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Probing the effect of superplasticizer adsorption on the surface forces using the colloidal probe AFM technique

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Abstract

The interactions between adsorbed superplasticizer layers have been studied using direct force measurements, with an atomic force microscope. MgO was used as a nonreactive model system for cement, and a novel freeze granulation method for the production of spherical particles suitable for the colloidal probe atomic force microscope (AFM)-technique is reported. We found that the interactions induced by the adsorption of the anionic acrylic ester–ethylene oxide (AAE–EO) copolymers can be described as electrosteric, with an electrostatic and steric contribution. The range of the steric repulsion varied between 1.5 and 5 nm and could be related to the length of the grafted ethylene oxide chains. The lignosulfonate also induced a significant steric contribution that could be related to a dense coil conformation of the adsorbed superplasticizer.

Keywords: Dispersion; Cement; MgO; Superplasticizer; Atomic force microscope (AFM)

1. Introduction

Superplasticizers are a type of dispersants that have been used to improve the flowability of cementitious systems for the last four decades [1]. The use of the first generations of superplasticizers, e.g., sulfonated naphthalene formaldehyde (SNF) and modified lignosulphonates (LS), resulted in significant improvements of the properties of fresh concrete and are still widely used. However, increasing demands on good flowability, extended working time and an increased need for a reduction in concrete porosity have created an interest in new types of superplasticizers, e.g., anionic acrylic ester–ethylene oxide copolymers (AAE–EO). Self-compacting concrete (SCC) is one application where it is especially important to have a good flowability because this concrete is not vibrated during placement [2].

Most of the different types of superplasticizers, both the early, first generation admixtures and the novel AAE–EO, are polyelectrolytes. Polyelectrolytes are a type of dispersant that is commonly used in, e.g., ceramics, paints, paper coatings and refractories [3]. Polyelectrolytes adsorb at the solid–liquid interface and infer a repulsive force, thus reducing or eliminating the adhesion between particles in close proximity. Polyelectrolyte adsorption is highly dependent on the electrostatic interactions between the polyelectrolyte and the surface; hence, the surface chemistry of the solid phase and the solution properties of the polyelectrolyte are important parameters, regulated by the pH and the ionic strength [4]. The pH controls the sign and density of charges on the surface and the degree of dissociation and the conformation in solution of a weak polyelectrolyte. The salt concentration also affects the conformation of the polyelectrolyte in solution and the screening of the electrostatic interaction between charged polymer segments and the surface charges.

The term electrosteric stabilization is often used to describe how polyelectrolytes act as dispersants. Electrosteric stabilization is a combination of an electrostatic double-layer repulsion and a steric repulsion, where the relative importance of the respective contributions is closely

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related to the polymer segment density profile at the interface. If the polyelectrolyte adsorbs in a flat conformation, the steric repulsion is short range and the stabilization mechanism is mainly electrostatic. This is usually the case when the polyelectrolyte is highly charged, having an extended conformation, and the particle surface is oppositely charged. With thicker adsorbed layers, having chains protruding into the solution, the steric contribution will become more important. However, there is always an electrostatic contribution because the adsorption of a charged polyelectrolyte usually induces a net surface charge. The relative importance of the steric and electrostatic contributions to the repulsion inferred by the adsorption of superplasticizers on cementitious particulate systems is still an unresolved issue, mainly because of the complex nature of the system. Superplasticizers that impose a significant change in the zeta-potential when adsorbed on the particles are usually interpreted to disperse cement through electrostatic stabilization, whereas steric stabilization is assumed to be the main mechanism when bulky polymers are adsorbed [5,6]. Lewis et al. [7] also suggested that depletion forces are important for the stabilization of cementitious systems.

The effect of a dispersant is often investigated with methods providing macroscopic (sedimentation and rheology), as well as microscopic information (electrokinetics). These methods, however, contribute only with indirect information on the actual interaction between the particles constituting the colloidal dispersion. Direct measurements using the Surface Forces Apparatus (SFA) or the Atomic Force Microscope (AFM) offer a possibility to directly probe the interactions between surfaces. The AFM method for measuring surface forces, often referred to as the "colloidal probe method", was first used by Ducker et al. in 1991 [8] and has, since then, been applied to a number of different systems [9–13]. The AFM method has also been applied to cement and cement-like systems immersed in a liquid with [14,15] and without the addition of polymer [16,17]. However, the use of reactive surfaces with a poorly defined geometry and surface roughness makes a thorough evaluation of the details of the inferred surface forces difficult.

