Neutron and X-ray Reflectivity Studies of Water-Soluble Block and Statistical Copolymers Adsorbed at the Air−Water Interface

T. J. Su, D. A. Styrkas, and R. K. Thomas*

Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, U.K.

F. L. Baines, N. C. Billingham, and S. P. Armes

School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.

Received February 13, 1996; Revised Manuscript Received July 16, 1996[⊗]

ABSTRACT: We describe surface tension and neutron and X-ray reflectivity measurements on layers of poly(2-(dimethylamino)ethyl methacrylate-*block*-*n*-butyl methacrylate) copolymer (poly(DMAEMA-*b*-BMA)) (72 mol % DMAEMA) adsorbed at the air−water interface, together with parallel measurements on the statistical DMAEMA−BMA copolymer (90 mol % DMAEMA). The DMAEMA block is a weak polyelectrolyte, and we have studied the properties of these two adsorbed layers as a function of pH and ionic strength. The variation of the surface tension with the three variables, polymer concentration, pH, and ionic strength, is somewhat complex, but combined with the adsorbed amounts determined from the reflection experiments, we have been able to give semiquantitative explanations of this variation using the Gibbs equation. The main factor that must be taken into account is the adsorption (or depletion) of the large number of ions associated with a single copolymer molecule. Different conclusions can be reached about the relative surface activity of the diblock and statistical copolymers depending on whether surface coverage or surface tension is used as the measure of surface activity. The coverage of the two copolymers in terms of the average number of segments adsorbed is comparable under most conditions, but the surface tension of the diblock is always significantly higher than that of the statistical copolymer. This is the opposite of what is usually supposed, but we argue here that, when the hydrophilic or polyelectrolyte block is the larger block and hence dominates the space occupied at the interface, the hydrophobic block has little effect on the surface tension. However, by ensuring strong adsorption of the copolymer as a whole, the hydrophobic block indirectly causes a large surface concentration of ions, which raises the surface tension to a higher value than would normally be expected. The combination of neutron and x-ray reflectivity shows that there is a thin copolymer layer, typically about 6 Å thick, protruding out of the aqueous surface and a thicker one, typically about 15 Å, immersed in the water. Under all conditions of pH and ionic strength the surface layer remains fairly concentrated (area per average segment less than about 70 Å^2). When the DMAEMA segments are fully charged and the ionic strength is high, this layer is more extended into the solution.

Introduction

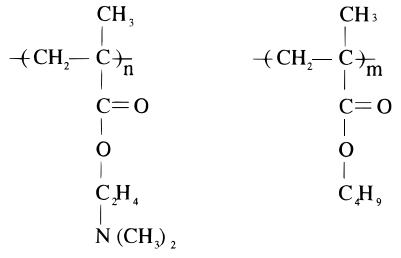
There is considerable interest in water-soluble hydrophilic−hydrophobic diblock copolymers as surface active agents because the hydrophobic component confers surface activity on the copolymer. It is therefore not surprising that many water-soluble block copolymers have been demonstrated to be effective stabilizers,[1−3] emulsifiers,[4,5] or dispersants,[6] a particularly well-known example being the poly(ethylene oxide-*b*-propylene oxide) diblock and triblock copolymers,[7−9] which are commercially successful macromolecular surfactants. A further interesting variant for water-soluble copolymers is the possibility of changing the characteristics of the amphiphilic behavior by using strong or weak polyelectrolytes as one of the blocks, the latter having the further flexibility of charge density variation on the soluble block.

There is also strong interest in the preparation of amphiphilic diblock copolymers using living polymerization. For example, styrene, which is relatively straightforward to polymerize *via* classical anionic polymerization, has been widely used to synthesize polystyrene based block copolymers which incorporate a range of nonionic, anionic, and cationic hydrophilic components. Barker and Vincent[10] have synthesized poly(ethylene oxide-*b*-methacrylic acid) copolymers, Munk and co-workers[11,12] have synthesised poly(styrene-*b*-methacrylic acid) copolymers, and several groups have reported the synthesis and solution behavior of poly(styrene-*b*-vinylpyridine) copolymers.[4,13−18] Poly(alkyl (meth)acrylate)s have also been utilized as the hydrophobic component in conjunction with various hydrophilic blocks such as poly(2-vinylpyridine)[19−21] and sulfonated poly(glycidyl methacrylate).[22,23]

As well as the interest in the practical aspects of amphiphilic copolymers at interfaces, there has been a fair amount of theoretical attention recently devoted to aspects of the self-assembly of copolymers in solution and at interfaces. Thus, Scheutjens and co-workers have used self-consistent field methods to examine the effect of composition on the adsorption of copolymers at interfaces and have considered the differences between diblocks and random copolymers,[24,25] Zhan and Mattice[25] have used Monte Carlo methods to study the self-assembly of diblocks into both micelles and adsorbed layers, and Marques *et al.*[26] have used scaling arguments to study the adsorption and the structure of the adsorbed copolymer layer. The added complication of the water-soluble block being a polyelectrolyte has been considered by Wittmer and Joanny[27] and Dan and Tirrell,[28] who have used scaling arguments to assess the balance between self-assembly into micelles or into an adsorbed layer. Some of the important issues are the relative stability of micelles and adsorbed layers as a function of fractional composition, charge on the polyelectrolyte block, and ionic strength. Also of interest

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

S0024-9297(96)00218-5 CCC: $12.00



DMAEMA n-BMA

Figure 1. Chemical structure of the monomer residues in the copolymers.

are the effects of changes in all these parameters on the structure of micelles and adsorbed layers.

There have been several experimental studies on the micellization of hydrophilic−hydrophobic block copolymers in aqueous solution[2,7−9,11−16] but relatively few reports concerning their adsorption and structure at the air−water interface. This is partly because traditional surface measurements are often difficult to interpret. The study of insoluble diblocks using Langmuir film balances has been more useful and Eisenberg and coworkers[29] have deduced various morphologies for spread block polyelectrolytes. Neutron and X-ray reflectivity are powerful techniques for investigating the air−liquid interface[30] and the former has been widely used to study the adsorption and structure of anionic, cationic, and nonionic small molecule surfactants,[31] spread monolayers of water-insoluble polymers such as poly(methyl methacrylate),[32] and spread layers of diblock copolymers.[33] Neutron reflection studies on soluble copolymers have been made by Phipps *et al.*,[34] who attempted to study the structure of three copolymers at the liquid−liquid interface (water−hexane), and Dai *et al.*[35] and Kent *et al.*,[36] who have respectively studied block copolymers adsorbed at the air-toluene and air-ethyl benzoate interfaces.

Here we describe surface tension and neutron and X-ray reflectivity measurements on layers of a hydrophilic−hydrophobic poly(2-(dimethylamino)ethyl methacrylate-*b*-*n*-butyl methacrylate) copolymer adsorbed at the air−water interface. The hydrophilic block is a weak polyelectrolyte, and the charge can be varied by varying the pH of the solution. In order to assess the effects of copolymer architecture we have carried out parallel experiments on the equivalent statistical copolymer.

