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Neutron Scattering from Adsorbed Polymer Layers

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ABSTRACT: An analysis of the neutron scattering from adsorbed polymer layers is presented. In particular, it is found that the scattering, with zero contrast between the particle and the solvent (matched scattering densities), is determined by the average structure of the adsorbed layer and not by fluctuations in the structure. The data can therefore be used to obtain the volume fraction profile of the adsorbed layer. The scattering away from zero contrast can also be used to obtain these profiles and the agreement between the two methods is satisfactory. However, when the mismatch is large, the scattering is dominated by that from the particle.

Introduction

Small-angle neutron scattering (SANS) has been used extensively to probe the structure of the interfacial region.[1-3] In particular the bound fraction, the adsorbed layer thickness, and volume fraction profiles have been determined, using a formalism developed by Crowley.[4] Recently, Auvray and de Gennes[5] have criticized this approach, in that the scattering from fluctuations in the structure of the adsorbed layer had been neglected in interpreting the experimental data. In particular, when the particle is at zero contrast with the solvent, they have proposed that the ratio of the scattering arising from fluctuations, $\tilde{I}$, to that from the first structure sensitive term of the layer, $I_0{}^*$, scales as

$$\tilde{I}/I_0{}^* \sim (Qa)^{1/3} \tag{1}$$

where Q is the scattering wave vector and a is a monomer size. They state that "although this ratio is somewhat small, since $Qa \ll 1$, this is not very small in practice". However, it is the absolute value of these terms which is important in determining their contributions to the observed scattering.

Auvray and de Gennes[5] have also concluded that the best experimental strategy would be to obtain data when there is a large difference in scattering density between the particle and the solvent. Although this approach will minimize fluctuation terms, as discussed by Crowley,[4] it does mean that the experimental scattering, from which these data have to be extracted, is dominated by the scattering due to the particle.

In this paper we show that the previous analysis of data at zero contrast gives unambiguous information about the volume fraction profile, with no evidence of scattering from fluctuations in the structure. We also demonstrate that the scattering term, I_1, which arises from interference between the particle and the adsorbed layer can also be used to obtain the volume fraction profile.[6]

Experimental Section

The adsorption systems consisted of monodisperse poly(ethylene oxide) (PEO) and fractionated 88% hydrolyzed poly(vinyl acetate) (PVA) adsorbed on poly(styrene-d_8) (dPS) latex. The details of the polymers are given in Table I. All the experimental samples were prepared to give adsorbed amounts in the pseudoplateau region of the adsorption isotherms.[7-9]

The SANS data were obtained at the Institut Laue Langevin, Grenoble. The scattering data were obtained by using sample–detector distances of 5.5 and 2.8 m and wavelengths of 0.7 and 1.4 nm, on the D11 and D17 instruments, respectively.

Table I
Sample Details of Polymers in SANS Studies

sample	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	source
PEO-50	51900	1.23	K. G. Barnett[7]
PEO-280	280000	1.04	Toya Soda Co.
PVA-37	37000	*a*	Revertex

[a] Fractionated by GPC.

Scattering Theory

The specular scattering, $I(Q)$, from a dispersion of N spherical particles, each described by a spherically symmetrical scattering density, $\rho(r)$, is given by

$$I(Q) = 16\pi^2 N Q^{-2}\left[\int_0^\infty \sin (Qr)\rho(r)\,\mathrm{d}r\right]^2 \tag{2}$$

where Q is the scattering vector defined as $4\pi\lambda^{-1} \sin (\theta/2)$.

