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Probing effects of polymer adsorption in colloidal particle suspensions by light scattering as relevant for the aquatic environment: An overview

Alberto Tiraferri *, Michal Borkovec

Department of Inorganic and Analytical Chemistry, University of Geneva, Sciences II, Quai Ernest-Ansermet 30, 1205 Geneva, Switzerland

HIGHLIGHTS

- Polymer adsorption on the surface of particles governs their environmental behavior.
- Light scattering techniques help in studying the adlayer formation and properties.
- DLVO theory describes the behavior of modified particles at least qualitatively.
- Fundamental knowledge of polymer adsorption can be applied to environmental systems.
- Light scattering can probe natural NOM sorption and guides NZVI design strategies.

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ABSTRACT

Modification of particle surfaces by adsorption of polymers is a process that governs particle behavior in aqueous environmental systems. The present article briefly reviews the current understanding of the adsorption mechanisms and the properties of the resulting layers, and it discusses two environmentally relevant cases of particle modification by polymers. In particular, the discussion focuses on the usefulness of methods based on light scattering to probe such adsorbed layers together with the resulting properties of the particle suspensions, and it highlights advantages and disadvantages of these techniques. Measurement of the electrophoretic mobility allows to follow the development of the adsorption layer and to characterize the charge of the modified particles. At saturation, the surface charge is governed by the charge of the adsorbed film. Dynamic light scattering provides information on the film thickness and on the behavior of the modified suspensions. The charge and the structure of the adsorbed layer influence the stability of the particles, as well as the applicability of the classical theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO). This fundamental knowledge is presented in the light of environmental systems and its significance for applied systems is underlined. In particular, the article discusses two examples of environmental processes involving adsorption of polymers, namely, the modification of particles by natural adsorption of humic substances and the tailoring of surface properties of iron-based particles used to remediate contaminated aquifers.

1. Introduction

Adsorbed polymers on particle surfaces govern the behavior of these materials in aqueous suspensions (Russel et al., 1989; Fleer et al., 1993; Elimelech et al., 1995). In the natural environment, particles are typically modified by adsorption of natural organic matter (NOM), which affects their fate and transport (Liang and Morgan, 1990; Tiller and O'Melia, 1993; Wilkinson et al., 1997; Lowry et al., 2012; Philippe and Schaumann, 2014). In engineered processes, adsorption of polymers is commonly exploited to either enhance colloidal stability or to induce particle aggregation. Particles functionalized by polymers for industrial applications may enter the environment and interact with the natural systems (Klaine et al., 2008). One example is the modification of nanoscale zerovalent iron (NZVI) used to remediate contaminated aquifers by means of polymers that prevent its deposition in the subsurface (Li et al., 2006; Phenrat et al., 2009; Lowry et al., 2012). On the other hand, the addition of polyelectrolytes, metal salts, or both, is an established procedure to achieve enhanced particle aggregation and sedimentation in both wastewater and water treatment plants (Bolto and Gregory, 2007; Mackenzie, 2010).

There are various routes for modification of particle surfaces with polymers, of which the simplest is physical adsorption to the surface (Russel et al., 1989; Fleer et al., 1993; Kango et al., 2013; Szilagyi et al., 2014). Polymer adsorption processes are often irreversible, which leads to a rapid and durable modification. The adsorbed mass and the conformation of the adsorbed film are dictated by properties of the polymers, such as molecular mass, composition, architecture, and type

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* Corresponding author.
E-mail address: alberto.tiraferri@unige.ch (A. Tiraferri).

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of charged groups; by the solution properties, for instance pH, ionic strength, and the type of ions present; and finally they are influenced by the particle characteristics, particularly, their surface charge density. In turn, the resulting layer properties control the suspension stability and the interaction of particles with other surfaces. In various situations, these interactions are dominated by forces described by the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) (Russel et al., 1989; Elimelech et al., 1995). This classical theory suggests that particle stability is governed by attractive van der Waals forces and repulsive double layer forces. For particles coated with adsorbed polymer layers, additional non-DLVO forces may come into play, such as patch–charge attractions, bridging interactions, and steric forces (Russel et al., 1989; Szilagyi et al., 2014).

Numerous techniques are available to characterize the adsorption of polymers on particle surfaces and to address their effects on the properties of particle suspensions. The relevant methods include microscopy techniques, especially electron microscopy or atomic force microscopy (AFM) (Donald et al., 2000; Minko and Roiter, 2005; Lead and Wilkinson, 2006; Domingos et al., 2009a). Microscopy techniques have the advantage of excellent resolution, but the disadvantage that they mostly operate ex situ, sometimes causing substantial disturbances to the original particle suspension. Sorption isotherms can be used to estimate the mass of adsorbed polymer, while techniques such as isothermal titration calorimetry, infrared spectroscopy, or nuclear magnetic resonance can be employed to gain information on the chemical and physical structures of the polymer and of the polymer layer. Other powerful methods that operate directly in the modified suspensions are light scattering, centrifugation, particle tracking analysis, field flow fractionation, or fluorescence correlation techniques. When such procedures are coupled with appropriately selective detectors, they become powerful methods for the analysis of naturally occurring particles (Baalousha et al., 2011; Lespes and Gigault, 2011).

