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NEUTRON AND X-RAY REFLECTIVITY FROM POLYMERS AT THE AIR WATER INTERFACE

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Abstract The applications of grazing incidence X-ray and neutron reflection to the study of interfaces are discussed. The method is applied to the study of polyethylene oxide adsorbed at the air-solution interface. Isotopic substitution is used to show that the surface is roughened to a thickness comparable with the statistical segment length of the polymer and that the segment length density profile into the solution is Gaussian in shape. Heavy ion substitution is used to obtain the volume fraction profile of a polystyrene sulphonate at the air-water interface.

SPECULAR REFLECTION OF NEUTRONS AND X-RAYS

The variation of the reflectivity of light, X-rays, or neutrons with incident angle from any surface depends on the variation of the appropriate refractive index normal to the surface. For neutrons and X-rays the refractive index is simply related to the composition. For neutrons

$$\eta = 1 - (\lambda^2/2\pi)\rho_s \qquad (1)$$

where ρ_s is the scattering length density given by

$$\rho_s = \sum n_i b_i \qquad (2)$$

where n_i is the number density of the ith nucleus and b_i its scattering length. There is a similar formula for X-rays but now the scattering length is simply the atomic number of the element. Because X-rays and neutrons probe matter at much higher momentum transfers than light they are sensitive to smaller distance scales at the interface.

The reflectivity profile for any model structure may be calculated exactly using the optical matrix method for the reflection of light polarized perpendicular to the reflection plane[1]. For X-rays only one state of polarization need normally be taken into account because at the low angles to be considered here, the reflectivity is independent of polarization. An alternative is to use the kinematic approximation[2]. In this approximation, the reflectivity, $R(\kappa)$, is given by

$$R(\kappa) = \frac{16\pi^2}{\kappa^4} |\rho_s'(\kappa)|^2 \qquad (3)$$

where κ is the momentum transfer normal to the interface, $4\pi\sin\theta/\lambda$, and $\rho_s'(\kappa)$ is the one dimensional Fourier transform of $\rho_s'(z)$, the derivative of the variation of the mean scattering length density normal to the surface.

It follows from (3) that the reflectivity of an interface with an abrupt step $\Delta\rho_s$ of scattering length density between the two media will vary as $1/\kappa^4$. A layer adsorbed at this interface will give rise to a series of interference fringes superimposed on the $1/\kappa^4$ decay of the

reflectivity. The spacing of the fringes is related inversely to the thickness of the adsorbed layer. It is not generally possible to invert the reflectivity data to obtain the interfacial scattering length density profile because it is the squared modulus of the Fourier transform which determines the reflectivity. In most cases it is necessary to use isotopic substitution to overcome this problem, which is the analogue of the phase problem in crystallography.

The difficulty in performing reflectivity experiments with X-rays and neutrons is that the intensity is low. However, for most materials total reflection occurs on going from the vapour to the condensed phase. In the region of total reflection the reflectivity is close to unity and so an acceptable signal can be obtained. Since the critical angle for total reflection is of the order of a degree (grazing incidence) the experiments must therefore be done at very low angles. Equation (3) shows that the resolution will be limited by the maximum value of momentum transfer to which the reflectivity can be measured. At present this is about 0.5 $Å^{-1}$ for X-rays, and about 0.3 $Å^{-1}$ for neutrons. This is a higher resolution than attainable in a small angle scattering experiment and is a result of the scattering not being spread over a large solid angle.

CONTRAST VARIATION IN THE NEUTRON EXPERIMENT

An important difference between X-ray and neutron reflection is the possibility of using the change of

neutron cross section for different isotopes of the same element. For interfacial systems of chemical interest the most important pair of isotopes are H and D whose scattering lengths are of opposite sign. Their magnitudes are such that, for example, the scattering length densities of D_2O and H_2O, are also of opposite sign. It is therefore possible to make an H_2O/D_2O mixture which has the same scattering length density as air and therefore gives no specular reflection at any angle. We refer to this mixture as null scattering water. At low concentrations of solute in null scattering water the contrast of the bulk solution may remain sufficiently close to that of air for there to be negligible reflection unless the solute is adsorbed at the surface. Thus the reflectivity depends *only* on the solute profile at the surface. As well as being able to examine the solute profile independently of the solvent, it is also possible to measure just the solvent profile by matching the scattering length density of the solute to that of air. This is often achieved approximately by using the fully protonated solute in D_2O. A a set of reflectivity measurements on different isotopic species can lead to a precise structural characterization of the surface region[3].

