The Influence of Pluronic P123 Micelles on Corrosion Behaviour of Steel in Cement Extract and Bulk Matrix Properties of Cement Paste

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Summary

The influence of Pluronic P123 (PEO\textsubscript{20}-PPO\textsubscript{20}-PEO\textsubscript{70}) micelles (of 10 nm size) on the corrosion behaviour of low carbon steel in cement extract (CE) was studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PDP). Additionally, mercury intrusion porosimetry (MIP) was employed to derive the impact of admixed micelles on porosity and pore-size distribution of cement paste. The motivation for carrying out this investigation has two main aspects: first, previous studies on the effect of micelles in model solutions and reinforced mortar proved to be very promising; secondly, an upscale approach was sought in terms of cost-effective polymer type. Previously studied was the influence of polyethylene oxide-b-polystyrene (PEO\textsubscript{113}-b-PS\textsubscript{70}) micelles (of 50 nm size) on steel corrosion resistance and microstructural properties of cement-based materials. It was concluded that a very low concentration of these PS-based micelles (0.024 g/l) added to CE results in an increased steel corrosion resistance. As far as cement-based matrix is concerned, significantly reduced porosity and permeability were recorded. Despite the positive results, two drawbacks appear with this application: on one hand the increase of corrosion resistance was isolated to early stages of treatment and no significant influence was observed later on. On the other hand, PEO-b-PS is a rather costly material, especially with regard to civil engineering applications.

This work aimed to explore the possibility for using the significantly lower in cost and commercially available tri-block copolymer, Pluronic P123. The PEO\textsubscript{20}-PPO\textsubscript{20}-PEO\textsubscript{70} micelles feature a PEO “shell” as well and the expectation therefore was to achieve similar to the previously recorded or improved performance in their presence. The results, however, show different trends of materials’ behaviour: as far as steel corrosion resistance is concerned, a positive effect was observed, initially denoted to the presence of the polymer itself, rather than the presence of micelles. There was no significant influence of the P123 micelles on cement-based microstructure. The P123 micelles were found to mainly affect the steel corrosion resistance in the presence of NaCl as corrosion inducing factor. The related phenomenon is that the P123 micelles tend to self-assemble only within higher ionic strength of the medium, when the critical micelle concentration is reduced i.e. at the hereby tested concentration of 0.024 g/l the control cases (and the solid cement paste specimens respectively) actually contain unimers, whereas the composition of the medium for the corroding (Cl\textsuperscript{-} containing cases) leads to micelles self-assembly, which actually contributes to the observed positive effects.
1. Introduction

The steel reinforcement in civil structures is normally in a passive state due to the high alkalinity (pH=12.9-13.5) of the pore solution and the cement paste respectively. However, corrosion can be initiated due to carbonation or chloride contamination. The result is accelerated damage of the reinforcing steel and rapid failure of reinforced concrete. In the frame of a novel approach to corrosion control in reinforced concrete, the application of polymeric nano-aggregates was recently investigated. The challenge was to ideally make use of self-healing processes in the event of detrimental influence and/or internal damages.

The investigated nano-aggregates (micelles, vesicles, hybrid core-shell particles of a polymer shell and a metal oxide core) proved to result in superior properties of reinforced concrete systems [1-7]. The studies with PEO$_{113}$-b-PS$_{218}$ and PEO$_{113}$-b-PS$_{70}$ micelles in model solutions (cement extract), mortar and reinforced mortar showed promising results in terms of increased corrosion resistance and significantly altered bulk matrix properties [1,5,8-10]. In model liquid environment (cement extract) a very low concentration of micelles (0.024 g/l) resulted in increased corrosion resistance: steel electrodes, treated in chloride containing (1 % NaCl), micelles-modified solutions exhibited reduced anodic current densities by approximately one order of magnitude, whereas an effect on cathodic currents was not observed. Morphological observations and surface analysis confirmed that a more uniform and compact layer (i.e. homogeneous and protective Fe$_2$O$_3$ and/or Fe$_3$O$_4$ and Ca-substituted such) was formed on the steel surface in the presence of micelles [1]. The influence of micelles on the bulk cementitious matrix was studied in plain (non-reinforced) mortar [5, 8-10]. This investigation was essential for evaluating microstructural properties and possible alterations in the presence of micelles (i.e. the polymeric nano-aggregates themselves) when no corrosion and/or self-healing agents and mechanisms respectively were yet involved. The main outcomes refer to three orders of magnitude decreased permeability and two times lower porosity in the presence of only 0.016 wt.% (cement paste) or 0.025 wt.% (mortar) micelles per dry cement weight.