Experimental Details

The poly(2-(dimethylamino)ethyl methacrylate-*b*-*n*-butyl methacrylate) block copolymer (henceforth abbreviated to poly(DMAEMA-*b*-BMA), see Figure 1) was prepared by group transfer polymerization[3,37] at 298 K using 1-methoxy-2-methyl-1-(trimethylsiloxy)propene initiator and a tetrabutylammonium dibenzoate catalyst *via* sequential monomer addition, the DMAEMA being polymerized first. ^{1}H NMR spectroscopy and CHN microanalyses indicated a BMA content of 28 mol %. Gel permeation chromatography (solvent, tetrahydrofuran; refractive index detector; polystyrene standards) showed that this block copolymer had a narrow unimodal distribution with an M_n of 19 500 and an M_w/M_n of 1.14. The statistical copolymer was synthesized using identical conditions except that the two comonomers were premixed in a 9:1 molar ratio before copolymerization. The resulting copolymer contained 10 mol % BMA and had an M_n of 8300 and an M_w/M_n of 1.10.

Sodium chloride (BDH, AnalaR) was roasted before use to remove surface active organic impurities. All the glassware and PTFE troughs were cleaned by soaking them in alkaline detergent (Decon 90) overnight and then rinsing several times with ultrapure water (Elgastat UHQ, Elga, U.K.). The pH of the solutions was adjusted using sodium hydroxide and hydrochloric acid and maintained constant during the measurements by keeping the samples under a nitrogen or argon atmosphere.

The surface tension of the aqueous copolymer solutions was determined on a Krüss K10T digital-tensiometer using the du Noüy ring method with a Pt/Ir ring. The surfaces of the solutions took some time to reach equilibrium and all measurements were made after the solution had stood for 30 min. Before each measurement, the ring was rinsed with pure water and flamed to remove contaminants. The temperature was maintained at 298 ± 0.2 K.

Dynamic light scattering experiments were carried out on 1% w/v copolymer solutions at pH 7.3 using a Malvern PCS 4700 spectrometer equipped with a 40 mW He−Ne laser. Measurements were made at an angle of 90° to the incident beam.

The neutron reflection measurements were carried out on the reflectometer CRISP at Rutherford Appleton Laboratory (Didcot, U.K.). The instrument and the procedure for making the measurements have been fully described elsewhere.[38,39] A pulsed, polychromatic neutron beam impinges on the sample at a fixed angle of incidence, which was set at 1.5° for the work in this paper. The neutrons specularly reflected from the sample are detected by a single detector and their wavelengths analyzed by time-of-flight. The reflectivity is determined by the ratio of the reflected neutrons at each wavelength to the number incident on the sample. The neutron reflectivity is measured as a function of momentum transfer Q (=$(4\pi \sin \theta)/\lambda$ where θ is the glancing angle of incidence and λ the wavelength of the neutrons). The reflection intensities were calibrated with respect to pure D_2O. Incoherent scattering from the bulk solution gives rise to a background, which was determined by measurement of the signal out to large values of Q. This background was assumed to be flat, which has been shown to be approximately valid, provided any small angle scattering from the bulk solution is small.[40]

The grazing incidence X-ray reflection measurements were made on a laboratory based X-ray reflectometer using a conventional X-ray tube (Cu Kα, 1.54 Å).[41] A monochromatic X-ray beam is incident on the sample over a range of angles giving a good reflectivity signal over the range of Q of 0.01−0.6 Å^{-1}. The reflected X-ray beam is detected by a proportional gas ionization counter. The procedure for subtracting the background scattering, which is lower than in the neutron experiment, was the same as in the neutron experiment.

Results and Discussion

(a) Surface Tension and Dynamic Light Scattering. Figure 2 shows the surface tension variation with copolymer concentration of both the diblock and statistical copolymers in aqueous solution at 298 K and a pH of 7.3. The surface tension decreases as the copolymer concentration increases up to about 0.1% w/v. There is then a well-defined break (indicated by an arrow in the figure) at 0.087 ± 0.005% for the diblock copolymer and possibly also one at 0.082 ± 0.005% for the statistical copolymer. Over most of the concentration range, if surface tension is taken as a measure of surface activity, the statistical copolymer is more surface active than the diblock copolymer, although its molar percentage of hydrophilic monomer residues (DMAEMA) is larger. A similar phenomenon has also been observed by Ishihara *et al.*,[42] who used surface tension and fluorescence techniques to investigate the properties of the water-soluble graft copolymer, poly(((2-(methacryloyloxy)ethyl)phosphoryl)choline-*graft*-BMA), which we abbreviate to poly(MPC-*g*-BMA). The surface activity of the diblock was only slight whereas the statistical copolymer was strongly surface active. Ishihara *et al.* interpreted this as the hydrophobic BMA moieties in the graft copolymer being completely covered by the hydrophilic MPC chains and therefore losing their surface activity. In the present study the difference

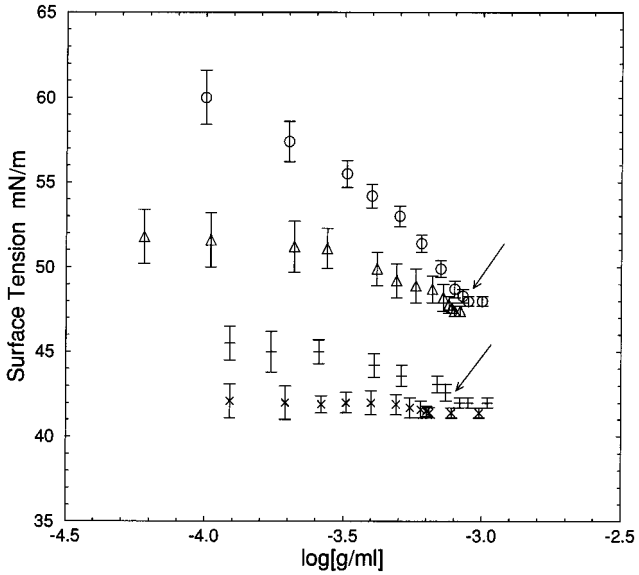


Figure 2. Surface tension measurements of the diblock copolymer aqueous solutions without (○) and with (△) 0.02 M NaCl and of the statistical copolymer aqueous solutions without (+) and with (×) 0.02 M NaCl.

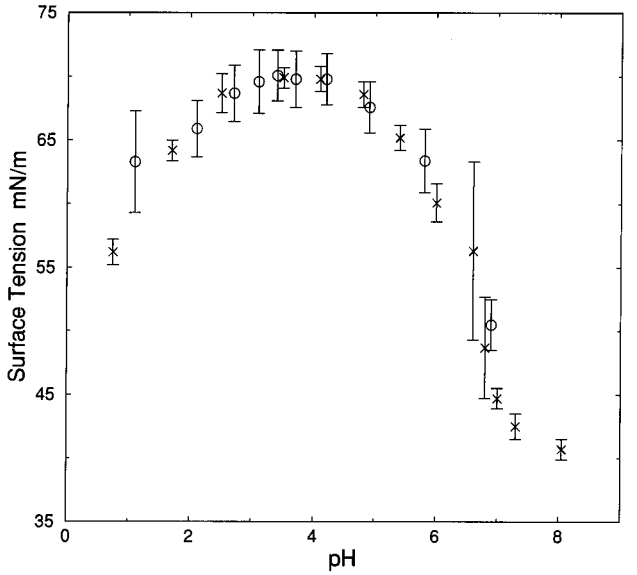


Figure 3. Effect of pH on the surface tensions of the two copolymers at a concentration of 0.087 w/v % for the diblock (○) and 0.082 w/v % for the statistical copolymer (×).

between the surface tension of our block and statistical copolymers is not as marked as for poly(MPC-*g*-BMA) and we discuss the question of relative surface activity further below.

