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The determination of segment density profiles of polyethylene oxide layers adsorbed at the air–water interface

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The adsorption of polyethylene oxide of molecular weight 17 800 and 87 000 at the air/water interface has been studied by neutron reflection and surface tension measurements. Over the concentration range 10^{-4}–10^{-1} wt% of polymer the surface excesses determined by neutron reflection were consistent with the results derived from the surface tension using the Gibbs equation. Reflectivity measurements were made on three samples of different isotopic composition at a fixed concentration of 0.1 wt%. The adsorbed polymer layers were found to be essentially completely immersed in the water, contrary to earlier suggestions that a significant fraction of the polymer protrudes into the vapour phase. The distribution profiles of the polymers with respect to the surface normal direction are composed of two major blocks, one constituting the layer at the top surface and the other forming a diffuse region extending into the bulk solution. Over 90% of the homopolymer is in the first region with a thickness of 18 ± 2 Å, and the remaining diffuse region has a thickness of 35 ± 5 Å. Alternatively, the volume fraction profile of the polymer can be described as a 1 : 1 sum of two half Gaussians of widths 10 and 35 Å. Change of molecular weight and addition of salt do not change either the surface coverage or the segment density profiles significantly.

(Keywords: polyethylene oxide; polyethylene oxide adsorption; air/water interface)

INTRODUCTION

Polyethylene oxide (PEO) is well known for its surface active behaviour in aqueous solution. The solution behaviour has been systematically characterized with respect to solubility[1,2], viscosity or rheology[3,4], configuration[5–7], dielectric behaviour[8,9] and thermodynamic properties[10,11]. A recent review by Bailey and Koleske[12] summarizes the literature.

Studies on the surface activity of PEO can be broadly divided into work on spread monolayers, which are not necessarily at equilibrium with the sub-phase, and work on monolayers adsorbed from solution, which would normally be expected to be equilibrium monolayers and would therefore obey the Gibbs equation. Since the work by Shuler and Zisman[13] who reported that a stable PEO monolayer could be spread on an aqueous substrate and compressed and expanded reversibly, there have been many investigations undertaken to examine a variety of features of the layer, for example, the structure and the effects of temperature and salt[12,14–16]. Recently Henderson *et al.* have used neutron reflection to study PEO monolayers spread on the solution of $MgSO_4$[17]. A number of studies on the adsorption of PEO from solutions have also been reported in the literature. Lovell *et al.*[18], Couper *et al.*[19], Glass[20], Kim and Cao[21], Daoust *et al.*[22], and Rennie *et al.*[23] have examined the effects of molecular weight, concentration, substrate conditions and temperature on the coverage of PEO at the air/water interface. The packing of PEO at the surface with respect to the degree of polymerization has been interpreted in terms of the relative contribution of enthalpy and entropy[13,20]. Some authors have speculated that, whatever the molecular weight, portions of the polymer are oriented out of the aqueous phase into the air. There is also the interesting question as to whether the spread and solution monolayers are the same.

The techniques used so far have been mainly surface tension measurements[18,19], light scattering[24,25], and ellipsometry[21,26,27]. The last of these methods gives some information concerning the structure of the adsorbed monolayer, but is not sensitive to the extent of mixing of polymer and solvent at the interface. Specular reflection of neutrons has been shown to be an effective technique for examining polymers adsorbed or spread at the air/water interface[23,28]. Its main advantage is that, with the help of isotopic substitution, the reflectivity can be

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made selective to the polymer layer by matching the scattering length density of the solvent to that of air so that it does not contribute to the signal.

In the present study we have used neutron reflection to investigate the segment distribution profiles of surface films of PEO at the air/water interface formed by adsorption from aqueous solutions.

EXPERIMENTAL

Both deuterated and protonated PEO samples were made as previously described[17]. Monomer ethylene oxide samples were first dried in calcium hydride and then passed onto sodium mirrors a few times until no tarnishing was observed. The polymerization reaction was performed in dry tetrahydrofuran. Diphenylmethyl potassium was used as initiator and glacial acetic acid was used to terminate the reaction. The resultant solutions were poured into *n*-hexane and the final products were obtained as precipitates. M_n was found to be 17 800 and 24 900 for the first pair of deuterated and protonated polymers, denoted as *d*-PEO1 and *h*-PEO1 respectively, and 87 000 and for the second sample, denoted as *d*-PEO2.