Although previous investigations proved the significant positive effect of limited concentration from the above mentioned nano-aggregates, a drawback with regard to practical applications of this approach is the cost of the PEO-b-PS used for their synthesis. In order to achieve an upscale of the already documented performance for civil engineering applications, a cost-effective alternative is necessary and this was one of the objectives of the present study. For that purpose, micelles from commercially available Pluronic P123 were tested in model solutions and cement paste in the same concentrations as within the previously reported studies. This paper presents the initial, preliminary results from this investigation.

2. Experimental materials and methods

2.1. Materials

2.1.1. Steel electrodes: low-carbon steel (St37) electrodes with a surface area of 4 cm$^2$ were used; all electrodes were equally treated prior to investigation in the model medium i.e. they were grinded with no.500 to no.4000 grinding papers and polished;
further, just before immersion in the relevant solutions, they were cleaned with acetone. Three replicates were measured for each time interval and condition.

2.1.2. Cement extract: the cement extract (simulated cement pore solution) was prepared from Ordinary Portland Cement OPC CEM I 42.5N and tap water by mixing in a weight ratio of 1:1; the suspension was filtrated after 24h rotation and thus a simulated pore solution (CE) was obtained. The pH of CE is 12.6 – 12.9. The chemical composition (wt. %) of OPC CEM I 42.5N (ENCI, NL) is as follows: CaO 63.9%; SiO$_2$ 20.6%; Al$_2$O$_3$ 5.01%; Fe$_2$O$_3$ 3.25%; SO$_3$ 2.68%; K$_2$O 0.65%; Na$_2$O 0.3%. The chemical composition of the CE (derived chemically by ICP analysis) is as follows: Ca – 201 mg/l; K – 3.85 mg/l; Na – 1.33 mg/l; Al – 4 mg/l and Fe - < 1 mg/l. The originally received CE (modified and prepared) was the environmental medium for testing the electrochemical behaviour of the steel electrodes. The CE modification was in terms of adding micelles (details specified below) and/or NaCl (10 g/l), thus ending up with 4 solution types: CE only (as control case); CE + micelles; CE + NaCl and CE + micelles + NaCl. The so received solutions determine the samples groups and designation within the electrochemical measurements, which is provided further below.

2.1.3. Cement paste: the same cement type (as for cement extract) i.e. OPC CEM I 42.5N, was used to prepare the cement paste specimens with a water-to-cement ratio of 0.5. These were used for microstructural investigation. The specimens were cast in plastic containers, tightly sealed and rotated for 8 hours to avoid sedimentation. They were further cured in sealed condition at room temperature for 7 days. At 7 days age samples for microstructural analysis (approx. 20 g per specimen) were taken (sample preparation followed well known and applied techniques [11-13], including ceasing cement hydration in liquid nitrogen and freeze-drying at -28°C until reaching a constant sample weight). Three groups of cement paste samples were investigated in this study: “TAP”, “DEMI” and “PL”. The difference between these three groups was in the type of mixing water i.e. “TAP” used regular tap water; “DEMI” used demineralised water and “PL” used demineralised water, containing 0.024 g/l micelles.