The aim of the present work is to use the AFM colloidal probe technique to directly measure the interactions inferred by adsorption of different superplasticizers and elucidate the characteristics of the electrosteric repulsion. We have used MgO as a nonreactive model system for cement. Previous work by Flatt et al. [18] showed that the surface chemistry and adsorption properties of MgO are quite similar to cement when the powder is immersed in an electrolyte that mimics the ionic composition of cement water. We have developed a technique to produce spherical MgO probes suitable for accurate direct force measurements using the AFM. The direct force measurements suggest that the adsorbed layer thickness is relatively thin (1–5 nm) and that the electrostatic interactions are of importance, also for the novel AAE–EO superplasticizers.

2. Experimental

2.1. Materials

2.1.1. Polymers

Two modified anionic acrylic ester type polymers with grafted ethylene oxide chains are used in this study. The two polymers mainly differ with respect to the length of the grafted ethylene oxide chains. The ethylene oxide (EO) branches of Conpac 30 (Perstorp Speciality Chemicals, Sweden) are about 60–80 units long and the overall molecular weight around 100,000 g/mol. The length of the EO chains for Ultra 1 (Cementa, Sweden) are shorter; FTIR and GC-MS analysis indicates a length between 25 and 60 units. The backbone of both Conpac 30 and Ultra 1 contains charged sulfate and carboxylate groups.

The lignosulfonate (DP563 from Borregaard Lignotech, Norway) is a highly branched sodium-based softwood lignosulfonate. The sugar has been fermented away, and the product has been ion exchanged and repeatedly ultra filtrated. The molecular weight distribution is very wide, with M_W/M_n 65000/6500 Da. DP 563 contains quite a large amount of sulfonate groups, and the sodium content is 4.8%.

2.1.2. MgO

The spherical MgO probes for the AFM surface force measurements were produced from a freeze-granulated magnesium hydroxide powder (Martin Marietta Magnesia type MH-10, 325 mesh). Flat MgO substrates for the AFM-force measurements were drilled out of 96% dense MgO crucibles containing 2% Y_2O_3 as sintering agent (Ozark Technical Ceramics). The substrates were polished to mirror quality, and the surface roughness was estimated to R_q=7 nm and R_a=6 nm over an area of 1×1 μm using scanning AFM. The adsorption measurement of the lignosulfonate polymer was performed on a MgO powder (Martin Marietta Magnesia type P 98, 325 mesh) with a specific surface area (BET) of 0.64 m^2/g.

2.2. Methods

2.2.1. Adsorption

The adsorption of the lignosulfonate DP563 on MgO was measured using UV-VIS spectroscopy (Perkin-Elmer Lambda 6 spectrometer). The lignosulfonate, dissolved in 10 g of electrolyte was added to 10 g of MgO powder, and the polymer was allowed to adsorb for 20 min before the suspension was filtrated and the remaining amount of lignosufonate was determined. The adsorption measurements were performed in an electrolyte that mimics the ionic composition of the cement water. We have used an electrolyte composition that mimics the composition of the water phase of cement slurry (CEM II/A-LL 42,5 R type cement, Cementa Byggcement Slite) at a water/cement ratio of 0.5 after 30 min of water contact. The electrolyte composition is $[Ca^{2+}]$=10 mM, $[Na^{+}]$=60 mM, $[K^{+}]$=220 mM, $[OH^{-}]$=100 mM and $[SO_4^{2-}]$=100 mM.

2.2.2. Freeze granulation

The technique of freeze granulation was used to produce the spherical MgO colloidal probes that were needed for the AFM force measurements. The freeze granulation equipment is a PowderPro Freeze granulator of type LS-2 (Powder Pro, Göteborg). The pumping of a slurry through a nozzle into a beaker filled with liquid nitrogen produces frozen granules. The size and shape of these granules can be tuned by changing the slurry parameters, the slurry pump speed and the air pressure in the nozzle.