It is difficult to use the Gibbs equation to determine the surface coverage of the copolymers from $\gamma - \ln c$ plots because the degree of ionization is not known. The authors have not been able to find a detailed discussion of the Gibbs equation for this type of system, and here we extend the approach of Hall *et al.*[43] The full expression for the Gibbs equation for these copolymers may be written

$$-\frac{\mathrm{d}\gamma}{RT} = \Gamma_{\mathrm{pol}}\mathrm{d}\ln f_{\mathrm{pol}}c_{\mathrm{pol}} + \Gamma_{\mathrm{ion}}\mathrm{d}\ln f_{\mathrm{ion}}c_{\mathrm{ion}} + \Gamma_{\mathrm{coion}}\mathrm{d}\ln f_{\mathrm{coion}}c_{\mathrm{coion}} \quad (1)$$

where Γ represents surface excess (measured relative to water), c is concentration, f is the activity coefficient, and the subscripts refer to copolymer, counterion, and co-ion. When the copolymer is the only source of counterions and the surface is neutral, then, if we assume that the copolymer charge is the same in solution and at the surface, the equation becomes

$$-\frac{\mathrm{d}\gamma}{RT} = \Gamma_{\mathrm{pol}}(1+n)\,\mathrm{d}\ln c_{\mathrm{pol}} + \Gamma_{\mathrm{pol}}\,\mathrm{d}n + \Gamma_{\mathrm{pol}}(\mathrm{d}\ln f_{\mathrm{pol}} + n\,\mathrm{d}\ln f_{\mathrm{ion}}) \quad (2)$$

where n is the total charge on an average copolymer chain. In the concentration range where the copolymer does not form aggregates in the bulk solution n should be constant at a given pH. Neglecting any contribution from variation of the activity coefficients with concentration the apparent surface excess Γ^a will be given by

$$\Gamma^{\mathrm{a}} \approx \Gamma_{\mathrm{pol}}(1+n) \quad (3)$$

The maximum values of n are about 90 for the diblock and about 50 for the statistical copolymer and at all the pHs studied n is expected to be very much greater than unity. In the special case where the fractional charge on the adsorbed DMAEMA and the coverage of the surface by DMAEMA segments are the same for the two copolymers then

$$\Gamma^{\mathrm{a}}_{\mathrm{ran}} \approx \left(\frac{50}{90}\right)^2 \Gamma^{\mathrm{a}}_{\mathrm{di}} \quad (4)$$

Thus the apparent adsorption of the statistical copolymer, as determined from the slope of the plots in Figure 2, would be expected to be about one-third of that of the diblock. Given the large errors in determining these slopes, this condition is approximately fulfilled, which implies that the surface coverage, in terms only of DMAEMA segments, is comparable for the two copolymers. The reflection results discussed below are approximately consistent with this estimate.

It is interesting to examine the behavior of the surface tension, eq 2, at the critical micelle concentration (CMC). If, as is common for small molecule surfactants, the surface coverage does not change significantly over a small range of concentration through the CMC[44] then the slope of the plots in Figure 2 may change either because $\ln c_{\mathrm{pol}}$ becomes very different from $\ln f_{\mathrm{pol}}c_{\mathrm{pol}}$, as for small molecule surfactants, or because the ionization of the copolymer in the micelle may be different from the free copolymer; i.e. n may change. It is of course also possible to have a break caused by a change in surface structure, i.e. a change in Γ_{pol}.

Both the solubility and the surface activity of the copolymers are sensitive to pH, the diblock being insoluble above a pH of about 7.5 and the statistical copolymer insoluble above about 8. Thus a proportion of the hydrophilic DMAEMA monomer residues must be protonated for the copolymers to dissolve, and the surface activity can also be expected to be sensitive to the pH. The variation of the surface tension at a fixed copolymer concentration near 0.1% w/v and varying HCl concentration is shown in Figure 3. This shows how, as the pH is lowered below about 7, the copolymers become less surface active, presumably because they become more fully extended with their extra charge and cannot then accommodate themselves to the steric restrictions imposed by the surface.[45] Provided the pH is not too high, its main effect is to change n and the response of the surface tension is then determined by

$$-\left(\frac{d\gamma}{RT}\right)_{c_{pol}} = \Gamma_{pol}\, dn + \Gamma_{pol}(d \ln f_{pol} + n\, d \ln f_{ion}) \quad (5)$$

where c_{pol} has been taken as constant. It is not possible to give explicit expressions for the two activity coefficient terms. However, at the low concentrations being considered, both should decrease with increasing n and because of the prefactor n in the counterion term this term will dominate. If we take as a guide the Debye–Huckel limiting law for the counterion we obtain

$$-\left(\frac{d\gamma}{RT}\right)_{c_{pol}} \approx \Gamma_{pol}(1 - Bn^{x})\, dn + \Gamma_{pol}\, d \ln f_{pol} \quad (6)$$

where B is a constant of order unity and x has a value between $^1/_2$ (appropriate for a 1:1 electrolyte) and 2 (appropriate for an n-valent ion and n counterions where n is large). In the pH range under consideration both the term in brackets and the d ln f_{pol} will be negative and, provided that the surface excess of copolymer remains positive, the surface tension will therefore increase as the pH is lowered until the degree of ionization no longer changes; i.e. γ should increase to a maximum value, irrespective of whether the amount of adsorbed copolymer changes. This is exactly as observed (see Figure 3). At still lower values of the pH the expression for the surface tension becomes more complicated because we must take into account the behavior of the co-ions (see eq 1) and allow for further variation of the activity coefficient of the counterions. Assuming that n no longer changes as the pH is lowered and including the co-ion term in eq 1 while maintaining electrical neutrality of the surface layer, we obtain

$$-\left(\frac{d\gamma}{RT}\right)_{c_{pol}} = (n\Gamma_{pol} - \Gamma_{co\text{-}ion})\, d \ln f_{ion}c_{ion} + \Gamma_{co\text{-}ion}\, d \ln f_{co\text{-}ion}c_{co\text{-}ion} + \Gamma_{pol}\, d \ln f_{pol} \quad (7)$$

The concentrations of counterions and co-ions will be approximately equal at low pH and their activity coefficients will also be similar. Then eq 7 becomes

$$-\left(\frac{d\gamma}{RT}\right)_{c_{pol}} = n\Gamma_{pol}(d \ln f_{ion} + d \ln c_{ion}) + \Gamma_{pol}\, d \ln f_{pol} \quad (8)$$

The dominant term will be the concentration term and therefore the surface tension will now decrease again as the pH is lowered, as observed.

