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The hydrodynamic thickness of adsorbed polymer layers measured by dynamic light scattering : effects of polymer concentration and segmental binding strength

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Résumé. — On étudie par diffusion dynamique de la lumière des couches de polyoxyéthylène (PEO) adsorbées sur de petites particules de silice (ludox) dans l'eau. On fait varier le pH de l'eau pour changer la force d'absorption des segments du polymère. Les résultats montrent que l'épaisseur hydrodynamique δ_h de la couche adsorbée reste constante ou croît légèrement avec le pH jusqu'à pH $\approx$ 10,5, puis tombe brutalement à zéro. La quantité adsorbée chute plus progressivement entre pH 8 et 11. L'ensemble des données est en accord avec la plupart des mesures antérieures sur différents substrats et aussi avec le résultat théorique d'après lequel l'énergie d'adsorption des segments n'a pas d'effet sur δ_h jusqu'à ce qu'on soit très proche d'une désorption complète. Les résultats fort différents obtenus précédemment pour l'adsorption sur le latex de polystyrène sont expliqués par la nature hétérogène de la surface du latex. Enfin, parce que les particules de silice sont petites, on prévoit des effets spéciaux à partir de masses moléculaires suffisamment élevées ; certains de nos résultats peuvent indiquer de tels effets.

Abstract. — Poly(ethylene oxide) (PEO) adsorbed on small silica (ludox) particles was studied by means of dynamic light scattering, as a function of segmental binding strength (pH). The results show that the hydrodynamic layer thickness δ_h is constant or increases slightly with pH up to pH $\approx$ 10.5 and then drops sharply to zero. The adsorbed amount drops much more gradually between pH 8 and 11. All data agree with most earlier measurements on different substrates, and agree with the theoretical result that the segmental adsorption energy has no effect on δ_h until very close to full desorption. The very different results obtained earlier for adsorption on PS latex are therefore explained as due to the heterogeneous structure of the latex surface. Finally, since the silica particles are small, special effects are expected for sufficiently high molecular weights. Some of our results are indicative of such small particle effects.

Introduction.

Measurement of the hydrodynamic thickness of adsorbed polymer layers has been frequently used to obtain insight into the structure of these layers [1-3]. In order to interpret the experimental data correctly, it is essential to have an understanding of the relation between structure and thickness. Theoretical calculations have shown very convincingly [4] that the thickness is entirely determined by the dilute periphery of the adsorbed layer, and that this periphery is dominated by free chain ends (so-called *tails*) [5]. Two effects should be emphasized here :

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1) long tails occur only in saturated adsorption layers, i.e., well into the plateau region of the adsorption isotherm. As a consequence, the hydrodynamic thickness increases very steeply with adsorbed amount as soon as the layer approaches saturation [4, 6] ;

2) the density profile of tails is almost independent of the segmental adsorption energy, in contrast to the density in *loops* which varies strongly with this parameter. Calculations have indeed shown that the hydrodynamic layer thickness δ_h is almost constant over a very wide range of adsorption energies. Of course, for non-adsorbing polymer $\delta_h = 0$. The transition between these two situations occurs around a critical adsorption energy χ_{sc} and is extre-

mely sharp, much sharper than the corresponding transition for the adsorbed amount [5]. In figure 1 we present theoretical curves which substantiate this conclusion.
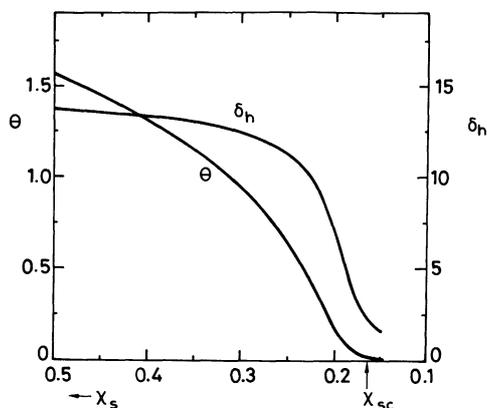

Fig. 1. — Hydrodynamic layer thickness δ_h and adsorbed amount θ as a function of segmental adsorption energy χ_s. Theoretical results taken from reference [5]. Crossover from adsorbed to non-adsorbed regime is located at χ_{sc}.