2.1.4. Polymeric micelles: The tri-block copolymer, Pluronic P123, was obtained from Sigma Aldrich. The structural composition of this polymer is HO(C$_2$H$_4$O)$_{20}$(C$_3$H$_6$O)$_{70}$(C$_2$H$_4$O)$_{20}$H. It has a number-average molecular weight of 5800 g/mol. P123 was used as received without further purification. Aqueous solution containing 1 g/l P123 was prepared by weighing. Part of this solution was added to the cement extracts (designation CEPL and CEPLn below) to obtain P123 concentrations of 0.0024 wt.% in the final samples i.e. 0.024 g/l of the micelles were present in chloride-free and chloride-containing cement extracts. The PEO$_{20}$-PPO$_{20}$-PEO$_{70}$ micelles are amphiphilic formations, consisting of a hydrophilic PEO shell and a hydrophobic PPO core. Dynamic light scattering (DLS) measurements were performed for the as received micellar solution (1 g/l), the micelle-containing CE solutions and the latter two with varied chloride concentration and pH. The DLS tests provide information for the hydrodynamic radius and stability of the micelles in each environment. The hydrodynamic radius of the micelles as received was 10 nm, however morphological changes as well as different ratio of micelles/unimers was relevant for different pH and/or chloride concentrations (results are presented further below).
2.1.5. **Sample designation:** the four testing solutions in this study define the samples designation as: control groups “CE” (without micelles) and “CEPL” (with micelles) and corroding groups “CEn” (without micelles) and “CEPLn” (with micelles) (for the “corroding” cases, NaCl was added to the CE in concentration of 10 g/l).

2.2. **Methods**

2.2.1. **Electrochemical measurements:** the hereby employed electrochemical methods were: electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP). A common 3-electrode electrochemical cell with a Saturated Calomel electrode (SCE) as reference electrode was used and the measurements were performed after open circuit potential (OCP) stabilization for all cells (the electrochemical measurements (as well as OCP readings) were performed on at least 3 replicates per sample type per age). The PDP measurement was performed in the range of −0.2 to +1.2 V vs OCP at scan rate 0.5 mV/s. The EIS measurements were carried out in the frequency range of 50 kHz to 10 mHz by superimposing an ac voltage of 10 mV. The used equipment was EcoChemie Autolab-Potentiostat PGSTAT30, combined with FRA2 module, using GPES and FRA interface.

2.2.2. **Mercury intrusion porosimetry (MIP).** Sample preparation for MIP analysis followed generally accepted procedure [11, 13]. The MIP tests were conducted by using Micrometrtics Poresizer 9320 (with a maximum pressure of 207 MPa) to determine the porosity and the pore size distribution of the specimens. The Washburn equation [13] was used to calculate the diameter of pores intruded at each pressure step, which is shown as: D=−γcosθ/P, where D is the pore diameter, γ is the surface tension of mercury, θ is the contact angle between mercury and the pore wall and P is the applied pressure. The surface tension of mercury was 484 ×10−3 N/m and the contact angle was 130°. The measurement was conducted in two stages: the first stage was at low pressure from 0 to 0.0036 MPa, the second stage was at high pressure running from 0.0036 to 210 MPa. According to Washburn equation [13], the pore size range detected is from 350 µm to 0.007 µm.

3. **Results and discussion**

3.1. **Electrochemical tests in cement extract**

3.1.1. **OCP values:** The evolution of open circuit potential (OCP) determines the time to corrosion initiation.