The surface tension measurements were made using a Krüss K10 tensiometer with a Pt/Ir du Nouy ring. Neutron reflectivity profiles were measured using isotopic combinations of the fully deuterated polymer (*d*-PEO1) in null reflecting water (n.r.w.) and D_2O, and protonated polymer (*h*-PEO1) in D_2O, at concentrations of 0.1 wt%. The surface tensions for both *d*-PEO1 and *h*-PEO1 were found to be the same within experimental error, as shown in *Figure 1*, and it was therefore assumed that the monolayers would have similar structures. This assumption allows the reflectivities from the different isotopes to be combined in the way described below. For *d*-PEO2 a set of reflectivity profiles in n.r.w. were measured at concentrations from 0.1 wt% to 10^{-4} wt%. The effect of salt on the structure of *d*-PEO1 monolayer was studied using $MgSO_4$ solutions.

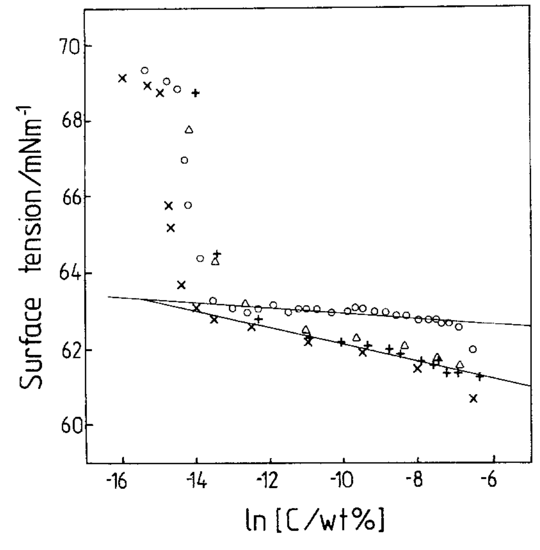

Figure 1 Surface tension of the three laboratory made polyethylene oxide samples in water at 25°C. The polymers are *d*-PEO1 (17 800) (+), *h*-PEO1 (24 900) (△), and *d*-PEO2 (87 000) (○), respectively. The continuous lines are the slopes of the Gibbs equation calculated using the measured neutron surface excesses

The procedures for determining the reflectivity profiles have been fully described elsewhere[29]. The measurements were made on the reflectometer CRISP at ISIS, UK. The instrument was calibrated using the reflectivity profile of pure D_2O, and the flat background measured at high momentum transfer was subtracted before interpretation. For the reflection measurements the solutions were contained in teflon troughs mounted in a sealed thermostatted container. All the measurements were made at 25°C.

RESULTS AND DISCUSSION

Surface tension measurements

Figure 1 shows plots of surface tension as a function of log (concentration/wt%) for the three samples used in the neutron reflection experiments over a limited range of concentration. The three plots are linear over much of the range shown. At high concentrations, however, the surface tension drops more rapidly as has already been noted by Kim and Cao[21]. At lower concentrations than shown in *Figure 1*, the equilibration time becomes very long and it is not possible to obtain good equilibrium values of the surface tension. This aspect of the problem was studied thoroughly by Couper and Eley[19]. We note that Glass[20] observed time dependence over much of the concentration range, although we found that 30 min were sufficient for equilibrium to be established for the concentration range shown in *Figure 1*. Within the experimental error the two samples with similar molecular weights (*h*-PEO1 and *d*-PEO1) show identical tension profiles with respect to the variation of concentration, indicating that their monolayers have similar properties. This is important for the later analysis of the neutron reflectivity profiles. The higher molecular weight sample has both a higher surface tension and a shallower slope, consistent with the observations of Couper and Eley[19].

