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Synthesis of phosphonated comb-like copolymers and evaluation of their dispersion efficiency on CaCO$_3$ suspensions part II: Effect of macromolecular structure and ionic strength

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A B S T R A C T

The aim of this paper is to investigate effects of macromolecular structure and ionic competition phenomena induced by an increase of ionic strength on the dispersive action of new superplasticizers. These superplasticizers were synthesized and their structure is based on that of polycarboxylates. These superplasticizers are comb-like copolymers with phosphonic acids. Macromolecular parameters studied are the monomer repartition along the carbon backbone and the chain length. Ionic strength is increased either by adding sulfate or nitrate ions. The effects of these factors are then investigated using adsorption, stability and rheology results. It appears that statistical copolymers with phosphonic acids having the shortest chain length are the most efficient in terms of fluidity improvement even in the presence of sulfate or nitrate ions.

1. Introduction

The incorporation of additional components (admixtures and mineral additions) to cementitious materials aims to control the reactivity of the material, as well as its fresh and hardened behavior [1,2]. This incorporation made it possible to formulate concretes that were previously impossible to produce, such as high-performance concretes (HPC) and self-compacting concretes (SCC) [3,4]. Superplasticizers or High Range Water Reducers (HRWR) are among the admixtures commonly added to the cementitious materials. These admixtures allow reducing the water content and thus improving the mechanical properties and durability of the hardened concrete while maintaining workability, or without changing the water content, they allow improving the workability of the fresh concrete by increasing its fluidity.

The most efficient superplasticizers are polycarboxylates PCEs, which allow reducing the water content by 40% [5]. These admixtures are a class of synthetic *comb*-like copolymers possessing poly(ethylene oxide) (PEO) side chains and anionic moieties [6]. In addition to their high efficiency, PCEs also have a good compatibility with different type of cements. In fact, the dispersive action of superplasticizers, such as PCEs, can be influenced by on the chemical composition of the pore solution of cement paste. This chemical composition can vary depending on the type of cement, which can cause incompatibilities with superplasticizers leading to a loss of fluidity [2,3,7]. It is then possible to modify the macromolecular structures of PCEs to avoid these incompatibilities phenomena by adapting their structural parameters (molecular mass, side chain length and ratio, nature and distribution of anionic moieties) to the type of cement [8].

It is well known that sulfate concentration in the pore solution of cement paste significantly affects the action of superplasticizers [9–11]. Superplasticizers can be consumed to form organo-mineral phases (OMP) in the early stages of hydration at low sulfate concentration [12] [13]. Furthermore, ionic competition at high sulfate concentration can occur [14]. The adsorption of superplasticizer on cement particles can be hindered, resulting in loss of the dispersive action.

In the context of nuclear wastes storage, one of the main concerns is the behavior of fresh concrete in the presence of high concentration of nitrates [15]. At such concentration, the phenomenon of ionic competition could potentially take place. Recent studies have been conducted to develop new superplasticizers more resistant to ionic competition [16,17]. These new superplasticizers, based on the PCEs structure, were designed by changing the nature of anionic moieties, with dicarboxylate function [18], or phosphonic acid functions instead of carboxylic acids [19,20]. Pourchet et al. have modified the monomer distribution along the macromolecule backbone, resulting in a gradient

copolymer [17]. These new PCEs revealed a good dispersive action and an improved sulfate resistance.

In our previous work [21], the synthesis of several comb-like copolymers with phosphonic acid moieties and PEG side chains was described. These copolymers were tested on calcite suspensions in alkaline conditions through adsorption measurement, stability with Turbiscan MA2000, and rheology. Calcite suspensions are commonly used as a model material to overcome the complexity of cementitious materials [22,23] . In fact, physical properties of calcite suspensions are close to that of cement pastes. It has to be kept in mind that the use of calcite suspensions cannot account for the effects of early stages of hydration that occur in the case of cementitious materials. In our previous study, we found that dispersive action is improved when phosphonic acid content in macromolecular structures increased.

The aim of this paper, which is the second part of the previous work, is to investigate the effects of macromolecular structure (monomer repartition along carbon backbone and macromolecular chain length) and ionic competition phenomena on the dispersive action of new synthesized superplasticizers. These effects were studied through adsorption measurement by total organic carbon (TOC), stability by turbiscan, and rheology. The ionic competition phenomena were investigated by increasing the ionic strength of solution by adding sodium sulfate or sodium nitrate.

2. Experimental

2.1. Materials

The new synthesized superplasticizers were tested on calcite suspensions in different ionic media by adding sodium sulfate or sodium nitrate. The calcite BL was supplied by OMYA France. Sodium nitrate and calcium hydroxide were provided by Panreax AppliChem, and sodium sulfate was purchased from Prolabo. The granular and physicochemical characteristics of calcite powder were determined in a previous work [21]. Measured density was of about 2.75 g/cm^3 and specific surface area was 1.25 m^2/g. Calcite particles are of monomorphic angular shape. The particle size distribution was determined by a laser granulometer S13320 from Beckman Coulter Company. Calcite exhibited particle size distribution ranging from 0.1 to 30 μm, with a main mode of about 8 μm. Pourchet et al. [24] found that the zeta potential of calcite clearly depends on the sulfate concentration. In limewater, the zeta potential of calcite is of about 20 mV and decreases with increasing sulfate concentration. For sulfate concentrations higher than 20 mmol/l, Pourchet et al. [24] found that the zeta potential becomes negative. It would have been interesting to measure the zeta potential to understand the effect of ionic strength [25]. However, this measurement was not made, due to the difficulty of performing it at high ionic strength using electrophoresis, and it should be done in a future work.

2.2. Sample preparation

Calcite suspensions were prepared using limewater to ensure alkaline conditions (pH ≈ 12.8) close to cement pore solution. Ionic strength was evaluated using the freeware Phreeqc [26] (Table 1). Ionic salts were added to a milk of lime obtained with an excess of lime Ca(OH)$_2$ in deionized water. Then, the milk of lime containing ions is filtered through a Büchner funnel with a sintered glass disc, resulting in a totally clear limewater containing ions. Note that the formation of gypsum is taken into account by Phreeqc calculations. The solution is re-filtered if precipitated solid particles due to carbonation and/or formation of gypsum are detected.