![Figure 1: Evolution of OCP values for the steel electrodes, treated in the various cement extract solutions from 24h until 7 days.](image-url)
In chloride-containing medium, corrosion initiation is due to the passive layer breakdown on the steel surface i.e. localized corrosion. For reinforced concrete, and simulated pore solution as the hereby used cement extract respectively, the steel surface is (in general) considered passive if OCP is equal or more anodic than -270 mV [14-16]. Figure 1 shows the OCP evolution for the steel electrodes in the testing solutions (readings are the average value of 3 samples per condition). As can be observed, the micelles did not significantly influence the OCP of the steel for the control groups (specimens CE and CEPL); both specimens showed OCP values more anodic than -270 mV i.e. a stable passive layer formed on the steel surface in chloride-free cement extracts (both with and without micelles). For the corroding groups (specimens CEn and CEPLn), a positive effect (in terms of OCP readings) was observed for the steel immersed in the micelles-containing cement extract (specimen CEPLn), but only at earlier stages (24h to 3days), evidenced by more anodic OCP values. However, even at the stage of 7 days where OCP values are comparable to the steel treated in micelle-free solution, corrosion resistance was maintained approximately two to three times higher. Additionally, corrosion current density values for the steel treated in Cl-containing, micelle-modified solutions (samples CEPLn) were significantly lower and comparable to the non-corroding samples (presented further below). This behaviour, in the simplest approximation, can be attributed to the impact that the micelles would have on diffusion limitations within the formation/restructuring of the product layer on the steel surface. OCP monitoring in that sense can not thoroughly differentiate evolution of polarization resistance from altered charge transfer resistance i.e. more cathodic OCP values, as well known, do not always account for low corrosion resistance.

3.1.2. EIS and PDP results: Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) provide insight in the development (and/or limitations) of the corrosion process in the presence of micelles. Figs. 2 and 3 depict the recorded EIS response at certain time intervals. Fig.2 presents (as an example) the response (symbols) and goodness of the fitting (lines) for a CEPL sample after 6h treatment, using an equivalent circuit (inlet in Fig.2a) of two time constants in series with the electrolyte resistance.

![Figure 2: Experimental EIS response and fit for specimen CEPL in Nyquist (a) and Bode (b) formats; equivalent electrical circuit as inlet in Fig. 2a); best-fit parameters: $R_{el} = 9.4 \text{ Ohm}$; $R_1 = 12.4 \text{ Ohm}$; $Q_1 = 0.5814 \times 10^{-4}$; $n = 0.94$; $Q_2 = 0.2449 \times 10^{-3}$; $n = 0.92$; $R_3 = 23 \text{ kOhm}$](image)

In general, different equivalent electrical circuits (as well both pure capacitances, C and/or constant phase elements, CPE (Q)) can be used for interpretation and data fitting of the experimental EIS response. The CPE is an empirical mathematical de-
The observed impedance response and is defined as [17]:

\[ Z = (j \omega)^n Y_0 \]

being further quantified by the parameters \( Y_0 \) and \( n \) (CPE constant and CPE factor respectively); where \( Y_0 \) is a parameter with units \( \Omega^{-1} s^n \) and \( 0 < n \leq 1 \). When \( n = 1 \) a CPE simplifies an ideal capacitor; when \( n = 0 \), CPE simplifies a pure resistor; when \( 0 < n < 1 \), characteristic is a non-ideal capacitive response.

**Figure 3:** Overlay of EIS response for control and corroding specimens at time intervals of 2h (a,b); 24h (c,d) and 3d (e,f)

Bearing in mind the duration of the tests, the addition of more time constants would not add more clarity and accuracy in the results. Therefore the hereby used circuit is considered to be sufficiently describing the behaviour of the steel electrodes and pro-
vides a clear physical meaning to each parameter involved. The first time constant (R₁ and Q₁) deals with the charge transfer resistance and pseudo-double layer capacitance; the second time constant (R₂ and Q₂) presents the contribution of product layer properties and transformations (e.g. Fe²⁺/Fe³⁺ in the surface layers).

