

Collapsed structure of hydrophobically modified polyacrylamide adsorbed at the air-water interface: the polymer surface excess and the Gibbs equation

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Abstract

Neutron reflectometry has been used to measure the surface excesses and structures of hydrophobically modified polyacrylamide polymers (HMPAM) at the air-water (A-W) interface. The HMPAM were based on a range of commercially available PAM, which were modified by the N-alkylation of the amide group to give an N-C_nD_{2n+1} hydrophobic group with $n = 8, 12$ and 16 at levels of 0.5, 1, 2, 4 and 6 mol%. A further HMPAM was synthesized in two isotopic forms with either N-C_nD_{2n+1} or N-C_nH_{2n+1} as hydrophobes.

For moderate and high MW species the near surface structure at the A-W interface consists of two layers. All the hydrophobic units are in these two layers, as well as a large fraction of backbone units, often amounting to a total volume comparable with

that of the hydrophobes. The outer layer next to air contains no water but the residual volume in the inner layer is filled with water. A further large fraction of the backbone units also forms a diffuse third layer extending a substantial distance into the solution. In a low MW HMPAM there was preferential adsorption of species with higher mol% of hydrophobe and a tendency to form apparently non-equilibrium structures, which in some cases resulted in more complex structures than the simple one characteristic of the large MW polymers. With the exception of this polymer, the variation of the patterns of surface excess and structure with solution concentration suggested that systems containing hydrophobic units at a level of 0.5, 1 and 2 mol% formed equilibrium or near equilibrium surface layers at bulk concentrations of 0.01 - 0.35 wt% for C₈ to C₁₆ units. However, higher levels of 4 and 6 mol% of the C₁₂ hydrophobe led to much less regular patterns of adsorption indicating that equilibration is more difficult once the molar fraction of hydrophobe exceeds 2 mol%.

The behaviour of the surface tension (ST) over the same concentration range as the NR experiments could be accounted for by the Gibbs equation using the directly measured surface excesses and the incorporation of a low charge on the polymers (about 1 charge per 100 backbone units). The presence of such a charge in PAM can arise from hydrolysis of some amide to carboxylate and was known to be present for one of the polymers. The extra structural information obtained by NR on these HMPAM combined with more recent measurements of the state of ionization in polyacrylates (PAA) allowed us to reinterpret earlier ST and x-ray reflection results on hydrophobically modified HMPAANA containing a similar level of 1 and 2 mol% C₁₂H₂₅ hydrophobes. The Gibbs equation again accounted quantitatively for the ST behaviour using the correct state of ionization of the polymer. Although the adsorption of hydrophobic groups in HMPAANA is about one tenth of that for the corresponding HMPAM, the ST drops more quickly to lower values for HMPAANA because of its higher level of dissociation, which increases the magnitude of the slope in the Gibbs plot.

Introduction

The hydrophobicity of a polymer can be manipulated in several different ways but the term hydrophobically modified polymer (HMP) usually refers to a mainly water soluble polymer that contains a fraction of more or less randomly distributed hydrophobic groups introduced either post-polymerization or by copolymerization. There is a limit to the amount of hydrophobicity that can be introduced while maintaining water solubility and therefore a balance has to be maintained between the degree of substitution and the hydrophobicity (usually chainlength) of the hydrophobic groups. Typically for a C_8H_{17} chain the chain substitution must be less than about 5 % if water solubility is to be maintained.

The individual hydrophobic segments in an HMP tend to self-associate intra- or inter-molecularly,¹⁻³ which strongly affects the viscosity of the aqueous solution and this makes HMPs useful viscosity modifiers, e.g.^{4,5} However, the incorporation of hydrophobic groups into an otherwise water soluble species also creates local amphiphilicity in the structure and the resultant surface activity of the amphiphilic fragments can be tuned over a wide range. This leads to the widespread use of HMPs as agents either for removing unwanted particles or chemical species from contaminated water, or for solubilizing species of low solubility into solutions or colloidal suspensions, e.g.⁶ To make full use of this second property requires an understanding of the surface behaviour of the HMP, particularly at the molecular level. Thus, whereas the adsorption of a simple amphiphile involves an energy of adsorption and a packing energy, the adsorption of an HMP involves an additional large component from changes in the configurational energy of the polymer, which is more complicated than for the simple backbone because of the presence of the amphiphiles.

Although most applications of the surface activity of HMPs can be expected to be mainly at the solid-liquid interface, the complications above suggest that it would be useful first to understand the surface behaviour at the simpler air-water interface (A-W). This has the advantages that its surface energy/surface tension (ST) can be measured and used to monitor the approach to equilibrium. In addition the average composition normal to the

surface can be determined by neutron reflection (NR) and/or x-ray reflection (XRR) and in principle can be resolved into the contributions from the different types of fragment, amphiphilic chain, polymer backbone and solvent. So far, however, there have been relatively few studies of the surface properties of HMPs. Most of these have focussed on the dynamics of adsorption. Thus, Kopperud and Hansen¹ observed strong surface activity at the air-water (A-W) interface for a series of HMPAM prepared by polymerisation under micellization conditions. There was an initial limited drop in the surface tension (ST) at times less than 1000 s, which then decreased more substantially and more rapidly at longer times. Their polymers were prepared by copolymerization under conditions where the hydrophobe formed micelle-like aggregates, which produces bulk behaviour dominated by the hydrophobe clusters. Monteux et al., used random post-polymerization to prepare a hydrophobically modified polyacrylic acid, HMPAA, and found an almost opposite behaviour of the ST from that described by Kopperud and Hansen. Thus, they found a significant drop in ST in the first 1000 s, which was followed by a gradual and smaller drop over much longer times.^{7,8} Millet et al. investigated the surface of HMPAANA where the hydrophobe was dodecyl or octadecyl at a molar percentage of 1-20%, and was introduced post-polymerization.⁹ The surface was examined by ST and x-ray reflectivity (XRR). Their equilibration times for the surface were generally much slower than those of Monteux et al., but in both cases the surface equilibration was much slower than expected for simple diffusion. On the basis of a comparison of the adsorbed amount from ST, via the Gibbs equation, with that determined separately by XRR, Millet et al. concluded that the polymer loops and tails do not contribute to the surface excess in the Gibbs equation. In a later paper, Millet et al. demonstrated that a logarithmic variation of the surface excess variation with time can be explained with a reptation-diffusion based model.¹⁰

Deme and Lee used neutron reflection (NR) to study a hydrophobically modified polysaccharide (native pullulan modified by grafted hydrophobic cholesteryl groups).¹¹ The pattern of ST behaviour was similar to that observed for HMPAA by Monteux et al. except that its

variation with time was much slower, as might be expected from the more rigid backbone of the polysaccharide. Nevertheless, the adsorption as measured directly by NR showed negligible time dependence. When coupled with the ST behaviour this suggests that the changes to the ST are a result of rearrangement of the polymer at the surface. There was, however, insufficient contrast between backbone and hydrophobe for the surface distributions to be determined independently, so that details of any surface rearrangement involving redistribution of these groups could not be followed.

In general, unfolding of a randomly hydrophobically modified polymer is expected to lead to a brush-shaped adsorption layer, with the hydrophobic groups as anchors and hydrophilic loops extending into the solvent and this has been supported by a number of theoretical or modelling calculations, e.g. see Jamadagni et al.¹² At the solid-solution interface Argillier et al¹³ have compared the adsorption behaviour of HMPAM and PAM at mineral surfaces, and interpreted the shape of the adsorption isotherm as arising from the formation of multilayers due to hydrophobic association. Poncet et al¹⁴ studied the adsorption of HMPAA onto hydrophobic surfaces by ellipsometry. The results indicated that the surface anchoring of the alkyl groups is accompanied by repulsion between the acrylate groups, which is thought to result in the formation of loops at the interface, separated by short chains. The addition of electrolyte results in a reduction in the mean thickness due to the partial collapse of the loops.

In this paper we focus on the adsorption behaviour of a range of randomly modified HMPAM at the A-W interface, studied by ST and NR measurements. The ST is a measure of the surface activity associated with these polymers, but NR has the capability to provide direct access to the adsorbed amounts. By contrasting the hydrophobes with the backbone, using deuterated hydrophobes and a protonated backbone, it should further be possible to distinguish the distribution of the different parts of the HMPAM. Of particular interest is the location of the hydrophobic chains at the surface, which can be determined by using deuterium labeling in conjunction with NR.

Experimental Details

Methods

NR provides information about inhomogeneities normal to an interface or surface, and is particularly effective for the study of the air-water interface. The basis of the experiment is that the variation in specular reflection with Q (the wave vector transfer normal to the surface, defined as $Q = (4\pi \sin \theta / \lambda)$ where λ is the neutron wavelength and θ is the grazing angle of incidence) is simply related to the composition or density profile along the direction normal to the interface.^{15,16} In the kinematic or Born approximation,^{17,18} the reflectivity is the square of the Fourier transform of the scattering length density profile, $\rho(z)$,

$$R(Q) = \frac{16\pi^2}{Q^2} \left| \int \rho(z) \exp(iQz) dz \right|^2 \quad (1)$$

where $\rho(z) = \sum_i n_i(z)b_i$, $n_i(z)$ is the number density of the i th nucleus, and b_i is its scattering length. Although the kinematic approximation is a useful way of describing neutron reflection, in practice the reflectivity is calculated using the accurate optical matrix formulation.¹⁹ The key to the use of the technique for the study of interfacial adsorption is the ability to manipulate the scattering length density or neutron refractive index profile at the interface using hydrogen/deuterium (H/D) isotopic substitution. The neutron refractive index is defined as $n^2 = 1 - \lambda^2 \rho(z) / \pi$ and H and D have very different neutron scattering cross sections.^{20–22}

The analysis of the neutron reflectivity from partially labelled hydrophobically modified polymers presents a number of intricacies, which are presented as part of the analysis of the results. The basis of the analysis requires a knowledge of the scattering length densities of the various components, which are given by the known scattering lengths of the constituent atoms²³ and the partial molar volumes of the fragments, which, for the hydrophobic fragments, have been given by Tanford.²⁴ These values are assembled in Table 1 and they are

Table 1: Scattering lengths and molecular volumes for the different components at the surface.

fragment	scattering length $b \times 10^5/\text{\AA}$	scattering length density $\rho \times 10^6/\text{\AA}^{-2}$	volume per fragment $v/\text{\AA}^3$
C ₈ D ₁₇	166.6	6.65	225
C ₈ H ₁₇	-10.4	-	225
C ₁₂ D ₂₅	234.6	7.59	325
C ₁₂ H ₂₅	-13.7	-	325
C ₁₆ D ₃₃	320	7.68	425
C ₁₆ H ₂₅	-17.0	-	425
C ₂ H ₃ CONH ₂	16.1	2.06	78
C ₂ H ₃ COND ₂	36.5	4.68	78
D ₂ O	19.1	6.35	30
H ₂ O	-1.7	-0.56	30

based on the specific volumes of both solid and liquid alkanes. The molar volume of the polymer backbone has been assumed from the bulk density of the solid. However, the more relevant quantity is the *partial* molar volume of a polymer fragment in aqueous solution, which may differ significantly from the value assumed from the bulk density, although there appear to be no available measurements and such measurements might not be easy. The value given in Table 1 for a PAM fragment has been deduced from the fitting of the NR profiles and this is discussed as part of the analysis of the results.