For polymers at interfaces the large difference in scattering length of H and D also gives neutrons a distinct advantage over X-rays. This is because the adsorbed layer is usually a mixture of polymer and solvent, but with solvent the dominant component. The difference in the X-ray scattering lengths of polymer and solvent is usually small and, when the composition of the

adsorbed layer is taken into account, the contrast between the interfacial and bulk regions becomes very small indeed. Furthermore, the sensitivity of the X-ray experiment to the adsorbed layer cannot be enhanced by contrast matching the bulk solution to air.

NEUTRON REFLECTION FROM A POLYMER SOLUTION

Polyethylene oxide(PEO) is surface active in water. Its adsorption at the air-solution interface has been studied by surface tension measurements[4] and π-A isotherms of the spread monolayer have also been extensively studied[5]. However, neither of these techniques can give any information about the surface structure.

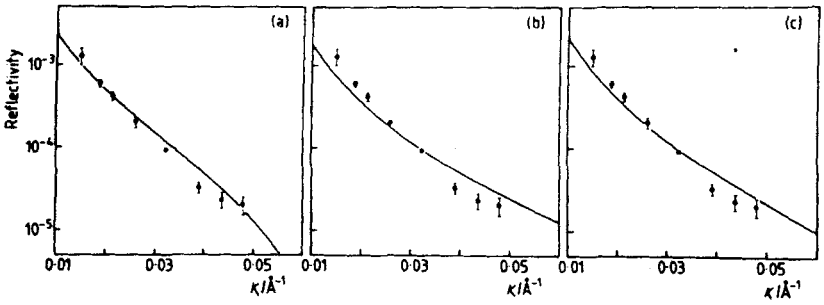

FIGURE 1 The fit of calculated reflectivity profiles to 0.1% dPEO in null water at 294 K, (a) single layer, thickness 90 Å and scattering length density 0.45×10^{-6}Å^{-2}, (b) the Schjeutjens-Fleer mean field profile with adsorption parameter 0.4, (c) the mean field reflectivity profile with adsorption parameter of 0.18 for the first and second layers.

Figure 1 shows the reflectivity of a 0.1% by weight solution of PEO (R.M.M. = 20000) in null scattering water[6]. The incoherent background has been subtracted and so the signal shown in the Figure is entirely from the