The replacement of pure capacitance (C) with constant phase element (CPE or Q) in the equivalent circuits is widely accepted for systems as in this study [18-21], denoted to inhomogeneities at different levels, hereby being mainly relevant to the heterogeneity of hydration/corrosion products, that form on the steel surface, in addition to the participation of micelles in the product layer formation. Figure 3a) to Fig. 3f) depict an overlay of the EIS response for the control and corroding specimens after 2h (Fig.3a,b), 24h (Fig.3c,d) and 3days (Fig.3e,f) of treatment. The best fit parameters are summarised in Table 1: R_{el} was stable and in the interval of 7 to 10 Ohm for all cases (therefore not listed in the table); the calculation of global polarization resistance (R_p) values derived by EIS is based on a well known simplified calculation i.e. R_p = R_{ct} (R₁) + R_{red} (R₂) when the overall reaction rate and R_p respectively are related to product layer transformations, including both oxidation and reduction [22].

The shape of the experimental curves (Fig.3) for all specimens reflects the typical response of steel in chloride-free or chloride-containing alkaline medium, simulating cement paste [23-25]. After product layer stabilization at later time intervals and at low frequencies (0.01 Hz) a close to capacitive behaviour was observed for the control specimens CE and CEPL, whereas inclined to the real axis semi-circles are characteristic for specimens CEn and CEPLn (corroding cases). The response for specimens CEn and CEPLn reflects the evolution of corrosion with time, also evidenced by the more significant phase angle drop for CEn specimens (from 80 to approx. 60 degrees and lower), compared to the control ones CE and CEPL (phase angle of 76 - 85 deg.).

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As seen from Fig.3a)b) initially (2h) the micelles do not exert any significant positive effect. On the contrary, the lowest magnitude of impedance was recorded for the steel electrodes treated in micelle containing solutions, both control and corroding ones (CEPL and CEPLn). The behaviour is, however, very similar to that for the elec-
trodes treated in micelle-free solutions (both control and corroding cases), visualised by almost equal phase angle (Fig.3b). It can be also observed that an initially higher contribution of product layer formation (second time constant) is relevant only for the case of specimens CEPLn. Within further treatment, stabilization of the passive layer for the control specimens CE and CEPL takes place, evidenced by increase in polarization resistance (both charge transfer and resistance of the product layer, Figs.3 c-f and Table 1). Despite the fact that these two groups are control ones (i.e. there are no corrosion initiators in the medium for CE and CEPL) the resistance of the CEPL samples is lower, meaning that none or minimal effect of the micelles is relevant for the control cases. In contrast, a different trend was observed for the corroding cases: with prolonged treatment, the CEPLn specimens exhibit significantly higher magnitude of $|Z|$, accompanied by higher phase angles (Figs. 3d,f) with no pronounced contribution of a second time constant. Should be noted, that a more significant alteration in polarization resistance values (Table 1) without a distinct contribution of product layer transformation (mainly one time constant observed), can only be denoted to transformations in the environment (initial existence of unimers rather then micelles and further self-assembly of the latter) and thus contribution to a relatively stable ratio of cathodic/anodic processes on the steel surface. This is not the case for the CEn specimens, where a gradual decrease of polarization resistance was recorded. After 24h of treatment, a pronounced contribution of a second time constant was observed for specimens CEn (Fig.3d), charge transfer slightly increases (due to diffusion limitations) but maintains lower values. The resistance of the product layer ($R_2$, denoted to oxi-redox transformations on the steel surface) gradually decreases, corresponding to enlargement of the area of corrosion damage on the steel surface. In contrast, for specimens CEPLn, the increased $R_1$ and $R_2$ values and decrease of $Q_2$ values denote for barrier effects on the steel surface and therefore higher charge transfer and higher $R_p$ values are relevant. For the corroding cases the corrosion resistance of the steel electrodes treated in micelle-containing solutions (CEPLn) remains higher, compared to those treated in micelle-free solutions (CEn) until the end of the testing period.

The EIS results indicate that the micelles result in a corrosion resistance improvement for the corroding cases (CEPLn) but do not have any pronounced contribution in chloride-free medium (CEPL cases). Further, the improvement in specimens CEPLn was pronounced after some hours of treatment i.e. initially (2h) the steel treated in micelle-free, chloride containing solutions has higher corrosion resistance.

