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Experimental determination of the effective anionic charge density of polycarboxylate superplasticizers in cement pore solution

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ABSTRACT

The specific anionic charge density of polycarboxylate superplasticizers can be determined experimentally by titration with a cationic polyelectrolyte. In this study, the anionic charge densities of several polycarboxylates based on methacrylate ester chemistry were measured in aqueous solution at pH 7 and 12.6, resp., and in cement pore solution. The anionic charge of the polycarboxylates increases with increasing pH value as a result of deprotonation of the carboxylate groups in the polymer backbone. Addition of Ca^{2+} ions generally causes a decrease of the anionic charge density. The reduction in anionic charge varies and depends on the architecture of the polycarboxylate. The effect results from the binding of calcium ions by the carboxylate groups, both through complexation and counter-ion condensation. Consequently, the effective anionic charge density of polycarboxylates in cement pore solution can differ significantly from the charge density which is calculated based on the chemical composition. Generally the $-COO^-$ functionality may coordinate Ca^{2+} as a monodentate or bidentate ligand. The type of coordination depends on the steric accessibility of the carboxyl group. In PC molecules possessing high side chain density, the $-COO^-$ group is shielded by the side chains and coordinates as bidentate ligand, producing a neutral Ca^{2+}–PC complex. Accordingly, this type of PC shows almost no anionic charge anymore in cement pore solution. In PCs possessing high amount of $-COO^-$, Ca^{2+} is coordinated monodentate, resulting in an anionic complex. Consequently, this type of PC shows significant anionic character in pore solution. Its adsorption behaviour is determined by a gain in enthalpy which derives from the electrostatic attraction between the PC and the surface of cement. This way, by utilizing the relatively simple method of charge titration, it is possible to assess the electrostatic attraction which, besides entropy gains, is the driving force behind the adsorption of polycarboxylates on the cement surface and thus determines their effectiveness as dispersing agent. The findings are generally applicable to other anionic admixtures used in cement.

1. Introduction

Polycarboxylates (PCs) are commonly used as superplasticizers to disperse cement particles in concrete and mortar [1]. They are comb polymers which consist of a negatively charged backbone with carboxylic groups and grafted side chains mainly composed of polyethylene oxide units. The charged backbone adsorbs on the surface of the hydrating cement particles. The non-adsorbing graft chains extend away from the cement surface into the pore solution. As a result, the cement particles are dispersed via a steric repulsion mechanism caused by the side chains [2–4]. The steric mechanism was confirmed via zeta potential measurements [5,6]. The adsorption process of PCs on the surface of hydrating cement is a subject of ongoing research. It is generally accepted that the anionic charge density of a PC macromolecule determines the electrostatic interaction with cement. Thus, it represents a major factor which influences its adsorption behaviour and, in consequence, its dispersing power [7]. At the same molecular weight, PC molecules with high anionic charge density are expected to adsorb in higher amount before they reach the plateau (saturation point) of the adsorption isotherm, and vice versa. In previous studies, the dispersive force of PC molecules often was correlated with their anionic charge density calculated from the chemical formula. This approach ignores, for example, the high concentration of calcium ions present in the cement pore solution which may significantly affect the anionic charge of the PC. Additionally, PC adsorption is influenced by entropy changes derived from immobilization of the macromolecule adsorbed on the binder surface and the simultaneous release of a large number of water molecules and ions into the pore solution replaced on the surface by PCs. Thus, adsorption of a PC generally can be described as an exchange process which is determined by the exchange enthalpy as well as entropy. Adsorption occurs if the resulting GIBBS free exchange energy is negative (Eq. (1)). The enthalpic contribution mainly is

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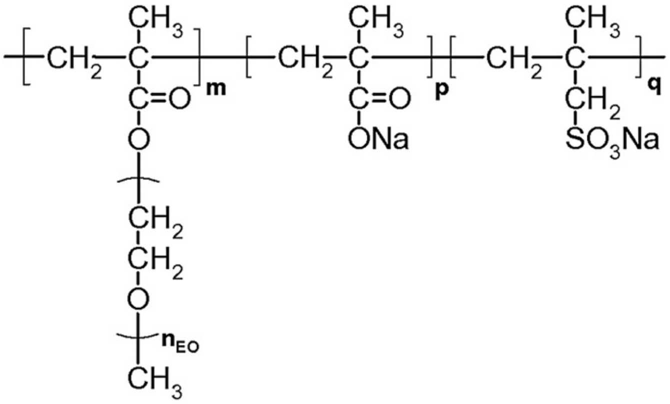