It may be considered that $\rho(r)$ consists of two components: one due to a particle, p, of radius, r_0, at a contrast, $\Delta\rho_p$, with respect to the solvent and the other due to a surface adsorbed layer, s, with a scattering density distribution, $\rho_s(z)$, at a contrast, $\Delta\rho_s$, with respect to the solvent; z, given by $r - r_0$, is the distance from the particle surface. Averaging over the particle size distribution and finite detector resolution, gives the following relations:

$$I(Q) = I_0(Q) + \Delta\rho_p I_1(Q) + \Delta\rho_p{}^2 I_2(Q) \tag{3}$$

where $I_0(Q)$ is a term arising from the adsorbed polymer layer, $I_2(Q)$ is a term arising from the particle, and $I_1(Q)$ is a particle–surface interference term. At zero contrast, $\Delta\rho_p = 0$ and

$$I(Q) = I_0(Q) = \frac{8\pi^2 r_0{}^2 \Delta\rho_s{}^2}{Q^2}\left|\int_0^t \phi(z) e^{iQz}\,\mathrm{d}z\right|^2 \tag{4}$$

ignoring scattering from structural fluctuations, $\phi(z)$ is the volume fraction profile of the adsorbed polymer normal to the interface, and t is the maximum extent of the adsorbed layer. The scattering from the particle is given by

$$I_2(Q) = \frac{8\pi^2 r_0{}^2}{Q^4}[1 + (Qr_0)^{-2}] \tag{5}$$

When $Q^2 r_0{}^2 \gg 1$, the intensity follows a Q^{-4} dependence. The interference term is given by

$$I_1(Q) = \frac{16\pi^2 r_0 \Delta\rho_s}{Q^4}\left[\int_0^t \phi(z) \cos (Qz)\,\mathrm{d}z - Qr_0\int_0^t \phi(z) \sin (Qz)\,\mathrm{d}z\right] \tag{6}$$

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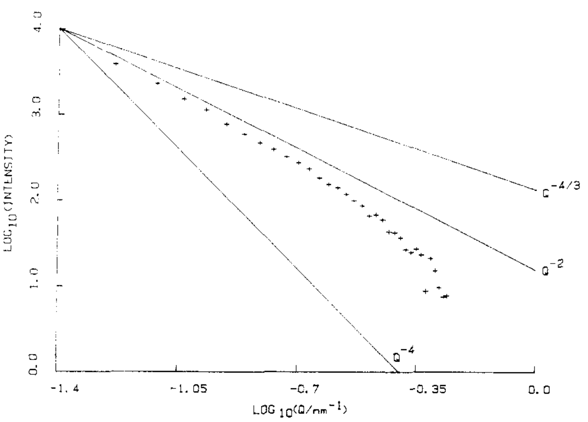

Figure 1. Log of intensity of scattering, $I(Q)$, as a function of log of the scattering vector, Q, for poly(ethylene oxide) 280 000 adsorbed on deuteriated polystyrene latex in D_2O, obtained by using D17 (+++). Also shown are lines indicating Q dependencies of Q^{-4}, Q^{-2}, and $Q^{-4/3}$.

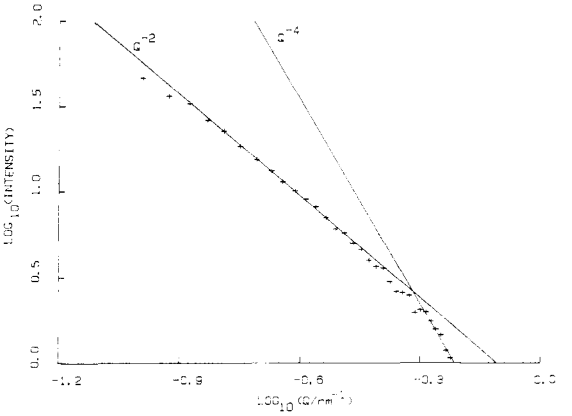

Figure 2. Log of intensity of scattering, $I(Q)$, as a function of log of the scattering vector, Q, for poly(ethylene oxide) 50 000 adsorbed on deuteriated polystyrene latex in D_2O, obtained by using D11 (+++). Also shown are lines indicating Q dependencies of Q^{-4} and Q^{-2}.