Among these techniques, light scattering probably represents the simplest and most versatile in situ procedure to investigate particle suspensions. There are numerous variants of light scattering techniques available (Russel et al., 1989; Berne and Pecora, 1990; Pusey, 2002). Static light scattering explores the variation of the scattered light intensity as a function of the scattering angle, and provides access to gyration radii. While static light scattering is very powerful for micron sized particles, this technique becomes less useful for nanosized particles. Dynamic light scattering (DLS) explores the temporal fluctuations of scattered light, and therefore provides direct access to the diffusion coefficient or the hydrodynamic radius of the particles. This technique is applicable over a wide size range down to nanosized particles, and when conducted in a time-resolved fashion, it further provides a direct probe of suspension stability (Holthoff et al., 1996; Chen et al., 2007; Hierrezuelo et al., 2010c). Electrophoretic light scattering is carried out in an external electric field and relies on a setup that is similar to that of DLS. This technique measures the electrophoretic mobility, and provides information concerning the particle charge (Russel et al., 1989; Kleimann et al., 2005; Chen et al., 2007). Electrophoresis also allows the determination of the adsorbed amount of a charged polymer (Mezei and Meszaros, 2006; Adamczyk et al., 2010; Sadeghpour et al., 2011). Therefore, techniques based on light scattering provide valuable information on polymeric layer formation and its influence on suspension properties.

The advantages and limitations of light scattering techniques when used for environmental samples were thoroughly reviewed elsewhere (Schurtenberger and Newman, 1993). The detection limit for nanosized particles strongly decreases with their size, and is situated in the mg/L range. The backscattering geometries introduced in recent years are capable to improve these detection limits. When DLS is used to analyze polydisperse samples, larger particles scatter more strongly, thus leading to a larger average particle size (Grolimund et al., 2001; Hierrezuelo et al., 2010b; Baalousha et al., 2012; Gottselig et al., 2014). These aspects can be remedied by introducing appropriate intensity weighting in the analysis of DLS data or by combining this technique to field flow fractionation or centrifugation (Baalousha et al., 2011; Baalousha and Lead, 2012).

The present overview evaluates the application of light scattering techniques to study adsorption of polymers to colloidal particles, and it discusses the relevance of these phenomena in environmental aqueous systems. We focus on the simplest case of physical adsorption, which occurs when particles are dispersed in an aqueous medium with dissolved polymers. Initially, we review our current understanding of adsorption phenomena in well-defined particle–polymer systems and their underlying mechanisms. Then, we emphasize the significance of this knowledge in applied systems, by investigating two representative cases of environmental relevance, namely, adsorption of NOM to metal oxide particles in the natural environment and modification of NZVI for aquifer remediation.

2. Adsorption of polymers governs particle aggregation

In the following, light scattering methods will be illustrated by discussing the representative case of adsorption of positively charged poly(diallyldimethyl ammonium chloride) (PDADMAC) on negatively charged sulfate-terminated polystyrene latex particles. Fig. 1a presents electrophoresis results of latex particles as a function of PDADMAC dose (Hierrezuelo et al., 2010c). The electrophoretic mobility expresses the ratio of the migration velocity of the particle relative to the applied electric field, and is approximately proportional to the surface potential (ζ-potential) (Russel et al., 1989). The polymer dose is the ratio between the mass of added polyelectrolyte and the mass of particles in suspension. At low polyelectrolyte dose, the mobility reflects that of the bare particles. With increasing dose, the adsorbed amount of the polyelectrolyte increases, and progressively neutralizes the particle charge. When the particle charge is precisely neutralized, the mobility vanishes. This condition is referred to as the isoeletric point (IEP). Further addition of polyelectrolyte leads to overcharging, whereby the mobility changes its sign and is dominated by the charge of the adsorbed polymer. When the dose is increased further, the adsorption saturation plateau (ASP) is reached. Beyond this point, the adsorbed layer is saturated and no further adsorption occurs. The charge reversal mechanism is depicted in Fig. 1c.

Measurements by electrophoretic light scattering are quickly carried out with suspensions of appropriate concentrations, and this technique thus permits to measure the electrophoretic mobility in a straightforward way. The disadvantage is that the technique averages the signal of all particles in solution, and thus leads to a relatively poor resolution. One possible way to circumvent this problem is to use video microscopy for electrophoresis measurement (Solomentsev et al., 2000; Jones et al., 2003). However, this technique is only applicable to larger particles, and the sample concentration must be chosen carefully. For polydisperse or non-spherical particles, reporting electrophoretic mobility avoids the problem of the conversion to the electrokinetic surface potential (ζ-potential). This conversion is relatively straightforward for monodisperse and spheroidal particles (O'Brien and White, 1978). However, it becomes particularly problematic for particles with differently charged crystal faces (e.g., clay minerals).

Fig. 1a illustrates two additional characteristic features for such polyelectrolyte–particle systems. The first feature is the decrease of the magnitude of the electrophoretic mobility with increasing salt level, including the value of the saturation plateau. This phenomenon is related to the decrease of the surface potentials with increasing salt level (Russel et al., 1989). The second feature is that the mobility is independent of the particle concentration when plotted versus the polymer dose. The lack of particle concentration dependence indicates that all added polymer molecules below the ASP adsorb to the particles. This behavior is consistent with irreversible adsorption, since this process will deplete the entire dissolved polymer from the solution. The fact that the mobility is independent of the particle concentration was