Results from neutron reflection

Surface excess. The neutron reflectivity can be calculated exactly for any model of the neutron scattering length density ρ normal to the interface using the optical matrix method[30]. The scattering length density is given by

$$\rho = \sum_i b_i n_i(z) \qquad (1)$$

where n_i is the number density profile of atom i and b_i is its empirical scattering length. The optical matrix method of analysis requires the fitting of a structural model to the data, which may lead to ambiguities in that more than one structural model may give the same reflectivity profile. Fitting the same structural model to reflectivities from different isotopic compositions reduces the number of possible alternatives and may be used to determine the structure with more certainty. For the measurement of the deuterated PEO in null reflecting water (NRW), the specular reflectivity is only from the polymeric material adsorbed at the surface and there is no contribution from either the solvent or the bulk solution except some non-specular and some incoherent scattering which contribute to the background. The simplest model which can be used to fit the reflectivity profiles is the uniform layer model and the most directly obtained parameter from fitting the reflectivity profiles in this way is the area per monomer segment A, which is given by

$$A = \frac{\sum m_i b_i}{\rho \tau} \tag{2}$$

where m_i is the number of ith atom in the segment and τ is the thickness of the layer.

The fits of the uniform layer model to *d*-PEO1 in NRW with and without $MgSO_4$ are shown in *Figures 2a* and *b*. It can be seen clearly that a uniform layer model does not fit either of the two reflectivity profiles well. The poorly fitted region is at low κ, where the calculated profiles fall below the measured profiles, indicating the presence of regions of greater thickness, probably diffuse layers extending into the bulk solution. Merely increasing the thickness of the single uniform layer can be used to fit the low κ data, but then the rest of the profile is not accounted for correctly. The fits of the uniform layer model to the two profiles result in an area per segment of 16.5 ± 2 Å^2 for the measurement in pure water and 16 ± 2 Å^2 for that in the salt solution with corresponding thickness of 18 ± 2 Å^2 and 20 ± 2 Å, respectively. The surface excesses are found to be 0.48 and 0.51 mg m^{-2} in the presence and absence of the salt. The only usefulness of these values at this stage is for comparison because the absolute values of both parameters are model dependent, as we will discuss below. It is perhaps not surprising to note that the difference in surface excesses is small because the salt concentration used here is much less than that used to obtain theta conditions.

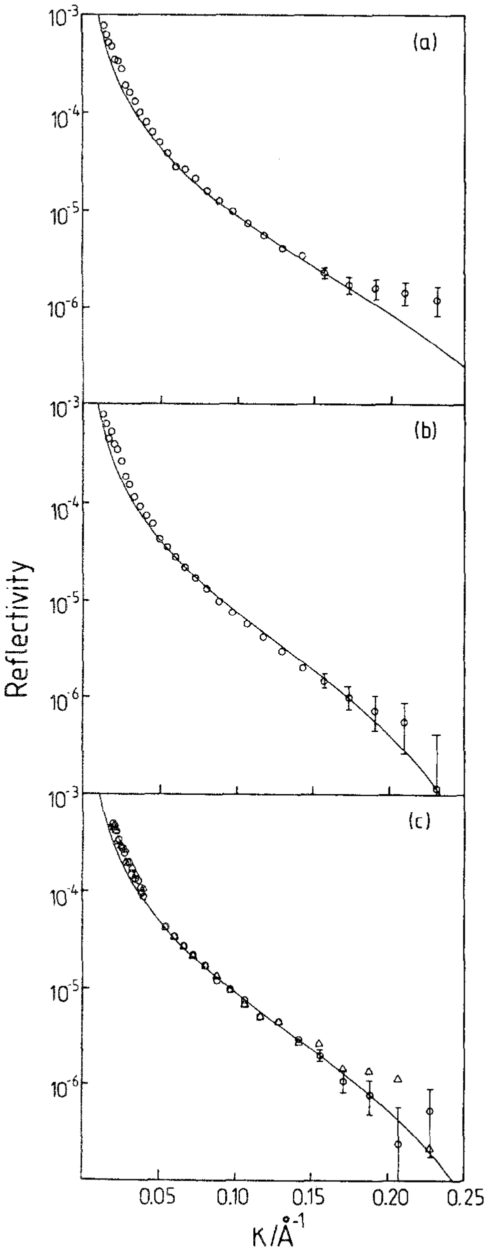

Figure 2 Uniform layer model fits to the reflectivity profiles of deuterated polyethylene oxides in null reflecting water (NRW) at 25°C. (a) 0.1 wt% *d*-PEO1 in NRW; (b) 0.1 wt% *d*-PEO1 in 0.3 M $MgSO_4$; (c) *d*-PEO2 in NRW at 0.1 wt% (○) and 10^{-4} wt% (△)