The NR measurements were made at the A-W interface using the reflectometers CRISP and SURF at the ISIS pulsed neutron source.²⁵ Measurements were made at two fixed angles of incidence, 0.8 and 1.5°, covering a neutron wavelength range of 0.5 to 6.8 Å which gives a Q range of 0.027 – 0.5 Å⁻¹. At high Q ($\approx 0.25 - 0.5 \text{ \AA}^{-1}$) the reflectivity is dominated by the incoherent scattering from the aqueous solution, representing the background, which is subtracted from the data before any detailed analysis. The absolute reflectivities were established by reference to the reflectivity from D₂O.²⁶ The measurements were all made at 25° C and the samples of volume about 30 mL and depth about 8 mm were contained in Teflon troughs in a sealed atmosphere. Each measurement lasted about 30-60 min but

each sample was typically in place for 1-5 hr before the actual measurement. In the time of flight method for measuring the NR the reflectivity is measured at two angles, each giving a range of momentum transfer. For each of these two segments of the profile, the reflectivity at different wavelengths is measured simultaneously, so that each segment is an average over the time of measurement. There is no variation in time across one segment. A mismatch of the small overlap region between the two segments is a useful indicator of incomplete equilibration.

The surface tension measurements were made using a Krüss K10 maximum pull digital tensiometer and a Camtel CIT-100 interfacial tensiometer, with a Pt/Ir du Noüy ring. All associated glassware was cleaned by soaking in Decon-90 solution and rinsing thoroughly in UHQ water. The measurements were made at 25°C, and the du Nouy ring was flamed and rinsed between measurements. The ST was not measured as a function of time and the measured values given here were taken when the variation of ST with time was less than 0.05 mN m⁻¹ over a period of 10 minutes. Surface properties may be sensitive to the dilute-semidilute crossover at c^* (see e.g. Huang and Wang²⁷). The radius of gyration (R_g) of PAM in the *absence* of any hydrophobic modification has been determined by François et al.²⁸ to be

$$\langle R_g^2 \rangle^{1/2} = 7.49 \times 10^{-10} M^{0.64} (cm) \quad (2)$$

The NR experiments were done at concentrations from 0.001 to 0.35 wt%, and at 0.35% Eqn (2) shows that c^* is not reached until the MW is above about 750k, i.e. of the five polymers studied c^* is reached only for the polymers labelled A and possibly those of C in Table 2 below.

Materials

Two synthetic routes were used to prepare the different HMPAM samples used in this study. In method 1 the hydrophobic groups were introduced into an already prepared polymer,

Table 2: Samples prepared, A, B, C and D were prepared post-polymerization as described in the text, using sources of PAM from (A) BDH, MW = $> 5 \times 10^6$), (B) ACROS, MW = 2×10^5), (C) Polysciences, MW = $6 \times 10^5 - 10^6$), and (D) Polysciences, MW = 10^4). The samples labelled E were made by copolymerization as described in the text.

sample label	polymer source X	hydrophobe	mol% hydrophobe
d-C ₈ PAM-X-0.5	A, C	C ₈ D ₁₇	0.5
d-C ₈ PAM-X-1.0	A, C, D	C ₈ D ₁₇	1.0
d-C ₈ PAM-X-2.0	A, B, C, D	C ₈ D ₁₇	2.0
d-C ₈ PAM-X-4.0	B	C ₈ D ₁₇	4.0
d-C ₈ PAM-X-6.0	B	C ₈ D ₁₇	6.0
d-C ₁₂ PAM-X-0.5	C, E	C ₁₂ D ₂₅	0.5
d-C ₁₂ PAM-X-1.0	C, D, E	C ₁₂ D ₂₅	1.0
d-C ₁₂ PAM-X-2.0	B, C, D, E	C ₁₂ D ₂₅	2.0
d-C ₁₆ PAM-X-1.0	C, D	C ₁₆ D ₃₃	1.0
d-C ₁₆ PAM-X-2.0	B, C, D	C ₁₆ D ₃₃	2.0
h-C ₁₂ PAM-X-0.5	E	C ₁₂ H ₂₅	0.5
h-C ₁₂ PAM-X-1.0	E	C ₁₂ H ₂₅	1.0
h-C ₁₂ PAM-X-2.0	E	C ₁₂ H ₂₅	2.0

i.e. post-polymerization, and this was done using the selection of commercially available polymers in Table 2. This method used partial N-alkylation of the PAM by the appropriate deuterated or protonated alkyl bromide in anhydrous DMSO under a nitrogen atmosphere, using potassium t-butoxide as catalyst^{2,29}. In the absence of water the alkyl groups will attach singly to the PAM backbone and are expected to be randomly distributed. The final HMPAM was purified by dialysis in water.

In method 2, N-dodecylacrylamide was copolymerized with acrylamide following Deguchi and Lindman.²⁹ This required the initial synthesis of N-d-dodecylacrylamide, where d denotes perdeuteration of the chain. This was done by the reaction of d-dodecanoic acid with urea to give d-dodecanamide,³⁰ which was then reduced to d-dodecylamine using LiAlD₄³¹ and the product purified by distillation under reduced pressure. The amine was then reacted with acryloyl chloride to give N-d-dodecylacrylamide following the procedure of Effing et al.³² The copolymerisation to give the HMPAM used radical copolymerisation in t-butyl alcohol with acrylo-bis(isobutyronitrile) as initiator. The copolymer precipitated from the reaction

was extensively washed with acetone to remove the monomer. The MW was assumed to be comparable with the 130k value of the original preparation. The partially deuterated polymer samples prepared are given in Table 2. The level of deuteration of the hydrophobic chains was 98%.

Results

The obvious labelling for exploring the surface structure of HMPAM adsorbed at the A-W interface has the hydrophobic moieties deuterium labelled rather than the backbone of the HMPAM because the hydrophobic units are expected to dominate the surface. However, the low stoichiometric level of the hydrophobic groups combined with the non-zero scattering of the acrylamide units potentially reduces any domination of the reflectivity by the deuterium labels. In addition to the measurement of polymers with deuterated hydrophobes (dHMPAM where d indicates that the hydrophobe is deuterated) in both D₂O and NRW, we therefore also made measurements for some of the polymers using dHMPAM in D₂O and hHMPAM in D₂O. Measurements of the three different contrasts provide better information on the structure of the adsorbed layer. The model used for fitting the data is described as part of the analysis of the results below. Table 1 shows that for a 1 mol% dHMPAM the scattering length of the 100 fragment backbone in NRW is $100 \times 16.1 = 1610 \times 10^{-5}$ Å, compared with 234.6×10^{-5} for the single attached C₁₂ hydrophobe. Thus, although a layer of hydrophobic units at the surface might give rise to a strongly reflecting thin layer, the signal from the more diffuse and thicker backbone region is not negligible. Further complications are that the scattering length of the backbone may depend on isotopic exchange with the solvent (see Table 1), and that in D₂O the reflectivity depends substantially on the displacement of D₂O by the backbone. For the first of these complete exchange with the solvent is often assumed and for the second there is uncertainty in the molar volume of the backbone, which leads to a corresponding uncertainty in the volume of displaced D₂O. The use of three different isotopic

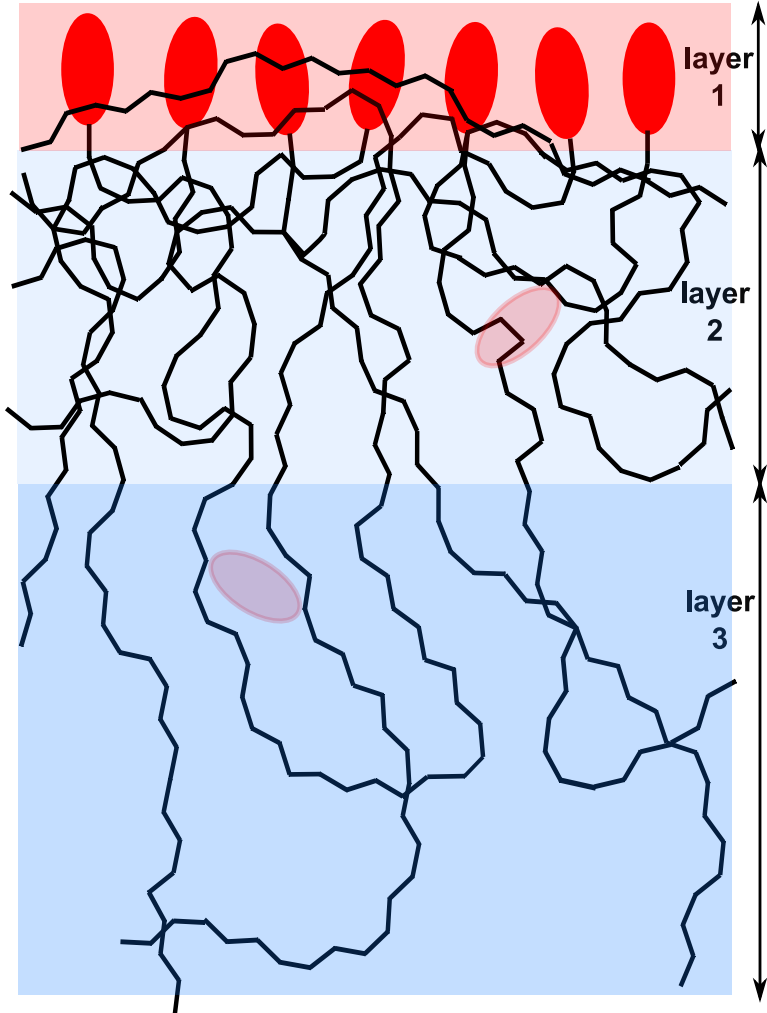


Figure 1: Schematic diagram of the layer model used for fitting the reflectivity of HMPAM at the air-water interface. Hydrophobic units are the red ellipses, backbone chains are black lines and the presence of water is indicated by blue shading. There is no water in layer 1 and not all the hydrophobic units are necessarily in layer 1, as is indicated by the presence of a hydrophobe in each of layers 2 and 3.

contrasts made it possible to assess these factors directly in the case of the E HMPAM and we therefore analyse the experimental results for these in detail before discussing the results for the other polymers.

On the basis of preliminary fits to some of the data we chose the relatively simple three layer model shown in Figure 1. This consists of a surface layer, layer 1, that contains only

hydrophobe and polymer backbone and is not necessarily space filling, a middle layer, layer 2, which is usually significantly thicker than layer 1 and may again contain hydrophobe and polymer but with the remaining space filled by water, and layer 3 which contains polymer backbone with the remaining space filled with water. The division into sharply defined layers is unrealistic and we allowed for this by introducing roughness parameters directly into the optical matrix method for calculating reflectivity following Névot and Croce.³³ The roughness was generally found to be small for interfaces 0-1, 1-2 and 2-3, i.e. comparable with roughnesses in simpler systems, and we therefore further assumed that it has the same value for these three interfaces. However, the roughness between layer 3 and the bulk solution has to account for the diffuse nature of the polymer in this region and can be expected to be large and may even have a specific functional form. Any particular shape in the distribution at this interface is, however, likely to be lost in the strong signals from other parts of the layer and we have therefore retained the simpler approximation of Névot and Croce, but with a much larger value for the roughness than for the other three interfaces. In the kinematic model any roughness can be Fourier transformed to give a structural roughness and the volume fraction profiles shown below have been obtained by this means. This method leads to shapes of the divisions between the layers that are approximate, but this will not affect significantly the accuracy of the measured compositions of the layers and the thicknesses of layers 1 and 2 measured as simple slabs.