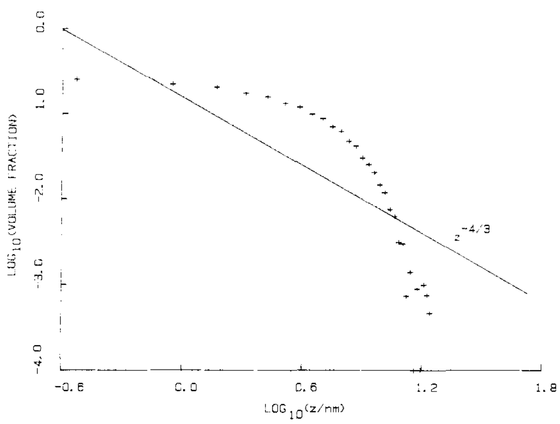

Figure 3. Log of the volume fraction of adsorbed polymer, $\phi(z)$, as a function of log of the distance from the surface, z, for poly(ethylene oxide) 280 000 adsorbed on deuteriated polystyrene latex in D_2O (+++). Also shown is the profile predicted from scaling theory.

When $Qr_0 \gg 1$, eq 6 simplifies to a sine transform of the volume fraction profile.

Analysis of Scattering at Zero Contrast

As $Q \rightarrow 0$, eq 4 becomes

$$I_0(Q) \sim Q^{-2}e^{-\sigma^2Q^2} \sim Q^{-2} \qquad (7)$$

where σ is the second moment of the volume fraction distribution. As $Q \rightarrow \infty$

$$I_0(Q) \sim Q^{-4} \qquad (8)$$

which is Porod's law.[10] Fluctuation terms are predicted to give a weak dependence on Q

$$\tilde{I} \sim Q^{-4/3} \qquad (9)$$

Figure 1 shows $I(Q)$ as a function of Q for adsorbed PEO-280 on dPS latex in D_2O, at zero contrast, obtained by using D17. For comparison, the Q dependencies predicted in eq 7–9 are also shown. Figure 2 shows low Q data obtained on D11 for PEO-50, also adsorbed on dPS latex. At high Q, the data are consistent with Porod's law (eq 8). At low Q, a Q^{-2} dependence is expected for $\sigma^2Q^2 \ll 1$. Both sets of experimental data are consistent with this. In particular, the smaller value of σ for the low molecular weight sample leads to an extended Q^{-2} region. Equation 1 predicts that fluctuation terms will become more important at high Q, causing a deviation from Porod's law. However there is no evidence for this in the data. At low Q, when the contributions from the fluctuation terms are predicted to be small, there is a reasonable fit to eq 7. Hence the low Q data can be used to obtain the second moment, σ, of the segment density distribution.[7]

In order to use these data to obtain the volume fraction profile, it is necessary to extrapolate the $I(Q)$ data at both high and low Q. At low Q, this necessitates obtaining good data in the Guinier regime, $\sigma^2Q^2 \ll 1$, which is only possible close to the zero contrast condition (see below).[8]

At high Q a good estimate to the base line is essential and this can be difficult if there is a large contribution to the data from incoherent scattering, which is predominantly due to protons. This rather limits the range of aqueous particulate dispersions that can be used for these experiments. Typically, dPS latex is at zero contrast with a 98% D_2O/H_2O mixture, which gives an acceptable amount of incoherent scattering. However, to take this system significantly away from zero contrast necessitates using high concentrations of H_2O, with a concomitant increase in the incoherent scattering.

The resultant profile, obtained by transforming the data shown in Figure 1, is shown in Figure 3, and for comparison the scaling prediction

$$\phi(z) \sim z^{-4/3} \qquad (10)$$

is included. It would appear that the slow decay predicted by scaling theory is not observed at this molecular weight and coverage: the profile follows no simple scaling law.

Analysis of Scattering Away from Zero Contrast

An alternative approach to the determination of the volume fraction profile is to carry out experiments away from zero contrast and use the interference term, $I_1(Q)$, as originally proposed by Barnett et al.[6] This can be obtained by subtraction of the I_0 and I_2 terms from the total scattering away from zero contrast, using eq 3. The relative contributions, away from zero contrast, of the three terms given in eq 3, depend on the ratio $|\Delta\rho_p/\Delta\rho_s|$. Figure 4 shows these contributions with $|\Delta\rho_p/\Delta\rho_s| = 0.03$, calculated by using equations 4–6 and the experimental profile shown in Figure 3. The scattering is still dominated by the I_0 term. At strong contrast, with $|\Delta\rho_p/\Delta\rho_s| = 1.00$, the scattering is dominated by the I_2 term (Figure 5). At, or close to zero contrast, the I_0 term will always dominate the scattering. By comparison, the I_1 term always represents a small proportion of the total scattering.[11] Hence, experimentally, the measurement of the I_1 term will always be substantially less favorable than the I_0 term and not

