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Regular Article

Effect of Ca^{2+} ion concentration on adsorption of poly(carboxylate ether)-based (PCE) superplasticizer on mica

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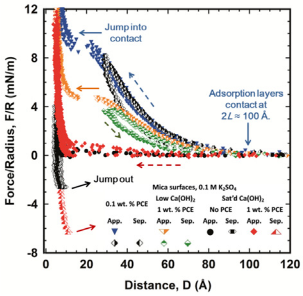
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Poly(carboxylate ether)-based (PCE) superplasticizers consist of a carboxylic acid backbone and grafted poly(ethylene glycol) (PEG) side chains. Ca^{2+} ion bridging mechanism is commonly purported to control PCE's adsorption on negatively charged cement particle surfaces in cement suspension, thus PCE was expected to adsorb on negatively charged surfaces in synthetic pore solutions via Ca^{2+}/—COO^- interactions.

Experiments: Adsorption behaviors of a commercial PCE on negatively charged mica were studied in aqueous electrolyte solutions by a surface forces apparatus.

Findings: Direct force measurements indicated that the PCE adsorbed onto mica from 0.1 M K_2SO_4 due to K^+ ion chelation by the ether oxygen units —CH_2CH_2O— on the PEG chains, but surprisingly did not adsorb from either 0.1 M K_2SO_4 with saturated $Ca(OH)_2$ or 0.1 M $Ca(NO_3)_2$. The adsorption in K_2SO_4 was weak, enabling the adsorbed PCE layers to be squeezed out under modest compression. Upon separating the surfaces, the PCE immediately achieved an identical re-adsorption. In high-calcium conditions, the PCE was highly positively charged due to Ca^{2+} ion chelation by PEG chains and backbone carboxylic groups —COO^-, and mica also underwent charge reversal due to electrostatic adsorption/binding of Ca^{2+} ions. Consequently, the interaction between mica and PCE was electrostatically repulsive and no PCE adsorption occurred. These findings can be explained by the complex interplay of ion chelation by PEG chains, electrostatic binding and screening interactions with charged surfaces in the presence of monovalent and divalent counterions, and ultimately charge reversal of both the charged surfaces and polyelectrolyte in high divalent ion conditions.

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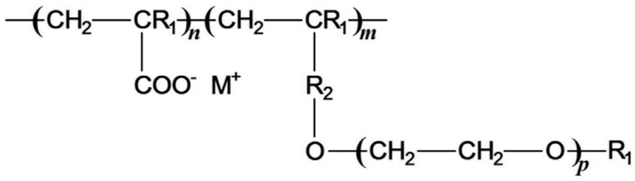
1. Introduction

Polyelectrolytes are extensively used as dispersing agents to improve the rheological properties of colloidal suspensions in a great variety of industries including paints, ceramic slurry processing, cement and concrete placement, cosmetics and pharmaceutical formulations [1,2]. In the case of cement, polyelectrolyte additives enable improved flowability at reduced water to cement ratios [3–5]. Lower water content in cement suspension contributes to higher mechanical strength and chemical resistance [6–9]. A variety of water-reducing admixtures, also called superplasticizers, are incorporated into high performance cement as essential components to improve effective flowability of hydrating cement paste. The mechanism for improved workability is thought to rely on adsorption of superplasticizers onto cement particle surfaces through their charged backbones. The adsorbed polymer layers prevent the agglomeration of cement particles by electrostatic and/or steric repulsions and release entrapped water to reduce the viscosity of cement suspension [10].

Comb-like (or bottle-brush) polymers have a linear backbone with grafted side chains [11–13]. Steric repulsion between bulky side chains can cause both the backbone and side chains to highly extend [14,15]. This unusual molecular configuration makes this class of polymers attractive for a wide range of applications such as cement dispersion [16], boundary friction modification [17], biomimetic lubrication [18] and protein adsorption [19]. Comb-like poly(carboxylate ether)-based (PCE) superplasticizers are the most common type of superplasticizer in aqueous systems [16]. They consist of a negatively charged carboxylic backbone and grafted side chains mainly composed of poly(ethylene glycol) (PEO or PEG), as shown in Fig. 1. PEG side chains are used because of their high osmotic repulsion in water and insensitivity to ionic strength [20]. In a hydrating cement system, the anionic backbones are electrostatically attracted onto positively charged cement particle surfaces (e.g., tricalcium aluminate (C_3A) and ettringite (AFt)) and are also thought to be bridged to negatively charged particle surfaces (e.g., tricalcium silicate (C_3S) and calcium silicate hydrate ($C-S-H$)) through electrostatic and entropic $Ca^{2+}/-COO^-$ interactions [16,21], with the side chains extending away from the particle surfaces into the cement pore solution. Consequently, the cement particles are dispersed primarily by the steric hindrance produced by the side chains. PCE polymers exhibit superior dispersing ability compared to conventional dispersants such as lignosulfonate and naphthalene or melamine formaldehyde condensates based superplasticizers [10]. Large bodies of research on zeta potential [5,6,8,10], adsorption isotherm [4–10] and rheological properties [4,5,10] of model cement suspensions and/or actual cement pastes have indicated the significance of added PCE dispersants, where enhanced flow properties were ascribed to strong steric repulsion of the side chains.