Some experimental evidence corroborating (1) has been obtained [7]. In this paper we want to focus on (2). Part of our interest stems from the fact that χ_{sc} values can be used to determine segmental adsorption energies [8, 9], and that the sharp transition in δ_h seems ideally suited to determine an accurate χ_{sc}-value. Also, we are motivated by the fact that some authors have invoked differences in segmental adsorption energy to explain differences in δ_h for a given polymer on different substrates [10]. This is clearly at variance with theoretical results and needs to be checked.

In principle, layer thicknesses can be obtained by several techniques. However, methods like optical reflection [11] which yield essentially the first moment of the density distribution are less sensitive to the effects we are interested in and hence we prefer to study δ_h. The technique we use to obtain δ_h is dynamic light scattering on polymer-coated colloidal particles. Several authors have studied δ_h with this technique [3, 10]. Provided particle-particle interactions (structure factors) and effects of free polymer on particle diffusion are properly ruled out, reproducible thicknesses can be obtained.

As the experimental system we choose poly (ethylene oxide) (PEO), adsorbing from aqueous solution onto silica particles. Results on a similar system were obtained by Killmann [10] so that comparison is possible. With this system it is easy to vary the effective adsorption energy by changing pH. Several studies [12, 13] have shown that PEO may be completely desorbed at high pH,

so that OH⁻ can be regarded as a *displacer* [8]. In terms of figure 1, this would mean that the adsorption energy parameter χ_s decreases with increasing pH. Adsorbed amounts as a function of pH have been reported, which show that between pH 6 and 10.5 the coverage decreases gradually at least on non-porous silica [12, 13].

Experimental.

For our experiments, we have used Ludox AS-40 colloidal silica (Du Pont). According to the manufacturer the silica particles have an average diameter of 22 nm and a specific surface area of 140 m²/g. Before using the dispersion, it was dialysed against Millipore Super Q deionized water. This water as well as analytical grade chemicals were used throughout.

PCS measurements were done with silica concentrations between 5.0 and 8.2 g/l.

Several properties of PEO samples, used in this study are listed in table I.

Table I. — *Polymer samples.*

Sample		$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
PEO SE-30	(Toyo soda)	2.7×10^5	1.09
PEO SE-70	(Toyo soda)	5.7×10^5	1.10
PEO PD	(Aldrich)	6×10^5	polydisperse
PEO SE-150	(Toyo soda)	8.6×10^5	1.17

The aqueous PEO solutions were kept in the dark as much as possible to prevent photochemical degradation of the polymer. In order to avoid aggregates of silica particles with adsorbed polymer, the silica dispersion was poured into a polymer solution of the appropriate concentration. Equilibrium between the adsorbed phase and the bulk phase was established by rotating the dispersion end-over-end for about fifteen hours.

Immediately before the PCS-measurements, the pH of the samples was adjusted by adding 0.1 M NaOH or 0.1 M HCl (titrisol, Merck). Dust and aggregates were removed by centrifugation during 10 min at 10.000 r.p.m.

For the determination of adsorption isotherms, we have used the depletion method. The samples were centrifuged for one hour at 20.000 r.p.m. The PEO concentration of the supernatant was then determined colorometrically [14]. Absorbance measurements were done with a Beckman 3 600 spectrophotometer.

A Malvern 4 700 photon correlation spectrometer was used to measure the diffusion coefficient of the silica particles with and without PEO. For polydisperse samples, this measured diffusion coefficient

generally depends on the scattering angle. However, our particles are so small that they may be regarded as Rayleigh scatterers, so that the auto-correlation function should be independent of the wave vector. We found indeed that this was the case. Therefore all further data were taken at a scattering angle of 90.00°. The temperature was always 20.00 °C.

DATA ANALYSIS. — With the Siegert relation [15], the normalized intensity autocorrelation function, $g^{(2)}(\tau)$ for a monodisperse dispersion can be written as :

$$g^{(2)}(\tau) = 1 + \beta S(K)(\exp\{-2 K^2 D\}).\quad (1)$$

Here, τ is the autocorrelation decay time. K represents the scattering vector and $S(K)$ is the static structure factor. In dilute dispersions, as in our case, $S(K)$ is equal to one. D is the translational diffusion coefficient and β an experimental fitting parameter.