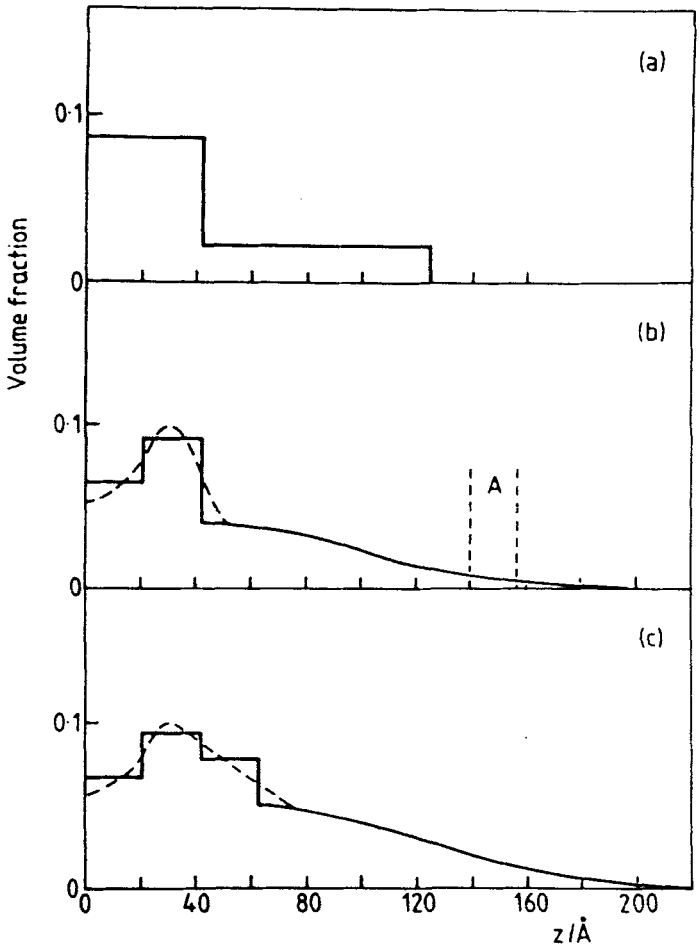

FIGURE 2 Segment density profiles for 0.1% PEO in water, (a) the simplest model that fits the observations at 294 K, (b) an equivalent two layer model in the interfacial region and a half Gaussian distribution of the loops and tails, (c) a similar model for a temperature of 318 K. Both (b) and (c) fit the data satisfactorily. The dashed lines represent smoother distributions which would also fit the data.

adsorbed layer. Figure 1(a) also shows the calculated profile for a model consisting of a single adsorbed layer of uniform scattering length density of thickness 90 Å.

The fit is remarkably good. However, when the scattering length density is converted to a segment density profile and then a prediction made of the reflectivity of the corresponding solution of hPEO in D_2O, the result does not fit the observations. Two new features have to be introduced to the model. Firstly, there is a region near the surface which contains a relatively larger amount of polymer of thickness about 45 Å. Secondly, the scattering length of this region shows that it contains a significant fraction of air, i.e. it is considerably roughened. The simplest model which will fit both sets of isotopic data is shown in Figure 2(a). However, given that the layer next to the surface contains air and given also that the tail region of the polymer is likely to decay into the bulk of the solution, more realistic models, which also fit the data, are those shown in Figure 2(b) and (c).

The statistical segment length of PEO is about 20 Å[7] and it seems likely that this will induce a roughening of the normally smooth water surface (mean square roughness about 3.3 Å) of about this characteristic length. It has been shown that the adsorption of polymer is greater at a rough surface than at a smooth one[8]. This greater adsorption may be the cause of the unexpected shape of the tail of the segment density distribution shown in Figure 2(b) or (c).

Mean field and scaling law predictions of the segment density profile[9] predict a rather more rapid decrease in the segment density than observed in these experiments. Indeed the reflectivity profile calculated using the Schjeutjens-Fleer mean field model[10] is shown in Figure 1(b) and for the same model but with adsorption into the

first two layers in Figure 1(c). These fit the data rather poorly. Better fits are obtained when the decay has the more Gaussian shape shown in Figure 2(b) and (c). The region marked A in Figure 2 is the maximum distance at which a repulsive force can be measured in a mica plate experiment[11].

X-RAY REFLECTION FROM POLYELECTROLYTE SOLUTIONS

Most theories of adsorbed polyelectrolytes start from theories of the conformation of neutral polymers at surfaces, adding the extra factors involved in the charged system in an ad hoc manner (see, for example, Hesselink[12]). Apart from the changes in the segment interactions resulting from the charges, in which the solvent will be more strongly involved than for neutral polymers because of charge screening effects, there are two additional components affecting the adsorption of polyelectrolytes compared with neutral polymers. There will be a change in the free energy of the electrical double layer upon adsorption of charged trains at the surface and there will be an electrostatic contribution to the surface train interaction resulting from the charged surface and image charges.

For polyelectrolytes the X-ray scattering of the polymer can be boosted considerably by incorporating heavy ions. This is what we have done to study polystyrene sulphonates at the air-solution interface. We have studied a range of concentrations, from 0.001% to 0.2% by weight of polymer in water, in both 0.1 M Cs_2SO_4 and 0.1 M

Na_2SO_4. The effects of the adsorbed layer on the reflectivity can be observed with X-rays even with the sodium form but become very large when Cs^+ is incorporated as the counterion. Figure 3 shows the reflectivity profiles of 0.1 M Cs_2SO_4 in water and a 0.05% by weight solution of sodium polystyrene sulphonate (molecular weight 74000) in 0.1 M Cs_2SO_4. There are large differences in the two profiles, which can be attributed to adsorption of the polyelectrolyte at the air-solution interface. There are even signs of an interference fringe in the profile, suggesting the formation of a structurally well defined layer.