There are several uncertainties in the application of the model of Figure 1. The first is that the *partial* molar volume of the PAM backbone in water or in hydrocarbon is not known. The bulk density leads to a molecular volume of about 90 \AA^3 , but this includes no effect of mixing. For measurements in D_2O the displacement of the D_2O by backbone residues has a large effect on the reflectivity. This is most noticeable for the contrast with protonated hydrophobe in D_2O , where the contribution of layer 1 is small and the reflectivity is dominated by the volume fraction of D_2O missing from layers 2 and 3. Fits of this contrast for the E HMPAM required a value of not more than 78 \AA^3 , significantly less than the bulk

density value of 90 \AA^3 , i.e. mixing the backbone with water has a partial molar volume lower than the volume obtained from the bulk density. A second possible uncertainty arises from H/D exchange. As shown in Table 1, the scattering length of the amide group depends significantly on H/D exchange with the solvent. Use of the three contrasts for the E HMPAM is sensitive to the extent of this exchange and inclusion of the effect showed that exchange was complete. A final important feature of the fitting is the volume of total backbone per hydrophobic unit. For a single C_{12} hydrophobic unit with a molar volume of 325 \AA^3 there is an associated volume of backbone in a 0.5 mol% HMPAM about $50\times$ greater than that of the single hydrophobe. In principle, this volume is determined by the stoichiometry. Since preferential adsorption of species that differ significantly from the average composition may occur, the surface stoichiometry is in principle uncertain. The most probable preferential adsorption will, however, be of species with a higher fraction of hydrophobe. In the fitting process this leads to unacceptably high volume fractions of backbone, i.e. backbone volume fractions greater than 1. The use of this as a constraint identifies preferential adsorption of more hydrophobic species, but it was only observed in one set of polymers, the D HMPAM, which have a low MW. The choice of value for the volume of a backbone unit may also have a small effect on the apparent stoichiometry. Thus, the value of 78 \AA^3 derived as described above differs by 15% from the value of 90 \AA^3 from the bulk density. In the absence of measurements using the hHMPAM in D_2O contrast, the equivalent effect could alternatively be caused by preferential adsorption of species with a mole fraction of hydrophobe $1.15\times$ higher than the nominal value. However, this is usually within the estimated overall error.

We divide the results into three groups. The first set of results is for the samples labelled E, in which the hydrophobic units were incorporated in the actual polymer synthesis. For the remaining polymers the hydrophobic chains were introduced post-polymerization and these divide into two groups. Groups A, B and C are all large MW (10^6 or more) and are treated together, while the group of D polymers are of low MW ($\approx 10^4$). In the D polymers the number of hydrophobic units per molecule is small, e.g. a single 2 mol% D

polymer molecule has an average of only 3 hydrophobic units. Statistically this will lead both to a large variation in the number of hydrophobes per polymer molecule and a higher chance of the behaviour being dominated by end effects. Thus, the surface behaviour might become sensitive to polydispersity not just in composition and MW but in the distribution of hydrophobes within a molecule. For example, if 2 of the average of 3 hydrophobic units above happen to be close to one end the adsorption of the small polymer might have close to normal surfactant like properties and would then displace a more uniformly hydrophobed molecule from the surface. As will be shown below the surface behaviour of the D polymers is indeed erratic.

Results from Copolymerized HMPAM (E HMPAM)

The hydrophobic unit in the E HMPAM is the dodecyl group, $C_{12}D_{25}$, attached to the amide nitrogen at molar ratios of 1:50, 1:100 and 1:200 N-dodecylacrylamide:acrylamide and incorporated by copolymerization. Reflectivity measurements were made of the three isotopic contrasts of dHMPAM in NRW and D_2O , and hHMPAM in D_2O . The results for the highest level of hydrophobicity (50 backbone units to 1 hydrophobic residue) at a solution concentration of 0.1 wt% are shown in Figure 2. The fits of the model of Figure 1 to the three isotopic contrasts are shown as lines in Figure 2(a) together with the corresponding set of volume fraction profiles out to 200 Å in (b). The fitted thicknesses and volume fractions of backbone, hydrophobe and water are given in Table 3. Values of the errors are given for the overall coverages but not for the thicknesses or volume fractions within the layer because these are often strongly coupled. In most cases, however, the errors are generally about $\pm 15\%$ for the volume fractions and $\pm 20\%$ for the thicknesses. The volume fractions (ϕ) given in Table 3 refer to the volume fraction separately from any smearing effects of roughness.

The good fit of the reflectivity from this set of polymers goes some way to supporting the main features of the model assumed in Figure 1. For the 0-1, 1-2 and 2-3 interfaces the

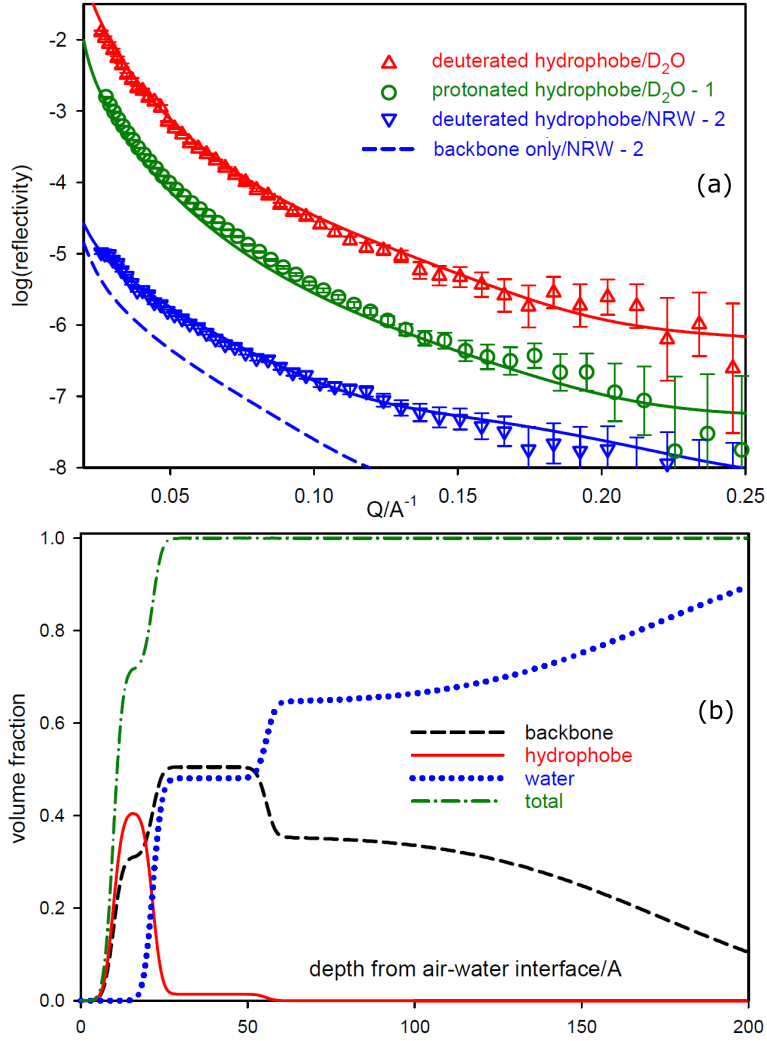


Figure 2: (a) Observed and fitted reflectivities from the air-water interface of three isotopic contrasts of hydrophobically modified PAM, dC₁₂PAM in D₂O and NRW, and hC₁₂PAM in D₂O, all containing 2 C₁₂ chains per 100 backbone residues at a total polymer concentration of 0.1 wt%. The dashed line shows the reflectivity calculated for the artificial situation of dC₁₂PAM in NRW with the contribution from the dC₁₂ groups removed. Note that, apart from the deuterated hydrophobe in D₂O, the values of $\log(\text{reflectivity})$ in (a) are offset by -1 or -2 as indicated in the legend. (b) The volume fraction profiles used to fit the data in (a).

roughnesses were assumed to be the same, and were found to be relatively low at 3.5 Å for the samples shown in Figure 2. The roughness of the layer 3-water interface has, however, to account empirically for the shape of the tails of the backbone distributions and is generally found to have a large enough value to damp out sharper oscillations in reflectivity that would result from the thick layer 3 slab, i.e. up to about 80% of the thickness of layer 3. That air/empty space is usually present in layer 1 confirms that this is not a space-filling layer. For the other two layers the partial molar volume of 78 Å³ was included as part of the analysis. In some cases, e.g. 1 mol% at 0.1 wt% and 0.5 mol% at 0.1 wt%, the volume fraction of backbone equals or is close to 1 in one of the layers. In these cases the excess may be caused by the mol% of hydrophobe in the overall surface layer being slightly larger than the nominal amount.

Table 3: Volume fractions (ϕ), thicknesses (t), total surface excesses (Γ_{total}), and areas per hydrophobe (A_c) characterizing the structure and composition of layers of PAM hydrophobically modified by the incorporation of a fraction of dodecylacrylamide (E polymers) and adsorbed at the air-water interface. For reasons of space the roughnesses between the layers are not included. A single value in the range 3 - 6 Å was used for the air-chain, chain - layer 2 and layer 2 - layer 3 interfaces and a much larger value 30 - 100 used for layer 3 - water. Full structural analyses are given only for measurements with more than one isotopic contrast.

C ₁₂ mol%	c wt%	t_1 Å	ϕ_{b1}	ϕ_{c1}	t_2 Å	ϕ_{b2}	ϕ_{c2}	t_3 Å	ϕ_{b3}	Γ_{total} mg m ⁻²	$A_c/\text{Å}^2$ ±15% * ± 20%
2	0.1	12	0.3	0.4	34	0.5	0	120	0.4	10.2	60
2	0.05	-	-	-	-	-	-	-	-	3.8	160*
2	0.01	11	0.5	0.2	20	0.8	0	41	0.2	4.8	130
2	10 ⁻³	-	-	-	-	-	-	-	-	0.2	3000*
1	0.1	10	0.5	0.3	19	1.0	0	73	0.7	11.2	110
1	0.05	-	-	-	-	-	-	-	-	4.8	250
1	0.01	8	0.2	0.3	25	0.5	0	77	0.3	6.0	200
1	10 ⁻³	-	-	-	-	-	-	-	-	3	400*
0.5	0.1	10.5	0.9	0.1	25	0.6	0	59	0.3	6.2	380
0.5	0.05	-	-	-	-	-	-	-	-	4.4	540*
0.5	0.01	-	-	-	-	-	-	-	-	3.4	700*
0.5	10 ⁻³	-	-	-	-	-	-	-	-	3	795*

The significant contribution of the backbone to the reflectivity and the difference of this

contribution to the reflectivity from that of the hydrophobic units is demonstrated in Figure 2(a) by the hypothetical reflectivity profile for dHMPAM in NRW with the contribution of the deuterated hydrophobe removed. The effect of the large amount of low contrast backbone is to introduce a steeper component of the reflectivity at low Q values because of the more extensive distribution of the backbone into the solution. If modelled as a simple slab of material, this would give rise to maxima and minima in the reflectivity, and the large roughness/diffuseness at the layer 3 - water interface is required to damp out any such interference. This is indeed observed in the reflectivity of some of the reflectivity profiles of the low MW D polymers.