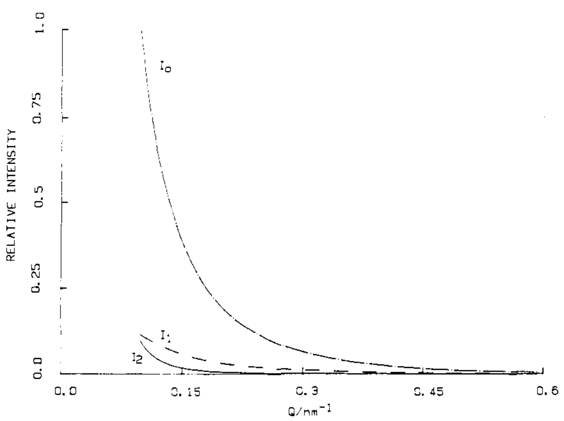

Figure 4. Relative contributions to the total scattering intensity, $I(Q)$, for $I_0(Q)$ (-·-), $I_1(Q)$ (---), and $I_2(Q)$ (—) with $|\Delta\rho_p/\Delta\rho_s| = 0.03$.

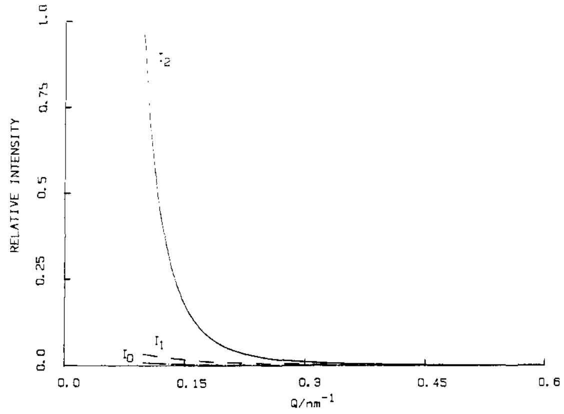

Figure 5. Relative contributions to the total scattering intensity, $I(Q)$, for $I_0(Q)$ (-·-), $I_1(Q)$ (---), and $I_2(Q)$ (—) with $|\Delta\rho_p/\Delta\rho_s| = 1.00$.

more favorable, as suggested by Auvray and de Gennes.[5] Using the volume fraction profile given by scaling theory (eq 10), the I_1 term should scale as

$$I_1(Q) \sim Q^{-8/3} \tag{11}$$

assuming no cutoff of the function at the chain length.

Figure 6 shows the $I_1(Q)$ data generated by using eq 6 and the experimental profile shown in Figure 3. At high Q when $Qr_0 \gg 1$, assuming for example, an exponential profile, eq 6 reduces to

$$I_1(Q) \sim Q^{-4} \tag{12}$$

which is rather different from the scaling prediction and highlights that the form of the I_1 term, as expected, is sensitive to the shape of the profile. The experimental data used in the calculation of Figure 6 show a much closer resemblance to the Q^{-4} prediction than to the scaling prediction of $Q^{-8/3}$. Auvray and Cotton[12] have presented I_1 data for poly(dimethylsiloxane) (PDMS) adsorbed on porous silica in cyclohexane. Their data suggest a Q dependence close to the scaling prediction. The concentration range over which scaling arguments are appropriate is limited, though agreement with theory extends to higher concentrations for flexible polymers, such as PDMS, than for the less flexible PEO.[13]