The behavior of the solubility and surface activity with pH indicates that the hydrophilic groups are partially charged at a pH of 7.3 and addition of electrolyte should screen this charge, reducing the repulsion between positive DMAEMA fragments, and increasing the surface activity. The surface tension in the presence of 0.02 M NaCl is shown as a function of polymer concentration in Figure 2 and it does decrease significantly over much of the concentration range, except above the break point in the surface tension curve, where the changes are relatively small. The main effect of added electrolyte will be to suppress the variation of c_{ion} in eq 1, which becomes

$$-\frac{d\gamma}{RT} \approx \Gamma_{pol}\, d \ln f_{pol}c_{pol} \quad (9)$$

and there should therefore be a dramatic reduction in the magnitude of the slope of the plot, exactly as observed. In Figure 4 we show the variation in surface tension of both copolymers as a function of salt concentration and at fixed copolymer concentration close to 0.1% w/v and a fixed pH. At pHs of 3.5 and 7.3 the surface tension of the statistical copolymer decreases systematically with added salt. The behavior of the diblock is more complicated. Its surface tension is generally slightly higher when the ionic strength is high but at low ionic strength the surface tension behavior is more erratic, there even being a clear minimum at pH 3.5. The appropriate surface tension equation is derived from (1) and is

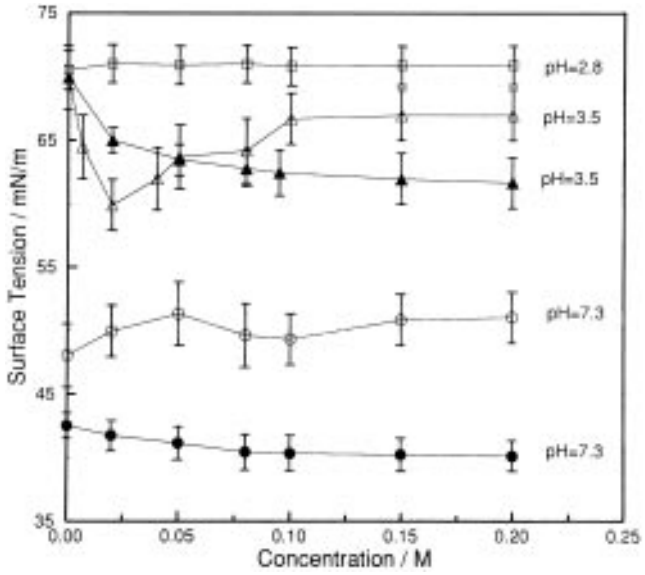


Figure 4. Surface tension measurements of the diblock (open symbols) and statistical random (filled symbols) copolymer aqueous solutions at different pHs as a function of added NaCl concentration. The copolymer concentration was kept constant at 0.087 w/v % for the diblock and 0.082 w/v % for the statistical copolymer.

$$-\left(\frac{d\gamma}{RT}\right)_{c_{pol,pH}} = \Gamma_{pol}\, d \ln f_{pol} + (n\Gamma_{pol} - \Gamma_{co\text{-}ion})\, d \ln f_{ion}c_{ion} + \Gamma_{co\text{-}ion}\, d \ln f_{co\text{-}ion}c_{co\text{-}ion} \quad (10)$$

The concentrations of co-ion and counterion under these conditions will be approximately the same, and if we make the further assumption that their activity coefficients vary similarly with concentration, we obtain

$$-\left(\frac{d\gamma}{RT}\right)_{c_{pol,pH}} \approx \Gamma_{pol}\, d \ln f_{pol} + n\Gamma_{pol}\, d \ln f_{ion}c_{ion} \quad (11)$$

This differs from eq 2 in that the concentration of counterion is being varied independently of copolymer. It should also be noted that we have neglected any variation of n with changes in the activity coefficients. The main change is in ln c_{ion}, which will cause γ to decrease as c_{ion} increases, as observed for the statistical copolymer. $n\Gamma_{pol}$ occurs as a prefactor for the ln c_{ion} terms, and the results for the statistical copolymer in Figure 4 indicate that $n\Gamma_{pol}$ is larger at pH 3.5 than at pH 7.3. The ionization, i.e. n, is expected to be larger but Γ might be expected to be smaller since the surface tension is only slightly lower than for water. Nevertheless the results show that n must more than compensate for any changes in Γ. This is confirmed by the reflection results below.

For the diblock copolymer we first consider the behavior at pH 7.3. Since the concentration of the copolymer is close to the critical micelle concentration,

addition of electrolyte will probably cause micellization. Above the CMC the activities of copolymer and co-ion will then be approximately constant and the surface tension variation will be

$$-\left(\frac{d\gamma}{RT}\right)_{c_{pol,pH}} \approx \Gamma_{co\text{-}ion}\, d \ln f_{co\text{-}ion} c_{co\text{-}ion} \qquad (12)$$

Since co-ions would be expected to be partially excluded from the copolymer layer, $\Gamma_{co\text{-}ion}$ should be negative and the surface tension should increase with added electrolyte, as observed. At pH 3.5 micellization will not occur immediately when electrolyte is added. The effect of added salt should then be the same as for the statistical copolymer at the same pH except that n is larger and the initial decrease in the surface tension is more rapid, as observed. From the observed surface tension behavior it would seem that at an electrolyte concentration of about 0.02 M micellization occurs and the behavior then follows eq 12.

We have been able to explain semiquantitatively the main features of the surface tension behavior mainly in terms of the variation of the adsorption of counterions and co-ions, which evidently have a strong influence on the surface tension behavior. As far as we are aware, this is the first time such a systematic study of the consequences of the Gibbs equation for the behavior of such a system has been made. The magnitude of the copolymer adsorption is of little relevance to most of the phenomena observed, and this emphasizes the dangers of interpreting surface activity in terms of surface tension rather than in terms of surface coverage. We will show below that the reflection results give values of the copolymer surface coverage that largely confirm the interpretations above.

By analogy with the results of others (see, for example, ref 46) the break point at about 0.1% w/v in the absence of salt is probably the critical micelle concentration (CMC) of the diblock copolymer. The much weaker break for the statistical copolymer is unlikely to be a genuine CMC, especially when the differing effects of added electrolyte on the surface tension are taken into account. The dynamic light scattering experiments on relatively concentrated solutions (1% w/v) showed that the scattering from the statistical copolymer was little different from that from water, *i.e.* the copolymer is dissolved molecularly, but there was substantial scattering from the diblock copolymer, indicating a high degree of association. The hydrodynamic radius of these aggregates was of the order of 100 nm, which, from our experience with similar diblock copolymers and also in the light of results from Selb and Gallot[13] and Stejskal *et al.*,[47] is not necessarily true micellization. The light scattering result shows, however, that the break in the surface tension curve for the statistical copolymer cannot be associated with micellization in the bulk solution. An important difference from small molecule surfactants is that the copolymer may change either its surface-adsorbed phase or its bulk aggregation, whereas for small molecule surfactants realistically only the bulk phase can change. Thus it has been suggested that the structure of an adsorbed copolymer layer changes at a different concentration from that at which micellization occurs.[25] It is possible that the very weak change in gradient in Figure 2 for the statistical copolymer corresponds to a change in the surface phase of the copolymer.

(b) Specular Reflection. Neutron reflection profiles were measured for D_2O solutions of the diblock and statistical copolymers at the break point in the surface tension plots of Figure 2, with and without NaCl and at pH values of 7.3, 3.5, and 1.1. The results for pH 7.3, where the surface tension is at its lowest, are shown in Figure 5 and compared with the reflectivity from D_2O on its own. The polymers have a marked effect on the reflectivity of D_2O and there are small differences between the statistical and diblock behavior. The addition of salt reduces the reflectivity somewhat further.