The radius of spherical particles can be calculated from the diffusion coefficient by the Stokes-Einstein formula

$$D = k_B T/6 \pi \eta R \quad (2)$$

where k_B is Boltzmann's constant, T the absolute temperature, η the viscosity of the continuous phase and R the particle radius. We note that the Stokes-Einstein equation can fail for (spherical) particles in polymer solutions. Ullmann et al. [16] investigated the validity of this relation for small particles in PEO-water solutions. The conclusion which can be drawn from that work is that for small particles (as in our case) and for PEO ($M_w = 3 \times 10^5$) concentrations up to 500 ppm the Stokes-Einstein relation can be safely used to determine the hydrodynamic radius of the particles. This is corroborated by the fact that we did not found a significant difference in the hydrodynamic radius between bare particles in water and in aqueous PEO-solutions (at desorption).

Since our silica is to some extent polydisperse, an average particle radius is determined. Several methods are available for this purpose. The matter has been reviewed by Stock et al. [15]. Due to the difficulty in obtaining an average diffusion constant from the autocorrelation function, the results of various methods are not identical. We have used for our data the method of cumulants [15, 17]. This method is based on equation (3), which relates $g^{(2)}(\tau)$ to moments of the distribution function of translational diffusion coefficients

$$\ln (g^{(2)}(\tau) - 1)^{1/2} =$$

$$= \ln \beta^{1/2} - \bar{\Gamma}\tau + \frac{\mu^2}{\bar{\Gamma}^2} \frac{(\bar{\Gamma}\tau)^2}{2!} - \frac{\mu_3}{\bar{\Gamma}^3} \frac{(\bar{\Gamma}\tau)^3}{3!} + \cdots \quad (3)$$

where $\bar{\Gamma} \equiv D_{\bar{z}} K^2$ and $D_{\bar{z}}$ is the z-average of the translational diffusion coefficient. The parameter

$\frac{\mu_2}{\bar{\Gamma}^2}$ measures the polydispersity of the sample since it is equal to the normalized variance of the distribution function of D. The asymmetry of this distribution is given by $\frac{\mu_3}{\bar{\Gamma}^3}$.

The Stokes-Einstein relation (Eq. (2)) is used to obtain from $D_{\bar{z}}$ an average radius of the particles which can be shown to be :

$$\bar{R} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i^2 R_i^{-1}}. \quad (4)$$

Here n_i is the number of particles with a mass M_i and hydrodynamic radius R_i. Finally, the hydrodynamic thickness δ_h can be determined by substracting the hydrodynamic radius of bare particles from the radius of particles with adsorbed polymer.

Results and discussion.

The diameter of the bare silica particles was found to be 32 ± 1 nm, at ionic strength of about 2×10^{-3} M (NaCl). Since this value is different from that quoted by the manufacturer, the silica sample was also characterized by static and dynamic light scattering as a function of scattering angle in the Van't Hoff laboratory at Utrecht. These results agree nicely with ours. The fact that the manufacturer states a lower particle diameter (22 nm) may be due to a different way of averaging over the certainly polydisperse sample. It is not very likely that aggregates were present (or only such a small fraction that it does not show up in the angular dependence). The particle volume fraction was approximately 0.3 % so that electrostatic interactions were considerably screened and it is probably justified to neglect all structure factor effects. Still, we checked by dilution that this was indeed the case. Also we observed no dependence of δ_h on pH for the bare particles.