We used a concentrated suspension (60 wt.%) of a fine $Mg(OH)_2$ powder (Martin Marietta Magnesia type MH-10, 325 mesh) as our base slurry for the MgO sphere production. The $Mg(OH)_2$ powder was dispersed with 1 wt.% Ultra 1, and 1 wt.% PVA was added as a binder. The freeze granulation was performed with a pump speed of 30 rpm and an air pressure of 0.4 bar. Water was then removed through freeze drying without losing the spherical shape of the frozen drops. The next step was that the porous dry spheres were heated to 1700 °C for 1 h, which densified the spheres and resulted in a transformation from $Mg(OH)_2$ to MgO. Fig. 1 shows a typical MgO sphere attached to the AFM cantilever. The spheres that we used for the direct force measurements were in the size range 50–100 μm. The particles with smaller diameters were rejected because they were not spherical, and larger particles demands a stiffer cantilever, due to their higher weight, and this leads to a lower sensitivity in the force measurements.

2.2.3. Force measurements with AFM

The surface force measurements were performed on a Nanoscope IIIa atomic force microscope (AFM; Digital Instruments, USA) using the colloidal probe technique. Spherical MgO probes were attached to the apex of tipless, V-shaped cantilevers (Digital Instruments) using a minute amount of a fast curing epoxy (Araldite, Casco Akzo Nobel, Sweden). The AFM measurements were carried out in aqueous solutions using a sealed liquid cell. All the solutions were pH adjusted using ammonia, and the electrolyte solutions contained KCl (Merck, Suprapur).

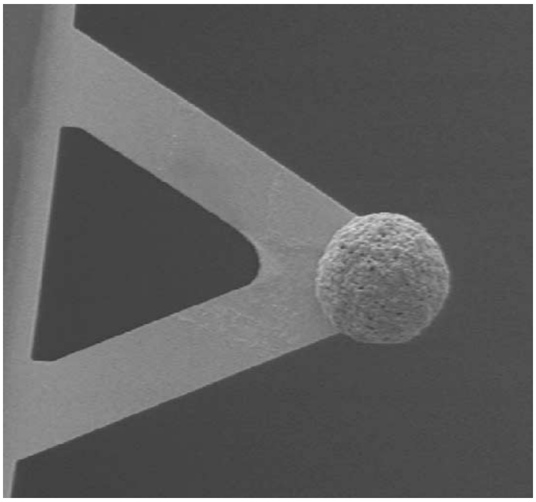

Fig. 1. SEM picture of an MgO sphere glued onto an AFM cantilever. The sphere has a diameter of about 65 μm and is used as a colloidal probe in the force measurements.

The normal surface forces between the MgO sphere and flat surface were evaluated by approaching and retracting the surfaces with a piezoelectric crystal scanner. The deflection of the cantilever was registered as a function of the movement of the scanner in the Z direction using a laser beam, reflected off the cantilever onto a photodiode detector. The raw data were transformed into true force curves by a series of manipulations. The zero force level and the point where the surfaces are in hard contact were established from the raw data. The spring constant of the cantilever was used to transform the deflection data into force units, and a force curve as a function of surface separation was obtained. Both attractive and repulsive forces can be measured, corresponding to negative and positive deflections, respectively.

The spring constants of the cantilevers were determined using the added mass technique [19]. The probes were rinsed with ethanol and distilled water and exposed to UV light for 30 min, prior to the experiments, to remove any organic contamination. The flat MgO surface was cleaned for 15 min in an air plasma cleaner (PDC-3XG, Harrick, USA), with subsequent rinsing in ethanol and water.

3. Results and discussion

The adsorption of superplasticizers at the solid–liquid interface induces interparticle forces that are of both steric and electrostatic origins. The range and magnitude of each contribution depends on several parameters, e.g., adsorbed amount, degree of dissociation of the polyelectrolyte backbone, net surface charge density and ionic strength [19]. Having a reactive system, i.e., cement, where the surface chemistry of the solid phase and the electrolyte composition changes with time creates a very complex situation. In this study, we have chosen to work with a nonreactive powder, MgO, that has been shown to be good model system for cement, displaying similar surface charge behaviour and adsorption properties at high pH [18,22].

The use of a nonreactive system is also warranted by the need to use surfaces with a small surface roughness in the colloidal-probe AFM measurements. The accuracy of the direct force measurements is determined by the surface roughness and geometry of the colloidal probe and the flat substrate. To accurately probe the short-range interactions inferred by the adsorption of superplasticizers, we need a probe-substrate system that has a surface roughness smaller than the range of the interaction of interest and a probe that has a well-defined geometry, preferably spherical.