Calcite suspensions were mixed in a beaker using a magnetic stirrer according to the following sequence: (1) aqueous solution of superplasticizer is added to the freshly prepared ionic solution according to the amount of liquid required, (2) calcite is added with the respect of liquid to solid ratio (L/S) of 0.5, which corresponds to mass fraction ϕ_m of 66.7% and volume fraction ϕ_v of 43%, (3) the suspension is kept under magnetic stirring for at least 10 min before being diluted. Superplasticizer dosage corresponds to the mass of polymer added by the mass of calcite.

2.3. Methods

2.3.1. Total organic carbon (TOC)

The concentration of free polymer in the pore solution extracted from calcite suspensions was measured with the total organic carbon (TOC) analysis. The TOC analysis was performed using a Vario TOC Cube from Elementar. Calcite suspensions were prepared with superplasticizer dosage of 0.5%. This dosage is chosen for different reasons. As described in our previous work [21], there is no marked adsorption difference between superplasticizers for dosages lower than 0.5%. Moreover, limited amounts of polymers have been synthesized. The 0.5% dosage therefore seems to be a good compromise to limit the amount of polymer used for the TOC analysis and to observe adsorption differences between superplasticizers. It should be noted that this dosage is at the plateau for some molecules (statistical PCE-30P and PCE-15P), whereas for others (statistical PCE and Block PCE), this dosage is not yet at the plateau.

Calcite suspension is centrifuged (at 7000 rpm during 7 min) after 10 min of magnetic stirring. Supernatant liquid is filtered with 0.45 μm PTFE filter. Part of this solution (4 mL) is diluted with deionized water with a factor of 5, and then acidified with some drops of concentrated sulfuric acid to prevent carbonation. Different concentrations of ethanol are used to calibrate the device. All the tests were performed in triplicate. The TOC analyzer is calibrated with unadmixtured calcite suspension to take into account the amount of organic carbon in calcite. The standard deviation of TOC measurement is of about ±2.3%.

2.3.2. Stability measurement

Stability measurements were performed by using an optical analyzer Turbiscan MA2000 from Formulaction. This device is an optical analyzer well suited for the study of concentrated suspensions. It is composed by a light source (λ = 860 nm) moving along a glass tube with a step of 40 μm. The light transmitted across the sample is collected by a transmission detector (0° from incident beam) whereas backscattered light is analyzed by a backscattering detector (135° from incident beam). Evolutions of transmitted and backscattered lights are plotted as a function of column height and time, and are linked to the mean diameter of particles and solid volume fraction from the Lorentz and Mie theory [27]. From sedimentation studies, it is possible to access information about mesostructural organization of suspensions and dispersion/agglomeration phenomena.

Table 1
Quantities of salts to add in order to reach ionic strength targeted. Ionic strength and molar concentrations computed by Phreeqc.

Ionic strength mmol/L	NaNO$_3$					Na$_2$SO$_4$				
	Mass to add g/L	[Na$^+$] mmol/L	[NO$_3^-$] mmol/L	pH $_{measured}$	σ $_{measured}$ mS/cm	Mass to add g/L	[Na$^+$] mmol/L	[SO$_4^{2-}$] mmol/L	pH $_{measured}$	σ $_{measured}$ mS/cm
66	Limewater: 4 g of Ca(OH)$_2$/L (excess)								12.8	11.4
171	9.4	110	110	13	17.05	7.1	95.3	37.37	13.3	16.75
855	65	760	760	13.1	54.3	48,3	595	225	13.3	65

In order to observe particle migration in a short analysis time, dilution with a factor of 3/10 is performed leading to mass concentration of 20 wt%. After 5 min of magnetic stirring, 7 mL of diluted suspension are pipetted into the Turbiscan cell. This cell is then introduced in the device, and analysis is started as soon as possible in order to neglect initial sedimentation. Turbiscan analyses last 30 min, with a scan every minute.

2.3.3. Rheological measurements

Rheological measurements were carried out using an experimental Couette rheometer AR2000 ex from TA instruments equipped with a four blades vane geometry. Calcite suspensions were prepared with liquid to solid ratio of 0.36. This ratio, which corresponds to a volume fraction of 50.6%, makes it possible to better highlight the dispersing effect of superplasticizers Due to the limited amount of synthesized superplasticizers, measurements were carried out with a dosage of 0.05%. Calcite suspensions were mixed during 10 min at 500 rpm. The measurement procedure is similar to that used by Mahaut et al. [28–30]. After a strong pre-shear phase ($60 \, s^{-1}$ during 30 s) followed by a resting time (30 s), a small rotational velocity corresponding to a shear rate of $0.006 \, s^{-1}$ is applied to the vane geometry (stress growth). On the shear rate vs. strain curve obtained for yield stress measurement, it can be noted that the stress begins to increase linearly with the strain (elastic behavior in the solid regime [31]) to reach a peak followed by a slow decrease corresponding to destructuration of the suspension (viscous behavior in the liquid regime [31]). The peak defines the static yield stress which corresponds to the minimum stress to induce flow.

2.4. Superplasticizers macromolecular synthesis

2.4.1. Reagents

Poly(ethylene glycol) methyl ether methacrylate of 950 g/mol ($MAPEG_{950}$), cyanoisopropyl dithiobenzoate (CIDB), 4,4′-Azobis (4-cyanovaleric acid) (ACVA), methacrylic acid (MAA) and methanol (MeOH) were purchased from Sigma-Aldrich. Dimethyl (methacryloyloxy)methyl phosphonate (MAPC1(OMe)) was purchased from Specific Polymers. Thioglycolic acid (TA) was purchased from Acros. Trimethylsilyl bromide (TMSBr) was purchased from Fluka Analytical and 2,2-Azobisisobutyronitrile (AIBN) was purchased from Fluka Chemika. Reagents were used as received, without any further purification.

(Methacryloyloxy)methyl phosphonic acid (MAPC1(OH)) was obtained from MAPC1(OMe) hydrolysis; corresponding procedure is detailed in [21].

2.4.2. Statistical copolymers synthesis

Syntheses of three statistical copolymers (Stat PCE, Stat PCE-15P and Stat-PCE-30P) have been detailed in the previous work [21]. We present hereafter the synthesis of Stat PCE-30P DPn10.