Reflectivity profiles were obtained for the larger molecular weight *d*-PEO2 in the concentration range 0.2–10^{-4} wt%, where the surface tension is almost constant (see *Figure 1*). The reflectivity profiles in NRW were found to be identical within error over the whole concentration range, indicating that there is no observable change in the surface coverage or the structure of the layer over this range of three orders of magnitude. *Figure 2c* shows two measurements at the extreme concentrations of 0.1 wt% and 10^{-4} wt%, together with the best uniform layer model fits. Using the single uniform layer model the thickness is found to be 21.5 ± 2 Å, thicker than the value obtained from *d*-PEO1 in the absence of $MgSO_4$, while the area per segment is found to be 15.5 ± 2 Å^2, slightly smaller than that of *d*-PEO1. The surface coverage was found to be 0.52 mg m^{-2}. The poor fit at low κ once again indicates that the diffuse part of the layer is not adequately taken into account in the uniform layer model.

Although we tested a two layer model, the simplest model which adequately fits the data is a three layer model. *Figure 3* compares reflectivities calculated using a three layer model with the experimental results. *Figures 3a* and *b* are the plots for *d*-PEO1 in NRW in the presence and absence of salt and *Figure 3c* for *d*-PEO2 in NRW. Because these models now fit the measured data well, the surface coverage, Γ, can be obtained with better reliability. Γ is found to be 0.53 ± 0.05 mg m^{-2} for *d*-PEO1 in the pure water system, 0.57 ± 0.05 mg m^{-2} for *d*-PEO1 in the system containing 0.3 M $MgSO_4$ and 0.56 ± 0.05 mg m^{-2} for *d*-PEO2 in pure water. We note here that there are three sources of error contributing to the fitted surface excess, calibration and sample errors, incorrect background subtraction, and fitting errors. For the surface coverage determination the latter is the least significant of the three and any fitted curve that passes through most of the points, as in *Figure 3*, will give an accurate coverage. The other errors are difficult to estimate, except by experience with the reproducibility of the experiment, but it is these that contribute mainly to the ± 0.05 mg m^{-2} above. It appears that addition of salt and increase of molecular weight have marginally increased the amount adsorbed, although the extent of the increase is smaller than the quoted error. The surface coverage obtained from the three layer model fitted in *Figure 3* is about 10% higher than from the uniform layer model fitted in *Figure 2*, the difference mainly arising from the poor fit of the latter in the low κ region, where the reflectivity would be affected most by polymer existing in a diffuse region. The surface excess obtained here is lower than that obtained from a previous neutron reflection measurement where it was found that the surface excess at saturation concentration was about $0.7\,\mathrm{mg\,m^{-2}}$ [23]. Although this difference is outside the experimental error, the properties of PEO films are thought to be sensitive to the type of end group, polydispersity, and molecular weight.

It is interesting to compare the neutron surface excess with that deduced from the plot of *Figure 1* using the Gibbs equation. Since the neutron surface excess is constant over the range shown, the surface tension should vary linearly with log *c*, provided also that the activity coefficient of the polymer does not vary with concentration. The line obtained from the neutron measurement is superimposed on the surface tension measurement in *Figure 1* and the agreement is well within the error in the surface tension measurements for both molecular weights. The change in slope between the two molecular weights results only from the change in molecular weight since the amount adsorbed, in terms of segments, is almost identical. That the Gibbs equation analysis works for the higher molecular weight polymer over most of the concentration range shows that the activity coefficient is not varying significantly with concentration, which is as expected from the Flory-Huggins theory[31]. It should also be clear from the scatter of the points in *Figure 1* that it would be very difficult to obtain an accurate surface excess from the surface tension measurements on their own, especially as the slope decreases.