![Figure 4: DLS measurements for varied micelle concentration in MILIQ water at varying pH (a); DLS result for 1% and 3.5% NaCl solutions in the presence of 1% micelles (b).](image)
The explanation lies in the stability of these type of micelles in the relevant solutions and apparently, their critical micelle concentration (cmc), differently affected in the hereby investigated environments. For PEO\textsubscript{20}-PPO\textsubscript{20}-PEO\textsubscript{70} micelles, in general, the cmc is 0.004wt.% at 25 °C and neutral pH [26] Fig. 4 presents DLS measurements for several cases where micelle concentration, pH and chloride concentration varies. The plots depict measurements for micelle concentration higher than the one used for the testing solutions (i.e. 0.05% and 0.1%) since no clear dependencies (low intensity and lack of correlation function) were observed for 0.0024% (therefore these results are not presented). As seen from the plots a distinctive micelle formation (presence) was observed at 0.1% concentration at neutral pH (Fig.4a, 10 nm peak). Lower concentration of the micelles (0.05%) at neutral pH and pH 13 led to appearance of large aggregates, which can be observed when the concentration of the Pluronic block copolymers is near the cmc [27]. These aggregates have been assigned to impurities such as di-block copolymers. At pH 3, the portion of micelles was already more significantly reduced as reflected by a clear decrease of the scattered light intensity (i.e. 88 kHz at neutral pH and 38 kHz at acidic pH). On the other hand, when NaCl was present in the cement extract solutions (pH of 12.6 – 12.9) and at higher block copolymer concentration, well defined fraction of spherical micelles was observed (Fig.4b). The spherical micelle fraction reduced with increase of the NaCl concentration from 1% to 3.5%, probably due to a morphological transition (from spherical to elongated or worm-like shape). More than ten-fold increase of the scattered light intensity further supports a possible shape transition, but direct morphological observations such as TEM will be needed to verify these observations. A sphere-to-rod transition has been previously observed in the presence of similar inorganic salts with ‘salting out power’, although at higher salt concentrations [28].

Hence, relevant to the hereby investigated solutions and cases, the following can be hypothesized: for the control specimens (CE and CEPI) the solutions are of pH 12.6 – 12.9, 0.0024wt.% micelles were admixed in the medium for CEPI specimens, whereas CE is micelle-free. Considering the results from Fig.4a), it can be stated that at the employed concentration (which was specifically chosen in order to compare this with previous investigations with PS-based micelles, [1,8-10]) the fraction of micelles is very low or just unimers were present. Therefore, there was no improvement of steel surface properties for the control specimens CEPL, compared to specimens CE (Fig. 3, Table 1); on the contrary, lower \( R_p \) values were recorded, accompanied by lower resistance of the product layer – these could be related to diffusion limitations at the steel/solution interface, resulting in an impeded formation of a stable passive layer.

For the corroding cases (CEn and CEPLn), the testing solutions are again of pH 12.6 to 12.9, containing 1% NaCl. Considering the DLS results (Fig.4b), it is most likely that the portion of micelles at the beginning of the test is very low. Reduction of cmc would be, however, relevant on later stages i.e. micelle re-assembly will take place as a result of altered ion transport/salt concentration gradients at the steel/solution interface within the Cl\textsuperscript{−}-initiated corrosion process (as well as the presence of Cl\textsuperscript{−} itself). In a simplified way: the anodic reaction of steel corrosion generates Fe\textsuperscript{2+}, the cathodic reaction for alkaline environment generates OH\textsuperscript{−} and subsequent formation of e.g. Fe(OH)\textsubscript{2} is relevant; within the corrosion-induced pits and with further Cl\textsuperscript{−} propagation, Fe(OH)\textsubscript{2} would oxidize to FeOH\textsuperscript{+} and H\textsuperscript{+}. These reactions will alter the balance of ions on the steel surface and will at the minimum increase the ionic strength; the result will be micelle re-assembly, which is known to be relevant for the
PEO$_{20}$-PPO$_{20}$-PEO$_{70}$ micelles in salt solutions, i.e. the Cl ions are expected to decrease cmc as well as cmt (critical micelle temperature) [29, 30]. Consequently, the initially observed corrosion behaviour for CEPLn specimens, compared to CEn specimens, would be affected only by unimers in the solution (the polymer itself), whereas later on, increased corrosion resistance is recorded, most likely relevant to micelle re-assembly and improved barrier effects on the steel surface. The above hypothesis for the mechanism of increased corrosion resistance in specimens CEPLn is supported by the electrochemical behaviour and response with external polarization – Fig. 5.