MAPC1(OH) (12.36 mmol), $MAPEG_{950}$ (28.84 mmol), thioglycolic acid (4.11 mmol) and 100 mL of distilled water were introduced in a 250 mL three-neck round bottom flask and kept under nitrogen flux. The mixture was heated to 70 °C and ACVA (0.4 mmol) was added. After 24 h of reaction, the solution was cooled and complete conversion was checked with ^{1}H NMR analysis. Water was then eliminated by lyophilization. The product was collected as white powder and dried under vacuum until constant mass. It was then solubilized in distilled water in order to reach a concentration of approximately 100 g/L. Finally, accurate mass concentrations were determined with thermobalance analyses.

2.4.3. Block copolymers synthesis

Block PCE, Block PCE-30P and Block PCE-10P are block copolymers synthesized by Reversible Addition-Fragmentation Chain Transfer (RAFT) copolymerization. This technique allows the preparation of diblock comb-like structures. The procedure was described in the previous work [21]. As an example, we present hereafter the synthesis of Block PCE. 24.55 mmol of methacrylic acid, 1.27 mmol of CIDB, 0.41 mmol of AIBN and 18 mL of DMF were introduced in a round bottom flask. The mixture was kept under nitrogen flux and heated to 70 °C. After 6 h, the reaction was stopped by immersing the flask in liquid nitrogen. ^{1}H NMR analysis was performed in order to check that the monomer conversion reached 80%. The solution was poured in a large volume of cooled diethyl ether to remove remaining monomer. The red precipitate was filtered, and then washed with diethyl ether, before being dried under vacuum until constant mass. The product was dissolved in 45 mL of DMF and 17.7 mmol of $MAPEG_{950}$ and 0.18 mmol of AIBN were added. The mixture was kept under nitrogen flux and heated to 70 °C. After 6.25 h, the reaction was stopped by immersing the flask in liquid nitrogen. ^{1}H NMR analysis was performed to check that the $MAPEG_{950}$ conversion reached 80%. The solution is poured in a large volume of cooled diethyl ether to remove remaining $MAPEG_{950}$. The pink precipitate was finally filtered, then washed with diethyl ether, before being dried under vacuum until constant mass.

3. Results and discussion

3.1. Macromolecular structure description

Seven comb-like copolymers were synthetized (Fig. 1): four of them are statistical copolymers obtained with conventional radical copolymerization whereas the three others were prepared by RAFT copolymerization. Stat PCE has a structure very similar to standard polycarboxylate, with 30% of carboxylic acids functions and 70% of $MAPEG_{950}$ units (Table 2). $MAPEG_{950}$ is a commercial monomer, having 20 units of PEG in each side chain. The degree of polymerization DPn (i.e ratio of molar mass of polymer and monomer) of Stat PCE is of about 50 and its molar weight is of about 40,000 g/mol. Stat PCE-30P has almost the same structure, except that carboxylic acid moieties are replaced by phosphonic acids. Stat PCE-15P is a terpolymer having 30% of anionic functions along the carbon backbone, but half of these functions are carboxylic acids and half are phosphonic acids. Stat PCE-30P DPn 10 has the same structure than Stat PCE-30P, but its length is shorter and molar weight is about 7000 g/mol. During the polymerization, DPn was controlled with a chain transfer agent: thioglycolic acid. Although chain extremities of statistical copolymers are assumed to be derived from thioglycolic acid, ^{1}H NMR signals intensities were unfortunately too weak to determine DPn from NMR spectra. That is why DPn and molar masses presented in Table 2 are theoretical, calculated from reactant quantities employed. It is important to note the presence of one carboxylic acid function per macromolecule due to thioglycolic acid; even if this end chain can be neglected, regarding the 17 anionic functions per macromolecule having a DPn close to 50, this is not the case for Stat PCE-30P DPn 10, which is supposed to have only 3 phosphonic acid moieties per macromolecule. For this superplasticizer, the presence of the terminal carboxylic acid might be important in its adsorption efficiency.

Concerning block copolymers, Block PCE and Block PCE-30P are assumed to have very similar structural parameters to Stat PCE and Stat PCE-30P, respectively, except their monomer repartition along the carbon backbone because it is diblock structures. It is important to note that Block PCE-10P was synthesized from the same macroinitiator as Block PCE-30P, which means that these macromolecules are supposed to have statically the same number of $P(O)(OH)_2$ moieties per macromolecule. However, Block PCE-30P and Block PCE-10P differ by their anionic molar content of phosphonic acid (only 10% for Block PCE-10P) and also by their total length, because Block PCE-10P has a total DPn close to 140 (Table 2).

With these different macromolecular structures, it will be possible to investigate the effect of the nature of anionic function, its repartition along the backbone and also the importance of the degree of polymerization (DPn) on the adsorption and the dispersive action.
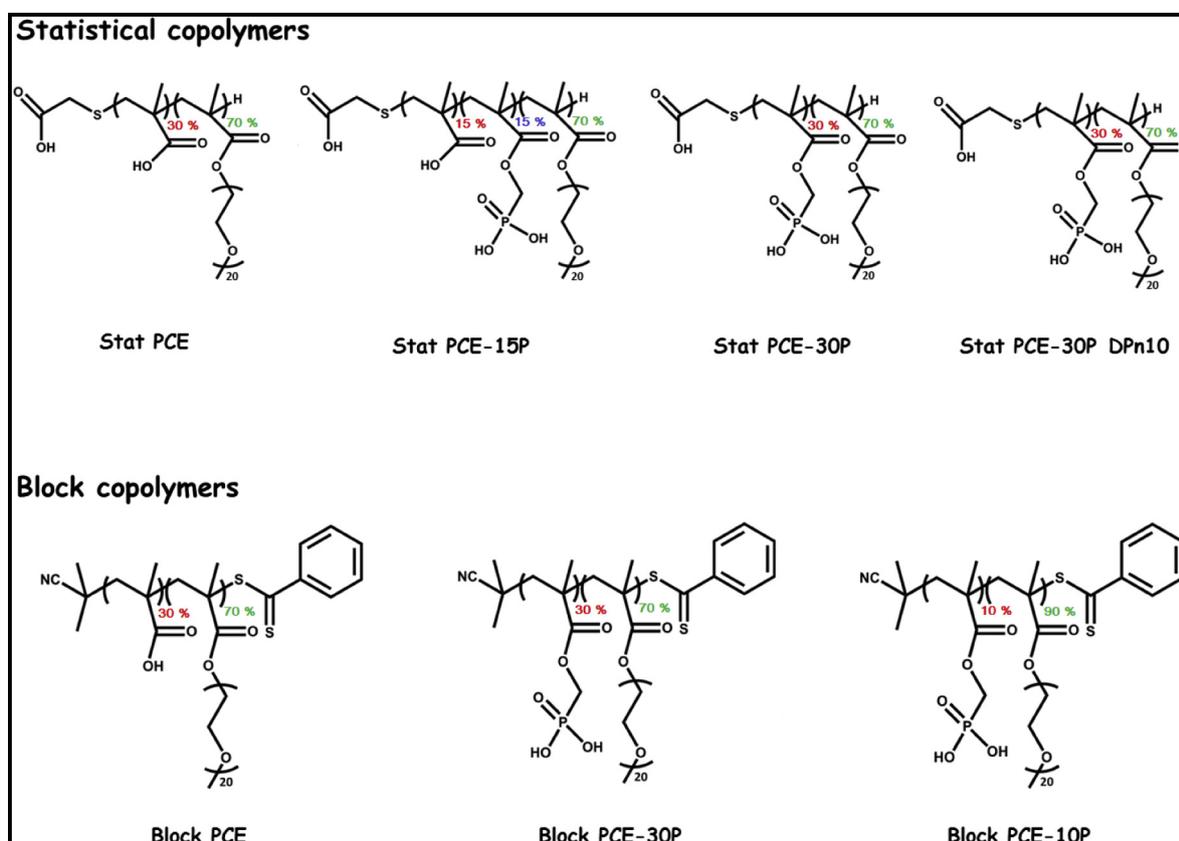
Fig. 1. Structural formulae of the seven synthetized superplasticizers, with molar proportions of each monomer.