Analysis of the data, using the optical matrix method, shows two main contributions to the reflectivity profile. The long tail of the polymer extending into the solution dominates the small momentum transfer region and causes the reflectivity at low angles to rise above that of the Cs_2SO_4 solution. The fringe occurring at high angles is caused by a very dense layer of polymer at the surface. Its intensity shows that the surface layer consists of an almost close packed layer of monomer units with the hydrophobic part on the air side of the interface and a quite well defined layer of ions on the solution side. The volume fraction profile can be calculated from the X-ray scattering length density profile taking the known scattering length densities of water and caesium polystyrene sulphonate. Figure 3(b) shows the volume fraction profile which when converted to a scattering length density profile gives the calculated reflectivity profile shown as the continuous line in Figure 3(a). The apparent value of more than 1 for the volume fraction at

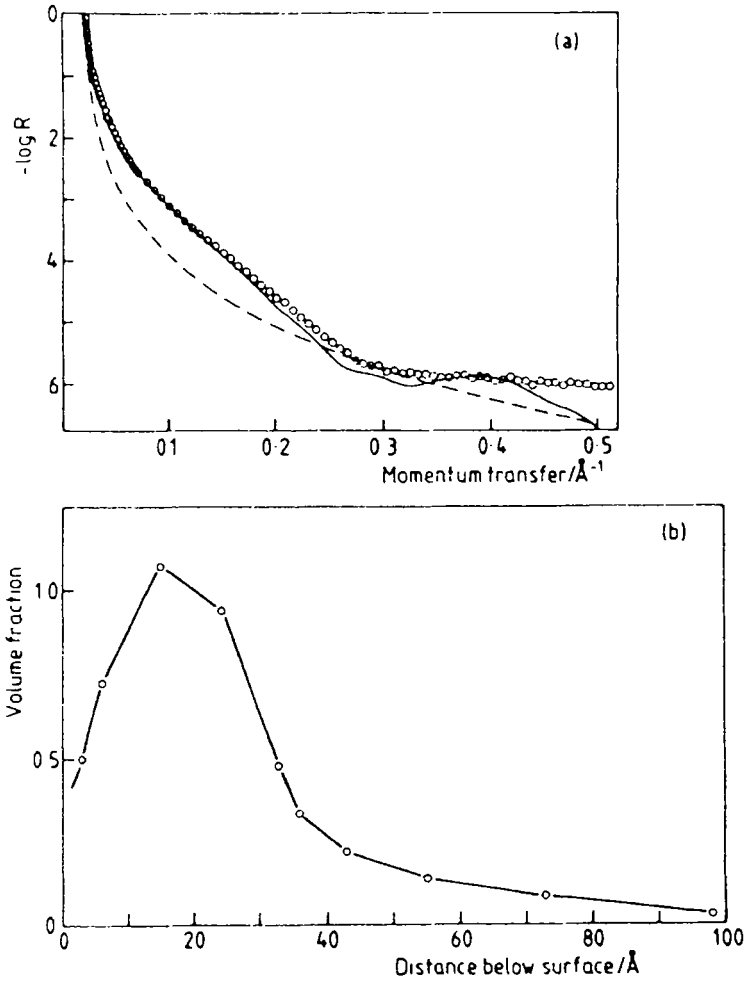

FIGURE 3 (a) X-ray reflectivities of 0.1 M Cs_2SO_4 in water (dashed line) and 0.05% sodium polystyrene sulphonate (molecular weight 74000, 100% ionic groups) in 0.1 M Cs_2SO_4. The continuous line is a calculated fit from which the volume fraction profile in (b) is derived.

about 15 Å occurs because there is almost a complete monolayer of ions just below the surface, which gives a very large peak in the scattering length density. Use of the average scattering length density in the conversion

from scattering length density profile to volume fraction profile cannot properly account for this.

This is the first detailed determination of the volume fraction profile of a polyelectrolyte at any surface, although Sansone et al.[13] have used evanescent wave techniques to study a solution of polystyrene sulphonate in dimethyl sulphoxide and have obtained the mean thickness of the layer assuming a particular shape for the profile. No such assumption has been made in our work. The profile was built up from a series of slabs until it give an adequate fit to the data.

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