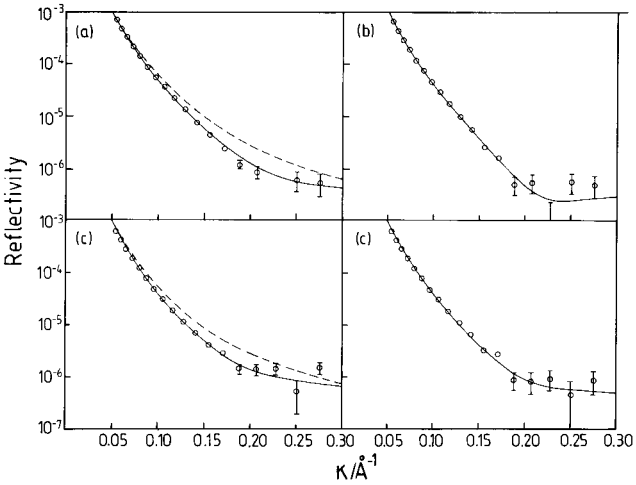


Figure 5. Neutron reflectivity profiles of the diblock copolymer aqueous solutions without (a) and with (b) 0.02 M NaCl and of the statistical copolymer aqueous solutions without (c) and with (d) 0.02 M NaCl. The continuous lines are the best fits using the parameters of Table 2, and the dashed lines are profiles calculated assuming the copolymer is entirely out of the water. The dashed lines are almost indistinguishable from those of pure D_2O.

The simplest analysis of neutron and X-ray reflection is *via* the optical matrix method.[48] The refractive index profile of the surface layer normal to the surface is divided into a number of uniform layers, the Fresnel reflection and transmission coefficients are calculated for each interface and combined to give the total reflectivity from the composite surface layer. The refractive index, n, of a layer is related to its scattering length density, ρ, by

$$n = 1 - (\lambda^2/2\pi)\rho \qquad (13)$$

For neutrons,

$$\rho = \sum n_i b_i \qquad (14)$$

where n_i is the number density of an atomic species i and b_i is its scattering length. b_i is an empirically determined quantity for neutrons but for X-rays is given by

$$b_i = (f_i + \Delta f_i)e^2/mc^2 \qquad (15)$$

where e and m are the charge and mass of the electron, c is the speed of light, and f is the atomic scattering factor which is approximately the atomic number at low scattering angles.

For the experiments here, the scattering length density of any component layer can be expressed in terms of the volume fraction, ϕ_p, of the copolymer in that layer:

$$\rho = \phi_p \rho_p + \phi_s \rho_s \qquad (16)$$

where ρ_p and ρ_s are the scattering length densities of the copolymer and solvent, respectively. If there is air

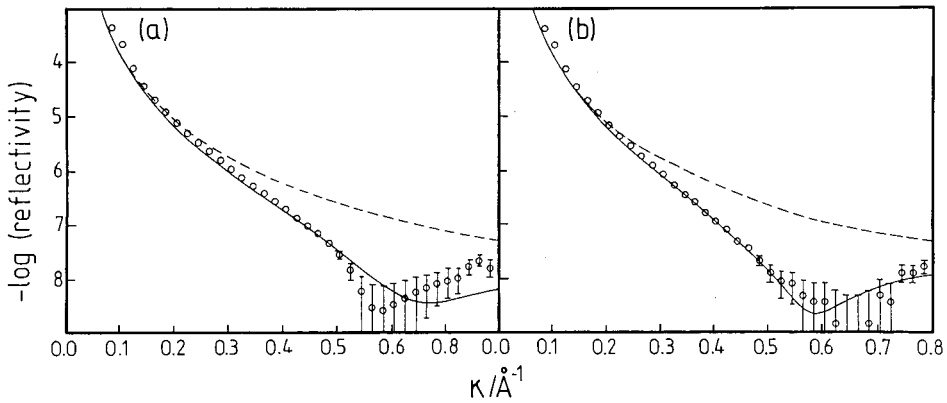


Figure 6. X-ray reflectivity profiles of (a) the diblock copolymer aqueous solution and (b) the statistical copolymer without salt. The continuous lines are the fits using the parameters given in Table 3. The dashed lines are the profiles calculated with the copolymer totally immersed in water.

Table 1. Volumes, Scattering Lengths, and Electron Numbers for Copolymer Subunits

unit	volume/Å^3	scattering length[a]/10^{-5} Å	electron no.
$CH_2C(CH_3)$	108.1[b]	1.25	23
C_4H_9	135.0[b]	−7.06	33
C_2H_4	53.8[b]	−1.66	16
COO	40.7[c]	18.25	22
$N(CH_3)_2$	110.1	0.26	25
H_2O	29.9	−1.68	10
D_2O	30.2	19.14	10

[a] Reference 49. [b] Reference 50. [c] Reference 51.

Table 2. Best Fits of the Neutron Reflection Profiles of the Two Copolymers Using a Uniform Layer Model

w/v % (±0.02)	pH	[NaCl]/M	$\rho_2/10^{-6}$ Å^{-2}, (±0.5)	τ_2/Å (±0.8)	$\rho_3/10^{-6}$ Å^{-2}, (±0.5)	τ_3/Å (±5)
			Diblock Copolymer			
0.08_5	7.3		4.9	14.5		
0.08_5	3.5		5.7	14.5		
0.08_5	1.1		5.7	14.5		
0.08	7.3	0.02	4.2	14.5		
0.08	3.5	0.02	5.6	18.0		
0.08	3.5	0.1	5.0	16.0	6.2	25
			Statistical Copolymer			
0.08	7.3		5.0	17.0		
0.08	3.5		5.5	15.0		
0.08	1.1		3.5	7.0	5.6	18
0.08	7.3	0.02	4.7	16.0		
0.08	3.5	0.1	4.3	14.0	6.2	25

in the layer ($\phi_p + \phi_s$) will be less than 1. In the neutron experiment the scattering lengths of the different components (see Table 1) are such that the density profile of D_2O normal to the interface is dominant because the scattering lengths of the copolymer fragments are very small. To illustrate this, the dashed lines in Figure 5a and c are for a compact layer of copolymer lying on the surface of the water; they are almost identical with the reflectivity of pure D_2O. The reflectivity profiles in Figure 5 are therefore approximately determined by the layer or layers where D_2O has been displaced by copolymer. Thus the simplest model that might fit the neutron data is of one uniform layer of scattering length density $\phi_s\rho_s$ where ρ_s is the scattering length density of D_2O. This does, indeed, give an adequate fit to the four profiles in Figure 5, and the fitted parameters are given in Table 2. Assuming that all the residual space in the lower layer is filled with D_2O, i.e. the volume fractions of copolymer and D_2O add up to unity, the volume fraction (%) of copolymer in the latter is found to be 20 and 25% for statistical and diblock copolymers in the absence of salt, increasing to 25 and 35% when 0.02 M NaCl is added (see Table 4). This parallels the lowering of the surface tensions of the two species when NaCl is added. The thickness of the layer is 14.5 Å for the diblock and somewhat larger at 17 Å for the statistical copolymer.

We have also studied the effects of pH on the reflectivity and the effects of added NaCl at the lower pH of 3.5. We do not show the reflectivity profiles, but the results of fitting the uniform layer model are included in Table 1. The neutron results indicate that the amount of copolymer in layer 2, the water-filled layer, is reduced substantially for both copolymers at the lower pH of 3.5, the volume fraction dropping to about 10% (see Table 4). The profiles at a pH of 1.1 show that the diblock has a reflectivity similar to that at pH 3.5 but the reflectivity of the statistical copolymer indicates greater adsorption and a significant thickening of the layer, which necessitated the use of a two-layer model to fit the data. Note that at a pH of 1.1 the ionic strength is also high. The effect of added NaCl at a pH of 7.3 was to increase the adsorption, and this is also true at a pH of 3.5. However, at pH 3.5 we studied the higher concentration of 0.1 M NaCl, which increases the adsorption for both copolymers and causes a thickening of the layer. The effect is much larger for the statistical copolymer and is consistent with ionic strength effects dominating pH effects at the very low pH of 1.1 for the latter.