3.2. Influence of macromolecular structure and ionic strength on copolymer adsorption

The results of adsorption are shown in Fig. 2. By considering adsorption in limewater, structures which bear only carboxylic acids (Stat PCE and Block PCE) seems to have the same adsorption efficiency, regardless of their macromolecule structures (statistical or block copolymers). As reported in the previous work for statistical structures [21], an increase of phosphonic acid content in copolymers leads to a decrease of the adsorbed amount. As shown in Fig. 2, the adsorbed amount of Stat PCE-15P in limewater is geater than that of Stat PCE-30P. Stat PCE-30P has two times more phosphonic acid moieties per molecule than stat PCE-15P. However, block copolymers do not follow the same trend. Block PCE-30P, which have 30 % of phosphonic acids on its backbone, has better adsorption efficiency than Block PCE-10P, which have three

times less anchor groups. It should be noted that Block PCE-10P has not only a different content of phosphonic acid but also a higher molecular weight and degree of polymerization DPn than Block PCE-30P (Table 2). Furthermore, these two copolymers are assumed to have different conformations at the particle surface. Stat PCE-30P DPn 10, which is the copolymer with the lowest molecular weight, presents the weakest adsorption efficiency in limewater (only 0.71 mg/g of calcite).

By comparing statistical and block structures, it appears that higher amount of block copolymers is adsorbed. The adsorbed amount of Block PCE-30P in limewater is of about 3 times higher than that of Stat PCE-30P and Stat PCE-30P DPn 10. This may be due to the compact conformation of block structures at the particle surface. Chen et al. [32] found similar observations for poly(acrylic acid) (PAA), which was adsorbed in higher amount on $BaTiO_3$ particles at low pH [32]. According to the authors, this is due to a poor affinity of PAA with water at low pH,

Table 2
Macromolecular parameters of synthetized superplasticizers.

Statistical copolymers					
Reference	Monomer content in copolymers (%)			Mn (g/mol)	DPn
	MMA	MAPC1(OH)	MAPEG$_{950}$		
Stat PCE	30	–	70	38,500	57
Stat PCE-15P	15	15	70	35,000	50
Stat PCE-30P	–	30	70	37,000	52
Stat PCE-30P DPn10	–	30	70	7000	10

Block copolymers					
Reference	MMA	MAPC1(OH)	MAPEG$_{950}$	Mn (g/mol)	DPn first block	DPn total
Block PCE	30	–	70	50,000	20	72
Block PCE-30P	–	30	70	38,500	14	52
Block PCE-10P	–	10	90	125,000	14	142
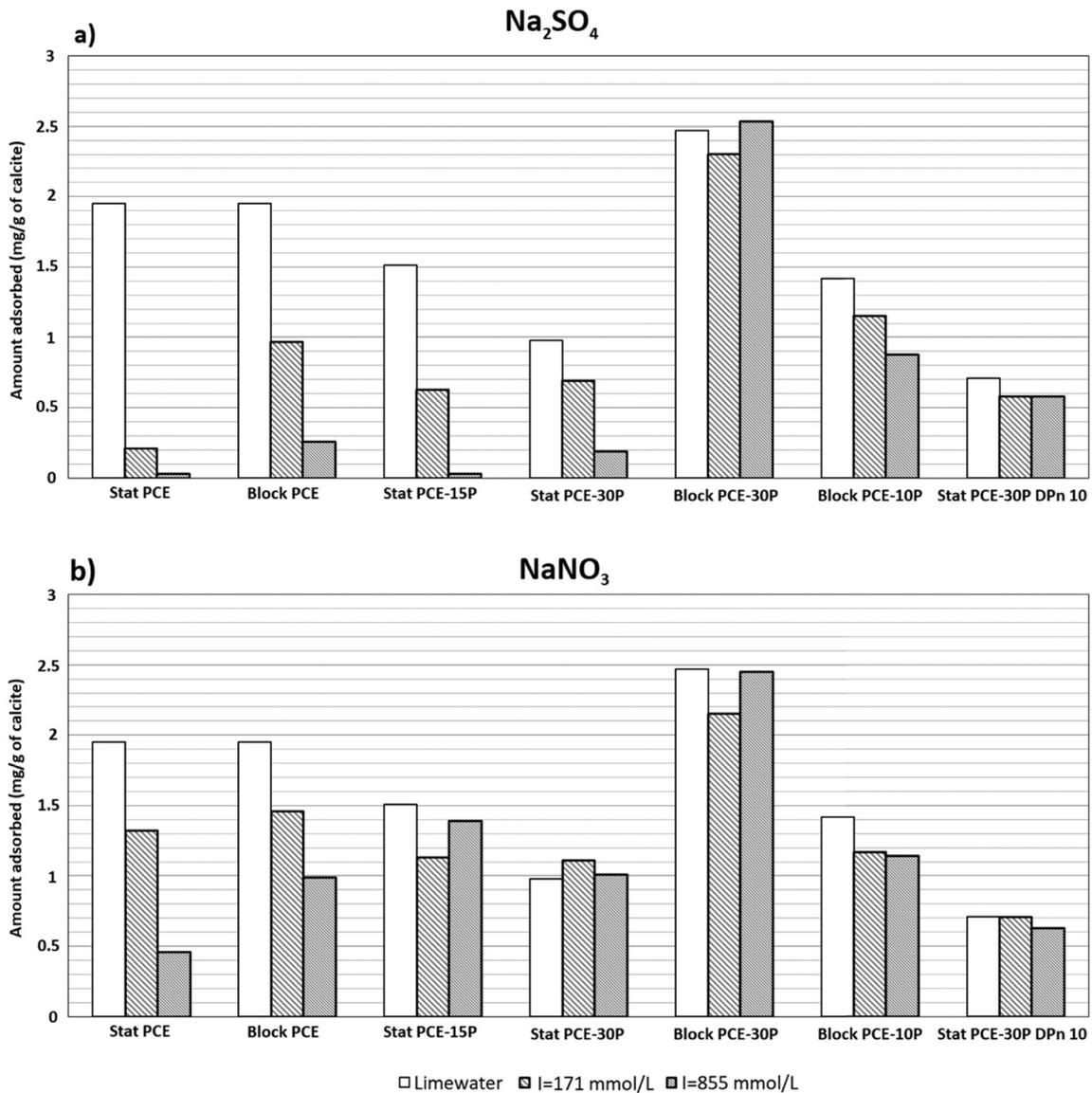
Fig. 2. Amount of adsorbed copolymer for different SO_4^{2-} (a) and NO_3^- (b) concentrations.