The overall model of the structure is consistent with the general behaviour of surfactants and other polymers at the air-water interface. Thus, in nearly all cases there is a similar layer of hydrophobic units containing little or no water next to the air and an inner layer containing both hydrophobe and head group (backbone units here) in which any remaining space is filled with water. What is distinctive in these HMPAM is the large volume of backbone material attached to each hydrophobic unit. Part of this effectively collapses on and/or into the outer, layer 1, and inner, layer 2, parts of the surface created by the hydrophobic units, while the remainder stretches into the solution (layer 3). Apart from the possible small discrepancy resulting from the molecular volume of the backbone and discussed above, the adsorbed species has the same composition as the bulk polymer, i.e. there is no preferential adsorption of species with a higher mol% of hydrophobe.

Figure 3 (a) shows the volume fractions in NRW of HMPAM containing 0.5, 1 and 2 mol% dC₁₂ chains at the same overall polymer concentration of 0.1 wt%. In each case the same three contrasts as used in Figure 2 were measured and fitted to a single set of volume fraction profiles (dC₁₂HMPAM in D₂O and in NRW, and hC₁₂HMPAM in D₂O). Figure 3 (b) shows the fits to the data for one of these contrasts, dC₁₂HMPAM in NRW. The reflectivities of dC₁₂HMPAM in NRW further illustrate the different contributions of the hydrophobic dC₁₂ unit (mainly towards higher Q) and the HMPAM backbone (mainly at lower Q values).

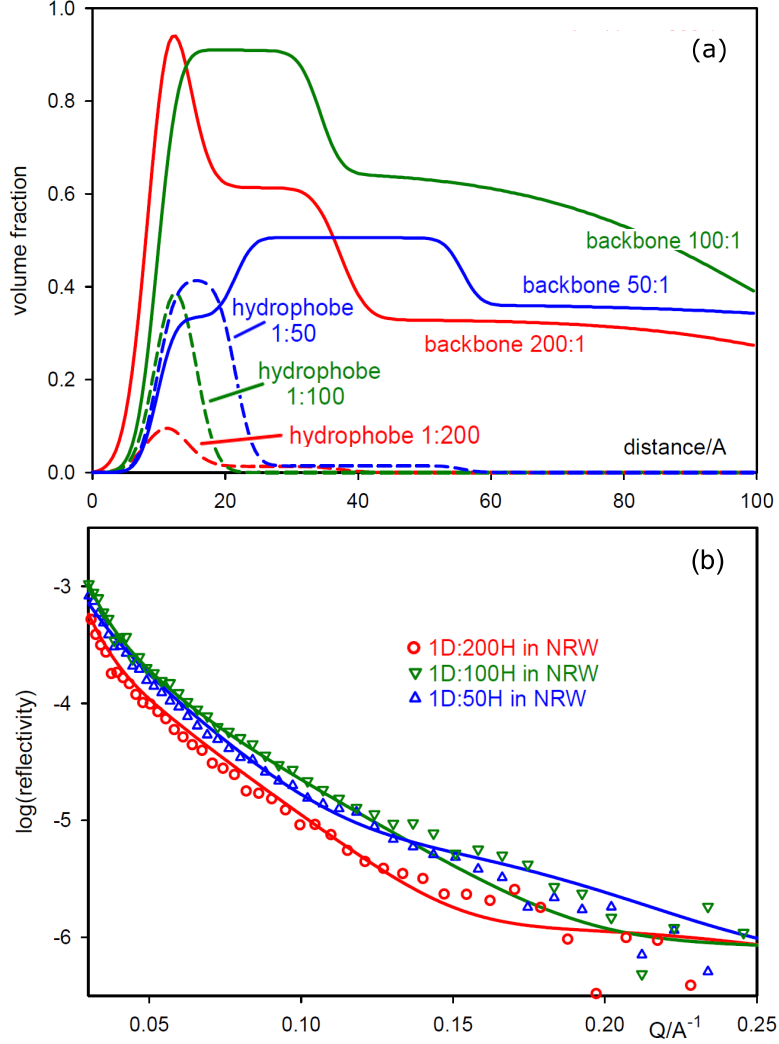


Figure 3: (a) Volume fraction profiles of C₁₂PAM at different levels of the attached hydrophobe C₁₂, all at a total concentration of 0.1 wt%. In each case the same three separate isotopic contrasts shown in Figure 2 were used for the structural determination. (b) shows the fitted reflectivity profiles and experimental points for the three compositions for the single contrast of dHMPAM in NRW.

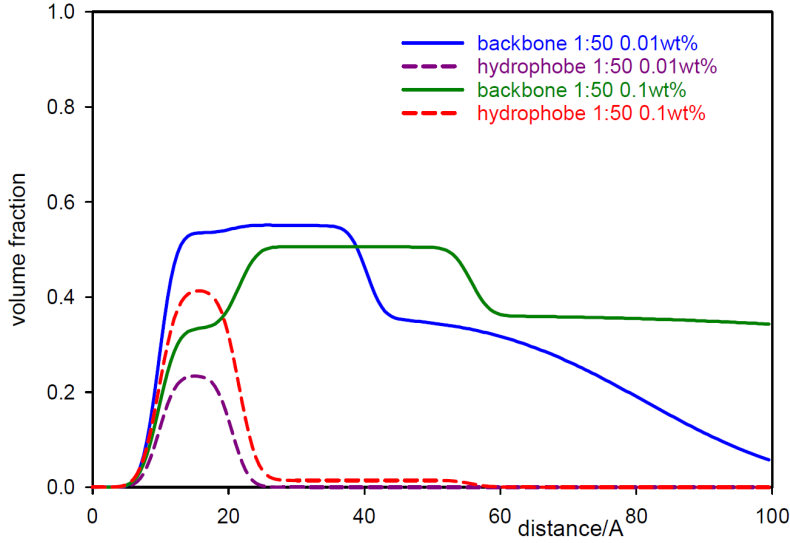


Figure 4: Volume fraction profiles of C₁₂HMPAM 1:50 (2 mol%) at two different concentrations, 0.1 and 0.01 mol%, determined using three and two isotopic contrasts respectively. The water, which fills the remainder of the volume in layers 2 and 3, is not shown.

These are interesting because, although the surface excess of the C₁₂ unit increases with its proportion in the polymer, as would be expected, the level of reflectivity of the three samples is not very different. Thus the areas per C₁₂ unit are 60 ± 10 , 110 ± 15 and 380 ± 50 Å² for 2 %, 1% and 0.5% respectively at a total concentration of 0.1 wt%, but the surface excess of the polymer as a whole varies less systematically. On the one hand, the surface excess of the polymer increases with the degree of hydrophobicity as would be expected but, on the other hand, it also decreases because there are fewer backbone residues attached to each hydrophobic unit. The corresponding areas per backbone residue therefore do not follow a simple progression and have values 1.2 ± 0.2 , 1.1 ± 0.2 and 1.5 ± 0.3 Å² for the 2, 1 and 0.5 mol% HMPAM respectively. These are high levels of adsorption and lead to substantial thickening of the layer, as can be seen in Figure 3(a). Normally, the contrast that is most sensitive to the surface excess is for a solution of deuterated adsorbate in NRW, i.e. the results in Figure 3(b). Although there are only relatively small differences in the three profiles, considering the large difference in areas per hydrophobe given above, this contrast still primarily determines the

measured surface excess, provided that the constraint of the fixed stoichiometry is applied in the analysis of the reflectivity. However, the surface coverages determined are significantly less accurate than when one or both of the alternative contrasts using D₂O is included. Both the amount and the profile of the adsorption change strongly with concentration and Figure 4 shows this change when the concentration is changed from 0.1 to 0.01 wt% for the 2 mol% polymer, using three and two contrasts respectively.

In principle, it should be possible to use the Gibbs equation to relate the adsorbed amounts, obtained from Table 3 using the arguments described above, to any changes in surface tension (ST) with concentration (c), provided that equilibration is at or close to completion in both NR and ST measurements. The values of surface excess per hydrophobic segment determined by NR are shown in Figure 5(a) and follow a systematic pattern with adsorption being stronger for both greater hydrophobicity and higher concentrations. In particular the surface excess increases approximately linearly with $\log c$. The ST results, shown in Figure 5(b), also show a systematic pattern of behaviour that is qualitatively consistent with the NR measurements in that the ST has a negative slope that increases with concentration and hydrophobicity, as expected from the Gibbs equation, which, for a single *nonionic* solute in solution, is

$$-d\sigma = \Gamma RT d \ln (fc) \quad (3)$$

where σ is the surface tension, Γ is the *molar* surface excess of solute at the A-W interface, c is the concentration and f is the activity coefficient of the solute. The molar surface excess of HMPAM is determined directly from Table 3 by combining the area per hydrophobic unit with the number of such units in each polymer. Thus, a 1:50 polymer of MW 160k consists of about forty 1:50 segments and, since the area per adsorbed segment is 60 Å² for a concentration of 0.1 wt%, the molar area at this concentration is 2400 Å², which is equivalent to a *molar* adsorbed amount of 0.07 μmol m⁻². In the volume defined by the measured total

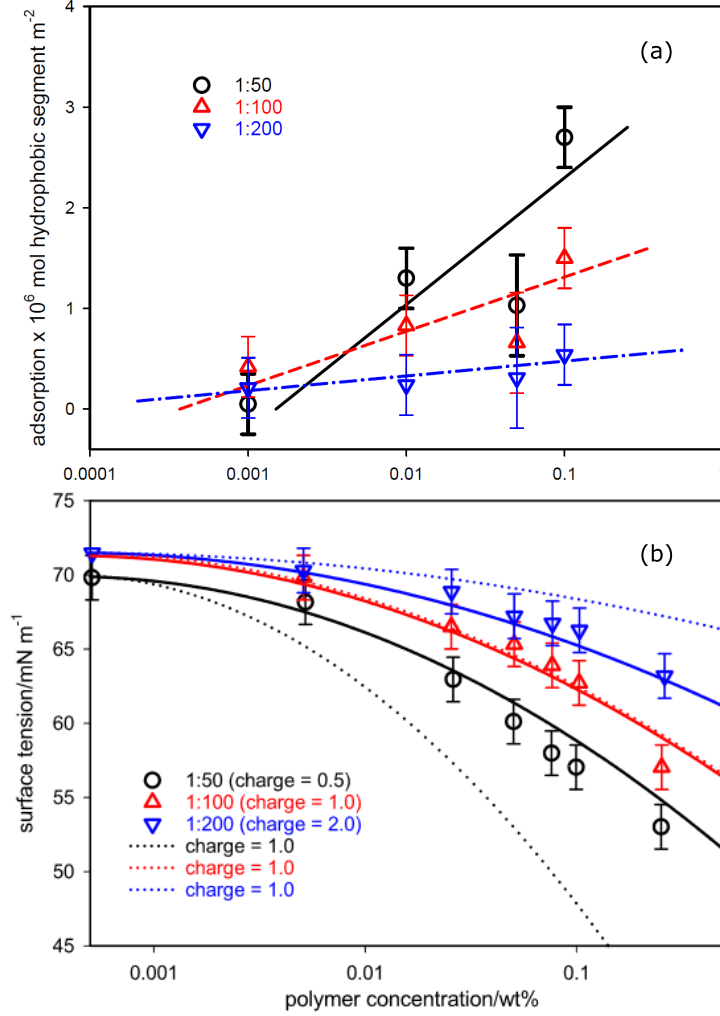


Figure 5: (a) Surface excess, Γ , per hydrophobic segment for 1:50, 1:100 and 1:200 E-HMPAM as a function of concentration. The linear variation of Γ with $\log c$ shown in (a) was used in the Gibbs equation to calculate the surface tension behaviour in (b) using two assumptions. In the first assumption (continuous lines) the charge on the PAM backbone was taken to be 1 per 100 backbone units, irrespective of hydrophobicity, making the charge per hydrophobic unit respectively 0.5, 1 or 2 for 2, 1 and 0.5 mol% HMPAM. In the second assumption (dotted lines) the charge along the backbone was taken to be one per hydrophobic unit.

