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ScienceDirect
Journal of Colloid and Interface Science 311 (2007) 430–437
Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

Interaction forces between particles stabilized by a hydrophobically modified inulin surfactant

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Received 4 December 2006; accepted 9 March 2007

Abstract

The adsorption isotherm of a hydrophobically modified inulin (INUTEC SP1) on polystyrene (PS) and poly(methyl methacrylate) (PMMA) particles was determined. The results show a high affinity isotherm for both particles as expected for a polymeric surfactant adsorption. The interactions forces between two layers of the hydrophobically modified inulin surfactant adsorbed onto a glass sphere and plate was determined using a modified atomic force microscope (AFM) apparatus. In the absence of any polymer, the interaction was attractive although the energy of interaction was lower than predicted by the van der Waals forces. The results between two layers of the adsorbed polymer confirms the adsorption isotherms results and provides an explanation to the high stability of the particles covered by INUTEC SP1 at high electrolyte concentration. Stability of dispersions against strong flocculation could be attributed to the conformation of the polymeric surfactant at the solid/liquid interface (multipoint attachment with several loops) which remains efficient at Na_2SO_4 concentration reaching 1.5 mol dm^{-3}. The thickness of the adsorbed polymer layer in water determined both by AFM and rheology measurements, was found to be about 9 nm.

Keywords: Hydrophobically modified inulin; Colloidal stability; Interaction forces; Atomic force microscopy

1. Introduction

Polymeric surfactants are commonly used in formulations that require high colloid stability, such as paints, cosmetics products, emulsion latexes, etc. [1]. The mains advantages of polymeric surfactants are their strong adsorption at the solid/liquid interface (lack of desorption) due to the multipoint attachment of the polymer chain to the surface and the strong steric repulsion between the stabilizing chains. This can be achieved using block or grafted copolymers, where the B part of the molecule acts to anchor the chain to the surface, and the A part is the stabilization chain [2–5]. The performance of a polymer depends not only upon its adsorption density but also on its conformation and orientation at the interface. For an adsorbing polymer system, the balance of interaction energies between the polymer and solvent, the polymer and surface, and the polymer with itself will determine the final conformation adopted at the interface [6]. It is essential to have an adsorbed layer thickness that is sufficiently large to screen the van der Waals attractive forces [7].

To achieve the above objective, a hydrophobically modified inulin surfactant (INUTEC SP1) has been recently synthesized [8,9]. This molecule is a graft copolymer consisting of an inulin (polyfructose) backbone (A) on which several alkyl groups (C_{12}) (B) are grafted. The inulin backbone has a degree of poly-

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doi:10.1016/j.jcis.2007.03.011

merization greater than 23 (i.e., a molecular weight greater than 3700 Da).

The alkyl groups provide the anchor points (multipoint attachment) at the solid/liquid interface, leaving the polyfructose loops dangling in solution. These alkyl chains are randomly distributed across the polyfructose backbone which implies a distribution of loop sizes. The polyfructose chain remains strongly hydrated even at high electrolyte concentration and high temperature [10,11]. The molecule was previously studied for his stabilization properties of O/W emulsions [11] and colloidal dispersions such as latex particles [12,13]. Preliminary investigations by dynamic light scattering (PCS) using polystyrene latex particles, indicated an adsorbed polymer layer thickness of 4 nm [12]. It proved to be very effective as a steric stabilizer [12,13] and indeed more efficient in comparison to classical surfactants, based on poly(ethylene oxide) [12–15].

For full characterisation of an adsorbed polymer layer, at a solid/liquid interface, one needs to know how much polymer is absorbed, where it is located on the surface, and how far it extends into solution away from the interface (the hydrodynamic layer thickness). Polymer adsorption has traditionally been studied quantitatively by classical solution depletion. More recently, the adsorbed polymer layer has been investigated by rheology [16] and by direct force measurements such as atomic force microscopy (AFM) [17]. Both techniques provide information about the adsorbed layer thickness as a function of polymer concentrations.