leading to a "globular" conformation of their homopolymers. Maybe such phenomenon is taking place for block copolymers, explaining their high adsorption efficiency, compared to statistical copolymers.

Increase of ionic strength with sodium sulfate (Fig. 2(a)) or sodium nitrate (Fig. 2(b)) leads to a reduction of the adsorbed amount. This decrease is more marked with sulfate and with copolymers bearing carboxylic acids moieties (Stat PCE, Block PCE and Stat PCE-15P, Fig. 2 (a)). Macromolecules including phosphonic acid functions seem to be less sensitive to ionic competition. In fact, Stat PCE-30P DPn 10, which presents the lowest amount adsorbed in limewater, is quite insensitive to the loss of adsorption efficiency due to ionic competition (0.71 mg adsorbed per gram of calcite in limewater versus 0.58 mg at high sulfate concentration).

3.3. Dispersion state of calcite suspensions

Characterization of the dispersion state of suspensions is essential to understand the rheological behaviors. However, the correlation between mesostructural organization of cement particles and fluidity is complex and it is not always established [33]. This is probably due to the high system complexity (particle size, phase composition, hydration reactions etc.). The mesostructure evolution of calcite suspensions as a function

of superplasticizer dosage was characterized by laser granulometry technique [21]. This characterization revealed no difference. The study of particle sedimentation behavior could give, indirectly, information on the dispersion state. Turbiscan device allows detection of the particle sedimentation and nascent instability phenomena in concentrated suspension over time by scanning transmitted and backscattered lights. It thus allows information about particle migration and agglomeration/dispersion phenomena to be determined. It is therefore possible to study the slowdown of the sedimentation rate as a function of superplasticizer dosage.

