Mode of Action of Anionic Surfactants for Air Entrainment in Cement Pastes w-w/o Fly Ash

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ABSTRACT

Using a simple paste air protocol, an extensive air entrainment investigation was initiated recently on a series of homologous surfactants comprising: n-alkylcarboxylates (n-RCOO⁻), n-alkylsulfonates (n-RSO₃⁻) and n-alkylsulfates (n-RSO₄⁻). Sodium salts of the latter, with hydrocarbon chain lengths varying between C₇ and C₁₂, were used to investigate, both the influence of different anionic head groups and of the varying hydrocarbon chain length on the air-entraining performance of these surfactants. Parallel measurements were performed on the solubility of the surfactants in the paste solution. The combined results provide a general basis for understanding the mode of action of anionic AEA’s in terms of a balance between their inherent surface activity (ability to reduce the surface tension of water) and the solubility of the surfactants in calcium-containing environments.

With several members of the homologous surfactants, the investigation was extended to FA-cement (50:50) pastes containing fly ash from different sources and having a range of residual carbon contents (LOI). The paste method was found most valuable to investigate quantitatively the influence of FA-carbon on air entrainment, and chemical approaches to mitigate the detrimental carbon effects.
INTRODUCTION

The benefits of air entrainment for improving the resistance of concrete towards degradation by freezing and thawing are now widely acknowledged and extensively documented\(^1\). Very small quantities of surfactants can indeed provide drastic improvements to the frost resistance of concrete, by promoting the formation of a highly dispersed network of fine air voids in the cement paste; the latter can accommodate in-situ volume expansion occurring upon freezing of the pore solution.

While the mode of action of the air-entraining surfactants (AEA) can be loosely associated to the formation of air bubbles\(^2,3,4\) in solutions or foams, the actual mechanism of air entrainment by different AEA’s remains largely speculative. The molecular and colloidal phenomena active at the paste-air surfactant interface may differ greatly from those acting in a surfactant film at an air-solution interface. Hence, the air void/bubble analogy can only be qualitatively valid, at best. The mode of action and performance prediction of AEA’s become even more elusive in blended cement pastes, particularly those containing fly ash with unburned carbon.

To help elucidate the mode of action of anionic surfactants, a broad study was recently undertaken on air entrainment in cement pastes, using series of homologous anionic surfactants\(^5\). The latter include: n-alkylcarboxylates (n-RCOO\(^-\)), n-alkylsulfonates (n-RSO\(_3^\text{(-)}\)) and n-alkylsulfates (n-RSO\(_4^\text{(-)}\)), with hydrocarbon chain lengths between C\(_7\) and C\(_{12}\). Within these series, variations in 1- the surface activity of the surfactant and 2- the solubility of their Ca-salt provided valuable insight into the physico-chemical processes which determine air entrainment in cementitious systems\(^5\).

The paste air protocol and experimental strategy developed earlier have now been extended to study the influence of Fly Ash and FA-carbon on air entrainment in cementitious pastes, again using model air-entraining surfactants. Means of mitigating the influence of FA-carbon on air entrainment were also explored in FA-cement pastes.

MATERIALS AND METHODS

Materials

The paste air data reported below were obtained with a portland cement having the composition reported in Table 1. For studies on FA-cement pastes, up to ten different fly ash materials were examined; two particularly different FA compositions are given in Table 1 (FA-B and FA-C). Detailed properties of these materials can be found elsewhere\(^6\). The data shown for FA-cement mortars were obtained with a different group of FA materials, again having a wide range of LOI and air entrainment behaviour.

The paste and mortar mix compositions and flow specifications are summarized in Table 2 for cement-only systems. In FA-containing systems, the degree of cement substitution was 50% in pastes and 30% in mortars, as also indicated with the corresponding data.
### Table 1: Composition and properties of cement and fly ash.