In figure 2 we give some adsorption data for PEO SE-70 and PEO-PD taken at pH $\approx$ 7. It can be seen that a plateau develops at about $A = 0.6$ mg m^{-2}, a value which is very close to what has been found by others [10, 21] and which was also found by us on different silica samples. It is important to note that the average number of polymer molecules per particle, n, calculated as $n = 4 \pi \bar{R}^2 AN_{av}/M$ with $\bar{R} \equiv$ particle radius (16 nm) and $M \equiv$ molecular weight (6×10^5 g mol^{-1}) gives n of order unity. Such a low number raises doubts about the applicability of a flat-plate model, as used to obtain the results shown in figure 1. Adsorption of polymers on small colloidal particles was considered by Alexander [18] and Pincus [19]. The later author pointed out that small spheres can accommodate only a limited
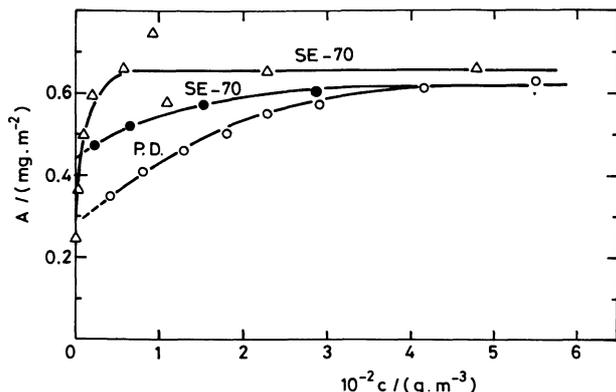
Fig. 2. — Adsorption isotherms for monodisperse (SE-70) (solid circles) polydisperse (PD) (open circles) PEO on ludox silica, at pH 7.5. For comparison, an adsorption isotherm for the same polymer, but on much larger particles (triangles), is shown (from Ref. [10]).

the introduction, the adsorbed amount is roughly constant up to pH $\approx$ 8 and then drops gradually to zero in the range pH 8-11. On the other hand, the parameter δ_h is very constant up to pH 10.5 and then drops sharply to zero. These experimental results agree very satisfactorily with the theoretical results (predictions) in figure 1 [5].

In figure 4 δ_h vs. pH is given for a higher molecular weight (SE-70) sample. Surprisingly, δ_h is not constant here, but increases substantially over the range pH 9.3-10.5 before it again drops sharply for pH > 10.5. At first sight this result appears very puzzling ; at least when compared with figure 1.

amount of polymer, A^*, which may be smaller than one molecule and scales like $A^* \sim \chi_s R^2$. If $A > A^*$ the rest of the polymer molecule extends far away from the particle as a long free end (eventually, more than one particle may adhere to a single chain). Hence, two effects are expected : a reduced adsorption affinity (which seems to show up in our results as a rather rounded isotherm) and probably a decreased diffusion coefficient due to the long free end. The latter effect would become more important for long molecules and as $\chi_s \rightarrow \chi_{sc}$. We note in passing, that the polydisperse sample has an even more rounded isotherm, which is in line with current understanding of polydispersity effects [20].

Our main results are given in figures 3-5, where adsorbed amounts, A and hydrodynamic thicknesses, δ_h of the adsorbed polymer layers are plotted vs. pH. The curve with the solid circles in figure 3 (PEO SE-30) denotes A as a function of pH. As stated in
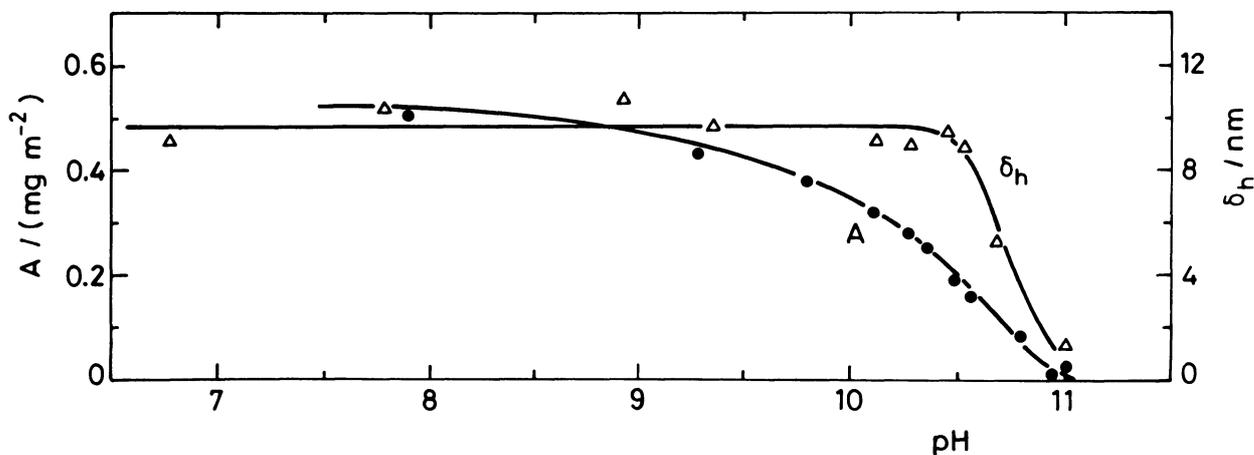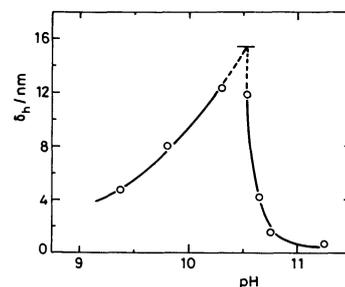