The direct observation of the I_1 term was first reported by Barnett et al.,[6] who used eq 6, in the limiting case when $Qr_0 \gg 1$, to obtain a crude volume fraction profile for 88% hydrolyzed poly(vinyl acetate) (PVA) on dPS latex in D_2O. There are, however, several difficulties with this approach. Firstly, the extrapolation of the data to low Q can be complicated, as both the sine and cosine terms in eq 6 may have to be taken into account. The earlier published volume fraction profile was obtained by extrapolating the experimental data back into the Guinier regime from a point in the data where $Qr_0 > 1$, using a limiting relationship analogous to eq 7. Secondly, at high Q, a good estimate of the incoherent background level is required, as with the I_0 inversion. However, this estimation is exacerbated for the I_1 term because of the necessity of adding H_2O to the dispersion in order to go away from zero contrast. These extrapolations are however not very satisfactory.

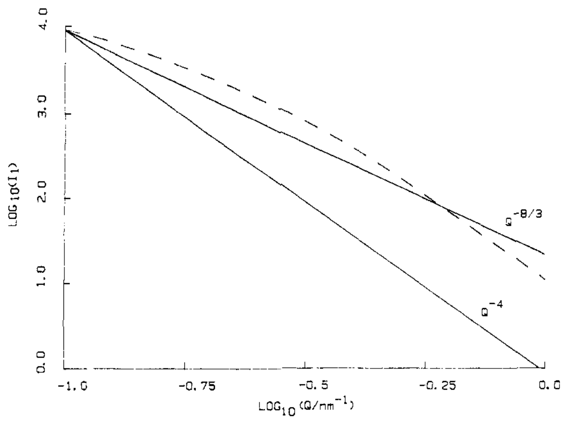

Figure 6. Log of intensity of scattering of the interference term, $I_1(Q)$, as a function of log of the scattering vector, Q, for poly(ethylene oxide) 280 000 adsorbed on deuteriated polystyrene latex in D_2O, calculated by using $|\Delta\rho_p/\Delta\rho_s| = 0.03$ (---). Also shown are lines indicating Q dependencies of Q^{-4} and $Q^{-8/3}$.

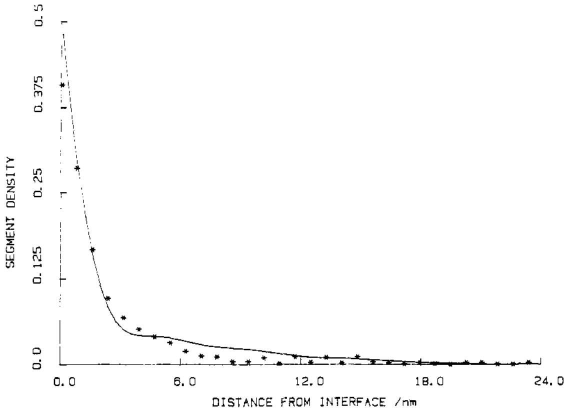

Figure 7. Normalized segment density distributions for 88% hydrolysed poly(vinyl acetate) 37 000 adsorbed on deuteriated polystyrene latex in D_2O, calculated by using the I_0 (—) and I_1 (* * *) terms of the total scattering.

I_1 data have been obtained for PVA adsorbed on dPS latex. This required three different scattering measurements to be made. The total scattering was measured away from zero contrast with $|\Delta\rho_p/\Delta\rho_s| = 0.1$ (92:8 D_2O/H_2O). The I_2 term was obtained from a dispersion of bare particles at the same contrast. The I_0 term was determined for the latex and adsorbed polymer at zero contrast (98:2 D_2O/H_2O) and corrected for the change in $\Delta\rho_s$ on adding the extra H_2O to the sample. In Figure 7 the PVA profile from the I_1 term is shown together with the profile obtained from the same sample at zero contrast. Within experimental error the two profiles are quite similar. The I_1 data, as emphasized above, are necessarily inferior.

Conclusions

In this paper we have shown that SANS data from adsorbed polymers, under experimental conditions when the substrate and the solvent/solution have matched scattering densities, can be used to generate volume fraction profiles.