Fig. 1. Chemical structure of the synthesized polycarboxylate copolymers.

determined by the electrostatic attraction forces between PCs and the surface whereas the entropy change depends on the molecular weight of PC and the number of H_2O molecules and ions desorbed from the surface.

$$\Delta G = \Delta H - T \bullet \Delta(\Delta S) \tag{1}$$

To profoundly understand the electrostatic attraction forces between a PC molecule and the cement surface (and thus the enthalpic contribution to the GIBBS exchange energy during adsorption), it is necessary to have experimental data on the anionic charge density of PC as it exists in cement pore solution. For this reason, we introduce a simple method to determine the effective anionic charge of PCs in cement pore solution. This method allows to investigate the influence of pH and calcium ions on the anionic charge of superplasticizers and other anionic admixtures. For this study, we synthesized four PC samples in our laboratory and compared their experimentally determined and calculated specific anionic charge densities.

2. Materials and methods

2.1. PCE preparation

Four methacrylic acid-co-ω-methoxy polyethylene glycol (MPEG) methacrylate polymers with side chains consisting of 17 and 45 ethylene oxide units, resp. (n_{EO} = 17 and 45) and different side chain densities (molar ratios of methacrylic acid: MPEG methacrylate ester 1.5:1 and 6:1, resp.) were prepared by radical copolymerisation in water using sodium peroxodisulphate as initiator and methallyl sulfonic acid as chain transfer agent [8]. The chemical structure of the synthesized polycarboxylates is illustrated in Fig. 1. After copolymerisation, all aqueous copolymer solutions were neutralized with NaOH and dialyzed over 2 days using a 6000–8000 Da cellulose cut-off membrane (Spectra/Por, Spectrum Laboratories Inc.).

The synthesized copolymers were characterized by gel permeation chromatography, using Waters 2695 GPC separation module containing a 2414 RI detector (Waters) and a Dawn EOS 3 angle light scattering detector (Wyatt Technology). A d*n*/d*c* of 0.135 mL/g was used to determine absolute molar masses [9]. Ultrahydrogel columns 500, 250, 120 (Waters) with an operating range (PEO/PEG) of M_w between 100 and 1,000,000 Da were used. Eluent was 0.1 N $NaNO_3$ at pH 12 adjusted by NaOH. The GPC data is shown in Table 1.

Table 1
Molar composition and GPC data for the polycarboxylate samples used in the study

Copolymer	Molar ratio methacrylic acid:ester	Side chain n_{EO}	M_w (g/mol)	M_n (g/mol)	Polydispersity Index (M_w/M_n)	Hydrodynamic polymer radius $R_{h(avg)}$ (nm)
17PC6	6:1	17	157,600	67,320	2.3	10.1
17PC1.5	1.5:1	17	141,300	43,160	3.5	8.1
45PC6	6:1	45	156,400	43,680	3.6	9.9
45PC1.5	1.5:1	45	170,600	60,500	2.8	9.5

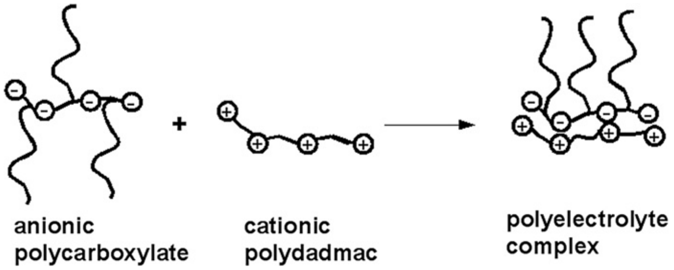

Fig. 2. Principle of charge neutralization during titration of a polycarboxylate polymer with cationic polydadmac.