<table>
<thead>
<tr>
<th></th>
<th>Cement</th>
<th>FA - B</th>
<th>FA - C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class (Coal type)</td>
<td></td>
<td>F (Sub-bit.)</td>
<td>C (Sub-bit.)</td>
</tr>
<tr>
<td>SiO₂ (%)</td>
<td>20.1</td>
<td>53.8</td>
<td>32.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.44</td>
<td>26.9</td>
<td>17.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.32</td>
<td>7.06</td>
<td>5.32</td>
</tr>
<tr>
<td>CaO</td>
<td>65.0</td>
<td>1.83</td>
<td>29.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.74</td>
<td>1.22</td>
<td>5.57</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.05</td>
<td>0.62</td>
<td>2.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.85</td>
<td>2.56</td>
<td>0.27</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.27</td>
<td>0.17</td>
<td>2.68</td>
</tr>
<tr>
<td>LOI (%)</td>
<td></td>
<td>4.36</td>
<td>1.62</td>
</tr>
<tr>
<td>BET (m²/g)</td>
<td>3.44</td>
<td>5.36</td>
<td></td>
</tr>
<tr>
<td>S.S.A. of FA-Carbon (m²/g)</td>
<td>34</td>
<td>265</td>
<td></td>
</tr>
<tr>
<td>Specific density (g/cm³)</td>
<td>3.19</td>
<td>2.33</td>
<td>2.76</td>
</tr>
</tbody>
</table>

### Table 2: Paste and mortar mix compositions.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Paste</th>
<th>Mortar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>400 g</td>
<td>350 g</td>
</tr>
<tr>
<td>0.6-0.85mm (20-30 mesh) standard sand</td>
<td></td>
<td>1400 g</td>
</tr>
<tr>
<td>Water (for 11 cm mini-slump)</td>
<td>170 -185 g</td>
<td>210-280 g</td>
</tr>
<tr>
<td>Water (for 80-95% - 10 table drops)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W/C</td>
<td>0.43-0.46</td>
<td>0.6-0.8</td>
</tr>
</tbody>
</table>
The surfactants series used in this study are presented in Table 3 together with key properties of these compounds, namely, their critical micelle concentration (CMC) and the solubility of their Ca-salts, as available. The CMC is the solution concentration at which the surfactant undergoes spontaneous aggregation, the more active surfactants forming micelles more readily, i.e., at lower surfactant concentration. The CMC is thus appropriately taken as a measure of the surface activity of a surfactant.

Table 3: Properties of surfactants investigated.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Symbol</th>
<th>CMC of Na salt at 25°C (mM) (^{(1)})</th>
<th>Solubility of Ca salt (^{(a)}) at 25°C (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carboxylates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Octanoate Na</td>
<td>C(_7)COO</td>
<td>345</td>
<td>9.5 (20(^o)) (^{(2,3)})</td>
</tr>
<tr>
<td>n-Nonanoate Na</td>
<td>C(_8)COO</td>
<td>230</td>
<td>3.95 (20(^o)) (^{(2,3)})</td>
</tr>
<tr>
<td>n-Decanoate Na</td>
<td>C(_9)COO</td>
<td>95</td>
<td>1.31 (^{(4)})</td>
</tr>
<tr>
<td>n-Dodecanoate Na</td>
<td>C(_{11})COO</td>
<td>25</td>
<td>0.09 (15(^o)) (^{(5)})</td>
</tr>
<tr>
<td><strong>Sulfates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Octyl sulfate Na</td>
<td>C(_8)SO(_4)</td>
<td>130</td>
<td>na</td>
</tr>
<tr>
<td>n-Decyl sulfate Na</td>
<td>C(_{10})SO(_4)</td>
<td>33</td>
<td>na</td>
</tr>
<tr>
<td>n-Dodecyl sulfate Na</td>
<td>C(_{12})SO(_4)</td>
<td>8.2</td>
<td>4.57 (50(^o)) (^{(2)})</td>
</tr>
<tr>
<td><strong>Sulfonates</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Octyl sulfonate Na</td>
<td>C(_8)SO(_3)</td>
<td>148</td>
<td>na</td>
</tr>
<tr>
<td>n-Decyl sulfonate Na</td>
<td>C(_{10})SO(_3)</td>
<td>40</td>
<td>3.21 (^{(2,3)})</td>
</tr>
<tr>
<td>n-Dodecyl sulfonate Na</td>
<td>C(_{12})SO(_3)</td>
<td>9.8</td>
<td>0.2 (^{(2,3)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Ca salt under the form of \((n\text{-alkylcarboxylate})_2\text{Ca}\) or \((n\text{-alkylsulfate})_2\text{Ca}\) or \((n\text{-alkylsulfonate})_2\text{Ca}\).