We have developed a new, simple technique to produce spherical MgO probes in a size range between 5 and 100 μm. The spheres were produced using freeze granulation, followed by freeze drying and calcining at 1700 °C, as described in the Methods section above. This technique is very versatile, and it should be possible to use it to produce spherical particles of a wide range of inorganic materials. The first step in producing good-quality spheres is to have a well-dispersed slurry of the powder in question. A higher solids loading of powder in the slurry will give more dense spheres, and a powder with smaller average particle size will give smoother spheres. However, the slurry must be well dispersed with a good flowability because a stiff slurry with agglomerated particles will get stuck in the spray nozzle. Two parameters remain to vary once a good slurry is obtained: the pump speed and the air pressure in the spray nozzle. We have found that a lower pump speed and a higher air pressure decrease the average size of the spheres produced, but too high air pressure tends to deform the spheres produced into ellipsoids. In our experiments, we finally decided to use a slurry with 60 wt.% $Mg(OH)_2$ at the pump speed of 30 rpm and the air pressure 0.4 bar. This produced spheres of MgO with a good spherical shape in the size range 50 to 100 μm after sintering and calcining.

Direct force measurements were performed using the MgO colloidal probes attached to cantilevers and a flat MgO substrate attached to the piezoelectric scanner. The measured force–displacement data were converted into real force versus separation data following the principles of Ducker et al. [8]. This involves the determination of a zero-force position, a zero separation position, the slope of the constant compliance region and the spring constant of the cantilever. The forces, F, we report are always normalised by the radius, R, of the MgO spheres.

Prior to the force measurement, the MgO surfaces were subjected to a solution of the superplasticizer for 1 h to allow the polymers to adsorb. The polymer was adsorbed from a solution of 1000 ppm of the superplasticizer in an electrolyte of 1 mM KCl at pH 10. The superplasticizer solution was then exchanged for pure electrolytes at different ionic strengths, and the forces were measured. This procedure has been used in previous studies to elucidate the range and magnitude of the two contributions to the electrosteric repulsion [9–11,13,22]. Fig. 2 shows the force–distance curves for Conpac-30-coated MgO surfaces at three different ionic strengths in polymer-free solutions. The adsorption of the AAE–EO superplasticizer induced a repulsion that is sufficiently strong and long range to prohibit the surfaces from jumping into contact. Force measurements between MgO surfaces that have not been exposed to a superplasticizer solution results in an attraction and displays a final jump into contact due to the ubiquitous van der Waals attraction.

Two different regions of the force–distance curves can be identified when plotting the data in a semilogarithmic manner (see insert in Fig. 2). The short-range part of the curves, up to a surface separation of 10 nm, is not affected significantly by the salt addition, whereas the distance dependence of the long-range section varies with ionic