Fig. 3 presents five Turbiscan profiles with transmitted light intensity (top) and backscattered light intensity (bottom) plotted as a function of column height, with a different curve for each time. In limewater, without admixture, a clarification of the turbid supernatant is observed over time and the evolution of a sedimentation front down to the bottom of suspension column (a). When a low quantity of polymer is added (typically, 0.05%), sedimentation is slowed (b): sediment front evolution cannot be followed anymore on backscattered profiles, and fine particles sedimentation is slowed, resulting in a fully opaque supernatant even after 30 min of settling. At high polymer concentration (c), sedimentation of all particles is hugely slowed, leading to stabilized suspensions. If addition of NaNO₃ salt (d) gives a profile similar to limewater profiles
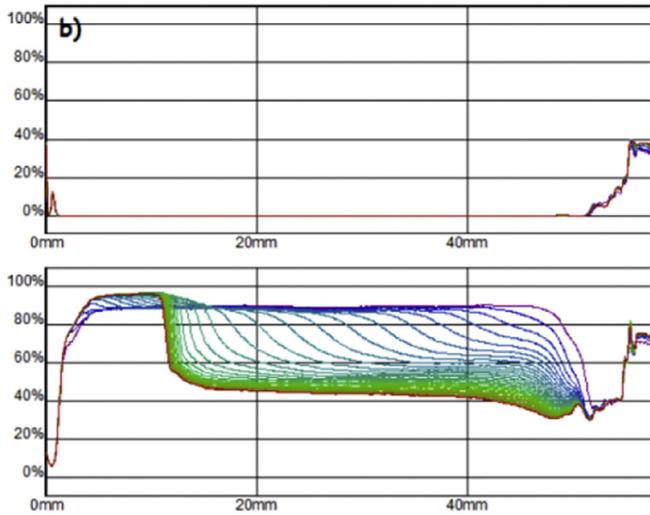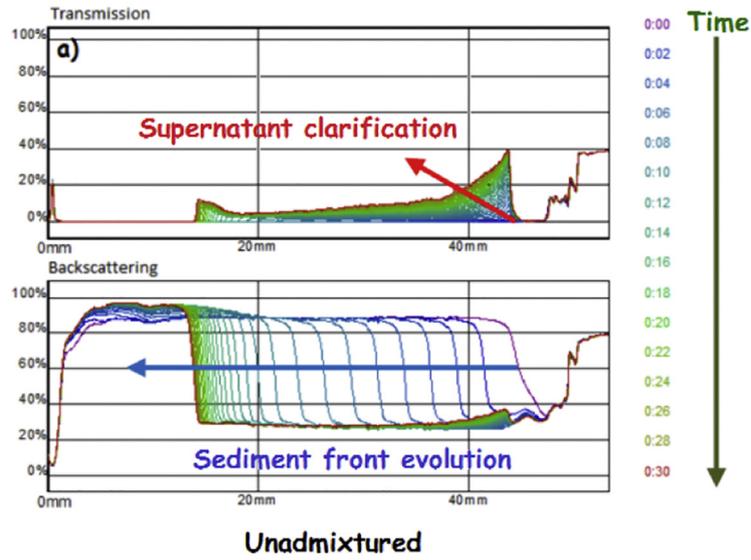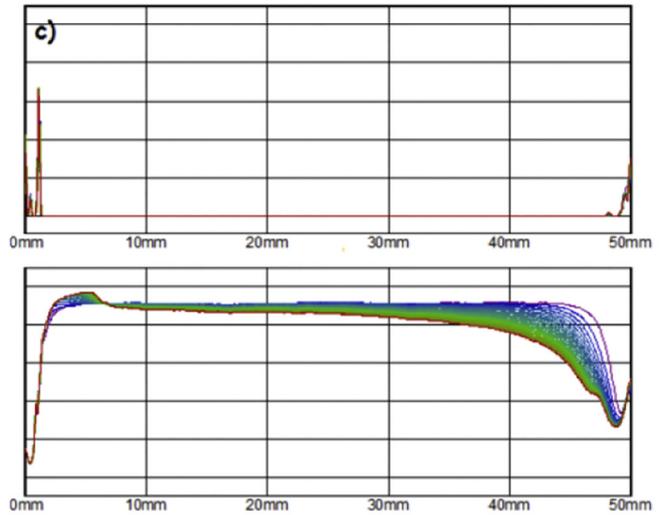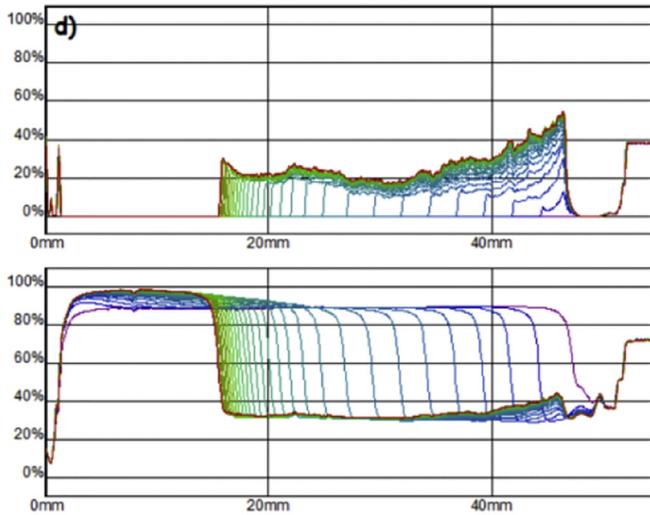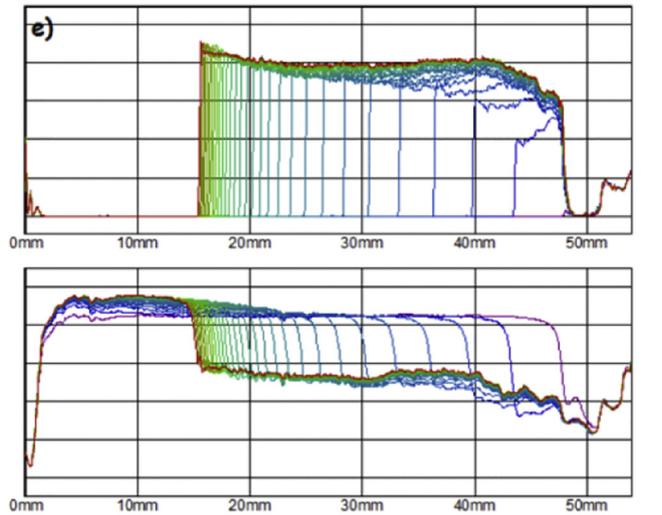
Fig. 3. Turbiscan profiles in limewater of calcite suspension unadmixtured (a), admixtured with different superplasticizer concentrations (0,1% for b) and 1% for (c). (d) and (e) correspond to Turbiscan profiles of unadmixtured suspensions in $NaNO_3$ and Na_2SO_4 solutions at $I = 171$ mmol/L, respectively. Each curve corresponds to a different analysis time, from 0 to 30 min.

(a), this is not the case for Na_2SO_4 (e). The presence of sulfate impacts fine particles dispersion, which leads to a sharp front between opaque sediment in formation and totally clear supernatant. This clear supernatant produces optical artifact in backscattered profile due to multiple reflections in glass tube. The measurements have to be corrected before being used in the sedimentation profile.

This change in behavior corresponds to hindered sedimentation regime. This may be explained either by a reduction of Debye length or a modification of the zeta potential [24] due to sulfate concentration, decreasing electrostatic repulsion between particles and leading to finest particles agglomeration into "flocs" which settle as quickly as largest particles. To fully understand the mechanisms behind this behavior, more detailed characterization with measurements of the zeta potential and modelling [34] should be done.

3.3.1. Influence of different formulations on fine particles dispersion

During sedimentation, two populations of particles can be identified. Largest particles are located in the opaque sediment, whereas a part of finest particles remains in suspension in the turbid supernatant. Laser granulometry analyses have shown that maximum diameter of this second particle population is about 8 μm (with a principal mode at 3 μm) [21]. When enough superplasticizer is added to the suspension, finest particles are dispersed and do not settle during the chosen analysis time. Table 3 presents the required dosage to reach a fully opaque supernatant at $t = 30$ min of analysis, i.e. when mean transmission in the sedimentation column equals zero.

As a general trend, addition of superplasticizer lowers mean transmission in supernatant; in limewater only 0.05–0.1% is required to have a fully opaque sedimentation column at 30 min (Table 3). In the presence of sulfate, a high dosage is required for copolymers including carboxylic acids (Stat PCE, Block PCE and Stat PCE-15P) to get an opaque supernatant. This is critical for Stat PCE because even with 1% dosage, the mean transmission in supernatant is totally clear, indicating a strong instability (profile similar to Fig. 3(e)). This loss of dispersion efficiency of fine particles is in accordance with adsorption results, for which copolymers with carboxylic moieties were found to have a loss of adsorption at high ionic strength (Fig. 2).