References:
Methods

Paste preparation
Pastes were prepared by 1 min rapid hand mixing of the solids (400 g of cement) and liquid (water and surfactant), followed by intense stirring at room temperature during 2 min using a kitchen mixer (BRAUN model MR400) positioned at 6.3 cm from the bottom of the mixing vessel. The type and mounting of equipment used are illustrated in Figure 1. Using this apparatus, the mixer blade can be displaced vertically through the paste/air interface in highly repeatable cycles. Typically, the displacement was performed with a 3-second cycle and a fixed stroke length of 6 cm.

Fluidity measurements
For fluidity measurements, a portion of the paste was poured to overflow into a mini-slump cone (5.63 cm height, 3.75 cm bottom interior diameter, 1.88 cm top interior diameter); after removing the excess paste with a straight edge, the cone is raised and the paste flow diameter (average of two) is recorded. The fluidity is measured 10 min after mixing. For both measurements, the paste is returned to the batch and retained for subsequent air entrainment measurements.

Air entrainment measurements
The total volume of air entrained in pastes was determined by density measurements; the difference in weight of a fixed volume of paste, mixed without and with added surfactant, was used to determine the quantity of air entrained by the surfactant. In practice, a portion of the paste was transferred to overfill a Plexiglas cylinder (9.5 cm height * 5.2 cm interior diameter), and the excess paste was skimmed-off with a straight edge. The total mass, minus the weight of the empty cylinder, was then recorded.

Figure 1: Illustration of paste mixing device for air entrainment and fluidity measurements.
This procedure was carried out at three time intervals (6, 36 and 66 min following initial cement-water contact), each time, after 1 min gentle hand mixing; this protocol enabled the evaluation of the rate of air loss.

**Surfactant adsorption/precipitation in cement pastes**

To determine the extent of surfactant adsorption or precipitation in the cementitious pastes, the amount of surfactant available (soluble) in the paste solution was measured as follows. Two 50 ml polypropylene centrifuge tube were filled with the paste (after 66min air measurement), and centrifuged for 10 min at 2300 rpm; the supernatant solution was then filtered (0.45 µm) and the surfactant content of the solution was determined by COD (Chemical Oxygen Demand) measurement. Additional details on the procedures described above and the reproducibility of their results were also reported elsewhere.

**Mortars**

The air entrained in mortars was evaluated following the ASTM C185 protocol.

**RESULTS AND DISCUSSION**

The air entrainment results reported below for cement and FA-cement pastes may be influenced by factors such as cement composition and paste fluidity. In previous work, part of the study was performed with three different cements; the results confirmed that, although the absolute values of air entrainment varied somewhat, the relative performance of the different surfactants remained unchanged. Changes in the fluidity of the cement paste were also found to impact significantly on air entrainment results; consequently, the initial fluidity of the cement paste was controlled throughout. The relevance of paste air measurements was also demonstrated from correlations of paste results with mortar and concrete data. Finally, the paste test was also found to yield more reliable predictions of air entrainment in concrete than the 'Foam Index' protocol.

**Air entrainment by the RCOO⁻, RSO₃⁻ and RSO₄⁻ surfactants in cement pastes**

Summarizing the experimental data reported earlier, the level of air entrainment by the various surfactants listed in Table 3 is illustrated in Figure 2. The concentration range investigated (0-15mM in solution, or 0-0.46wt% on cementitious) appeared adequate for all of the surfactants studied, although, the n-alkylcarboxylate data exhibit relatively early air entrainment saturation.

As is readily apparent from Figure 2, both the chemical functionality of the surfactant, and its hydrocarbon chain length, exert an important influence on air entrainment in cement pastes. Under the conditions of our experiments, the optimum air level was achieved with C₁₀ surfactants bearing sulfonate (SO₃⁻) or sulfate (SO₄⁻) head groups. The relative performance of the different surfactants can be traced to their molecular features and solution properties as discussed below.
Surfactant adsorption/precipitation in cement pastes

The solubility of the various surfactants was determined in cement paste extracts and related solutions and slurries. Detailed results of these experiments, as well as the Ca-salts solubility data reported in Table 3, show wide variations in the solubility of the homologous surfactants. As with the air-entrainment, the solubility is seen to depend on both the surfactant head group and the hydrocarbon chain length. Comparing surfactant solubility in solutions, slurries and pastes, it could be concluded earlier that most of the surfactant removed from the paste solution is precipitated as Ca-salts; only minor fractions appeared to be adsorbed onto the solid phases in the pastes.