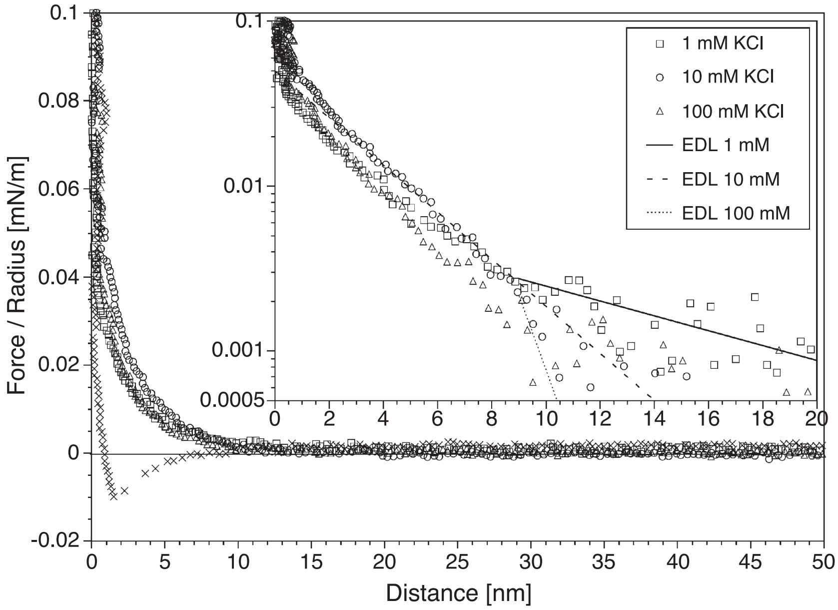

Fig. 2. AFM colloidal probe force curves for the modified polycarboxylate Compac 30, adsorbed on MgO surfaces. The forces are measured in electrolytes with the concentrations 1, 10 and 100 mM KCl at pH 10. The curve marked with × in the larger figure with linear scales corresponds to measurements in 1 mM KCl before the polymer was adsorbed onto the MgO surfaces.

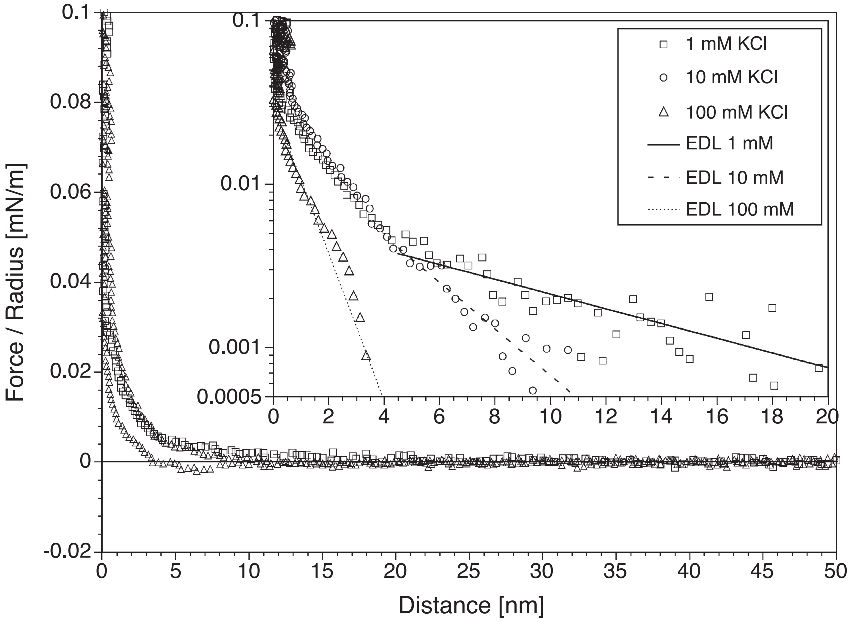

Fig. 3. AFM colloidal probe force curves for the modified polycarboxylate Ultra 1 adsorbed on MgO surfaces. The forces are measured in electrolytes with the concentrations 1, 10 and 100 mM KCl at pH 10.

strength. We have fitted this long-range part of the force–distance curves to the distance dependence predicted by theory for electrostatic interactions [20]. Electrostatic double-layer forces, EDL, decays exponentially following

$$F/R = Be^{-\kappa D}[\mathrm{N/m}] \tag{1}$$

where B is a constant, D is the distance between the surfaces, and κ is the Debye–Hückel parameter. The decay length of the electrostatic forces ($1/\kappa$) decreases with increasing electrolyte concentration according to

$$1/\kappa = \frac{0.304}{\sqrt{I}}[\mathrm{nm}] \tag{2}$$

at 25 °C in a 1:1 electrolyte, where I is the ionic strength.

The magnitude of the forces of the long-range tail is close to the resolution of the AFM, thus, there is a

