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POLYMER COLLOIDS

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Light scattering investigation of amphiphile and polymer adsorption on the surface of colloidal particles with low optical contrast

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Abstract We have exploited the peculiar optical properties of fluorinated polymer colloids, which have a very low refractive index and a partially crystalline internal structure, to obtain accurate adsorption isotherms by combining static and depolarized dynamic light scattering information. Due to the very weak optical contrast between perfluoropolymers and water, the intensity of the light scattered by suspensions of fluorinated colloids strongly depends on the presence of surface adsorbates. At the same time, the depolarized scattering contribution arising from the particle internal optical anisotropy allows to measure the rotational diffusion constant which is strongly dependent on the particle hydrodynamic radius. We have applied such technique to measure the adsorption isotherms of both nonionic and ionic surfactants, and of long-chain block copolymers.

Key words Light scattering – adsorption – amphiphile – polymer

The adsorption properties of polymer and surfactants on the surface of colloidal particles are particularly relevant in industrial applications related to the steric stabilization of emulsions and latices. To be effective, surfactants and polymers should adsorb in appropriate amount and form interfacial layers of sufficient thickness. Additional adsorbates may also be present on the surface of polymer latex particles as residuals of the polymerization process, and compete with the adsorption of the stabilizer. Careful monitoring of adsorption equilibria is therefore required. Traditional adsorption studies are often time-consuming, require a substantial amount of adsorbant, and are intrinsically invasive, since they generally require to separate out the colloidal phase from the supernatant [1]. Moreover, methods which detect variations of the concentration of the adsorbant in solution are not well suited to study weak adsorption effects, where the amount of adsorbate can be only a tiny fraction of the adsorbant remaining in solution.

Light scattering, as a powerful and non-invasive technique which can easily detect changes in the suspended particle morphology, could be a valid substitute to conventional chemicophysical analysis. However, for aqueous solutions of polymer colloids having a refractive index in the range 1.45–1.50, changes of the scattered intensity due to adsorption are very weak, due to the small fraction of particle volume occupied by the adsorbed layer. So far then, the application of light scattering to adsorption studies is confined to a few experiments in which dynamic light scattering was used to determine variations of the particle hydrodynamic radius as a function of the amount of added adsorbant. In the case of surfactant adsorption, changes of the translational diffusion coefficient of the order of a few percent must be detected [2].

We have used static and depolarized dynamic light scattering to probe the adsorption of ionic and nonionic surfactants, and of surfactant block copolymers, on the surface of monodisperse spherical particles made of FEP, a polytetrafluoroethylene copolymer. In the last few years our group has performed extensive studies of the peculiar optical properties of fluorinated polymer colloids [3], and in a preliminary paper we have shown that these properties can be profitably exploited to study surface adsorption processes [4]. Here we simply recall that FEP particles present two very interesting features: they have an average refractive index similar to that of water, and they yield a depolarized contribution to the intensity of the scattered light due to their intrinsic optical anisotropy. As we shall see, the former feature ensures a much stronger sensitivity of the scattered light intensity to the presence of adsorbate layers, while the latter yields a more precise determination of the particle hydrodynamic radius via the measurement of the rotational diffusion coefficient, which is inversely proportional to the particle volume.

Let us first consider a uniform layer of thickness d adsorbed on the surface of a spherical particle of radius R. We will call $\bar{n}$ the average refractive index of the particle, and n_a, n_s, the refractive indices of the adsorbate and of the solvent, so that we will refer to $\bar{n} - n_s$ and to $n_a - n_s$ as to the optical "contrasts" of particle and adsorbate with respect to the solvent. The field scattered by such a core-shell particle can be calculated with a simple trick by summing to the field scattered by a homogeneous particle of radius $R + d$ and refractive index n_a, the field scattered by a homogeneous particle of radius R and refractive index $\bar{n}$ imbedded in a medium of refractive index n_a. The total intensity of the light scattered by N noninteracting particles in the scattering volume V is then given by