The X-ray reflectivities of the two copolymers without salt at pH 7.3 are shown in Figure 6. In comparison with water the reflectivity is again strongly depressed, although now there is a noticeable interference minimum at about 0.6 Å^{-1}, indicating that the depression is not simply an increased roughness of the surface. If the values of the volume fractions obtained by fitting the neutron data are used to calculate an X-ray reflectivity profile using the single-layer model, the calculated profile does not fit the X-ray data at all (dashed lines in Figure 6). The calculated X-ray reflectivity for such a model is only slightly different from that of water because there is not much contrast between a close-packed copolymer/water layer and water on its own. The only possible explanation of the large difference between the X-ray reflectivities of the copolymer solutions and that of water is that some copolymer protrudes above the water to form a layer, which would be invisible to the neutrons because of its near zero scattering length density but which would have a significant effect on the X-ray reflectivity. Indeed, the X-ray reflectivity profile can be fairly accurately modeled with a single uniform layer of lower scattering length density than with a close-packed water/copolymer layer and of about 6 Å in thickness. Because each type of reflectivity is clearly

Table 3. Best Fits of the X-ray Reflection Profiles of the Two Copolymers Using the Model of Two Uniform Layers

w/v % (±0.02)	pH	[NaCl]M	$\rho_1/10^{-6}$ Å^{-2} (±0.8)	τ_1/Å (±0.1)	$\rho_2/10^{-6}$ Å^{-2} (±0.8)	τ_2/Å (±1)	$\rho_3/10^{-6}$ Å^{-2} (±0.8)	τ_3/Å (±1)
				Diblock Copolymer				
0.08_5	7.3		4.5	5.0	9.0	14.5		
0.08_5	3.5		3.0	8.0	8.0	14.5		
0.08_5	1.1		5.6	5.5	9.3	14.5		
0.08_5	1.1		5.6	5.5	9.3	14.5		
0.08	7.3	0.02	5.8	6.0	8.9	14.5		
0.08	3.5	0.02	3.0	10.0	8.0	18.0		
0.08	3.5	0.1	3.2	9.0	8.5	16.0	9.35	25
				Statistical Copolymer				
0.08	7.3		4.2	5.5	9.0	17.0		
0.08	3.5		3.5	7.0	9.0	15.0		
0.08	1.1		4.0	5.0	9.0	7.0	9.2	18
0.08	7.3	0.02	5.5	5.5	8.9	16.0		
0.08	3.5	0.1	3.2	6.5	8.7	14.0	9.35	25

Table 4. Structural Parameters Derived from the Neutron and X-ray Reflection Data

w/v %	pH	[NaCl]/M	A_{mol}/Å^2 (±10%)	A_{seg}/Å^2 (±10%)	γ/mN m^{-1}	ϕ_{p1} (±0.1)	ϕ_{p2} (±0.1)	ϕ_{p3} (±0.1)	g_{p1} (±0.05)	g_{p2} (±0.05)	g_{p2}
					Diblock Copolymer						
0.08_5	7.3		6300	49	48.0	0.6	0.25		0.47	0.53	
0.08_5	3.5		8470	66	70.0	0.4	0.1		0.68	0.32	
0.08_5	1.1		7160	56	63.5	0.7	0.1		0.73	0.27	
0.08	7.3	0.02	4080	32	47.5	0.75	0.35		0.48	0.52	
0.08	3.5	0.02	6380	50	60.0	0.4	0.1		0.64	0.36	
0.08	3.5	0.1	5260	41	67.0	0.4	0.2	0.02	0.5	0.43	0.07
					Statistical Copolymer						
0.08	7.3		2510	49	42.5	0.55	0.20		0.45	0.55	
0.08	3.5		3250	61	70.0	0.45	0.10		0.49	0.51	
0.08	1.1		2080	39	59.0	0.50	0.45	0.1	0.34	0.39	0.27
0.08	7.3	0.02	2000	37	41.5	0.70	0.25		0.49	0.51	
0.08	3.5	0.1	2170	41	62.5	0.40	0.30	0.02	0.35	0.59	0.06

sensitive to two distinct parts of the interface, we finally use a two-layer model with a layer of copolymer containing no water at all and a close-packed layer containing water and copolymer to model both neutron and X-ray reflectivities. From eq 16, the scattering length densities of the two layers must be

$$\rho_1 = \phi_{p1}\rho_p \tag{17}$$

and

$$\rho_2 = \phi_{p2}\rho_p + (1 - \phi_{p2})\rho_w \tag{18}$$

where the subscripts 1 and 2 denote the upper and lower layers, respectively. Since the neutron scattering length densities are estimated to be 0.5×10^{-6} Å^{-2} for the diblock and 0.6×10^{-6} Å^{-2} for the statistical copolymer, and the scattering length density of D_2O is 6.35×10^{-6} Å^{-2}, the contribution of layer 1 to the neutron reflectivity will be negligible. The fits to the neutron data in Table 2 will, however, give an accurate value of $(1 - \phi_{p2})$. Using the values of $(1 - \phi_{p2})$ and τ_2 from Table 2, we adjust the parameters of layer 1 until the X-ray data are satisfactorily fitted. The results of this are given in Table 3. These now show more definitely that there is a thin layer of copolymer, invisible to neutrons, protruding above the water. At a pH of 7.3 the thickness of the layer is not sensitive to the addition of 0.02 M NaCl but its composition is, there being a 50% increase in the amount of copolymer in this layer for both copolymers when salt is added. The effect of pH on the X-ray reflectivity has not been shown, but the results are given in Table 3. As the pH is lowered to 3.5, the density of copolymer in layer 1 decreases but because the layer thickens somewhat the total amount of polymer in the layer increases. For the diblock copolymer at the lower pH of 1.1 this effect is reversed and the upper layer becomes more dense. The effect is also reversed for the statistical copolymer but not as strongly. The effect of ionic strength on layer 1 at pH 3.5 is small for both copolymers.

The volume fractions of copolymer in the two layers can be obtained by using eqs 17 and 18. From the arguments already presented X-rays give the most reliable information about the composition of layer 1 and neutrons about layer 2. Therefore, combining the X-ray results on the first layer with the neutron results on the second layer, the average area per copolymer molecule, A, and the fraction, g, of a copolymer molecule above and in the water can be obtained from the following relations:

$$\phi_{p1} = g_{p1}V_p/\tau_1 A \tag{19}$$

$$\phi_{p2} = g_{p2}V_p/\tau_2 A \tag{20}$$

$$1 = g_{p1} + g_{p2} \tag{21}$$

where V_p is the volume of a copolymer molecule and τ is the layer thickness. The results of this calculation are given in Table 4. There are a number of sources of error in the estimates of the volume fractions. Neither neutron or X-ray reflectivity will be sensitive to diffuse copolymer layers in the situation where there is a substantial signal from an upper layer. Thus there is almost certainly a small fraction of polymer forming a diffuse layer which is not accounted for underneath the two or three layers already included. No allowance has been made for the contribution of the counterions to the reflectivity, although this is again expected to be very small. Finally, we have assumed that the copolymers are homogeneous. This would normally only be important for the neutron experiment because X-rays are scattered similarly by each of the fragments. However, even for the neutron experiment it is not likely to cause

serious error because what is being measured is the displacement of water rather than the aggregation of polymer. Taking all these errors together, the values of A in Table 4 will be overestimates of the area per molecule but experience with other systems suggests that the error will be at worst about 15%. At the level of accuracy needed for comparison with the surface tension results this is relatively small. To allow for the different molecular weight of the two copolymers, we have also included the mean area per segment.