Block copolymers including phosphonic acids seem to be less disturbed by high concentration. Block PCE-30P is able to disperse fine particles at very low dosages, whatever ionic strength. Only Block PCE, which has carboxylic acids, needs higher dosage (0.5%) to disperse particles in the presence of sulfate.

Stat PCE-30P DPn 10 is comparable to Stat PCE-30P, but it is also sensitive to sulfate: at $I = 855$ mmol/L, 0.5% dosage is needed to stabilize fine particles. This is surprising because its adsorption is practically not influenced by sulfate (Fig. 2).

3.3.2. Study of suspensions stability using backscattering profiles evolution

Study of transmission intensity in supernatant can only inform about "finest" particles in suspension (mode at 3 μm); study of backscattered intensity evolution of Turbiscan profiles is relevant because it gives information about global stability of the system. For example, in the first part of this study, it has been shown that, in some cases, addition of superplasticizer at low dosages (<0.05%) may increase sedimentation rate of largest particles [21]. These observations could possibly be explained by some bridging phenomena [35,36] and/or a change of carrier medium viscosity due to dispersion of finest particles.

In order to quantify impact of superplasticizers on system stability, a Stability Index was defined [21]. This Index corresponds to the area between curves at $t = 0$ and $t = 6$ min, on backscattered profiles. Stability index increases as a function of particle settling and variation of backscattered signal. The time $t = 6$ min is chosen to study the destabilization dynamic and to exhibit maximum differences, especially at intermediate dosages (Fig. 3(b)). In the presence of sulfate, the high transmission in supernatant induces optical artifact due to reflection on the wall of glass cell, which must be corrected before calculation of Stability Index (Fig. 3(e)).

Fig. 4 present Stability Index evolution as a function of superplasticizer dosage, at different ionic strengths. As a general trend, addition of copolymers lowers Stability Index value. This indicates system stability is enhanced, i.e. a slow-down of particles sedimentation. At high dosage, suspensions behaviors seem monotonous and reach a stability plateau close to 40–50 area units. At this plateau, Turbiscan profiles are similar to Fig. 3(c). Dosages needed to reach this threshold are systematically superior to those required for stabilizing finest particles (Table 3). In some systems, at low dosages (<0.2%), addition of superplasticizers increases Stability Index compared to unadmixtured suspensions (0%). This is the case of Block PCE-30P (Fig. 4(b)). As previously mentioned, this is the consequence of destabilization at low dosages, which could be caused by bridging phenomena.

As shown in Fig. 4(a) and (b) (limewater and $NaNO_3$ at low ionic strength), block PCE-10P presents the highest values of Stability Index. This indicates that it is not as efficient as others in dispersing particles: 0.5% of block PCE-10P is needed to reach the stability threshold. The results obtained in the presence of nitrate are close to that in limewater, except for Stat PCE at ionic strength of 855 mmol/l (Fig. 4(d)), which requires a high dosage (0.5%) to reach the stability plateau.

The effect of sulfate on the dispersive action of superplasticizers is shown in Fig. 4(e). It appears that macromolecules including carboxylic acid moieties (Stat PCE, Block PCE and Stat PCE-15P) are more affected by the presence of sulfate since dosage of 1% is not sufficient to stabilize calcite suspensions. This is consistent with adsorption results (Fig. 2) and finest particles dispersion (Table 3).

Phosphonated copolymers seem to be more resistant to high sulfate concentration as shown in Fig. 4(e). Furthermore, by comparing Stat PCE-30P and Stat PCE-30P DPn 10, it appears that the chain length plays a major role in terms of sulfate resistance. In fact, PCE Stat PCE-30P and Stat PCE-30P DPn 10 have the same parameters except the chain length. The shortest macromolecule (Stat PCE-30P DPn 10) has a good sulfate resistance.

3.4. Effect of superplasticizer macromolecular structure and ionic strength on calcite suspension rheological behavior

Most cementitious materials displays yield stress which is the shear stress below which the material stops flowing. According to Roussel et al. [31], the yield stress corresponds *to the energy that has to be applied to the system in order to break a network of interaction between particles.* It is a very relevant parameter to describe the effect of superplasticizers on the workability. Furthermore, possible correlations between the yield

Table 3
Required dosage to reach mean transmission in supernatant at 30 min = 0% as a function of ionic strength.

|		Required dosage to reach mean transmission in supernatant at 30 min = 0 (%)						
		Stat PCE	Block PCE	Stat PCE-15P	Stat PCE-30P	Block PCE-30P	Block PCE-10P	Stat PCE-30P DPn10
Limewater		0.05	0.05	0.05	0.1	0.05	0.1	0.1
I = 171 mmol/L	$NaNO_3$	0.1	0.05	0.05	0.1	0.05	0.05	0.05
	Na_2SO_4	>1	0.05	0.05	0.1	0.05	0.1	0.1
I = 855 mmol/L	$NaNO_3$	0.2	0.05	0.1	0.05	0.05	0.1	0.05
	Na_2SO_4	>1	0.5	0.5	0.2	0.05	0.05	0.5

Fig. 4. Evolution of Stability Index as a function of superplasticizer dosage in limewater (a), in the presence of nitrates (b and d) and in the presence of sulfates anions (c and e).

stress and stability of the suspensions (sedimentation) could be established [28]. In fact, sedimentation of the coarsest elements of the concrete is conditioned by the yield stress of the cement paste [33]. In this work, the yield stress is therefore chosen to compare the workability efficiency of the synthesized superplasticizers.

Fig. 5 presents the yield stress of calcite suspensions with 0.05% of superplasticizer for two ionic strengths, in the presence of nitrate or sulfate. It can be noted that increase of ionic strength leads to an increase of the yield stress for all studied suspensions. This effect is probably due to a change in particles dispersion state. In the presence of sulfate, the increase of the yield stress could be partly due the gypsum formation, but no formation of gypsum was detected by XRD analysis.

As shown in Fig. 5, addition of superplasticizers allows decreasing the yield stress and thus the fluidity of calcite suspensions, but this decrease is affected by the presence of sulfate and nitrate. The presence of sulfate is more detrimental than that of nitrate, which is in accordance with adsorption results (Fig. 2).

Copolymers including carboxylic acids (stat PCE, block PCE and stat PCE-15P) are much more sensitive to the loss of fluidity (Fig. 5). This may be due to the fact that adsorption of these copolymers is lower (Fig. 2). These macromolecules are therefore more sensitive to ionic competition phenomena.