2.2. Cement

OPC (CEM I 32.5 R) from HeidelbergCement, Rohrdorf (Germany) plant was used to prepare a cement paste at a water to cement (w/c) ratio of 0.5. Phase composition of the cement was determined by X-ray diffraction analysis including Rietveld refinement. The results were as follows (mass %): C_3S 54.6%, C_2S 20.6%, C_3A cubic 6.1%, C_3A orthorhombic 2.8%, C_4AF 8.5%, free CaO 1.7%, $CaSO_4 \bullet 1/2H_2O$ 2.2%, $CaSO_4$ 2.4%, $CaSO_4 \bullet 2H_2O$ 0%. Blaine value was at 3280 cm^2/g. From the cement paste, a filtrate was produced by filtration of the slurry with a vacuum pump. The Ca^{2+} content in the pore solution was analysed by atomic absorption spectroscopy and was found at 1 g/L. The pH of the pore solution was 12.6.

2.3. Charge titration

The method used in this study to determine the anionic charge density of superplasticizers is polyelectrolyte titration [10]. This method is based on the measurement of the streaming current produced by charged polymer molecules adsorbed on a moving surface. By addition of a second polyelectrolyte with opposite charge, charge neutralization is achieved from the formation of a

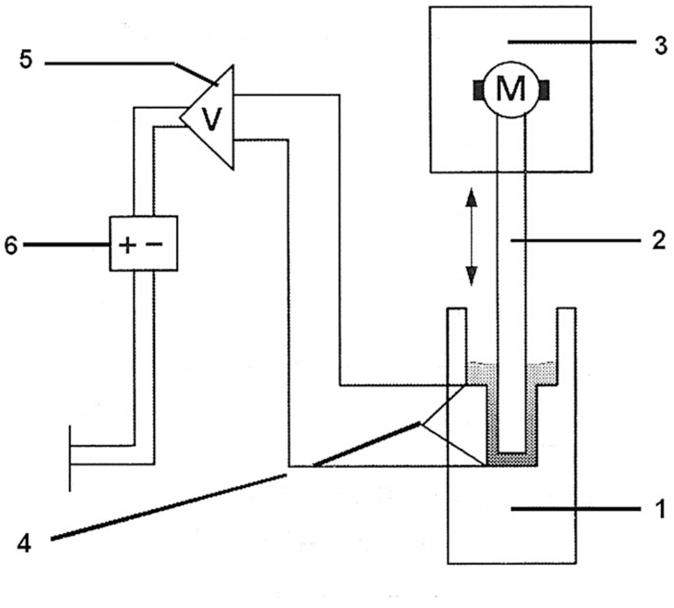

Fig. 3. Schematic of the charge titration device.

polyelectrolyte complex. Fig. 2 illustrates the principle of charge neutralization during polyelectrolyte titration of a polycarboxylate polymer with cationic poly diallyl dimethylammonium chloride (polydadmac). Charge neutralization is accomplished when the streaming current is zero (isoelectric point).

The anionic charge of the PCs was measured using a Mütek PCD 03 pH titrator. The build-up of the Mütek charge titration device is illustrated in Fig. 3. The device consists of a measuring cell (1) with fitted plunger (2). The aqueous sample is filled into the measuring cell. Dissolved polycarboxylates adsorb via van der Waals forces on the surface of the plunger and on the wall of the cell. The plunger is powered by a motor (3) and oscillates vertically. During the oscillating movement of the plunger, free counter-ions are removed from the immobilized adsorbed polycarboxylate macromolecules. The counter-ions induce a current at the electrodes (4). This current is amplified (5) and finally displayed (6).