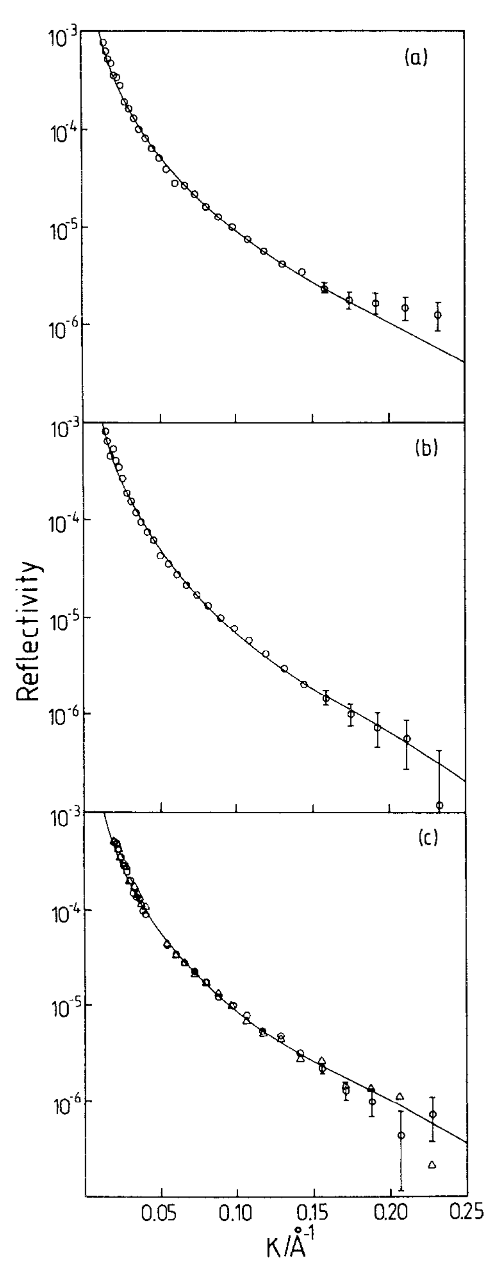

Figure 3 Three layer model fits to the reflectivity profiles of deuterated polyethylene oxides in null reflecting water (NRW) at 25°C. (a) 0.1 wt% *d*-PEO1 in NRW; (b) 0.1 wt% *d*-PEO1 in 0.3 M $MgSO_4$; (c) *d*-PEO2 in NRW at 0.1 wt% (○) and 10^{-4} wt% (△)

Figure 4 shows the polymer volume fraction profiles corresponding to the three layer model. Within the experimental and fitting errors, the distribution profiles for *d*-PEO1 (continuous line) and *d*-PEO2 (dashed line) are similar, indicating that the volume fraction profile is not sensitive to the molecular weight. Addition of 0.3 M salt also did not have much effect either on the density or distribution in the surface region (dotted line). For the spread monolayer, Henderson *et al.*[27] concluded that addition of magnesium sulfate increased the surface excess by less than 10%, which is consistent with our observation, but they found that the thickness of the top layer decreased by almost 40%. Rennie *et al.*[23] found that addition of $MgSO_4$ enhanced the surface excess.

The disadvantage of model fitting is that more than one model may fit a given reflectivity profile. This problem may be overcome by fitting a single model to profiles with different isotopic compositions. *Figure 5* shows the reflectivity profiles of *h*-PEO1 and *d*-PEO1 in D_2O, together with the fits of the three layer model

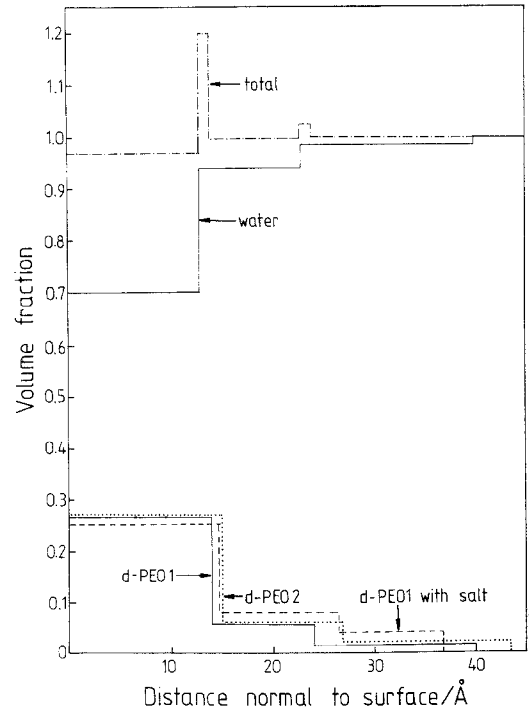

Figure 4 Segment density distribution profiles obtained from the three layer model fits. The distribution profile for the water corresponds to the adsorption of *d*-PEO1 and *h*-PEO1 at the air/water interface. The dash-dotted line is the calculated total volume fraction of *d*-PEO1 (*h*-PEO1) and water at the interface

corresponding to the exact distribution profiles in *Figure 4*. This structural model fits all three reflectivity profiles well, supporting the correctness of the model.