Fig. 4. — Hydrodynamic layer thickness δ_h as a function of pH for PEO SE-70 adsorbed on colloidal silica. The maximum corresponds to the (constant) value obtained when more free polymer is present (also see Fig. 6). The free polymer concentration is about 70 mg l⁻¹ at pH 7.5.

However, it should be realized that the theoretical result is based on a constant solution concentration, whereas in the results of figure 3 the total polymer dose was constant. Since the adsorbed amount decreases with increasing pH, the solution concentration will rise and as we have explained in the introduction, this has an important effect on layer

Fig. 3. — Hydrodynamic layer thickness δ_h (triangles) and adsorbed amount A (solid circles) as a function of pH for PEO SE-30 adsorbed on colloidal silica. The free polymer concentration is about 250 mg l⁻¹ at pH 7.5.

thickness. More polymer was therefore added to the samples in order to reduce these *undersaturation effects*. In figure 5 we give results for a still higher molecular weight (SE-150), but with much more polymer added. As can be seen, δ_h is now nearly constant over the range pH 8-10. There is still a slight increase between pH 10-10.2 before the final drop for pH > 10.5. It is tempting to interpret this maximum as due to the *finite capacity effect* discussed by Alexander [18] and Pincus [19], where a long free end and concomitant reduced diffusion rate is expected when the molecular weight is sufficiently high and χ_s low. Both the position of the maximum and the fact that it is absent for lower molecular weight (SE-30) agree with this explanation. We wish to stress here that a weakening of the segment-surface interaction does certainly not lead to a decrease in layer thickness until the very last molecules leave the surface.
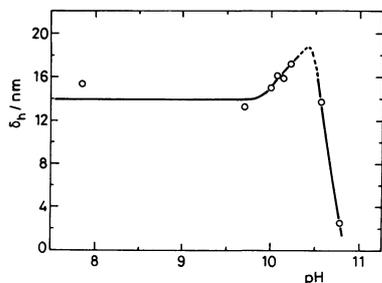
Having properly understood the effects of pH and polymer concentrations on δ_h we are now in a position to compare our data with those recently published by Killmann *et al.* [10, 21]. These authors have determined average particle radii in the same way as we did, but with much larger, fairly monodisperse precipitated silica (~ 100 nm). If we take as our δ_h (at full saturation) the value around pH ≈ 10, i.e. just before the sharp drop, we obtain the results shown in figure 7. The agreement between the data sets is very good, which suggests that a $\bar{\delta}_h(M)$ relationship is a good characteristic of a given polymer/solvent/substrate system, provided measurements are taken at taken at saturation. It is somewhat surprising, perhaps, that the size of the bare particles seems to have no effect. Anderson *et al.* [23] made detailed hydrodynamic calculations which suggest that δ_n should decrease with decreasing particle size. Our data would suggest that such corrections are negligible.

Fig. 5. — Hydrodynamic layer thickness δ_h as a function of pH for PEO SE-150 on colloidal silica. The free polymer concentration is about 400 mg l^{-1} at pH 7.5.

