \sin(\kappa \sigma / 2) \\ \kappa n_c''(\kappa) &= 4i n_{c2} \sin^2(\kappa \sigma / 4) \end{aligned} \quad (18)$$

and giving $\kappa^2 h_{cc} = 4n_{c1}^2 \sin^2(\kappa \sigma / 2) + 16n_{c2}^2 \sin^4(\kappa \sigma / 4)$ (19)

and $(h_{cc})^{1/2} \cos \kappa \delta' = 2n_{c1} \sin(\kappa \sigma / 2) \cos \kappa \delta + 4n_{c2} \sin^2(\kappa \sigma / 2) \sin \kappa \delta$ (20) where δ is defined as before. At the two limits where c becomes an even distribution δ' is found correctly to be δ when $n_{c2} = 0$ and $(\delta - \sigma/4)$ when

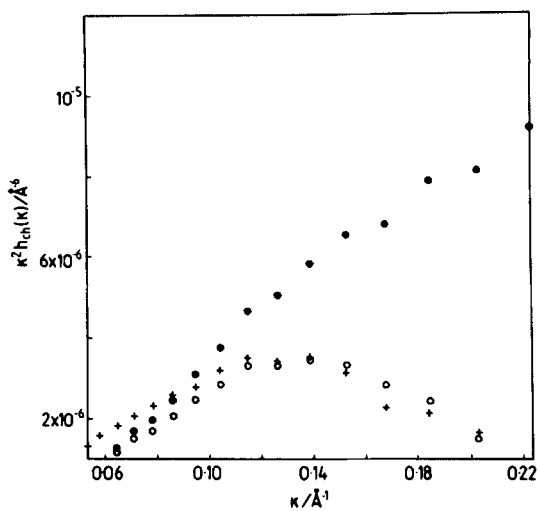


Figure 3 The chain/head partial structure factor of a C_{14} TAB layer calculated using equation (13). Experimental values of $(h_{cc}h_{hh})^{1/2}$ are (●) and of h_{ch} (+). The circles show the former multiplied by $\cos(\kappa\delta)$ with δ having a value of 7 Å.

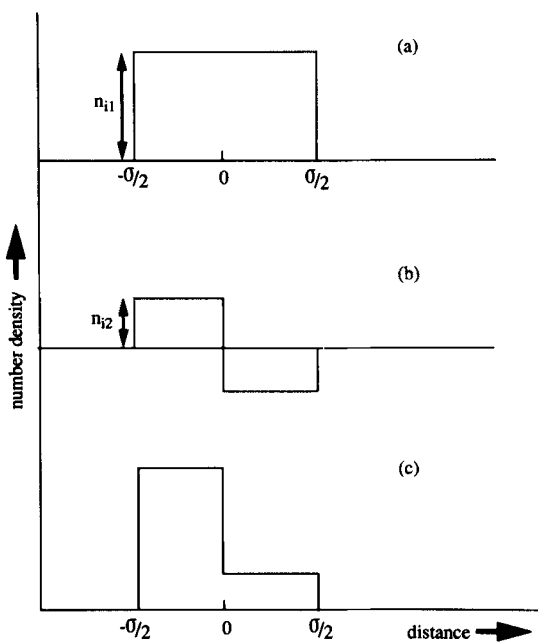


Figure 4. A simple distribution (c) consisting of even (a) and odd (b) components.

TABLE 1

$-\kappa\delta$	$-\kappa\delta'$	$-\kappa(\delta+\sigma/8)$
$\epsilon\pi$	$1.22\epsilon\pi$	$1.25\epsilon\pi$
0.25π	0.29π	0.31π
0.5π	0.60π	0.62π
0.65π	0.81π	0.81π
0.75π	0.97π	0.94π
π	$0.5\pi/1.5\pi$	1.25π

$n_{c2} = n_{c1}$. The most skewed distribution is when $n_{c2} = n_{c1}/3$, since at this point the left hand lobe of the distribution is twice the right hand lobe. For this special case we have, after some simplification,

$$\{9\cos^2(\kappa\sigma/4) + \sin^2(\kappa\sigma/4)\}^{1/2} \cos\kappa\delta' = 3\cos(\kappa\sigma/4)\cos\kappa\delta + \sin(\kappa\sigma/4)\sin\kappa\delta \quad (22)$$

To test the approximation further we need to make some assumptions about the relative values of σ and δ . The requirements of space-filling at the interface will often mean that the separation between the chain and its anchor will be about half the width of the chain distribution. Assuming that δ is exactly -0.5σ , which corresponds approximately to a chain next to a smooth wall, we obtain the values of $\kappa\delta'$ for different values of $\kappa\delta$ (the exact values are $\kappa(\delta + \sigma/8)$ ($1.25\kappa\delta$) when $n_{c2} = n_{c1}/3$). These are shown in Table 1. ϵ represents small values of $\kappa\delta$. From these figures it can be seen that for the particular case of this quite skew distribution the analysis we have used gives the separation of centres to an accuracy of better than 10% up to $\kappa\delta \approx 0.8\pi$. For surfactant layers δ will typically be not more than about 10 \AA and the analysis therefore holds up to values of κ of approximately 0.25 \AA^{-1} , which is at the present limit of the experimental measurements. However, for larger polymer molecules δ will be greater and the choice of range of κ over which the analysis is made will have to be made with care. For data of sufficiently high quality, however, there is the possibility of fitting data directly to equation (16) instead of the simplified form, equation (13). Two further difficulties are that at low values of κ the kinematic approximation, equation (1), may break down (typically $\kappa < 0.02 \text{ \AA}^{-1}$), and for polymeric species the fundamental assumption that the structure is unchanged by isotopic substitution will certainly need to be checked. However, for many interfacial systems the directness of the method makes it well worth attempting to apply.

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