Although the three layer model in *Figure 4* fits all three reflectivity profiles, it is very coarse grained and the actual segment distribution profile must be a smooth function. In our previous paper on PEO at the air/water interface[23] we discussed the possibilities of accounting for the PEO volume fraction profile in terms of continuous functions, either empirical, analytical, or numerically calculated. We attempted to apply the scaling predictions of de Gennes[32] for the case of a good solvent, an analytical mean field profile[33], and a numerical mean field profile[34]. For the latter we used the known χ parameter for PEO in water. The difficulty with all these profiles is that they generally decay rather rapidly at short distances and we were unable to account for our previous reflectivity data with any of them. The same is true for the present data, which also falls off more slowly than these models require. There may be two explanations of the problem. The first is that the surface is probably rough on a length scale comparable with a statistical segment length (for surfactants at this surface tension the Gaussian width of the interface (full width at $1/e$ of the height) at a comparable surface tension is of the order of 10–15 Å). This will have en effect on the predicted volume fraction profile, which is not taken into account in the above theoretical treatments. The second possibility is that we should include an initial proximal layer with arbitrary parameters. However, the sensitivity of the experiment would not then be good enough to extract any meaningful scaling exponent for the rest of the segment density profile. Empirically we find that the data are well fitted by two half Gaussians as shown in *Figure 6*. This does not mean that other functional forms of similar characteristics could not also be fitted, but it does exclude the smooth surface theoretical profiles discussed above.

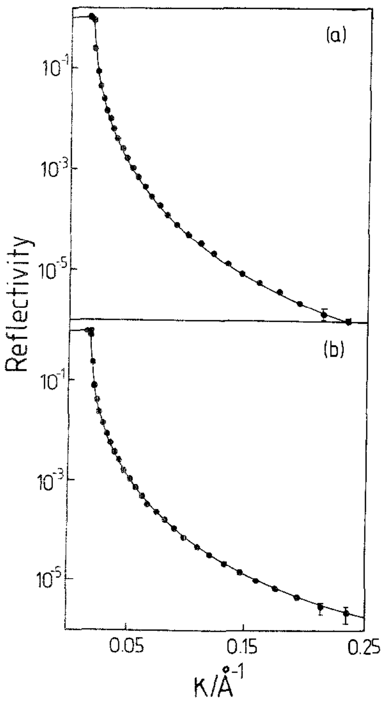

Figure 5 Three layer model fits to the reflectivity profiles of polyethylene oxide in D_2O at 25°C. (a) *d*-PEO1 in D_2O; (b) *h*-PEO1 in D_2O

Rennie *et al.*[23] deduced from the reflectivity of *h*-PEO in D_2O that the surface was abnormally rough, i.e. there was a thick surface layer with a significant proportion of empty space. The present measurements do not show any such effect. If there is no air in the top part of the PEO layer, the scattering length density of that layer will be either that of pure PEO or of the mixture of the PEO with water. Using either the three layer or the combination of two half-Gaussians we find that the fraction of the air involved in the top layer is less than 6%, indicating that the layer is almost completely immersed in the water. The presence of a small fraction of air in the top layer may also be explained in terms of thermal roughness[35]. It is important to emphasize that the data of Rennie *et al.* were obtained at an early stage in the development of the neutron reflection technique, and the sensitivity of their experiment was more than an order of magnitude worse than in the present one.