Anionic charge densities of the PC samples were determined in aqueous solution at (a) pH 7.0 and 12.6, resp., (b) at pH 12.6 in the presence of 1 g/L Ca^{2+}, and (c) in the filtrate of the cement paste (cement pore solution). Measurements were taken from PC solutions as follows: pH 7: add 0.1 mmol/L HCl to a 0.2 g/L PC solution until pH changes from around 9 to 7; aqueous pH 12.6: add 1.6 g NaOH pellets to 1 L deionised water, then add 0.5 mL of 40 M-% PC solution (this produces a PC concentration of 0.2 g/L); calcium loaded pH 12.6: add 3.675 g $CaCl_2 \bullet 2H_2O$ (1 g/L Ca^{2+}) and 1.6 g NaOH pellets to 1 L deionised water, then add 1.25 mL of 40 M-% PC solution (this produces 0.5 g PC/L). In a typical experiment, 10 mL of the sample solution were filled into the measuring cell and titrated with 0.001 N polydadmac solution (Mütek) until the isoelectric point was reached. Polydadmac solution was added continuously from a burette by an automatic feeder system according to a preset titration program (method 1) controlled by the decrease of the streaming potential. For preparation of the cement pore solution, 300 g of cement was added within 1 min to 150 mL of water (w/c = 0.5). Then, the paste was manually stirred over 2 min and filtrated through a blue ribbon filter (Schleicher & Schuell, Ø 125 mm) using a vacuum pump (10^{-3} Torr). 40 M-% PC solution was added to obtain the polycarboxylate concentrations described below. With increasing ionic strength of the solution, higher PC concentrations must be employed to obtain stable and reproducible results. In cement pore solution, this is particularly important when measuring PCs possessing low amount of methacrylic acid. When using cement pore solution as solvent, the potential often became unstable when approaching the isoelectric point. Obviously, the fluctuations were caused by the high ionic strength of the solution. Reproducible results were obtained when polydadmac was added at a slower rate of 0.1 mL portions per titration step until a potential of +3 mV was reached. Then the time interval between two titration steps was increased to 10 s. The volume of polydadmac solution consumed in each experiment was obtained by determining the intercept point between the regression line and the isoelectric point. From the consumption of polydadmac, the specific anionic charge density of the polycarboxylate can be calculated. 1 mL of 0.001 N polydadmac solution corresponds to an anionic charge density of 500 μeq/g polymer at a PC concentration of 0.2 g/L. In cement pore solution, PC concentrations were 0.5 g/L (17PC6), 2 g/L (17PC1.5 and 45PC6) and 5 g/L (45PC1.5), resp. The experimental anionic charge density can be calculated according to Eq. (2).

$$\text{exp. anionic charge density(eq/g)} = \frac{\text{consumption of polydadmac solution(L)} \bullet \text{concentration of polydadmac(eq/L)}}{\text{mass of PC in the sample(g)}} \quad (2)$$

3. Results and discussion

At first, the anionic charge of the PCs was calculated based upon their molar composition and assuming complete deprotonation of the carboxylic groups. Next, this data was compared with experimentally determined anionic charges measured at pH 7, pH 12.6, pH 12.6 plus 1 g/L Ca^{2+}, and in cement pore solution.

3.1. Calculated anionic charge of PC

At pH ≥ 10, polymethacrylic acid is fully deprotonated [11]. Thus, in highly alkaline cement pore solutions, the theoretical anionic charge of PCs can be calculated assuming that only COO^- functionalities are present. This theoretical charge density was calculated according to Eq. (3), where M_u is the molar mass of one repeating unit in the polymer chain, and n_{COO^-} represents the number of COO^- functionalities per repeating unit. n_{COO^-} corresponds to the molar ratio of methacrylic acid and methacrylate ester present in the polymer.

$$\text{calculated anionic charge density of polymer(eq/g)} = \frac{n_{COO^-}}{M_u} \quad (3)$$

The calculated anionic charge densities of the PC samples are presented in Fig. 4. As expected, the anionic charge density of the PC molecules generally decreases with increasing ester content in the polymer. For example, the anionic charge of 17PC1.5 is much less compared to 17PC6 which contains significantly more methacrylic acid. A similar trend exists when the side chain becomes longer. Therefore, on an equal gram basis, 45PC1.5 is less anionic than 17PC1.5. Generally, the calculated anionic charge densities of the PCs appear to be relatively high. They do not always correspond well with the known adsorption behaviour of some PCs. For example, 17PC6 adsorbs in lower amount than BNS, in spite of their similar anionic charge densities. The calculated anionic charge density of BNS is 4545 μeq/g versus 4418 μeq/g for 17PC6. In the OPC cement paste mixed at w/c = 0.5 and containing 0.2 M-% polymer by weight of cement (bwoc), however, 1.44 mg 17PC6/g cement and 1.78 mg BNS/g cement were found to adsorb. This difference is beyond the experimental margin of error and indicates that the theoretical anionic charge density of a polymer does not always allow to predict its adsorption behaviour.