Discussion

We first compare the surface tension and reflectivity results for the surface coverage. As noted in the discussion of the surface tension results, the surface tension behavior is mainly determined by the ion absorption or desorption. Thus, the slopes of the $\gamma -$ ln c plots in the absence of electrolyte in Figure 2 are approximately $(1 + n)$ times the true copolymer surface excess. The coverages from surface tension and reflectivity can then be combined to give an estimate of n. These values are found to be about 100 and 20 for the diblock and random copolymers, respectively, to be compared with maximum theoretical values of 90 and 50. The experimental value for the diblock copolymer seems to be too high, but there are considerable errors in the determination and the agreement demonstrates that eq 3 does account for the steep slope of the $\gamma -$ ln c curve as the CMC is approached from below. Also consistent with the presence of n in eq 3 and its absence in eq 9 is the change in both surface tension curves of Figure 2 when electrolyte is added. The slope of the γ - ln c plot changes by a very large factor, but as can be seen from Table 4, the change in Γ_{pol} is only by a factor of 20−50%.

When the pH is lowered, the surface tensions of both copolymers approach the value for pure water at a pH of 3.5. A naive interpretation, based only on the surface tension measurement, could have been that the amount of adsorbed copolymer drops to a very low value at this pH. The neutron and X-ray results, however, show quite clearly that the absorption is still strong, being only about 30% lower than at pH 7.3. Given this result, eq 6 shows that the increase in surface tension comes from forcing the number of adsorbed counterions to increase, because the net charge on the copolymer increases, and decreasing their chemical potential in the bulk (decrease in ln f), which makes adsorption of the ions less favorable. The hydrophobicity of the copolymer is strong enough to ensure adsorption, whatever its charge, but the lowering of the surface free energy is largely offset by the unfavorable free energy of adsorption of a large number of counterions. It is well-known that the surface tension of electrolyte solutions increases with electrolyte concentration because there is a depletion layer of electrolyte at the surface. These observations reinforce the earlier conclusion that it may be misleading to use surface tension as a measure of surface activity. The differences between surface tension behavior and adsorbed amounts are even more marked for the effects of electrolyte on the diblock copolymer at pH 7.3. The effect of a small amount of added electrolyte at pH 7.3 and just below the CMC causes little change in the surface tension of the diblock polymer, but the adsorbed amount changes by 50%.

The effect of adding 0.1 M electrolyte to the statistical copolymer at a pH of 3.5 was to decrease its surface tension substantially. This was earlier explained, using eq 11, as an increase in the chemical potential of the counterions in the bulk solution, which reduces the free energy penalty of adsorbing them at the interface. The reflectivity results now make it clear that the observed increase in Γ_{pol} can also explain the decrease in γ; i.e. the increased screening of the charged DMAEMA segments makes the copolymer more surface active. It would not have been possible to draw that conclusion from the surface tension results on their own.

The effect of added electrolyte on the behavior of the diblock copolymer is even more complex. At a pH of 3.5 the initial effect of electrolyte led to a sharp lowering of the surface tension, which then increased steadily on further addition of electrolyte above about 0.02 M. In contrast, the surface coverage, determined from the reflectivities, initially *decreases* on addition of electrolyte before *increasing* steadily on further addition. We have already used eq 12 to explain the increase of surface tension in terms of the co-ion behavior, the implied assumption being that Γ_{pol} was constant. Given that the diblock copolymer concentration was such that addition of electrolyte would take the copolymer above the CMC, the behavior of the surface coverage suggests that the adsorbed amount of copolymer also changes quite markedly across the CMC. This would be quite different from the behavior of small molecule surfactants, where the coverage only varies slightly through the CMC.[44] However, it has been suggested that the structure of the adsorbed layer changes for diblock copolymers at the CMC, the adsorption above the CMC being of micellar aggregates.[28] If this were the case, it would not be surprising if there were also a change in the adsorbed amount.

It is interesting to note that, in terms of surface coverage per average segment and allowing for the 10% error, there is no systematic difference between the surface activity of the two copolymers, and they are usually similar. However, in terms of the surface tension the statistical copolymer is always much more surface active. Van Lent and Scheutjens[24] showed that, when the hydrophobic monomer is the majority component, the diblock should be more surface active than the statistical copolymer. We have the opposite effect. The situation seems to be quite different when the hydrophilic (charged) monomer is the majority component. The BMA segments are strongly hydrophobic, and the DMAEMA segments will also be somewhat hydrophobic when uncharged and probably amphiphilic, and hence surface active, even when charged. Thus the copolymer as a whole will always tend to be strongly adsorbed. If the charged block occupies a much greater volume than the uncharged block at the surface, the amount of copolymer adsorbed will be determined by the size of the charged block. In the absence of screening by added electrolyte this will increase with the charge density. For a given fractional ionization of a DMAEMA segment the charge density will be about 10% greater on the DMAEMA sequence of the diblock because it is not diluted by occasional BMA fragments. Thus the density of DMAEMA segments at the surface should be less for the diblock. In terms of the average segmental coverage this is compensated by the addition of the BMA block and the values of A_{seg}(average) will therefore be about the same. There are two situations where the values are different. At a pH of 7.3 and electrolyte concentration of 0.02 M the diblock is more strongly adsorbed. As already suggested, this may be because the addition of electrolyte has taken the system into the micellar region and that micelles are actually adsorbed at the surface. At a pH of 1.1 the statistical copolymer is more strongly adsorbed, which must be caused by the charge

density on the DMAEMA block of the diblock copolymer being maximized under these conditions.

The surface tension will be dominated by the properties of the component occupying most of the surface, i.e. the DMAEMA block in the case of the diblock, although it is the presence of the BMA that ensures that the copolymer is always adsorbed. As noted earlier, the surface tension will be reduced by the presence of the copolymer at the air−water interface but this may be offset by the accumulation of charged counterions and co-ions at the surface. The latter will depend on the charge density in the DMAEMA component, and since this is larger for the diblock, the diblock will tend to have the greater surface tension. What is happening physically is that the BMA blocks are kept separate so that there are no favorable interactions between them. The situation is then rather like an insoluble copolymer monolayer where the concentration of copolymer is too low to cause any increase in the surface pressure. The presence of DMAEMA should also lower the surface tension but this is partly offset by the relatively high charge density at the surface.

Comparison of the distribution of the copolymers between the two layers shows that the protruding layer is usually more dense for the diblock than for the statistical copolymer and that there is always a greater proportion of the copolymer in this upper layer for the diblock. Given that the BMA block is insoluble in water, these observations are exactly as would be expected. Within the solvated DMAEMA chains there will be competition between the uncharged segments, which will want to be out of the water, and the charged segments, which will want to be well immersed, and this will cause any layer formed to be somewhat disordered. For the diblock copolymer there is nothing to prevent the BMA block from forming a relatively thin and compact layer on the surface. Thus, at the same average coverage per segment the diblock should form a thinner layer than the statistical copolymer, and this is as observed. The BMA comprises less than one-third of the monomer residues of the diblock copolymer, and given that these residues will be much more compacted within the layer than the DMAEMA component, much the larger proportion of the surface occupied by the diblock is occupied by the more solvated DMAEMA chains. This is consistent with the discussion in the previous two paragraphs.