thickness of the layer of just over 150 Å this would be a much higher concentration than in the bulk solution and therefore this adsorbed amount is a good approximation for the surface excess. Using Eqn (3) a constant surface excess of 0.07 $\mu\text{mol m}^{-2}$ would lead to a drop in ST of only about 0.4 mN m^{-1} for a 10 fold increase in the bulk concentration, assuming ideal behaviour in the bulk. This is much less than the observed drop of more than 10 mN m^{-1} when the concentration changes from 0.01 to 0.1 wt%. For the 1:100 and 1:200 polymers the molar areas are about 2200 and 3000 Å² respectively, which would similarly lead to respectively much smaller changes of ST than observed for the same 10 fold increase in concentration for these two polymers, i.e. there is a large discrepancy between the ST behaviour and the observed surface excesses.

Most surface active nonionic polymers do not exhibit the pattern of ST behaviour shown in Figure 5(b) for reasons that are not well understood but which seem to be associated with depletion or fractional depletion of different MW species in a polydisperse sample.³⁴⁻³⁹ In these systems the ST initially drops steeply at the lowest concentrations and then more gradually at higher concentration, which would require the apparent surface coverage to decrease at higher concentration, although NR indicates that there is no such effect.³⁸ However, for HMPAM the initial value of the ST at low concentration is that of water and the ST curves all remain convex downwards both as normally required by the Gibbs equation, but the decrease in ST is again much higher than can be accounted for by the observed molar surface excesses. It is, however, known that a small fraction of amide residues in PAM are often hydrolysed to carboxylic acid groups. Indeed, partial hydrolysis is used deliberately to improve the solubility of some commercial HMPAM.²⁸ Although carboxylic acids are weak, their presence would have the effect of converting the HMPAM from a nonionic species into a low charge density polyelectrolyte, for which the Gibbs equation changes from Eqn (3) to become^{40,41}

$$-d\sigma = \frac{(Z+1)}{Z} \Gamma_X RT d \ln c_X \approx \Gamma_X RT d \ln c_X \quad (4)$$

where Z is the total number of charges per polymer, the counterion is univalent, c_X and

Γ_X refer to the concentration and surface excess of *charged* polymer residues, and activity coefficient effects have been neglected. Thus, in the simple case where the mean charge is one per 100 backbone units Γ_X would become identical with the surface excess *per hydrophobic unit* for the 1 mol% HMPAM, but half and twice the surface excess per hydrophobic unit for the 2 mol% and 0.5 mol% HMPAMs respectively. Figure 5(b) shows fits of the Gibbs equation in the form of Eqn (4) to the experimental coverage data (from the fitted slopes in Figure 5(a)) combined with effective prefactors of 0.5, 1.0 and 2.0 based on the assumption that the average charge on the PAM is 1 per 100 backbone residues. The fit is remarkably good, considering the significant errors in Figure 5(a). The carboxylic acid group being a weak acid would require a higher concentration of carboxylic acid groups than 1 mol% to finish with a nett charge of 1 mol%. As far as we are aware, no explanation of this sort has been suggested for the ST behaviour of other nominally neutral polymers. The hydrolysis to give charged groups is known to occur in PAM that has not been hydrophobically modified, i.e. it should be a feature that is independent of any added hydrophobicity. That this is the case for the E HMPAM can be shown from the result above. Thus, if oxidation were associated with the introduction of a hydrophobe, the effective prefactors would be proportional to the mol% of the hydrophobic units. Then instead of the prefactors being 0.5, 1.0 and 2.0 they would all be 1.0. The result of this would be the behaviour shown as dotted lines in Figure 5(b) and is clearly not appropriate.

Post Polymerization B Polymers

All the remaining HMPAM were prepared by the post-polymerization method using commercially available PAMs. This allowed a wider range of hydrophobic units, C_8D_{17} , $C_{12}D_{25}$, and $C_{16}D_{33}$ to be explored but the range of isotopic contrasts investigated was more limited than for group E in the previous section. Under these circumstances the total adsorbed amount can be determined reasonably reliably by NR but the distinction between the backbone and hydrophobe distribution may then rely on the type of differences shown for the reflectivity in

NRW in Figures 2 and 3(b), which are significant but not large, and the assumption that the composition of the adsorbed species corresponds to the nominal stoichiometry. The greater number of isotopic contrasts used for the E polymers showed that the average adsorbed polymer had the average composition of the whole sample (apart from the uncertainty concerning the partial molecular volume of a backbone residue, which is equivalent to a maximum discrepancy of $1.15\times$). A similar analysis can be performed on the B polymers. However, for the A and C polymers, where there is only a single contrast, it has to be assumed that the surface composition is the same as that of the bulk, i.e. that there is no preferential adsorption of different compositions. This is not the case for the much smaller D polymers, as is discussed further below. Since the A, B and C polymers are all of larger MW than the E polymers, it is reasonable to assume that there is also no composition polydispersity in their adsorption because the attachment of hydrophobes to a sufficiently large precursor polymer in non-aqueous conditions should lead to a random attachment of hydrophobes. There may, of course, still be MW dependent preferential adsorption, i.e. smaller MW may adsorb more strongly than large MW, or *vice versa*, but this type of preferential adsorption will not affect the fit of the model of Figure 1, although it may affect the overall excess. In the smaller D polymers, however, the number of attached hydrophobes is small, e.g. a D polymer of 10k MW has a backbone of about 130 monomers and at 2 mol% hydrophobe there are only 2-3 hydrophobes per polymer molecule. This has two effects, the first of which is that the deviation from the average will be relatively much higher, and the second of which is that there is a higher probability of a hydrophobe being attached close to one of the two ends. This could create a species with a surface activity quite different from that where the hydrophobe(s) are attached closer to the middle of the molecule. Polydispersity in composition may therefore have a strong effect on the surface of the D polymers and we examine the behaviour of the D polymers separately.

The results of the analysis of the NR results for the B polymers, where two isotopic contrasts allow a characterization in terms of the model in Figure 1, are given in Table

4. The pattern of variation of the adsorbed amount can again be used as an approximate

Table 4: Surface structure and composition at the A-W interface of hydrophobically modified PAM (B polymers in Table 2) determined from two contrasts of the polymer with deuterated hydrophobe, one in NRW and the other in D₂O using the same method of analysis as for the E polymers in Table 3. The values in brackets are the equivalent measurements for polymer E from Table 3.

C_n (mol%)	conc. wt%	t_1 Å	ϕ_{b1}	ϕ_{c1}	t_2 Å	ϕ_{b2}	ϕ_{c2}	t_3 Å	ϕ_{b3}	Γ_{total} mg m ⁻²	$A_c/\text{Å}^2$ ±20%
C ₈ (2)	0.35	16	0.7	0.3	34	0.4	0	170	0.3	12	49
C ₈ (2)	0.10	19	0.4	0.4	29	0.9	0	101	0.4	21	29
C ₈ (2)	0.01	15	0.03	0.01	16	0.2	0.01	31	0.1	1	610
C ₈ (4)	0.35	19	0.6	0.3	21	0.6	0.0	51	0.6	9	36
C ₈ (4)	0.10	15	0.6	0.3	31	0.4	0.01	75	0.3	7	43
C ₈ (4)	0.01	-	-	-	-	-	-	-	-	0	-
C ₈ (6)	0.35	19	0.5	0.3	21	0.0	0.5	43	0.4	6	36
C ₈ (6)	0.10	15	0.3	0.5	31	0.5	0.0	57	0.4	8	28
C ₈ (6)	0.01	15	0.4	0.5	22	0.5	0.0	59	0.4	7	31
C ₁₂ (2)	0.35	18	0.5	0.5	26	0.6	0	193	0.4	17	37
C ₁₂ (2)	0.10	17	0.4	0.5	27	0.8	0	99	0.8	17(10)	37(60)
C ₁₂ (2)	0.01	14	0.03	0.03	19	0.1	0	89	0.1	2(5)	350(130)
C ₁₆ (2)	0.35	20	0.1	1.0	20	1.0	0.1	139	1.0	34	18
C ₁₆ (2)	0.10	15	0.5	0.5	18	0.0	0.4	117	0.45	11	57
C ₁₆ (2)	0.01	15	0.1	0.3	15	0.0	0.3	81	0.1	2.7	228

assessment of equilibration. That the values of Γ_{total} for C₁₂-PAM-B-2% and those for C₁₂-PAM-E-2% both decline with concentration suggests that this system is not very far from equilibrium in both systems for the C₁₂ hydrophobe, although the trend is occasionally just outside the error, which may alternatively be a feature of the difficulty of estimating the error. A decline with concentration also occurs for the C₁₆-PAM-B-2% system, and less regularly for C₁₂-PAM-B-2%. However, the presence of a greater number of hydrophobes in C₈-PAM-B-4% and C₈-PAM-B-6% leads to a level of adsorption that drops abruptly to zero for the 4 mol% compound but does not vary with concentration for the 6 mol% compound. Given that the 2 mol% compound adsorbs at a bulk concentration of 0.01 wt% the lack of adsorption for the 4% compound suggests that equilibration is not complete at the lowest concentrations. The most interesting result is that for the C₈ and C₁₂ systems

the limiting areas *per hydrophobe* are approximately constant irrespective of the mol% on the polymer and that they are also approximately what would be expected for a reasonably well packed monolayer of a surfactant with these chains. For C₁₆ the value at 0.35 mol% gives an unusually small value of the area per hydrophobe in a monolayer, which might seem physically improbable. However, this is accounted for by an unusually thick layer 1 (20 Å) fully filled with hydrophobe ($\phi_{c1} = 1$) and the presence of a further 10% of hydrophobe in layer 2, also about 20 Å thick. The backbone is therefore approximately completely squeezed out of layer 1. In contrast, the corresponding result for the C₈ hydrophobe has a thinner layer 1 of 15 Å, which contains a volume fraction of 0.3 hydrophobe and 0.7 backbone. The C₁₆ compound therefore conforms more to the traditional picture of how a hydrophobically modified polymer should adsorb, although the indications are that the C₁₆ layer is less likely to be a true equilibrium layer. This is also a rare example where the analysis leads to a total mole fraction in layers 1 and 2 that is greater than unity. Although the total volume fraction is within the experimental error of 1.0, this may alternatively indicate that the stoichiometry of the adsorbed complex is slightly richer in backbone than the bulk complex. This question will be considered more closely for the D polymers below.