Block copolymers including phosphonic acids, except Block PCE, seem to be the least efficient to fluidize calcite suspensions although they are adsorbed in higher proportions than statistical copolymers. Stat PCE-30 DPn 10 seems to be the best superplasticizer in terms of fluidity improvement, even in the presence of nitrate and sulfate. The adsorbed amount of Stat PCE-30 DPn 10 (mg/g of calcite) is the lowest, but it has to be kept in mind that this macromolecule is the smallest. It is therefore necessary to consider the surface coverage ratio (i.e. the adsorbed amount divided by the adsorbed amount at the saturation plateau) [28] rather than the adsorbed amount to correlate the rheological behavior and adsorption. This was not done because of the limited quantities of synthesized superplasticizers.

These results reveal that phosphonic acid moieties are helpful to preserve the dispersive action of copolymers from ionic competition phenomena, and a macromolecule with a shorter chain length (DPn $\approx$ 10) gives better fluidification efficiency and sulfate resistance than conventional structures (DPn $\approx$ 50).

4. Conclusion

The experimental program performed in this work has allowed the investigation of the effect of macromolecular structure and ionic
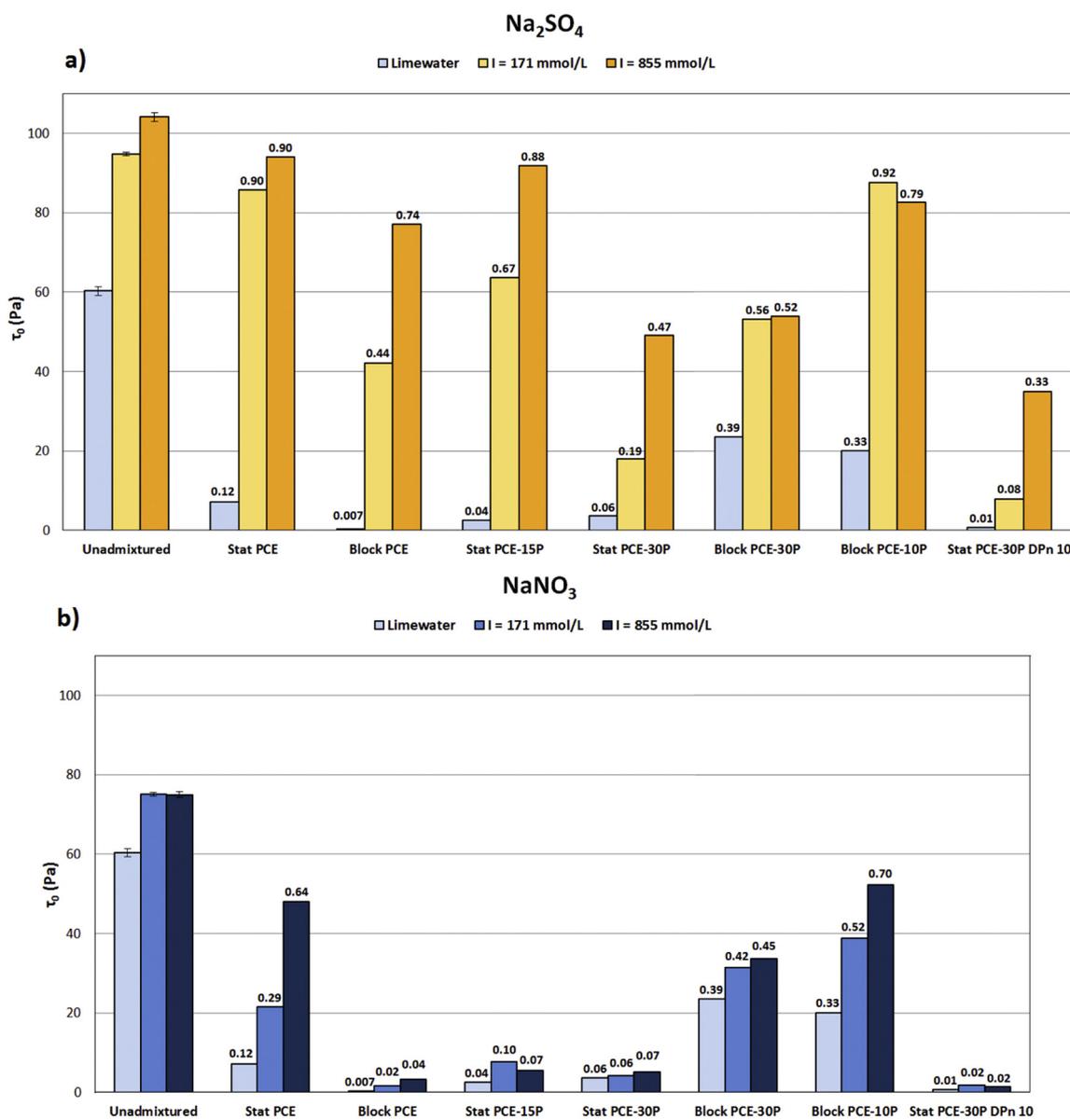
Fig. 5. Yield stress of calcite suspensions with 0.05% of superplasticizer for different ionic strength with sulfates (a) or with nitrates (b). The number above corresponds to yield stress of admixtured suspension divided by yield stress of corresponding unadmixtured suspension.

strength on the dispersive action of new superplasticizers. These superplasticizers are *comb*-like copolymers including phosphonic acid moieties and were synthesized starting from a structure similar to that of polycarboxylates. The dispersive action of these macromolecules was tested on calcite suspensions through adsorption, suspension stability and rheology measurements. This investigation reveals that:

- Block copolymers seem to be the least efficient in terms of dispersive action, although the adsorbed amount is the highest possibly due to effects of the quality of solvent.
- It is important to consider both anchor groups (per macromolecule) and degree of polymerization (DPn) for studying the effect of superplasticizers: Block PCE-10P with higher DPn and less anchor groups per macromolecule than others block copolymers is less effective to stabilize and to fluidize.
- In the presence of nitrate or sulfate, copolymers with phosphonic acids are more efficient than macromolecules bearing carboxylic acids moieties.
- The degree of polymerization (DPn) and thus the chain length is a "key" parameter to formulate superplasticizers: phosphonated

copolymer with the shortest chain length (DPn $\approx$ 10) is the most efficient even in the presence of sulfate and nitrate.

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