**Figure 5:** Polarization curves (PDP tests) for control and corroding cases after 2h (a), 24h (b) and 3d(c) conditioning in the relevant model medium.
The initial 2h response (Fig.5a) is similar for the control cases (curves 1 and 2). For the corroding cases (curves 3 and 4) similar corrosion current density, but higher anodic current densities were recorded for the CEn specimen, compared to CEPLn specimen. This is in addition to the lower resistance of the product layer on the steel surface in CEn (pronounced increase in current density around -270 mV after corrosion potential, Fig.5a). With further treatment (24h and 3d), the response for the control cases (CE and CEPL) depicts passive state.

A more pronounced difference was observed for the corroding cases. While for the CEn specimen corrosion and anodic current densities progressively increase, the specimens CEPLn behave as control such, presenting even lower anodic currents that the control CE and CEPL specimens. Since corrosion potential and corrosion current density do not significantly vary, this behaviour can only be denoted to increased barrier effects on the steel surface in the presence of micelles and consequently largely impeded anodic reaction. The derived corrosion current density values form PDP tests (using Tafel and Butler-Volmer equations and fitting of the GPES software and more particular, Tafel slope analysis for deriving Rp values and further substituting a constant B=0.026 V/dec in the Stern-Geary equation) are summarised in Fig.6. Clearly, no significant effect of the micelles in terms of increased corrosion resistance is evident at early stages – corrosion current densities at 2h time interval were similar for all control and corroding cases, even higher for the specimens CEPL and CEPLn treated in micelle-containing solutions. Here again, this behaviour is attributed to actually non-presence of micelles at this stage (as previously discussed) but diffusion limitations from the polymer itself, that result in impeding of the formation of a passive layer (as for the CEPL cases) rather than any impact on improved performance. On later stages, corrosion current densities for the specimens CEPLn decrease and are actually comparable to those for the control specimens (CE and CEPL), whereas the steel electrodes, treated in micelle-free solutions (CEn) are actively corroding, reaching corrosion current density values of more than 1 \( \mu \text{A/cm}^2 \).

The following needs to be mentioned: the corroding CEPLn specimens, although with significantly higher resistance than CEn specimens, behave as corroding such according EIS results (Fig.3) i.e. the magnitude of \(|Z|\) and phase angles are higher compared to CEn but lower compared to the control cases. On the other hand, corrosion current density derived from PDP is significantly low and similar to the control cases (Fig.6). The two measurements are not comparable in absolute values, since EIS is a “non-destructive” measurement, no polarization is involved, but only 10 mV
AC perturbation, whereas the PDP measurements provide information for electrochemical behaviour with external polarization. In other words, the very low corrosion current densities recorded for CEPLn via PDP tests are denoted to the significant limitation of the anodic reaction with external polarization, which is basically an indirect evidence for the barrier effect and possibly improved product layer characteristics on the steel surface in the presence of micelles. In order to clearly postulate this hypothesis, surface analysis of the steel electrodes is necessary and will be further performed and reported in a future work.

3.1.3. Microstructural analysis of cement paste with admixed PEO_{20}-PPO_{20}-PEO_{70} (P123) micelles – Mercury intrusion porosimetry (MIP).