The scattering is dominated by the average structure of the adsorbed layer; there is no observable contribution from fluctuations as has been recently suggested. The structure of the adsorbed layer does not follow any simple scaling law. Using SANS data away from the zero contrast condition is problematical and in general unsatisfactory due to difficulties of obtaining data for the Guinier approximation and because of scattering from the substrate itself. The experimental strategy suggested by Auvray and de Gennes is therefore impractical, and the best experimental results have been obtained at zero contrast.

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Registry No. PEO, 25322-68-3; dPS, 27732-42-9; neutron, 12586-31-1.

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Potentiometric Titration of Xanthan

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ABSTRACT: Potentiometric titration data were obtained for two samples of rigid double-helical xanthan in aqueous sodium chloride at salt concentrations C_s of 0.01, 0.02, 0.05, and 0.1 M at 25 °C, and from their comparison with typical theories along with some theoretical considerations the following conclusions were derived. (1) The solution of the complete Poisson–Boltzmann equation for a uniformly charged cylinder fails to describe the titration data, unless an unreasonably large value is chosen for the radius of the xanthan double helix. (2) The well-known expression $\mathrm{pH} - \log[\alpha/(1-\alpha)] - \mathrm{p}K_0 = -2\alpha\sum_j \log u_j$ for a long rod with randomly distributed discrete charges agrees with the result from the linear Ising model at degrees of ionization α of $^1/_2$ and 1, where $\mathrm{p}K_0$ is the logarithmic intrinsic dissociation constant and u_j, the statistical weight for the electrostatic interaction of a given ionized group with its jth neighbor group. (3) This equation combined with the Debye–Hückel screened Coulomb potential, an approximation to the pair interaction potential, describes the xanthan data only at the two higher C_s of 0.05 and 0.1 M. Its failure at the lower C_s is attributable to this approximation. Similar analysis of the published data for α-helical poly(glutamic acid), another rodlike polyelectrolyte, led to essentially conclusions 1 and 3.

Introduction

The pH of a polyelectrolyte solution is usually expressed by [1-3]

$$\Delta\mathrm{p}K \equiv \mathrm{pH} - \log(\alpha/1-\alpha) - \mathrm{p}K_0 = 0.434e\psi/kT \qquad (1)$$

where α is the degree of ionization of ionizable groups in the polymer, K_0 the intrinsic dissociation constant of a group ($\mathrm{p}K_0 = -\log K_0$), e the protonic charge, ψ the electrostatic potential at a point of a charge on the polymer surface, k the Boltzmann constant, and T the absolute temperature. For uniformly charged long cylinders, numerical values[4-7] of ψ were obtained from the complete Poisson–Boltzmann equation, while for discretely charged rods, various approximate expressions[8-15] for ψ (or more generally $\Delta\mathrm{p}K$) were derived on different assumptions. These theories of ψ or $\Delta\mathrm{p}K$ may be checked if data of pH $-\log(\alpha/1-\alpha)$ are obtained for polyelectrolytes having an intrinsically rigid backbone, i.e., those rigid even at high salt concentrations.

The present paper reports such an experimental study made on xanthan, a bacterial polysaccharide with ionic side chains, in aqueous sodium chloride (NaCl) of salt concentrations C_s of 0.01, 0.02, 0.05, and 0.1 M. This polysaccharide, whose repeating units are shown in Figure 1, should be eligible for use as the test sample, since its sodium salt has recently been shown to dissolve in aqueous NaCl as a rigid double helix[16-21] with a large persistence length of about 100 nm at infinite ionic strength.[22] We note that although comparisons between theory and experiment were already made by many workers,[3-6,12-15,23-25] the conclusions drawn were not always definite since intrinsically flexible polyelectrolytes were used except α-helical poly(glutamic acid).

Experimental Section

Potentiometric Titration. The previously investigated xanthan samples,[26] X12-2-3 and X14-2-3 with weight-average molecular weights of 3.31×10^5 and 7.44×10^5, respectively (both in the dimerized acid form), were used. Either sample was dissolved in deionized water at about 5 °C, and the solution was passed through a mixed-bed ion exchanger (Amberlite IR-120 + IRA-410), with the temperature of the solution kept at about 5

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