Atomic force microscope (AFM) [22,23] and surface forces apparatus (SFA) [24], two techniques for direct force measurement, have been widely employed to measure the interaction forces between polyelectrolyte adsorption layers in aqueous solutions [25–29]. Uchikawa et al. [30] used AFM for the first time to demonstrate the existence of steric repulsive force from the adsorbed superplasticizer on cement particle surfaces. Since this pioneering work, measurements of the steric force between PCE adsorption layers have been carried out by AFM and SFA. Ferrari et al. [31] used an AFM silicon tip to detect the interaction force with calcium silicate and ettringite surfaces in Milli-Q water with PCE. The measured force was very small, suggesting little PCE's adsorption under these conditions. In contrast, significant repulsion between mica surfaces was measured in aqueous PCE solution under both acidic and alkaline conditions by SFA [32]. Adhesion was observed upon separation in low PCE concentration conditions, which was explained by the bridging of the PCE molecules between the two mica surfaces through hydrogen bonding. Kauppi et al. [1] measured the interaction forces between MgO surfaces in KCl solution with anionic acrylic ester-ethylene oxide (AAE-EO) copolymer at pH 10 using AFM. Analysis of the force-distance curves revealed that the measured force had a long-range electrostatic component and a short-range steric component, suggesting that the acrylic backbone adsorbed onto the MgO surface with the PEG chains protruding into the solution in a coiled conformation. Ferrari and coworkers [8] also employed AFM to study the interactions between a silicon nitride tip and multiple substrates (calcite, quartz, mica and MgO) in Milli-Q water, K_2SO_4 and KOH solutions with PCE, respectively. Their force measurements showed that the addition of PCE eliminated attractive jump-into-contact behavior and induced repulsive force between the tip and substrate in all cases. Along with zeta potential measurements and adsorption isotherms, they concluded that the PCE did not adsorb on negatively charged substrates (calcite, quartz and mica) but adsorbed on the positively charged silicon nitride tip and MgO in these aqueous monovalent electrolyte conditions. However, reports on establishing PCE's adsorption through divalent cation bridging are very limited in the literature. Flatt and coworkers [2] investigated the interactions between $C-S-H$ surfaces in 5 mM $Ca(OH)_2$ solution with PCE at different ionic strengths (adding 10 or 100 mM NaCl) by AFM, but the adsorption of PCE on C—S—H could not be confirmed from the measured interaction forces. Similarly, direct measurements of adsorption of polyelectrolyte or comb-like polymer due to divalent counterion bridging are very sparse, though this mechanism is purported to explain phenomenological changes in such systems.



$$-(CH_2-\underset{COO^-\ M^+}{CR_1})_n-(CH_2-\underset{R_2-O-(CH_2-CH_2-O)_p-R_1}{CR_1})_m-$$

R_1 : H or CH_3
R_2 : $(CH_2)_q$ or C=O, q = 1–4
M^+ : alkali or alkaline earth metal cation

Fig. 1. Molecular structural schematic of the PCE polymer.

The goal of the present study was to determine the adsorption behavior of a commercial PCE on negatively charged mica in synthetic pore solution containing abundant Ca^{2+}, K^+, SO_4^{2-} and OH^- ions that mimics actual cement suspension conditions. Direct force measurements at the molecular level by SFA showed that the PCE polymer adsorbed onto mica from 0.1 M K_2SO_4 solution but did not adsorb from either the synthetic pore solution or 0.1 M $Ca(NO_3)_2$ solution. This work is relevant to understanding and improving PCEs as cement/concrete admixtures, not only in terms of their action as dispersing agents, but also their interaction with aggregate minerals such as alminosilicate clays. More broadly, the work increases our understanding of the properties of adsorbed polyelectrolyte in high-salt conditions in the absence and presence of divalent counterions.

2. Experimental

2.1. Materials

A commercial cement dispersant PCE polymer was utilized as received from GCP Applied Technologies (Cambridge, USA): 55 wt