3.2. Experimentally determined anionic charge of PC

In the following, the specific anionic charge densities of the polycarboxylate samples were experimentally determined under various conditions.

3.2.1. Effect of pH on anionic charge of PC

The results obtained for the anionic charge density of the synthesized PCs, measured at pH = 7 and 12.6, resp., are shown in Fig. 4.

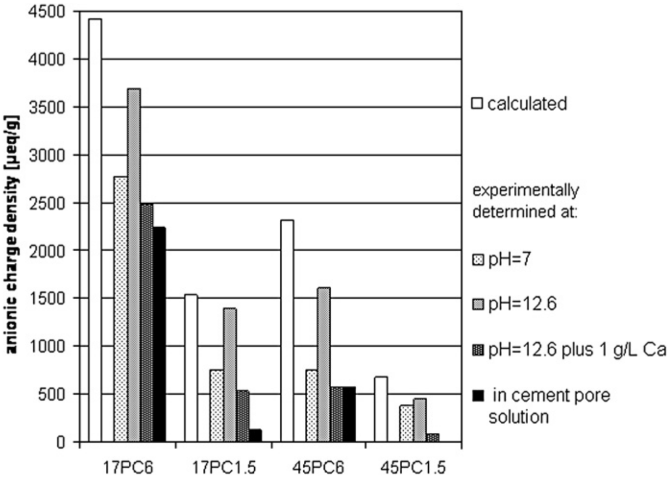

Fig. 4. Calculated and experimentally determined specific anionic charge densities of the synthesized polycarboxylate samples.

Generally, the anionic charge density of all polycarboxylate samples increases when the pH is raised from 7 to 12.6. The increase is between 20 and 110%, depending on the molecular structure. The reason for this effect is deprotonation of the carboxylic groups. Via potentiometric titration, other authors determined the portion of protonated carboxylic groups in polyacrylic acid, polymethacrylic acid and an acrylic acid–maleic acid copolymer at pH 7 to be around 20–40%. It varies with the ionic strength of the solution and the polymer concentration [12–14]. This portion will further decrease at higher pH. In our case, the experimentally determined anionic charges of the PC polymers never reached the values of their calculated charge, indicating that counter-ion condensation by Na^{+} ions is occurring. Na^{+} ions surrounding the negatively charged polymer backbone are not completely displaced by polydadmac. Thus, the consumption of polydadmac to achieve charge neutralization is less than the theoretically predicted. Another potential reason for the discrepancy is the steric effect of the side chains. In a highly coiled PC molecule, some carboxylate groups might be in the inner sphere of the macromolecule. Then, their charge is too distant for the polydadmac which interacts more with the –COO^{-} functionalities located on the surface of the macromolecule. The interaction between PC and a charged polyelectrolyte such as polydadmac is comparable with its interaction with the charged surface of hydrating cement. Therefore, experimentally determined anionic charge densities seem to represent better the effective electrostatic interaction between PCs and cement hydrates.