The variation of ST is to some extent consistent with both the analysis given for the E-polymers in Figure 5 and the NR results in Table 4. The first difference is that the ST of the original *unmodified* B polymer also varies with concentration, i.e. it also adsorbs. This was not the case for the E polymer and may result from an impurity in the commercial polymer. However, since the incorporation of the hydrophobe decreases the ST significantly more than just the polymer on its own, we can reasonably assume that adsorption of the HMPAM dominates the ST behaviour when HMPAM is present. Although the ST behaviour patterns of the 4 or 6 mol% polymer are comparable with those of the other polymers but with a steeper drop in ST, the NR fits to the data suggest that these systems may not be at full equilibrium. We therefore limit the analysis to the series of 2 mol% modified B polymers with different chainlength hydrophobes. We found that it was possible to follow a similar

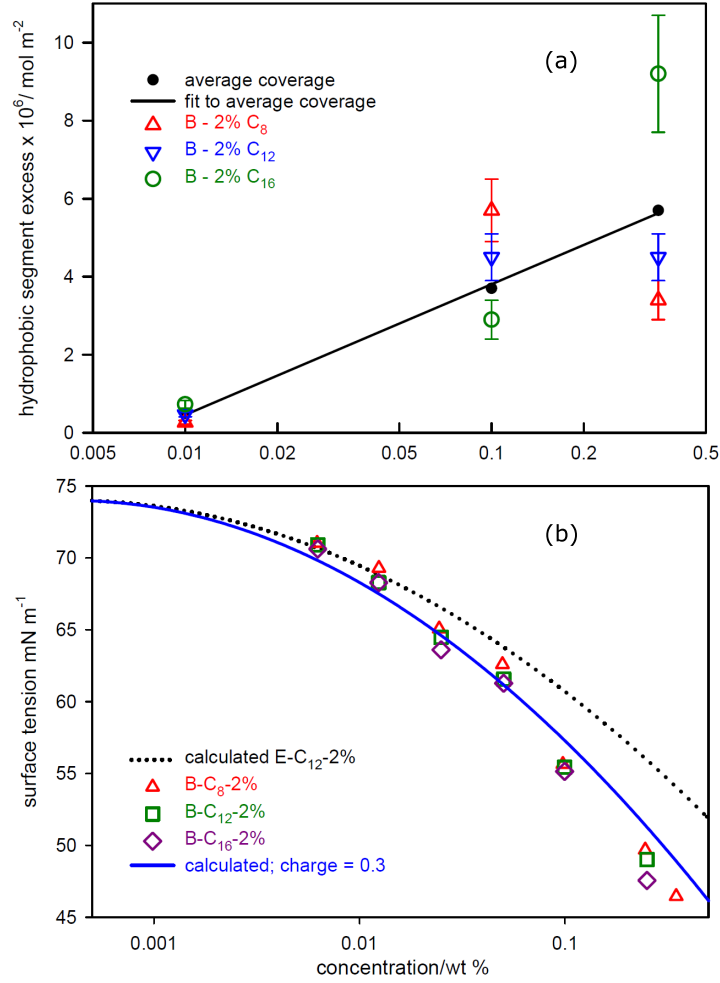


Figure 6: (a) Surface excesses per hydrophobic segment for B polymers modified post-polymerization with 2 mol% C₈D₁₇, C₁₂D₂₅ and C₁₆D₃₃ hydrophobes, and measured by NR. The average adsorption of the three species is fitted to the logarithmic dependence on concentration shown. (b) shows the fit of experimental measurements of the ST to the Gibbs equation using the isotherm from (a) and a charge of 0.3 per 50 backbone units. The corresponding fit of the E polymer with 2 mol% C₁₂D₂₅ and a charge of 0.6, which gives a better fit to the data than the 0.5 used in Figure 5(b), is shown as a dotted line for comparison.

procedure to that used in Figure 5 and the results are shown in Figure 6. The NR data show a logarithmic drop in adsorption as the concentration is lowered for the three 2 mol% B polymers with C₈, C₁₂ and C₁₆ hydrophobes. By the same arguments as used for the E polymers, the drop in ST will be driven by a combination of the variation of surface excess with concentration and the mean charge on the backbone. This was found to be close to 1 per 100 backbone units independent of the hydrophobe for the E polymers, i.e. it should be the same irrespective of the hydrophobe. We have therefore used an adsorption isotherm for the average coverage for the three different hydrophobes (Figure 6(a)) and then fitted the ST with this coverage and a common value of the backbone charge to obtain the plot in Figure 6(b). The charge per hydrophobe was found to be about 0.3, to be compared with the value of 0.6 obtained for the corresponding E polymer (the effect of the averaging of the measured adsorption in the case of the B polymers leads to a greater relative surface excess for the C₁₂ polymer). As can be seen, the fit of the Gibbs equation to the data under these circumstances is remarkably good for this second set of polymers. Furthermore, the key contribution of charge to the Gibbs behaviour must be relevant in the case of the B polymers because the manufacturer’s specification states that the B polymers are *carboxylated at a low level*. We return to the whole question of equilibration in the discussion.

Post Polymerization A and C Polymers

The NR measurements on the remaining polymers were less extensive in that only the dHM-PAM in NRW was measured. However, as discussed above this still gives the overall excess, although with a lower accuracy and with the same assumption that the adsorbed species has the same stoichiometry as the average bulk species. The results for the two large MW polymers A and C are given in Table 5. Taken with the data for the B and E polymers, the reproducibility of the coverage as determined by NR seems to be optimum for 2 mol% hydrophobe. For the higher 4 and 6 mol% B polymer and the lower 1 and 0.5 mol% E, A and C polymers, the deviations from a steadily increasing coverage with concentration are more

Table 5: Parameters characterizing the surface structure and composition at the A-W interface of PAM hydrophobically modified by the addition of different alkyl bromides (polymers A and C in Table 1) based on a single isotopic composition of the polymer with deuterated hydrophobe in NRW.

$C_n/\text{mol}\%$	conc/wt%	$\Gamma_{total}/\text{mg m}^{-2} \pm 20\%$	$A_c/\text{\AA}^2 \pm 20\%$
A-C ₈ (2)	0.35	7	87
A-C ₈ (2)	0.10	5	128
A-C ₈ (2)	0.01	1	610
A-C ₈ (1)	0.35	4	280
A-C ₈ (1)	0.10	2.5	480
A-C ₈ (1)	0.01	0.5	2400
A-C ₈ (0.5)	0.35	2.5	950
A-C ₈ (0.5)	0.10	0.7	3200
A-C ₈ (0.5)	0.01	2.7	865
C-C ₈ (2)	0.35	5	120
C-C ₈ (2)	0.10	5	120
C-C ₈ (2)	0.01	1.2	490
C-C ₈ (1)	0.01	2.2	530
C-C ₈ (0.5)	0.35	13.5	180
C-C ₈ (0.5)	0.10	13	180
C-C ₈ (0.5)	0.01	1.7	1330
C-C ₁₂ (1)	0.35	2	600
C-C ₁₂ (1)	0.10	9.5	130
C-C ₁₂ (1)	0.01	1	1200
C-C ₁₆ (1)	0.35	30	33
C-C ₁₆ (1)	0.10	35	34
C-C ₁₆ (1)	0.01	2.2	540

erratic and the variation in the chainlength of the hydrophobe does not have a comparable effect. Overall, this suggests that any difficulties associated with the HMPAM folding at the surface are determined more by the spacing between hydrophobes rather than by the individual surface activity of the hydrophobes.

Post Polymerization D Polymers

The relatively small D polymers show some dramatic variations in surface behaviour. As already mentioned above the small number of hydrophobes per polymer molecule and the process of post-polymerization are likely to result in significant variations of surface activity

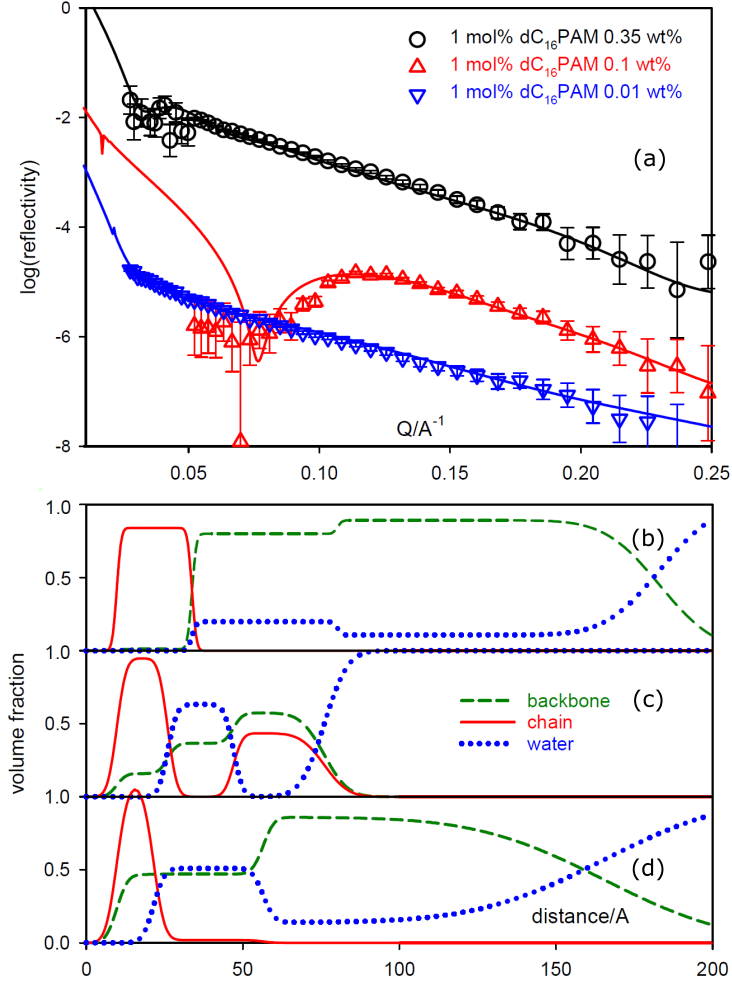


Figure 7: (a) NR from dHMPAM in NRW (points) for three concentrations of 1 mol% C₁₆D₃₃, 0.35, 0.1 and 0.01 wt% with best fits (lines) with the log(reflectivity) being respectively displaced by +1, -1 and -2. (b) The volume fraction profiles of backbone, hydrophobe and water used to fit the data in (a). The stoichiometries of the adsorbed layers are different from the nominal values and are given in Table 6.

Table 6: Parameters characterizing the surface structure and composition at the A-W interface of PAM hydrophobically modified by the addition of different alkyl bromides (polymer D in Table 1) based on a single isotopic composition of the polymer with deuterated hydrophobe in NRW.