Acknowledgment. F.L.B. wishes to thank the School of Chemistry and Molecular Sciences, University of Sussex, and Courtaulds Research for financial support in the form of a Ph.D. studentship. S.P.A. and N.C.B. acknowledge EPRSC (formerly the SERC) for continued support of their water-soluble polymers research program at Sussex. R.K.T. also thanks EPSRC for support.

References and Notes

(1) Baines, F. L.; Dionisio, S.; Billingham, N. C.; Armes, S. P. *Macromolecules*, in press.
(2) Arca, E.; Cao, T.; Webber, S. E.; Munk, P. *Polym. Prepr. (Am. Soc., Div. Polym. Chem.)* **1994**, *35*, 334.
(3) Beadle, P. M.; Rowan, L.; Mykytiuk, J.; Billingham, N. C.; Armes, S. P. *Polymer* **1993**, *34*, 1561.
(4) Biggs, S.; Vincent, B. *Colloid Polym. Sci.* **1992**, *270*, 505.
(5) Barker, M. C.; Vincent, B. *Colloids Surf.* **1984**, *8*, 297.
(6) de Laat, A. W. M.; Derks, W. P. T. *Colloids Surf. A: Physicochem. Eng. Aspects* **1993**, *71*, 147.
(7) Yang, L.; Bedells, A. D.; Attwood, D.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1447.
(8) Malmsten, M.; Lindman, B. *Macromolecules* **1992**, *25*, 5440.
(9) Mortensen, K.; Brown, W. *Macromolecules* **1993**, *26*, 4128.
(10) Barker, M. C.; Vincent, B. *Colloids Surf.* **1984**, *8*, 289.
(11) Munk, P.; Ramireddy, C.; Tian, M.; Webber, S. E.; Prochazka, K.; Tuzar, Z. *Makromol. Chem., Macromol. Symp.* **1992**, *58*, 195.
(12) Munk, P.; Qin, A.; Tian, M.; Ramireddy, C.; Webber, S. E.; Tuzar, Z.; Prochazka, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 1020.
(13) Selb, J.; Gallot, Y. *Makromol. Chem.* **1980**, *181*, 809.
(14) Selb, J.; Gallot, Y. *Makromol. Chem.* **1980**, *181*, 2605.
(15) Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 1491.
(16) Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 1513.
(17) Gao, Z. S.; Varshney, S. K.; Wong, S.; Eisenberg, A. *Macromolecules* **1994**, *27*, 7923.
(18) Biggs, S.; Vincent, B. *Colloid Polym. Sci.* **1992**, *270*, 563.
(19) Briggs, N. P.; Budd, P. M.; Price, C. *Eur. Polym. J.* **1992**, *28*, 739.
(20) Yin, R.; Hogen-Esch, T. E. *J. Polym. Sci., Polym. Chem.* **1994**, *32*, 363.
(21) Long, T. E.; Allen, R. D.; McGrath, J. E. *ACS Symp. Ser.* **1988**, *364*, 258.
(22) Leemans, L.; Fayt, R.; Teyssie, P. *J. Polym. Sci., Polym. Chem.* **1990**, *28*, 1255.
(23) Leemans, L.; Fayt, R.; Teyssie, P.; DeJaeger, N. C. *Macromolecules* **1991**, *24*, 5922.
(24) van Lent, B.; Scheutjens, J. M. H. M. *J. Phys. Chem.* **1990**, *94*, 5033.
(25) Zhan, Y.; Mattice, W. L. *Macromolecules* **1994**, *27*, 677.
(26) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(27) Wittmer, J.; Joanny, J. F. *Macromolecules* **1993**, *26*, 2691.
(28) Dan, N.; Tirrell, M. *Macromolecules* **1994**, *26*, 4310.
(29) Zhu, J.; Eisenberg, A.; Lennox, R. B. *Macromolecules* **1992**, *25*, 6547.
(30) Penfold, J.; Thomas, R. K. *J. Phys. Condens. Matter* **1990**, *2*, 1369.
(31) Lu, J. R.; Li, Z. X.; Thomas, R. K.; Staples, E. J.; Thompson, L.; Tucker, I.; Penfold, J. *J. Phys. Chem.* **1994**, *98*, 6559.
(32) Henderson, J. A.; Richards, R. W.; Penfold, J.; Shackleton, C.; Thomas, R. K. *Polymer* **1991**, *32*, 3284.
(33) Richards, R. W.; Rochford, B. R.; Webster, J. R. P. *Faraday Discuss. Chem. Soc.* **1994**, *98*, 263.
(34) Phipps, J. S.; Richardson, R. M.; Cosgrove, T.; Eaglesham, A. *Langmuir* **1993**, *9*, 3530.
(35) Dai, L.; White, J. W.; Kerr, J.; Thomas, R. K.; Penfold, J.; Aldissi, M. *Synth. Met.* **1989**, *28*, 69.
(36) Kent, M. S.; Lee, L. T.; Farnoux, B.; Rondelez, F. *Macromolecules* **1992**, *25*, 6240.
(37) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Ranjanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(38) Penfold, J.; Ward, R. C.; Williams, W. G. *J. Phys. E* **1987**, *20*, 1411.
(39) Lee, E. M.; Thomas, R. K.; Penfold, J.; Ward, R. C. *J. Phys. Chem.* **1989**, *93*, 381.
(40) Lu, J. R.; Simister, E. A.; Thomas, R. K.; Penfold, J. *J. Phys. Chem.* **1993**, *97*, 13907.
(41) Styrkas, D. A. Ph.D. Thesis. University of Oxford, 1994.
(42) Ishihara, K.; Tsuji, T.; Sakai, Y.; Nakabayashi, N. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 859.
(43) Hall, D. G.; Pethica, B. A.; Shinoda, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 324.
(44) Simister, E. A.; Thomas, R. K.; Penfold, J.; Aveyard, R.; Binks, B. P.; Fletcher, P. D. I.; Lu, J. R.; Sokolowski, A. *J. Phys. Chem.* **1992**, *96*, 1383.
(45) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993.
(46) Bedells, A. D.; Arafeh, R. M.; Yang, Z.; Attwood, D.; Heatley, F.; Padget, J. C.; Price, C.; Booth, C. *J. Chem. Soc., Faraday Trans.* **1993**, *98*, 1235.
(47) Stejskal, J.; Konak, C.; Helmsted, M.; Kratochvil, P. *Collect. Czech. Chem. Commun.* **1993**, *58*, 2282.
(48) Born, M.; Wolf, E. *Principles of Optics*; Pergamon Press: Oxford, U.K., 1970.
(49) Windsor, C. G. *Pulsed Neutron Scattering*; Taylor & Francis Ltd.: London, 1981.
(50) Tanford, C. *J. Phys. Chem.* **1972**, *76*, 3020.
(51) *Handbook of Chemistry and Physics*, 54th ed.; CRC Press: Boca Raton, FL, 1973−1974.

MA960218Z