Measures to determine the hydrophobicity of colloidal polymers

Abstract The role of latex dispersions as well as water-soluble polymers in industrial and pharmaceutical applications (i.e. analytical and drug delivery systems) is growing fast. An important attribute of polymer particles is the high adsorption capacity for organic moieties (e.g. of molecules of biological origin). It is important that the biologically active molecules remain fully hydrated during the adsorption by the colloidal system; therefore, it is essential to have a measure for the hydration of both adsorbent particles and adsorptive molecules and to correlate its value with other properties of the polymeric material. We have estimated the hydrophobic/hydrophilic balance with adsorption isotherms of polymethine dyes (surface probes). The adsorption of the anionic dyes is 10 times stronger on positively charged polystyrene particles compared to the adsorption of the corresponding cationic dyes on negatively charged particles. We found a redshift in the absorption maximum of the anionic dyes after adsorption onto the positively charged particles. A blueshift was observed for cationic dyes bound to negatively charged particles. We deduce from our measurements that the nature of the surface charges present at the particle-liquid interphase alters the surface characteristics of the particles. We suppose that cationic charged polymer particles are more hydrophobic than particles from the same matrix with negative surface charges. In a qualitative model, we illustrate the governing role of hydration forces on particle aggregation.

Key words Microgel · Dye adsorption · Polymer colloids · Water structure · Hydrophobic hydration

Introduction

There are only a few ways to measure or compare the hydrophobicity of surfaces in disperse systems. Contact-angle measurements cannot be applied to the hydrated colloidal particle in its original dispersion medium. Polymer particles need to be dissolved in an organic liquid to cast the polymer film for the contact-angle measurements. The properties of the dry polymer film certainly differ from the properties of a strongly curved surface; therefore, it is insufficient to determine only the contact angle on macroscopic surfaces with conventional measurements, by either the sessile-drop or the inverted-plate method. For polymer colloids in nonmiscible fluids, depending on the hydrophobicity the particles concentrate in either phase. Over the last few decades, several improvements to the investigation techniques have been suggested, but there is virtually no easy method to provide the desired information.

In the last few years, we have focused our intention on the determination of the so-called surface hydrophobicity of colloidal particles and biopolymers [1]. We were searching for simple and effective methods to measure the extent of hydrophobicity of polymer lattices and
developed a preferential solvent adsorption method from binary liquid mixtures. In this technique, the colloidal particles can preferentially absorb either the polar or nonpolar liquid from the liquid mixture. Careful analysis of the adsorption-excess isotherm gave us some useful information about the stagnant layer at the surface of the colloidal particles and the properties of the polymer network as well [14].

In a second set of experiments we investigated the adsorption of hydrophobic yet soluble organic dyes onto different polymer latices. The measurements were conducted using a UV–vis spectrophotometer. The advantage in measuring in the visible spectrum is that impurities (e.g., surfactants, monomers) released by the colloidal particles over time do not disturb the spectrum of the dyes. The shift in the absorption spectra of precipitated polymer dye conjugate and the shape of the adsorption isotherm of the dye provides information about the particles hydrophobicity.

**Experimental**

**Preparation of particles**

In general the polymerization was carried out in a 500-ml round-bottomed four-necked flask with stirrer, cooler and nitrogen purge.

**Preparation of negatively and positively charged polystyrene**

Water (200 ml, double deionized, Seradest) was stirred at 350 rpm and heated to 90 °C under a nitrogen blanket. After 10 min 25 ml, for negatively charged polystyrene, PS (−), or 12.5 ml, for positively charged PS, PS (+), styrene (stabilized with 12 ppm catechol, Hül), was added. Potassium persulfate (0.25 g), for PS (−), or 0.5 g ADMBA, (Wako), for PS (+)), in 25 ml water was added after 5 min. The stirrer was adjusted to 60 rpm. The warm dispersion was filtered through glass wool and after cooling was filtered through a nylon mesh.

**Preparation of negatively charged poly(butyl methacrylate)**

Water (480 ml, double deionized, Seradest) was stirred at 600 rpm and heated to 80 °C under nitrogen. Butyl methacrylate (BMA, 260 ml, Fluka), sodium dodecyl sulfate (2 g) and acrylic acid (2 ml) were added. After 30 min, 2 g potassium peroxodisulfate in 25 ml water was added. The stirrer was adjusted to 400 rpm. The reaction was started after 4.5 h and the latex was filtered.

**Preparation of positively charged poly(butyl methacrylate)**

Water (480 ml, double deionized, Seradest) was stirred at 600 rpm and heated to 65 °C under nitrogen. BMA (130 ml, Fluka), N-ethyl-N-hexadecyl-N,N-dimethyl ammonium bromide (1.3 g, Fluka), acrylamide (1 g) and, after 15 min, ADMBA (1.2 g) were added. The temperature was raised to 70 °C and the reaction started. Bluish opalescence was observed. The temperature was reduced to 60 °C. After 3 h the reaction was stopped and the latex was filtered.

**Preparation of negatively charged poly(methyl methacrylate)**

Sodium dodecyl sulfate (0.45 g) in water (500 ml, double deionized, Seradest) was stirred at 600 rpm and heated to 80 °C under nitrogen. A 1.3-ml aliquot of a 5.2% ammonium peroxodisulfate solution and 1.5 ml of a 7% potassium phosphate solution were added. One quarter of the monomer mixture as 124.8 ml methyl methacrylate (Fluka) and 4.7 ml ethylene glycol dimethacrylate (Fluka) was added. The rest of the monomer mixture was added over 90 min from an addition funnel. After the complete addition of the monomers over 2 h the reaction was stopped and the latex filtered.

**Adsorption experiments**

**The Rose Bengal method**

Rose Bengal (DAB 8, 46, 132–135) is a standard reagent to dye biological samples. The xanthene dye is adsorbed depending on how lipophilic the material is. The molecule is dipositive charged and soluble up to 1 mmol/l. Owing to its hydrophobic nature it is strongly adsorbed by polymer surfaces.

Standards of Rose Bengal (0.6–0.02 mmol/l) were used to measure a calibration curve. These standards (6 ml) were mixed with 1 ml PS latex (2.5 and 6% wt/wt), equilibrated for 3 h and centrifuged. The concentration of Rose Bengal in the supernatant (c_{equl}) was determined using a UV–vis spectrophotometer (Hitachi 2000) and the adsorbed amount, \( \Gamma \) (millimoles per gram), was calculated.

- **Rose Bengal, di-Sodium-tetrachlorotetraiodofluorescein**

**Adsorption of polymethine dyes**

The polymethine dyes were prepared by Dähne and coworkers [3–5]. They are available as both cations and anions. For the measurements, standards of the dyes were prepared and a calibration curve recorded. A 6-ml aliquot of the standards (4-0.0003 mmol/l) was mixed with 1 ml latex (solids: 2.5–6%), equilibrated for 3 h and centrifuged. The concentrations, c_{equl}, in the supernatant were measured with a UV–vis spectrophotometer (Hitachi 2000) and the adsorbed amount, \( \Gamma \), was determined by