C_n (mol%)	stoichiometry mol%	conc. wt%	$\Gamma_{total}/\text{mg m}^{-2}$ $\pm 20\%$	$A_c/\text{\AA}^2$ $\pm 20\%$	comment
D-C ₈ (2)	2.5	0.35	3.5	140	
D-C ₈ (2)	2.5	0.10	8.5	55	
D-C ₈ (2)	(2)	0.01	0	-	
D-C ₁₂ (2)	2	0.35	20	30	trilayer
D-C ₁₂ (2)	2	0.10	1.5	450	
D-C ₁₂ (2)	2	0.01	0.5	820	
D-C ₁₂ (1)	3.5	0.35	9.5	40	
D-C ₁₂ (1)	2.5	0.10	6.5	75	
D-C ₁₆ (2)	2	0.35	29	25	
D-C ₁₆ (2)	8	0.10	8.5	20	
D-C ₁₆ (a) (1)	5	0.35	12.5	20	trilayer
D-C ₁₆ (b) (1)	3	0.35	22	20	
D-C ₁₆ (1)	7	0.10	11.5	20	
D-C ₁₆ (1)	5	0.01	7.5	40	

within a batch of HMPAM. Thus, it may no longer be valid to assume that the polymers adsorbed at the surface will have the average composition of the bulk. However, the analysis of the NR data in Table 6 indicates even wider variations, suggesting that there are effects from either or both polydispersity and a failure to equilibrate. Thus, although the measured surface excess generally decreases sharply with concentration, there are exceptions, at 0.35 wt% dC₈PAM and at 0.35 wt% 1 mol% dC₁₆PAM (measurement (a)). A separate measurement of the latter gave a more consistent result but the difference between the two results clearly demonstrates that equilibration for this system is uncertain. The other important variation is that there are clear indications that the composition of the adsorbed layer is often very different from the nominal composition. This shows up in two ways. First, the application of the constraint that the volume fraction at any part of the interface must not increase above 1 can only be satisfied by attributing a greater fraction of the signal to the deuterated hydrophobes. Secondly, in two systems, a contribution from a second layer of

hydrophobes located at the layer 2 - layer 3 division in the model structure of Figure 1 becomes apparent. In the case of 1 mol% C₁₆TAB at a wt% of 0.1 this manifests itself as a distinct interference fringe, resembling those often seen in polyelectrolyte-surfactant mixtures,²² although the origins of the interaction must be different here. This is shown, together with the fitted structural profile in Figure 7. The deviations of the stoichiometry of the composite surface layer from the nominal bulk value stoichiometry are given in Table 6 and the results for almost all the C₁₆ modifications show that these adsorbed species contain mol% of hydrophobe much greater than the nominal value, whereas the two smaller hydrophobes showed little significant difference between the composition of the surface and that of the bulk. Thus, at the two lowest concentrations the adsorbed C₁₆PAMs contain 8 (2 mol%) and 7 (or 5 in a repeat run) (2 mol%) hydrophobes per molecule compared with the bulk average of 2 or 1 respectively.

The results for the large polymers A, B, C, E give adsorbed layers that, except for the possible 1.15 factor arising from the choice of partial molar volume, have the same composition as the nominal value. For such preferential adsorption there has to be a significant change in surface activity with composition. It is reasonable to assume that surface activity of the HMPAM increases with the number of attached hydrophobes. The preferential adsorption of more highly hydrophobed species will then be determined by the balance between the stronger tendency of more extensively hydrophobed species to adsorb and their lower than average concentration. The spread of composition about the average is expected to be narrower when the number of hydrophobic units per polymer *molecule* is large than when it is small. C and E are the smallest of the large polymers and at a composition of 1 mol% each molecule of these is attached on average to 20 hydrophobes, whereas a D polymer molecule is only attached to an average of 1.6. The relative width of the distribution of compositions about the average will clearly be much larger for the D polymers and this is likely to result in a relatively higher concentration of the more surface active species. The effect on the distribution will be more marked for a lower nominal mol% of hydrophobe

and the change of surface activity with mol% will be more marked for larger hydrophobes. Thus (i) the D polymers are much more likely to exhibit preferential adsorption than any of the others considered here, (ii) the effect will be larger the more strongly hydrophobic the added unit, and (iii) the effect will be larger the smaller the degree of modification. The first two effects are clear in Table 6. In spite of the substantial error the third effect can be observed in the average difference between the 1 and 2 mol% C₁₆ polymers, which are respectively 5.0 (4 measurements) and 2.5 (2 measurements) times the nominal average. Finally, as has been discussed elsewhere,^{34,38} preferential adsorption brings an extra level of possibilities for non-equilibrium adsorption. These arise because the spread of relative composition/hydrophobicity increases as the size of the polymer decreases. For example, smaller species containing a higher than average mol% of hydrophobes adsorb more rapidly than larger species, but are ultimately replaced by larger species with a larger total of hydrophobic groups. The patterns of both NR and ST results also indicate that the A-W surface of the D polymers is less well equilibrated than those of all the other polymers.

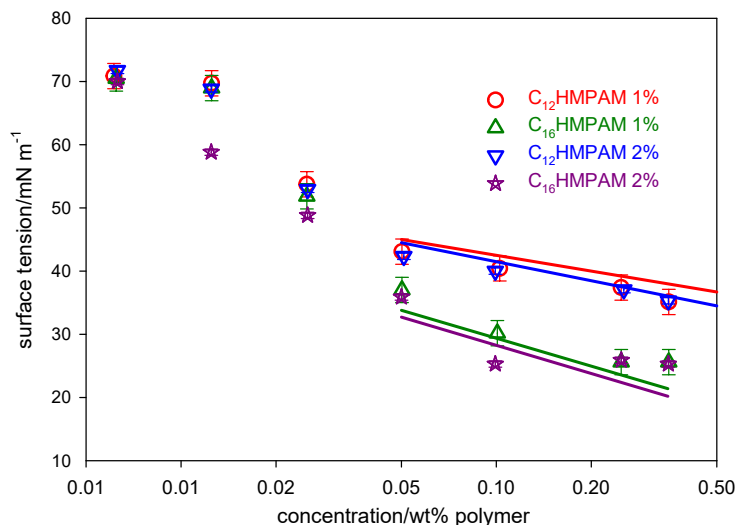


Figure 8: Surface tension of 1 and 2 mol% C₁₆D₃₃ and C₁₂D₂₅ hydrophobically modified D polymer. The lines show the calculated slopes of the Gibbs equation for the adsorbed amounts and stoichiometries observed by NR at a concentration of 0.35 wt% using a backbone charge of 1.6%.

Equilibration can also be judged by the ST behaviour, which is shown for the C₁₂ and C₁₆ modification of the D polymers in Figure 8. Unlike the ST behaviour of all the other polymers the gradient *decreases* with increasing concentration over the range up to about 0.05 wt%, which is not consistent with equilibrium adsorption unless there is an unusual behaviour of the activity coefficient. Thus, at high concentration there are signs of a plateau in the ST which could be associated with the activity of the polymer becoming constant because of aggregation in the bulk, which is also possible for these polymers. It could alternatively result from variation of the preferred adsorbed species with concentration.^{34,38} However, in spite of these differences from the behaviour of the larger polymers it is instructive to apply a similar model for the ST as used for them. We therefore make the same assumption, i.e. that there is sufficient hydrolysis in the backbone to give an effective charge of 1 per 100 backbone units, equivalent to a total charge of about 1.6 per complete polymer molecule. Using the coverage per hydrophobe and composition from the NR at 0.35 wt%, we then calculate the slopes of the ST-log c plots, just as in Figures 5 and 6. These are shown for the C₁₂ and C₁₆ polymers in Figure 8. Their reasonable agreement with the data suggests that (a) the flattening of the ST gradient is not necessarily a result of bulk aggregation and (b) that the behaviour of the ST at lower concentrations is probably not an equilibrium effect. They are also consistent with the conclusion that the ST behaviour in part results from charge on these polymers. The gradients of these lines would be significantly lower (1/1.6) without the charge.

Discussion

Results comparable with those above come from ST and XRR experiments by Millet et al. on hydrophobically modified sodium poly(acrylate), HMPAANa, at the A-W interface.⁹ Millet et al. used dodecyl or octadecyl as hydrophobes at between 1 and 20 mol%, which were introduced by copolmerization of poly(acrylic acid) with N-alkylacrylamide. Important differences of their experiments from those described here are that HMPAANa is a

polyelectrolyte and that XRR cannot contrast out the water signal, which makes it relatively insensitive to the loops and tails of the polymer, i.e. our layer 3. However, the level and type of added hydrophobe and the MW for some of their samples are comparable with those of our E or B polymers in Tables 3 and 4, e.g. their 120 1C₁₂ had a MW of 120k and 1 mol% of added C₁₂H₂₅ hydrophobe. However, Millet et al. concluded that only *part* of the excess, the part out of the water and easily detected by x-rays, is required to explain the ST behaviour for HMPAANa, i.e. their results are not consistent with the Gibbs equation. It is nevertheless interesting to compare their results for two strongly ionized hydrophobic polymers with our very weakly ionized, but otherwise similar species, where we do obtain approximate consistency of ST and NR results with the Gibbs equation.

The surface excesses determined by XRR for the 120 1C₁₂ and 120 3C₁₂ (3 mol% hydrophobe) of Millet et al. at the highest concentration of their measurements were both 1.2 mg m⁻², more than an order of magnitude less than our values for the B and E polymers with 2 mol% C₁₂. Although the polyelectrolyte HMPAANa is expected to be much less surface active than the nearly nonionic HMPAM, a significant part of this discrepancy must arise from the non-detection of layer 3 in Figure 1, which Millet et al. designate as the “loops and tails”. Millet et al. established the presence of such a layer in an earlier experiment on the measured thickness of a free-standing thin film drawn from the aqueous polymer,⁴² which was found to be significantly larger than expected from the directly detected material at the solution interface. If we now assume that this undetectable part of the HMPAANa layer is *relatively* in the same proportion to the measurable part of the layer as in our experiments on the the 2 mol% C₁₂ E HMPAM polymer (Table 3), then a correction of 2.9× should be applied to the measured XRR value of the surface excess of 1.2 mg m⁻², which increases the surface excess to 3.5 mg m⁻². Millet et al. also obtained a limiting value of 1.3 mg m⁻² for the surface excess of both 120 1C₁₂ and 120 3C₁₂ species from the analysis of their ST data. To do this they assumed that the HMPAANa was fully dissociated. However, HMPAA is a weak acid and HMPAANa therefore partially hydrolyses when dissolved in water. Because

of the interaction of charges along the chain, the mean dissociation constant varies with the degree of ionization and this variation can only be determined experimentally. Experimental titration curves have been determined and give the pH as a function of the fraction of added base.⁴³ This can then be combined with a measurement of the degree of dissociation as a function of pH, which has been determined since the experiments of Millet et al. by Laguecir et al.,⁴⁴ i.e. this information was not available at the time of the work of Millet et al. In the absence of any added electrolyte, which seems to be the condition used by Millet et al., HMPAANa has a degree of dissociation of only 0.79 instead of their assumed value of 1.0. The Gibbs equation for a polyelectrolyte including the Manning contribution to the activity coefficient is^{40,45}

$$d\sigma = -\frac{\Gamma_Y RT}{2\xi} d\ln c_Y \quad (5)$$

where Γ_Y refers to the coverage per *backbone segment*, not per hydrophobic unit (Γ_X) as in Eqn (4), and ξ is a measure of the charge density, which is inversely proportional to the charge separation along the polyelectrolyte chain. Millet et al. assumed complete dissociation to calculate ξ instead of the now known value of 0.79 above. In addition, they appear to have approximated the prefactor $(Z + 1)/Z$ to 2 instead of 1 because they took Z to be the charge per *monomer* instead of the charge on the whole polymer molecule.^{40,41,45} The combination of the two factors means that over the linear part of their ST plots for 120 1C₁₂ and 120 3C₁₂ their value of the surface excess has to be increased by a factor of 2.53, which changes it from their value of 1.3 to 3.3 mg m⁻² for both species. This agrees within error with the revised XRR/NR estimate, i.e. the Gibbs equation does in the end fit their set of data on the HMPAANa system. Interestingly, this now becomes one of very few results that confirm the contribution of counterion condensation to the ST behaviour.⁴¹

The comparison between HMPAM and HMPAANa is then between species with similar backbones and similar hydrophobes, the former having a high coverage but a low charge, and the latter having a lower coverage (1/3 – 1/5th) but also a higher charge, made up of a high stoichiometric charge offset by ion condensation. Thus the area per hydrophobic unit

is 60 and 37 Å² for the 2 mol% C₁₂ E and B polymers respectively, and is approximately 360 and 120 Å² respectively for the 120 1C₁₂ and 120 3C₁₂ polymers of Millet et al. The nonionic HMPAM should be substantially more surface active than the polyelectrolyte HMPAANa, as observed, and polymers with a higher hydrophobe content should also be more surface active, e.g. 120 3C₁₂ should be more surface active than 120 1C₁₂. As measured by the concentrations of the onset of the initial drop in ST, i.e. a lower value indicates greater surface activity, this is indeed the case. However, the steeper gradient of the Gibbs plot results in the 120 3C₁₂ polymer having a lower ST than 2% C₁₂ B when the concentration is at about 0.5 wt%.