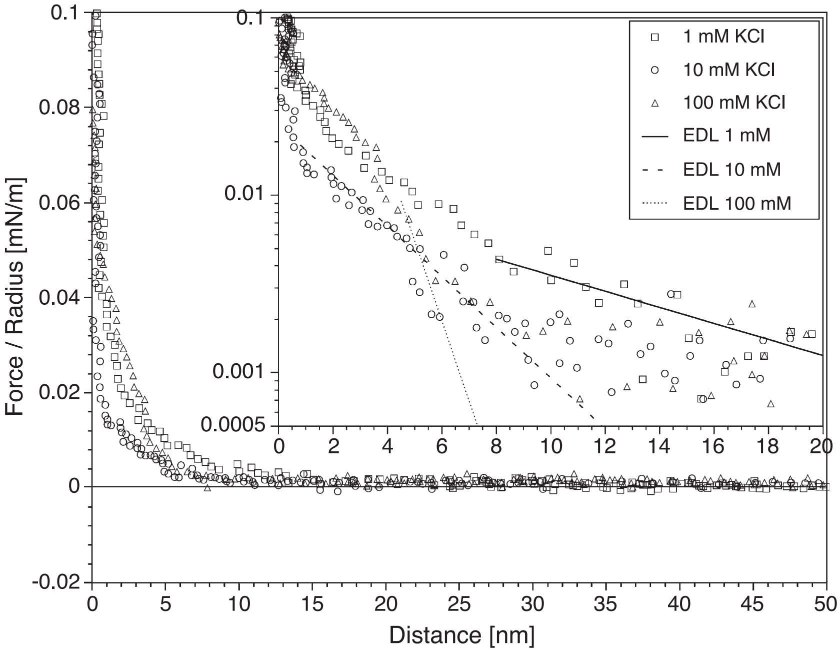

Fig. 4. AFM colloidal probe force curves for the lignosulfonate DP563 adsorbed on MgO surfaces. The forces are measured in electrolytes with the concentrations 1, 10 and 100 mM KCl at pH 10.

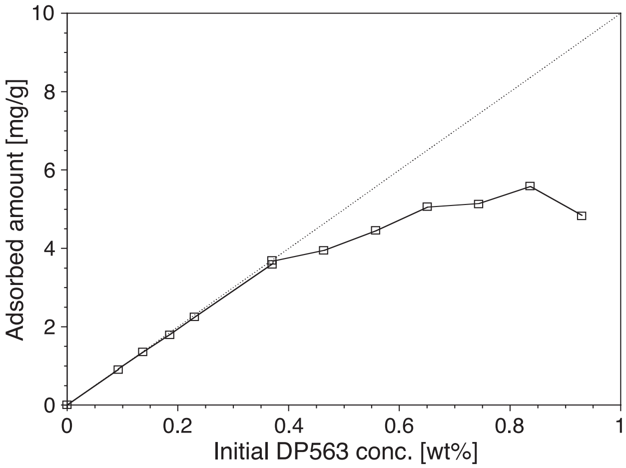

Fig. 5. Adsorption isotherm for the lignosulfonate DP563 on cement. The dotted line indicates 100% adsorption.

significant scatter in the data. However, it is clear that the range of the long-range repulsion decreases with increasing electrolyte concentration, suggesting that the long-range tail of the induced repulsion is of electrostatic origin. At closer separations, however, there is an additional repulsive contribution that cannot be attributed to electrostatic effects. This is most clearly seen at the highest ionic strength (0.1 M), where we measure a continuous and relatively long-range repulsion. The measured range of the repulsion of the superplasticizer-coated surfaces is ≈10 nm, which is significantly larger than the Debye length, $1/\kappa \approx 1$ nm, for a 0.1 M NaCl electrolyte. Hence, this part of the force–distance curves must be of steric origin, induced by the adsorbed superplasticizer. The fact that this part of force–distance curves is unaffected by the variation in ionic strength suggests that the conformation and thickness of the adsorbed superplasticizer, Conpac 30, do not vary much with ionic strength. Hence, the force–distance measurements indicate that the Conpac 30 superplasticizer adsorbs to the MgO surfaces with a layer thickness of the order of 5 nm.

Fig. 3 shows the force–distance curves for the other AAE–EO superplasticizer, Ultra 1, at the ionic strengths, 1, 10 and 100 mM KCl, in polymer-free solutions. Similar to the measurements on Conpac 30, we can identify two different regions of the force–distance curves for Ultra 1. Also for this superplasticizer, the long-distance tail is obviously of electrostatic origin because the measured forces display the predicted exponential distance dependence with a range determined by the ionic strength. The short-range steric interactions show some interesting features that differ significantly compared with the steric forces induced by the adsorption of Conpac 30. We find that the steric repulsion is more short range for Ultra 1; we estimate an adsorbed layer thickness of ≈1.5 nm at I=100 mM and ≈2.5 nm at 1 and 10 mM. Interestingly, the range of the steric repulsion appears to increase when the ionic strength is decreased, which suggests that the adsorbed layer swells. This indicates that the conformations and thickness of the adsorbed Ultra 1 layer are strongly influenced by electrostatic forces.