It is interesting to compare the segment distribution profiles between the spread and equilibrium monolayers. *Figure 7* shows the reflectivities of the *d*-PEO1 monolayer spread on (○), and adsorbed from (+), NRW. The spread monolayer was measured at the highest accessible pressure (9 mN m^{-1}) and the adsorption from the aqueous solution was at a concentration of 0.1 wt% (surface pressure 10.3 mN m^{-1}). The spread monolayer can be fitted very well by the model of a uniform monolayer with a thickness of 23 ± 2 Å and surface excess of 0.6 ± 0.1 mg m^{-2}, shown as a continuous line in *Figure 7*. The best fit of a single uniform layer to the adsorbed monolayer, at a similar coverage, gave a

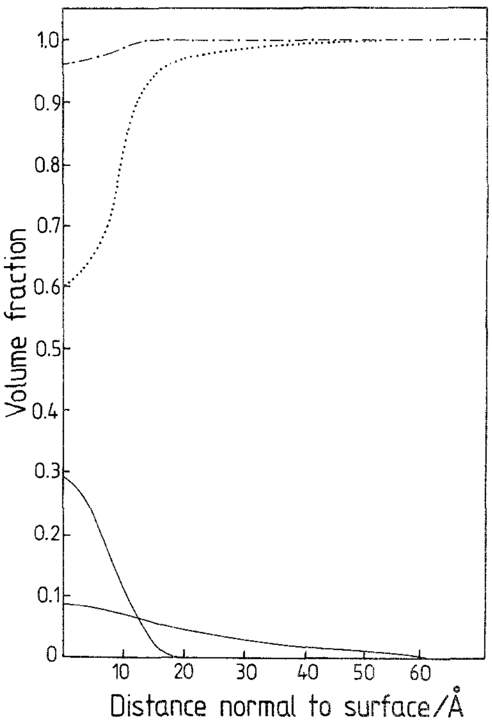

Figure 6 Segment density distribution profiles of *d*-PEO1 obtained from the fit of two half Gaussians of width 10 and 35 Å (defined as width ρ at $1/e$ of the maximum of $\exp(-4z^2/\sigma^2)$. The distribution profile for the water (dotted line) corresponds to the adsorption of *d*-PEO1 and *h*-PEO1 at the air/water interface. The dash-dotted line is the calculated total volume fraction of *d*-PEO1 (*h*-PEO1) and water at the interface

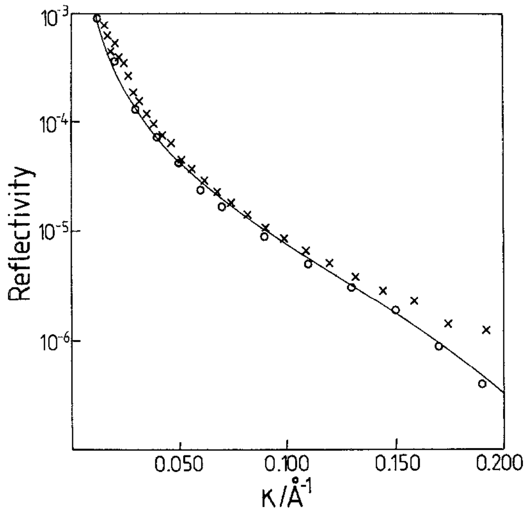

Figure 7 Comparison of the reflectivities of spread (O) and adsorbed monolayers (×) of *d*-PEO1 on null reflecting water. The continuous line fitted to the spread monolayer is for a uniform monolayer of thickness 23 ± 2 Å. Fits for the other profile with different models are shown in *Figures 2* and *3*

thickness of 18 ± 2 Å but this was a poor fit. The main differences in the two profiles occur at high κ and it is the shape in this region that determines the apparent single monolayer thickness. It would appear that there is no diffuse tail for the spread monolayer, but it is significant for the equilibrium layer. Sauer and Yu inferred from quasi-elastic light scattering that the spread and adsorbed PEO films were the same[24]. That the structure has been found to be different does not necessarily mean, however, that the dynamic properties of the layer, as measured by quasi-elastic light scattering, are also different. Two groups[26,27] have measured the thickness of the spread PEO layer using ellipsometry, both obtaining thinner layers than we observe here. However, since the polymer is mostly immersed in the water, it is very difficult to deduce an accurate thickness from ellipsometry owing to the lack of contrast between the layer and water.

CONCLUSIONS

We have obtained neutron reflection and surface tension results for an equilibrium layer of PEO adsorbed at the air/water interface. The neutron measurements are substantially improved over earlier work and, in contrast to the earlier work, indicate no abnormally large roughness at the surface. Over the concentration range 10^{-4}–10^{-1} wt% of polymer there is good agreement between the neutron surface excesses and those deduced from the Gibbs equation. We also observe differences between the structure of the spread monolayer and that formed by adsorption from bulk solution.

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