As previously introduced, the hereby investigated P123 micelles were tested in terms of their influence on steel corrosion behaviour, starting with tests in simulated pore solution (cement extract). Their influence on the bulk cement-based matrix had to be investigated as well, prior to any corrosion tests or microstructural analysis in reinforced cement-based systems. Therefore, 0.016 wt.% per dry cement weight micelles were admixed in cement paste specimens and microstructural properties in terms of porosity and pore size distribution were recorded. Two replicates per condition were investigated. The MIP results are plotted in Fig. 7.

The plots show the results for three types of samples: “demi” – cement paste cast with demineralised water; “PL” – cement paste cast with 0.0024wt.% micelles solution; and “tap” – cement paste cast with ordinary tap water. As can be observed, there is no positive influence of the admixed P123 micelles on microstructural properties. On the contrary – even slight increase in effective porosity was observed (Fig.7, left); the critical pore size for all three specimens is the same (Fig. 7, right). The slightly higher porosity of samples “demi” and “PL” compared to sample “tap” is due to the low (virtually zero) calcium hardness and total dissolved solids in the demineralised water, compared to tap water, which is known to exert microstructural alterations and increased internal leaching – therefore porosity ends up slightly higher, compared to the “tap” water samples. As for the influence of micelles – sample “PL” – clearly no such was observed, despite the expected densification of the matrix in their presence as previously observed for the same concentration of polystyrene-based micelles in cement-based materials [1,8-10, 31]. The result here is related to the instability of P123 micelles in this environment and their transformation to unimers (at pH 13, no chloride contamination, and at 0.0024 wt.% in the mixing water, these micelles are below cmc). Therefore, the expected “nucleation sites” effect for formation of uniformly distributed hydration products and decrease in porosity and
pore size was not observed at this stage. Clearly, stabilization of the P123 micelles would be required (as previously employed for PS-based micelles) or slightly higher concentrations (e.g. higher than 0.024g/l) need to be employed for these type of micelles in order to achieve improved performance in terms of microstructural properties.

4. Conclusions
This paper discussed an initial investigation on the influence of Pluronic P123 micelles in concentration of 0.0024 wt.% on corrosion resistance of steel electrodes in chloride containing alkaline model solutions. Additionally, the influence of 0.016 wt.% per cement weight P123 micelles on porosity and pore size of cement paste was studied. The employed concentration of P123 micelles (for both model solutions and cement paste) was specifically chosen to be equal to the concentration of polystyrene-based micelles, previously reported to exert superior performance for steel and cement-based matrix. A comparison for the influence of the polymer type was thus expected to bring about possible utilization of a cost-effective polymer, such as Pluronic P123. The following conclusions can be drawn at this stage:

- P123 micelles in the employed concentrations can increase the corrosion resistance of steel in chloride-containing solutions after longer than 2h treatment. There is no improvement of the steel passive layer in chloride-free model medium.

- Increased ionic strength and salt concentration at the steel/solution interface trigger micelle re-assembly and impede anodic reactions on the steel surface with external polarization. The result is significant reduction of corrosion current densities. The effect is related at the minimum to enhanced barrier effects on the steel surface. Microscopic investigation is necessary to confirm altered composition and compactness of the product layers.

- The P123 micelles (of 10 nm size) do not exert any superior performance of the bulk cement-based matrix when employed in the hereby investigated concentrations. Stabilization of the micelles, prior to admixing in cement paste, and/or concentrations higher than 0.024g/l in the mixing water would most likely lead to the desired reduction in porosity and critical pore size.

- P123 micelles are a suitable alternative of polystyrene-based micelles, however, optimization for concentration and admixing, as well as steel surface analysis and TEM investigation (for the micelles morphological transformations at varying Cl- concentration and pH) are necessary in order to claim better (or at least similar) performance to the previously studied polystyrene-based micelles.

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5. References:
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