$$I = CN \{(n_a^2 - n_s^2)\, \tfrac{4}{3}\, \pi (R + d)^3\, F[k(R + d)] + (\bar{n}^2 - n_a^2)\, \tfrac{4}{3}\, \pi R^3\, F(kR)\}^2 , \tag{1}$$

where k is the scattering wave vector, $F(kx)$ is the form factor of a spherical particle of radius x, and C an instrumental constant. When the particle core is optically anisotropic, an additional depolarized contribution, depending only on the internal anisotropy and not on the properties of the solvent, is also present. The depolarized "incoherent" scattering contributions is very weak compared to the polarized "coherent" component whenever $\bar{n}$ is even slightly different from n_s, and we will take it into account only when dealing with the scattering dynamics. In this work we consider particles which, even in presence of the adsorbed layer, have a radius which is smaller than 1/10 of the wavelength of the incident light beam. In such a case we can set $F(k(R + d)] \approx F(kR) \approx 1$, and we can recast Eq. (1) in a simpler and more useful form

$$I = C\, \frac{V^2}{N}\, \{(\bar{n}^2 - n_s^2)\, \Phi_p + (n_a^2 - n_s^2)\, \Phi_{aa}\}^2 , \tag{2}$$

where Φ_p is the particle volume fraction, and Φ_{aa} the volume fraction of *adsorbed* adsorbant. From Eq. (2) we clearly see that, just because we are summing *fields*, and not *intensities*, we obtain interference terms leading to a substantial increase of the scattered intensity whenever even a small quantity of high-contrast material is adsorbed on a low-constrast particle. Calling I_0 the intensity scattered by the core particles in absence of added adsorbant, the intensity increase due to adsorption is then given by

$$\frac{I}{I_0} = \left[1 + \frac{(n_a^2 - n_s^2)\, \Phi_{aa}}{(\bar{n}^2 - n_s^2)\, \Phi_p} \right]^2 . \tag{3}$$

The volume fraction Φ_{aa} of adsorbate can be simply evaluated from Eq. (3) in terms of experimentally measurable quantities. However, if the adsorption is not complete, as it happens when the amount of added adsorbant exceeds the value required for full surface coverage, the refractive index of the effective solvent in which the particles are dispersed is modified by the fraction of the adsorbant which remains in solution. Assuming additive optical polarizabilities, and calling n_w the refractive index of the original solvent (which in our case is water), and Φ_a the total amount of added adsorbant, the refractive index of the effective solvent in presence of dispersed adsorbant is given by

$$n_s^2 = n_w^2 + (n_a^2 - n_w^2)\, (\Phi_a - \Phi_{aa}) , \tag{4}$$

so that Φ_{aa} can be directly found by combining Eqs. (3) and (4).

The general trend which can be extracted from Eq. (3) is a steady increase of the scattered intensity as a function of the amount of added adsorbant until surface coverage saturation is reached. However, adding further adsorbant ends up in increasing the solvent refractive index, and in reducing then the refractive index contrast between the "dressed" particle and the solvent itself, with a consequent decrease of the scattered intensity. A strong increase of the scattered intensity, compared to the "bare particle" value, can be obtained by using particles which have a refractive index not too different from n_w. In our case, the average refractive index of FEP, as determined by measuring an index-matching curve, is $n_p = 1.353$, while the refractive indices of the used adsorbants, which are hydrogenated surfactants or polymers, is always in the range 1.45–1.50. The scattering "contrast" between FEP and water is then of the order of 1/10 of the one between water and adsorbate.

We present now some applications of the previous ideas. Suspensions of fairly monodisperse FEP particles having a radius $R = 41$ nm were extensively dialysed against water, and successively flushed through mixed-bed ionic exchange resins, in order to reduce to a minimum the amount of adsorbed ionic perfluorinated surfactant coming from the polmerization process. Light scattering measurements have been performed by means of our previously described apparatus [4] which includes selective