In this paper, we report the results of a study of the mechanism of stabilization of solid particles by the INUTEC SP1. The adsorption of INUTEC SP1 on PS and PMMA particles has been investigated. The polymer coated latex particles were used for rheological investigations as a function of the volume fraction of the particles. To fully understand the stabilization mechanism, a quantitative description of the interaction forces between the adsorbed polymer layers was obtained using AFM measurements. For this purpose, the interactions between a hydrophobized glass sphere and a glass plate, that were coated with INUTEC SP1, was measured as a function of polymer concentration, both in aqueous solution and in the presence of Na_2SO_4 (up to 1.5 $mol\,dm^{-1}$).

2. Experimental

2.1. Materials

INUTEC SP1 was supplied by ORAFTI Bio Based Chemicals (Tienen, Belgium), and was synthesized as described before [8,9]. It is a graft copolymer made of a polyfructose backbone on which some alkyl groups (C_{12}) are randomly grafted. Its average molecular weight is approximately 5000 $g\,mol^{-1}$ and it is quite polydisperse since inulin has a wide molecular weight distribution. The purity of such surfactant was higher than 97% and it forms a clear solution at concentrations less than 0.1 wt%, above which a turbid solution appears which is due to some association of the polymeric chains [13]. Recent studies using small angle X-ray scattering (SAXS) showed the aggregates to be approximately spherical with an hydrodynamical diameter about 9.5 nm.

Table 1
Main features of latexes. Particle diameter, polydispersity index (PI), monomer conversion (X), and critical coagulation concentration of $CaCl_2$ (CCC) of PS and PMMA particles

Sample	Particle size (nm)	PI	X (%)	CCC (M)
PS	321.6	0.031	91	0.018
PMMA	273.1	0.054	94	0.024

Styrene (Merck) or methyl methacrylate (Aldrich) were used as monomers. These were purified by passing them through basic chromatographic aluminum oxide in order to remove the hydroquinone inhibitor. Potassium persulfate, $K_2S_2O_8$, was obtained from Fluka with purity higher than 99%. Deionized water was further purified by filtration through a Milli-Q system. The electrolytes used were calcium chloride, $CaCl_2$. $2H_2O$ (purity >99%) supplied by SIGMA and sodium sulfate, Na_2SO_4 (purity >99%) supplied by BDH. For the AFM experiments, the water used was filtered through a Nanopure system (water resistance >10 MΩ, surface tension $= 72 \pm 0.2$ $mN\,m^{-1}$).

2.2. Methods

2.2.1. Latex particles

All latexes were prepared by emulsion polymerization as described before [13]. The reactions were carried out for 24 h for polystyrene (PS) particles and 6 h for poly(methyl methacrylate) (PMMA) particles, at a constant temperature of 80 °C under a controlled nitrogen atmosphere.

A complete characterization of both latexes was carried out. The main results, such as diameter, polydispersity index, conversion rate, and the critical coagulation concentrations (CCC) of $CaCl_2$, are shown in Table 1. The monomer conversion rates were determined at the end of the reaction, for each latex synthesized, by the gravimetric method based on evaporation of all volatile compounds of the dispersion, at 50 °C during 12 h. Particle size and polydispersity index of each particle were obtained by photon correlation spectroscopy, PCS. The CCCs were evaluated by measuring the turbidity as a function of time for different electrolyte concentrations. Details of the method have been reported elsewhere [13].

2.2.2. AFM experiments

The atomic force microscope (AFM) used was constructed at the Imperial College with the specific aim of examining the surface interactions between adsorbed polymer layers on glass surfaces. No scanning capability was incorporated into the instrument. A full description of the instrument and its operation was given elsewhere [18]. To minimize the drifts and noise from both the environment and the mechanical apparatus itself, the apparatus was set up in a basement laboratory, placed on an antivibration table and covered with a custom-made box to control the local environment.

The glass surfaces (30 ml Petri dish with flat bottom and glass spheres of about 30 mm diameters) were rigorously cleaned by ultrasonication in dilute RBS 50 detergent solution