The effect of added polymer is shown in somewhat more detail in figure 6, where the pH was fixed at 7.5. As is seen, the adsorbed amount does indeed increase slightly while the increase in δ_h is much more pronounced.
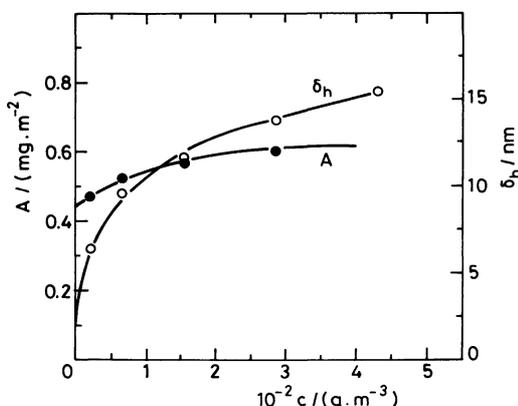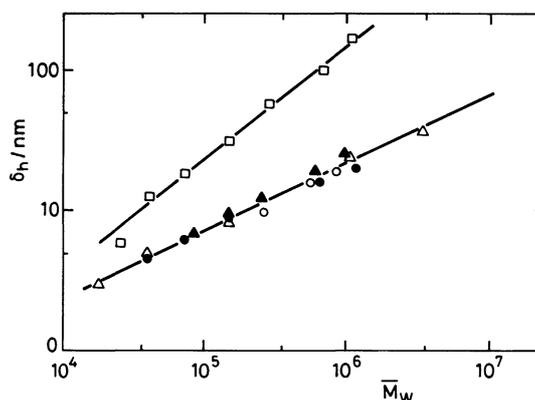
Fig. 6. — Hydrodynamic layer thickness δ_h and adsorbed amount A as a function of free polymer concentration of PEO SE-70 on colloidal silica at pH 7.5.

Fig. 7. — Double logarithmic plot of δ_h (at saturation) as a function of molecular weight for PEO/water. Data taken from : ($\triangle$) reference [10] ; ($\bigcirc$) this work ; ($\blacktriangle$) reference [21] ; ($\bullet$) reference [22] ; ($\square$) reference [4].

Our data makes it clear, however, that $\bar{\delta}_h$ at saturation is determined by the periphery of the adsorbed layer (i.e. by the tails) and that, therefore, the adsorption energy per segment plays no role. In other words : given a particular polymer/solvent pair δ_h (saturation) will be fixed, whatever the adsorption energy could be. This is further supported by data from Kawaguchi *et al.* [22]. These authors have determined the hydrodynamic thicknesses of PEO adsorbed in filter pores (millipore filters, made from cellulose esters), by measuring the flow rates of water through the filters. As can be seen in figure 7, their results fall exactly on the same line.

All this is hard to reconcile with the experimental fact that PEO on PS-latex spheres is often found to form layers which are at least four times thicker (some relevant data are given in Fig. 7) [3, 4].

We suggest that not the segmental adsorption energy, but the difference in surface structure (distribution of adsorption sites) is responsible for this difference. Further research is clearly needed to substantiate this conjecture but the fact that PEO adsorption on PS latex relies on a few (probably acidic) active surface sites [24] seems to corroborate the idea.

Conclusions.

The hydrodynamic thickness of an adsorbed polymer layer is virtually independent of the segment/surface interaction energy up to very close to the critical adsorption energy. The critical point is characterized by a very sharp drop of δ_h to zero. This conclusion is valid provided the concentration in the solution is constant, or at least high enough to be well into the plateau region of the adsorption isotherm (saturation). The effect had been predicted earlier on the basis of theoretical work [5]. For very high molecular weight, δ_h was found to have a small maximum just before the sharp drop which might signal a special effect predicted to occur in the case of small particles [18, 19].

Since the segment/surface interaction strength plays no role, δ_h at saturation would be expected to depend only on the properties of the polymer and the solvent. Hence, differences in δ_h between different substrates must be due to some other surface properties, which we suggest is the distribution and density of active surface sites.

Critical adsorption conditions can easily be determined with precision (even without keeping bulk concentrations rigorously constant, or using monodisperse polymer) because δ_h always drops very sharply to zero in the neighbourhood of the critical point.

Acknowledgments.

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