3.2.2. Effect of calcium ions

Addition of 1 g/L Ca^{2+} to the PC solutions at pH 12.6 results in a significant decrease of the experimentally determined anionic charge densities (Fig. 4). The decrease is between 35 and 80%. Surprisingly, it is extremely strong for PCs possessing low anionic charge density and high side chain density. This type of PC is commonly used in ready-mix concrete because of its superior slump retaining property. The effect is due to strong interaction between the carboxylic groups and the calcium ions. Polycarboxylates can form calcium chelate complexes of various compositions [15–17]. The calcium binding capability of a PC depends on the number of carboxylate groups and their steric position along the polymer trunk. Thus, the polymer architecture plays a significant role for the effective anionic charge of a PC in cement pore solution. As mentioned above, polymers with low amount of carboxylate groups (e.g. 17PC1.5 or 45PC1.5) show, in relative terms, a stronger reduction in anionic charge than PCs with high content of carboxylate groups. This can be explained by the steric accessibility of the –COO^{-} functionalities. Generally, for carboxylate groups, two different types of coordination with Ca^{2+} have been found [18]: a) monodentate, in which Ca^{2+} coordinates with only one oxygen atom of the –COO^{-} groups in an end-on configuration; this way, COO^{-} is a monodentate ligand for Ca^{2+}; or b) bidentate, in which Ca^{2+} is bound to both oxygen atoms of a –COO^{-} functionality in a side-on configuration, with the –COO^{-} group being a bidentate ligand. These different types of coordination are illustrated in Fig. 5. In a Ca^{2+}–PC complex with monodentate coordination of 4 –COO^{-} groups, the resulting charge of the chelate complex is −2 since each carboxyl oxygen atom carries a negative charge of −0.5. In Ca^{2+}–PC complexes with bidentate coordination of –COO^{-}, however, the resulting charge of the complex is zero (Fig. 6). This way, the type of coordination between –COO^{-} and Ca^{2+} greatly impacts the final charge resulting from the interaction between Ca^{2+} and PC. For monodentate binding of calcium ions, the preferred coordination number of Ca^{2+} was found to be 6 whereas in complexes containing –COO^{-} as bidentate ligand, the preferred coordination numbers are 7 or 8 [18]. In both cases, the remaining ligands are water molecules and the oxygen donor atoms in the polyethylene glycol side chains. Ca^{2+} complexation in PCs may occur either through intra- or intermolecular coordination of COO^{-} ligands in the polymer backbone. In PCs possessing a low side chain density and short side chain length with adjacent COO^{-} groups (e.g. 17PC6), Ca^{2+} is expected to preferably coordinate monodentate (Fig. 7). In this case, four carboxylate groups can easily chelate one Ca^{2+} ion. Because of this high amount of coordinating –COO^{-} groups, the charge of the resulting Ca^{2+}–PC complex remains negative and the decrease of the anionic charge from Ca^{2+} interaction is not so strong. In PC polymers with high side chain density and long side chain (e.g. 45PC1.5), however, the accessibility of the –COO^{-} ligands is stereochemically restrained. Thus, for steric reasons, calcium binds to the carboxylate groups in a bidentate way (Fig. 7). Consequently, the amount of Ca^{2+} bound per –COO^{-} group is considerably higher and the reduction of the anionic charge density, in relative terms, is much stronger. Such way, the differences in the decrease of the anionic charge densities of the PCs found in cement pore solution can be explained.

Fig. 5. Schematic illustration of different types of coordination between Ca^{2+} and –COO^{-} groups: –COO^{-} as monodentate (left) and as bidentate ligand (right).

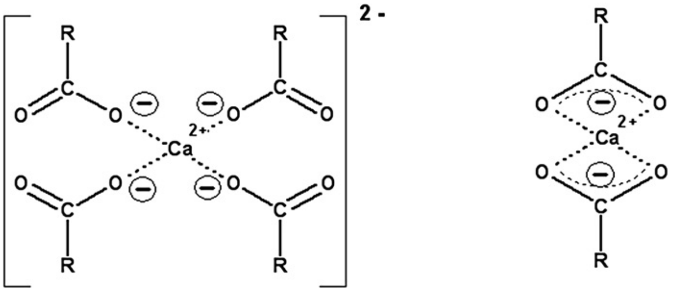

Fig. 6. Effect of coordination type in Ca^{2+}–carboxylate complexes on their electrical charge: monodentate coordination leading to a Ca^{2+}–tetracarboxylate complex possessing negative charge (left) and bidentate coordination, resulting in a neutral Ca^{2+}–bicarboxylate complex (right); note that Ca^{2+} will coordinate additional ligands not shown here (e.g. water molecules) to achieve coordination numbers between 6 and 8.