When the lignosulfonate superplasticizer, DP563, is adsorbed onto the MgO surfaces, we find that the force–distance curves for the three electrolyte concentrations, 1, 10 and 100 mM, coincide rather closely (Fig. 4). Although it is difficult to separate the electrostatic and steric contributions, it is clear that there has to be a significant steric contribution to the induced repulsion. If the repulsion had been dominated by electrostatics, the force–distance curve at the highest ionic strength (I=0.1 M NaCl) should have been much more short range (as indicated in the insert in Fig. 4). We have also measured the adsorption of the lignosulfonate on MgO. The adsorption isotherms clearly show that the lignosufonate DP563 adsorbs to MgO with a maximum adsorbed amount of about 8 mg/m^2 (Fig. 5).

We have summarised the direct force measurements in a schematic drawing of the inferred conformations of the adsorbed superplasticizers (Fig. 6). The anionic acrylic ester type polymers with grafted ethylene oxide chains probably adsorb in a conformation where the anionic backbone is adsorbed onto the MgO surface and the ethylene oxide chains are protruding into the solution. The characterisation of the polymers and the direct force measurements indicate that the shorter ethylene oxide chains of Ultra 1 lie quite flat on the surface, especially at the highest ionic strength. The slightly longer ethylene oxide chains of Compac 30 induce a more long-range steric repulsion, but the conformation is still rather compact. It is interesting to note that although the force results indicate a clear difference in the dispersion mechanisms between Conpac 30 and Ultra 1, both these polymers are commercial products that function well [21]. Somewhat surprisingly, there is a significant steric contribution to the repulsion induced by the adsorption of the lignosulfonate. This suggests that the polymer is adsorbed as a coil onto the MgO surface. Because lignosulfonate is a polymer with a relatively high degree of cross-linking, the

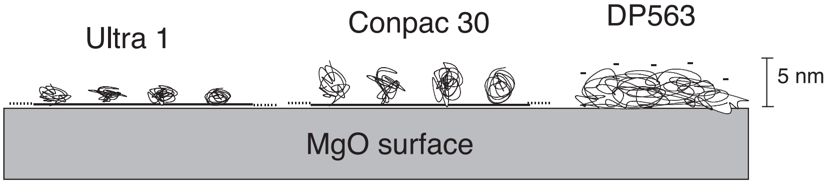

Fig. 6. Schematic drawing of the conformation of the polymers Ultra 1, Compac 30 and DP563 adsorbed on MgO.

adsorbed coils have a relatively high density and are thus expected to occupy a relatively small area on the MgO surface. This could explain why much more lignosulfonate usually has to be added to obtain a significant reduction in viscosity; more polymer is simply needed to fully cover the surface.

4. Summary and conclusions

A novel technique based on freeze granulation of a dense suspension of $Mg(OH)_2$, followed by sintering at 1700 °C, was developed to synthesize spherical MgO probes for atomic force microscopy. Direct measurements of the forces between such a spherical probe and a flat MgO substrate showed that the surfaces attract each other in an electrolyte that mimics cement water at pH 10. However, the adsorption of superplasticizers eliminates the attraction and induces a repulsive force between the surfaces. Analysis of the force–distance curves showed that superplasticizers of the modified anionic acrylic ester type with grafted ethylene oxide chains and a lignosulfonate induces an electrosteric repulsion with electrostatic and steric contributions. At the high ionic strengths of a cement slurry, the dominating stabilizing mechanism is steric stabilization. The range of the steric repulsion is closely related to the conformations of the adsorbed polymers, and the measurements suggest that the modified anionic acrylic ester type polymers with grafted ethylene oxide chains (AAE–EO) are adsorbed with the acrylic backbone to the surface and the PEG chains sticking out into the solution in a rather coiled conformation, with a characteristic thickness varying between 1.5 and 5 nm. Adsorption of the lignosulfonate induces a relatively long-range repulsion that is not much affected by a change in ionic strength. The direct force measurements suggest that the lignosulfonate adsorbs in a dense-coil conformation and thus induces a steric repulsion of significant range. The dense conformation can explain the need for a much higher dosage of lignosulfonates to fully cover the surface compared with the novel AAE–EO superplasticizers.

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