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## Solvent quality dependent interactions between adsorbed block copolymers measured by AFM

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### ABSTRACT

This paper describes experiments conducted with an atomic force microscope to investigate the manner in which the steric interactions between an adsorbed layer of the block copolymer synperonic F127 (an ABA copolymer of ethylene and propylene oxide) are modified when the solvency conditions are gradually changed from good to poor. The solvent quality was adjusted by varying either the temperature or the electrolyte concentration. By fixing one of the aforementioned parameters such as temperature, measurements were conducted at various electrolyte (sodium sulfate) concentrations. Alternatively at a fixed temperature, the electrolyte concentration was increased. It was found that as the solvency for the stabilising polymer, poly (ethylene oxide) (PEO) decreased the range of the interaction decreased and that at sufficiently high sodium sulfate concentrations, or temperature, the interaction switched from being repulsive to being attractive. The results were compared to the cloud points of F127, low molecular weight PEO, and the critical flocculation temperatures for polystyrene latex bearing the same adsorbed polymer adsorbed. The point at which the polymer interaction forces changes from repulsive to attractive, compares to, but is lower than the lower consolute solution temperatures (LSCT) for the copolymer and critical flocculation temperatures (CFT) for PEO stabilised polystyrene latex particles.

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### 1. Introduction

The stabilisation of colloidal particles by adsorbed polymers has been well studied scientifically for the last 50 years, although man has unwittingly been using such methods for many thousands of years when preparing early paints and inks. It has also been well recognised that for aqueous dispersions such polymer stabilised systems are much less sensitive to electrolyte concentration than simple charged colloids in terms of their aggregation. However, at sufficiently high electrolyte concentrations of the correct type, and or at high temperatures flocculation of the dispersion is possible. The reason for this behaviour is relatively simple to explain and that is at high electrolyte concentration and or at high temperatures, the structure of water, the solvent changes, and is significantly less hydrogen bonded. High temperatures reduce the hydrogen bonding in water and by adding electrolyte we are adding ions that wish to become hydrated, which also changes the water structure. Thus increasing the temperature or adding electrolyte, decreases the solubility of the polymer which has become dissolved in water due to hydrogen bonding of free water. For particles

that have become stabilised by adsorbed polymer therefore one would expect the stabilising polymer layer to become less effective as either the temperature or the electrolyte concentration is increased and eventually to become ineffective. In the 1970s Napper in Australia [1,2] and Vincent and co-workers in the UK [3,4] studied in detail the flocculation of particles, frequently polystyrene latex particles, bearing adsorbed layers of polymer such as poly (vinylalcohol), PVA and poly (ethylene oxide), PEO, and demonstrated these ideas. Following this came the measurement of the interactions between adsorbed polymers, pioneered by Klein using the surface forces apparatus, SFA [5]. Many of the systems investigated were non-aqueous, but some experiments were performed on aqueous systems [6–8]. In recent years the AFM [9–11] has largely replaced the SFA as a technique to measure the interactions between two surfaces coated with adsorbed polymer layers. A large number of systems have been studied, including in a recent publication of ours the ABA copolymer series commonly called 'Pluronics' [12], which are comprised of poly (ethylene oxide) as the A block and poly (propylene oxide) as the B block. Recently Butt et al. have studied the effect of temperature on the forces of interaction between polymer layers, but the layers were always in good solvent conditions [13]. A similar system to that studied here using atomic force microscopy has been studied by Bevan and co-workers using total internal reflectance microscopy, TIRM [14–16] a technique which

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is less direct than AFM, but more sensitive. In the TIRM technique the separation a particle is from a surface is measured over time and from the fluctuation in position the balance between gravitational forces, colloidal forces and diffusion forces the interaction between the particle and the surface can be inferred. In a series of papers the interactions between a Pluronic-coated particle and a Pluronic-coated surface has been measured at different temperatures. From the original study it was noted that as the temperature increases (and hence the solvency for the polymer decreases) the thickness of the polymer layer decreases [17]; in further work [14] the effect of both temperature and electrolyte concentration (or in the terminology of Ref. [14] specific ion concentration) was investigated.

The limitation of the TIRM technique is the range of force which can be covered, from approximately 5 kT to  $-5$  kT, although not as sensitive the AFM method can probe a wider force range and this is which this paper reports. The interactions between hydrophobic glass surfaces bearing adsorbed layers of the Pluronic F127 has been investigated in both good and poor solvent conditions.

## 2. Experimental

### 2.1. Materials

The ABA triblock copolymer used in this study, Synperonic F127, was obtained from ICI surfactant division (now Croda chemical) (UK). A summary of the properties of this copolymer is shown in Table 1. The polymer was used without any further purification to prepare stock solutions of 0.01% (w/w) in water.