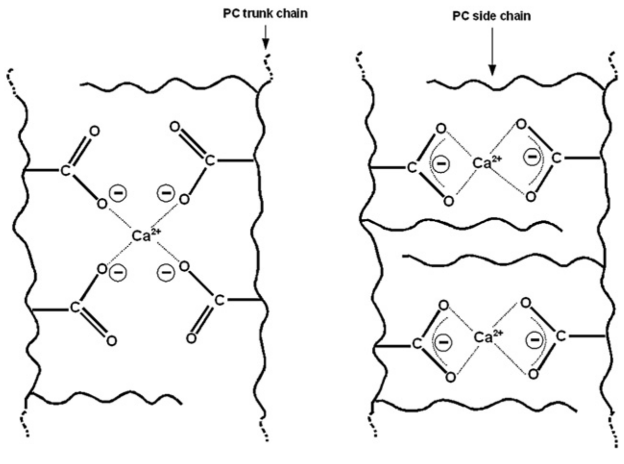

Fig. 7. Schematic illustration of monodentate complexation of Ca^{2+} by two PC strains possessing low side chain density (left) and bidentate complexation of Ca^{2+} by two PC trunks showing high side chain density (right).

3.2.3. *Effect of cement pore solution*

In cement pore solution, the anionic charge densities of the PCs are even more reduced. Again, PCs with high side chain density are most affected. For example, polycarboxylate 45PC1.5 shows almost no more anionic charge in pore solution. Obviously, there is a combined effect of calcium complexation and counter-ion condensation. Counter-ion condensation on polyelectrolytes is known to play a major role in fluids possessing high ionic strength, such as cement pore solution. Monovalent (e.g. Na^+) and divalent cations (e.g. Ca^{2+}) are attracted to the anionic PC backbone due to electrostatic forces. The charged polymer backbone then is surrounded by a cloud of counter-ions. As a result, the effective anionic charge is decreased [19]. This way, counter-ions may reduce the electrostatic attraction between the dissolved PC and the binder surface and thus can impact its adsorption behaviour. It has also been reported that polyethylene oxide can interact with Ca^{2+} through the free electron pairs of the ether oxygen in the absence of carboxylate groups. Thus, the anionic charge of polycarboxylates can be reduced further [20,21]. The result clearly demonstrates that the effective anionic charge of a PCs in cement pore solution as it is experienced by a cationic particle approaching the polymer, can differ substantially from the theoretical charge derived simply from its chemical composition. It also hints at the fact that the driving force behind adsorption of these polymers is a gain in entropy, rather than electrostatic attraction. Generally, the adsorption process is driven either through a gain in enthalpy or in entropy. The gain in enthalpy is determined by the electrostatic attraction between the polyelectrolyte and the surface. The entropy gain, in comparison, results from the release of water molecules and counter-ions bound on the binder surface and/or to the polymer. Both parameters determine the adsorbed amount of a superplasticizer molecule on the cement surface. Thus, adsorption of PC macromolecules possessing very low anionic charge density in cement pore solution (e.g. 45PC1.5) mainly is entropy driven, with the release of counter-ions contributing much to the entropy gain. In the case of PCs with high anionic charge density in cement pore solution (e.g. 17PC6), adsorption is more enthalpy driven. This way, the experimental determination of the anionic charge density of PCs in cement pore solution allows to distinguish whether the adsorption process of a specific PC molecule is more enthalpy or entropy driven.

4. Conclusions

Our experiments indicate that, in cement pore solution, polycarboxylate molecules exist as macromolecules with varying amounts of calcium ions bound to their main chain by ligand complexation. Furthermore, the polymer trunk is surrounded by a cloud of cations resulting from counter-ion condensation. Depending on the specific polymer architecture, these effects can lead to very low anionic charge densities which may reduce adsorption capability and, consequently, the dispersing power of a PC. During the adsorption process, the cations from counter-ion condensation and at least some of the calcium bound by chelation is released in favour of stronger bonds between the carboxylate groups and the calcium atoms present on the binder surface. Our experiments provide new insights into the processes determining the general adsorption behaviour of superplasticizers. By utilizing the relatively simple method of charge titration, the enthalpic contribution to the adsorption of an admixture molecule can be assessed. Knowledge of the actual anionic charge density of PCs in cement pore solution also may help to explain why, in multi-admixture systems, some PCs possessing relatively high theoretical anionic charge surprisingly do not adsorb well in the presence of other anionic admixtures possessing a relatively low anionic charge. Thus, this information can assist to solve admixture incompatibilities. The findings bear great significance for all anionic admixtures with calcium chelating capability of which many are used in concrete and mortar.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cemconres.2008.09.001.

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