The judgment as to whether a system is at equilibrium depends either on showing that it has reached a state where there is no further change or that its state is consistent with an appropriate thermodynamic equation. For the A-W interface this means that either the NR and/or ST have to be given time to reach stationary values or that the Gibbs equation is obeyed. In that the Gibbs equation requires input from both NR (or an alternative equivalent technique) and ST these two conditions would seem to be equivalent. However, the difficulty with polymers is that they are polydisperse. Even if the only polydispersity is that of MW (polydispersity of both composition and/or state of ionization are possible in HMPAM and HPAANa), it would make the Gibbs equation almost impossible to apply in practice.^{34,35} The key problems are the effect of time, which means that smaller than average MW species diffuse to the surface much faster at a given molar concentration than large ones, and the effect of depletion, which results from loss of a fraction of the material to the surfaces of all containers used for the measurements including the final one. Although simple analysis suggests depletion does not occur until the molar concentration is less than about 10⁻⁸ M, experiment shows that the depletion threshold can be as high as about 10⁻⁵ M.³⁹ Below this concentration initial adsorption will be lower than the value expected for the nominal concentration of the solution, but it may slowly increase with time, although not necessarily reaching the true value. Assuming that the binding energy to the surface

is approximately proportional to the number of segments, N , which is expected to be a reasonable assumption for many polymers, the dominant factors determining adsorption of the various species present in a polydisperse polymer sample are (i) the binding constant for adsorption, which increases as $\exp(N)$, i.e. large MW species adsorb more strongly than low MWs, (ii) short measurement times favour the adsorption of smaller over larger MW species at all concentrations, (iii) depletion occurs below a molar threshold concentration that increases with MW. We have discussed elsewhere how the first two factors lead to an artificially steep Gibbs plot in its initial drop in ST for PVME and poloxamer systems.^{38,46} The assessment of equilibration is more commonly made at higher concentrations where the surface excess has reached its saturation value and the ST is low. Here, the ST can be further lowered by the increasing gradual adsorption of the highest MW species into the surface layer. The threshold molar depletion concentration increases linearly with MW and lowering of the ST therefore proceeds gradually as higher and higher MW species reach their threshold depletion concentrations. If the ST is measured as a function of time at a fixed concentration it may also slowly decrease with time because of very slow diffusion of high MW species near their depletion threshold or if the now high concentration of low MW species drives release of higher MW species from surfaces of the container. Either mechanism could explain the slow decline in ST that is nearly always observed. This decline results from differences in the slope of the Gibbs plot, not from any change in the segmental coverage, which, in the simple model suggested here, will be constant with time, as is often observed in NR experiments.

The equilibration of the different MWs at the A-W interface is, of course, the true equilibrium process for a polydisperse polymer and this is not a situation in which it would be feasible to apply the Gibbs equation. However, from the discussion above equilibration can be considered as proceeding in stages, each of which can be regarded as a quasi-equilibrium, and to each of which the Gibbs equation might reasonably be applied. NR generally indicates that the segmental composition of the surface is reasonably constant and stable after 1-3

hrs. It is then plausible that the point at which a constant surface excess is reached, as measured by NR, corresponds approximately with the point at which the dominant MW in the mixture is fully adsorbed. Measurements of the ST made at a similar surface age should therefore fit the Gibbs equation using the NR surface excess and molar concentrations based on the known nominal MW. In practice, the errors arising from the use of measurements of the ST at longer times are probably small, but the important point is that the shorter time ST measurements should be more representative of the equilibrium behaviour of the average MW than the very long time measurements. This is a similar conclusion to that reached by Gilanyi et al. in a comprehensive study of the effects of MW and time on the adsorption of PEO at the A-W interface PEO.⁴⁷

In addition to polydispersity in MW, the present HMPAM polymers are likely to be polydisperse in composition, state of ionization, and in the composition of the counterion. We have shown here that polydispersity of composition in hydrophobically modified polymers can become a substantial effect when the MW drops to 10k but should not be noticeable at high MWs. For the same reasons, polydispersity of the state of ionization of the HMPAM should also only become significant at low MW. However, the presence of impurity counterions, which commonly have a significant effect on the ST of charged surfactants,³⁹ is a potential source of significant error for ST measurements on charged polymers. If, for example, Ca^{2+} ions are present at trace concentrations, as they often are in ionic systems, they may also progressively lower the ST at long times.

The “representative” surface as described above has a composition that is approximately constant with time, but an ST that is not necessarily constant. In the experiments described here the average age of the surface in the NR experiment was generally 2-3 hrs. Although the time dependence was not explicitly monitored, the expected effects of hydrophobicity and concentration form a regular pattern in the case of those E polymers for which all three contrasts were measured (Table 3). The pattern for the B polymers in Table 4 is less regular and becomes quite irregular for higher mol% of hydrophobe, i.e. 4 and 6 mol%. It

is not unreasonable that equilibration should be more difficult under these circumstances. On the other hand the more hydrophobic C_{16} chain at the low 2 mol% still appears to follow an equilibrium pattern. The disagreement between coverages for E and B polymers at 2 mol% C_{12} is as likely to be a genuine difference, possibly as a result of differing charge on the two polymers, as a non-equilibrium effect. The A and C polymers are larger in MW, which would make equilibration slower, and only one contrast was measured, so the measurement is less reliable. The surface coverages qualitatively mainly follow the expected pattern but there are some deviations. Finally, the very small D polymers show a whole range of irregular behaviour, which arises from the greater range of surface activity possible in a small hydrophobically modified polymer. On the basis of the discussion in the previous paragraph it is only the B and E HMPAM that might be expected to reach a “representative” equilibrium. An equilibrium system should be consistent with the Gibbs equation and, although an important assumption is required to show this, there are good reasons for believing it to be valid for these two systems. It is also significant that the data of Millet et al. for similar species of HMPAANa can also be fitted to the Gibbs equation via a different, though reasonable assumption.

Conclusions

The adsorption of HMPAM with a range of MW, containing a range of concentrations and length of hydrophobic chains from C_8D_{17} to $C_{16}D_{33}$, has been followed at the A-W interface using ST and NR measurements. The deuterium labelling of the hydrophobes and the use of both null reflecting water and D_2O as solvents has made it possible to determine the distribution of hydrophobes and backbone fragments in the surface region for HMPAM compositions with a range of stoichiometries and over a range of bulk concentrations. For four polymers with MW of 100k and above the composition of the surface is within error the same as the nominal bulk composition, i.e. there is no preferential adsorption of polymers with a composition significantly different from that of the bulk. For these polymers the

hydrophobes are entirely in the outer part of the surface, some in a thin outer layer with no water and a smaller number in an immediately adjacent thicker layer containing some water. More backbone is present than water in the two outer layers and it evidently collapses on to the hydrophobic layer, but the majority of the backbone segments form a thick and diffuse third layer below the two surface layers. The variation of the area per hydrophobic group with composition shows that it generally systematically decreases as the mol% increases from 0.5 to 2. The adsorption of these HMPAM mostly also decreases systematically as the concentration decreases suggesting that they reach a state either at or close to equilibrium. However, the adsorption becomes irregular when the mol% of polymer is increased above 2%. Low molecular weight (10k) HMPAM form a much wider and less regular array of surface structures. This is attributed to the greater spread of compositions and structures that form when the total number of hydrophobes per polymer is less than about 10. A wider spread of compositions and a greater effect of hydrophobe location on the chain leads to a large spread in surface activity within a single sample. Preferential adsorption of species with more hydrophobes occurs and more complex surface structures are observed. Some of these have been identified, although it is not possible to determine whether or not these represent equilibrium in systems that are polydisperse in composition.

A new feature has been identified in the ST behaviour. The ST of the two most completely studied series of polymers satisfy the Gibbs equation if it is assumed that they carry a small charge, at a level of about 1 charge per 100 backbone units. The charge arises from some acrylamide groups being partially converted to carboxylate groups. In one of the polymers, the B polymers, such groups are known to be present. The effect is a substantial increase in the slope of the Gibbs plot (σ against $\ln c$). For two of the groups of polymers the successful simultaneous fit of surface excess from NR and the ST is evidence of both very weak charge densities of the modified polymers and of these systems being at equilibrium. This analysis was further extended to earlier similar data obtained for HMPAANa, which has a similar structure except that it is a polyelectrolyte. The XRR and ST data for HMPAANa of similar

hydrophobic compositions could also be fitted to the Gibbs equation. In these cases the level of adsorption is much less than for the corresponding HMPAM but the higher effective charge leads to a stronger decrease in ST with increasing concentration.

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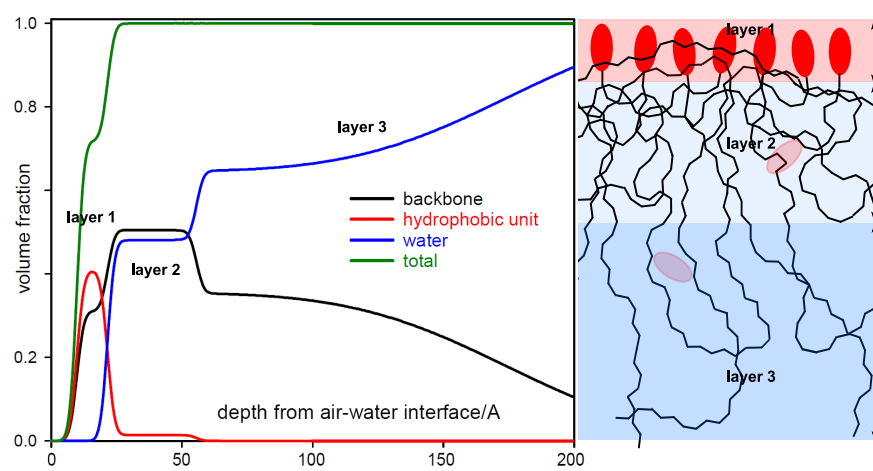
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TOC Graphic