The  $\text{Na}_2\text{SO}_4(\text{aq})$  (BDH) was of analytical grade and prepared to the required concentration with nanopure water. The glass surfaces (40 ml Petri dish; glass spheres of roughly  $30\ \mu\text{m}$  diameter) were made hydrophobic by silanisation with dichlorodimethylsilane (BDH) using the method described in an earlier paper of ours [18].

The adsorbed amounts were estimated from earlier work for the adsorption of the copolymer onto polystyrene latex particles, reported by Kim and Luckham [19]; we note that similar values were obtained by Kayes and Rawlins [20].

### 2.2. Experimental techniques and procedure

The force measurement apparatus used was by a custom built AFM, whose application and data interpretation techniques have been explained in detail elsewhere [9,21]. Before setting up the AFM rig, the hydrophobic glass sphere was mounted on a commercial silicon AFM single beam cantilever using a micromanipulator and video camera. The levers typically had spring constants in the range  $0.04$ – $0.4\ \text{N/m}$ . The spring constant was determined for each cantilever using a resonance shift technique [9], an approach similar to the one used by Cleveland [22] and the particle diameter was determined microscopically.

The hydrophobic Petri dish was then mounted on top of the AFM moving vertical stage and filled with the required electrolyte solution (40 ml). The two surfaces were brought in close proximity of roughly 2 mm apart after which 5 ml of electrolyte was replaced

with 5 ml of the copolymer stock solution (0.1%, w/w) using a hypodermic needle. The surfaces were left for around 12 h to allow the copolymer to adsorb on the silanised surfaces.

During the AFM experiments, an approach rate of 250 nm/s was used in all the experiments. At this slow rate hydrodynamic effects are minimal. The raw data were collected using a commercial software package called snapshot (Advantech, UK) and finally the data were processed using a written subroutine in commercially available spreadsheet software (Excel 2000).

Heating of the solution was achieved by passing a small current through a heating coil placed underneath the Petri dish. The degree of heating was controlled by the current supplied, rather than through a thermostating arrangement to reduce thermal drift. In this way the solution could be raised to  $40^\circ\text{C}$ , heating further to higher temperatures brought about unacceptable levels of thermal drift. At least 1 h of equilibration time was allowed before starting the measurements for each temperature change. The temperature of the solution inside the Petri dish was measured with a thermocouple. Typically, the temperature could be controlled to within  $0.2^\circ\text{C}$  using this setup.

In the experiments where the electrolyte concentration was increased a known volume of solvent was removed, typically 5–10 ml and replaced by a higher electrolyte concentration. Similarly when the electrolyte concentration was reduced a known volume of electrolyte was removed and replaced by pure water.

In all experiments a low concentration, around 0.02%, polymer solution was present enabling further polymer adsorption to occur on heating or on increasing the electrolyte concentration.

## 3. Results and discussion

### 3.1. Hydrophobic surfaces

To establish whether the copolymer had adsorbed onto the surfaces, one has to initially determine the interactions between the bare surfaces (hydrophobic). The force profiles between these surfaces in 0.4 M sodium sulfate solution are shown in Fig. 1. No interaction between the surfaces is observed until they are some 45 nm from contact, whereupon the surfaces spontaneously jump into contact. On separation, a very strong adhesion is noted. Also shown in Fig. 1 as a curve, is the estimated van der Waals attraction between the two surfaces assuming a Hamaker constant for glass of  $7.7 \times 10^{-21}\ \text{J}$  [23]. It is clear that van der Waals forces are much weaker than those being measured between these hydrophobic glass surfaces, although we do see a good agreement between hydrophilic glass surfaces (not shown). Long ranged, strongly attractive interactions between hydrophobic surfaces have periodically been reported in similar measurements over the last

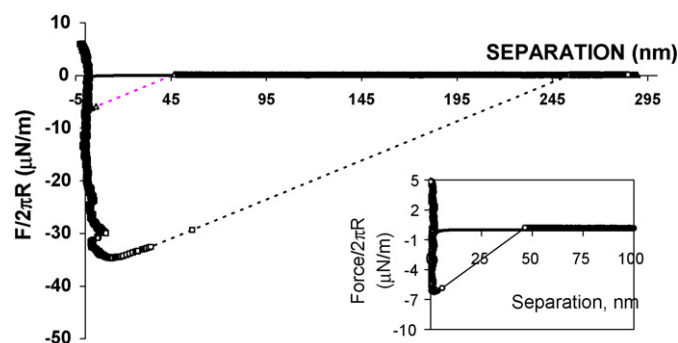


Fig. 1. Force–distance interaction profile between hydrophobic (silanised) glass immersed in 0.4 M sodium sulfate solution. ( $\Delta$ ) approach; ( $\square$ ) retraction of surfaces.

**Table 1**  
F127 copolymer property characteristics.

$M_w$	22,400
Polydispersity $M_w/M_n$	1.4
Average no. of PEO units per molecule	120
Average no. of PPO units per molecule	76
Adsorbed amount ( $\text{mg}/\text{m}^2$ )	1.3
Distance between adsorbed chain (nm)	1.23

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