The actual surfactant concentrations found in solutions extracted from pastes 66 minutes after mixing are plotted Figure 3 against the initial (added) surfactant concentration. The residual levels of surfactants in the paste extracts were found to vary in three distinct ranges (as indicated approximately by the three curves):
- with the higher homologs (C11, C12), the surfactant concentration in the paste extracts remains very low, regardless of the initial dosage;
- with the C7 carboxylate and C8 sulfonate and sulphate, the greater part of the surfactant remains soluble in the paste solution;
- the solubility of the C8 carboxylate is significantly lower than that of the C8 sulfonate, or sulphate.

To relate the air entrainment data and surfactant solubility, Figure 4 illustrates the paste air content obtained with the various surfactants at their corresponding concentration.
Figure 3: Residual surfactant concentrations in solutions extracted from cement pastes.

Figure 4: Air entrainment as function of residual surfactant concentration in cement paste extracts.
Interestingly, the most effective surfactants for air entrainment are those having intermediate solubility (C\textsubscript{10} sulfonate and sulfate). It is also noteworthy that some of the surfactants (particularly carboxylates) having very low solubility in cement paste solution can still entrain significant levels of air.

**Surfactant molecular features: Hydrocarbon chain length and ionic group**

The behaviour of surfactants in aqueous systems is usually related to two key features: 1) the composition and size of their hydrophobic chain (usually hydrocarbons) and 2) the nature and size of their hydrophilic head group\textsuperscript{10}. Typically, with ionic surfactants, the effectiveness (surface activity) increases with increasing hydrocarbon chain length, and increasing degree of ionization, i.e., salts of strong acids (e.g., sulfates) are more extensively ionized than salts of weak acids (e.g., carboxylates)\textsuperscript{11}.

An overall measure of the relative surface activity of surfactants is their critical micelle concentration (CMC). As noted earlier, the latter refers to the minimum surfactant concentration required to initiate the self-aggregation process called micellization: the higher the surface activity of the surfactant, the lower the CMC. For the surfactant series investigated in the present work, the available CMC values are given in Table 3; the [-log(CMC)] values are plotted in Figure 5 against the number of carbon atoms in the hydrocarbon chain (left-hand ordinate).

![Figure 5: Variation of surfactant activity (-log[CMC]) of Sodium salt and solubility of calcium salt as function of hydrocarbon chain length.](image-url)
As is generally found within homologous surfactant series, the \([-\log (\text{CMC})]\) values vary linearly with chain length, or number of carbon atoms in the chain. Comparing the data for different series, the CMC values decrease in the order COO > SO₃ > SO₄; the differences between the three series are fairly small, but significant, and in the same order as the corresponding acid strength of COOH, SO₃H and SO₄H. From these considerations, the surfactant activity and air-entraining effectiveness should be highest for n-alkylsulfates bearing the longest hydrocarbon chains, namely n-C₁₂SO₄.

This contrasts with the observation of maximum air entrainment with intermediate chain length surfactants (sulfonates and sulfates); the latter can, however, be understood from the relative solubility of the surfactants in cement paste solution. The available data on the solubility of Ca-salts of the various surfactants are shown in Figure 5, again plotted as function of hydrocarbon chain length (right-hand ordinate). Assuming that the insoluble Ca-salt of the surfactant contributes little to air entrainment, the opposite trends in surfactant activity (CMC) and solubility as function of hydrocarbon chain length provide a rational explanation for maximum air entrainment at intermediate surfactant chain lengths. As suggested from Figure 5, the optimum air entrainment should occur near the intersection of the two curves, where the combined effects of solubility and activity of the surfactant are optimal.

The relative position of the intersection points in Figure 5, corresponding respectively to RCOO, RSO₃ and RSO₄ surfactants, is qualitatively consistent with the air entrainment observations in these series (Figure 3). Note, however, that the right- and left-hand ordinates are not uniquely related; hence the optimal chain length (position of the maximum) cannot be predicted from Figure 5.

**Paste air stability**

As further insight into the phenomenology of air entrainment, the stability of the surfactant-promoted air voids was assessed through the relative rate of air loss; the latter was defined as the time required for reaching a 50% loss from the initially entrained air volume \(t_{1/2}\). The rate of air loss depends, of course, on the surfactant concentration, so \(t_{1/2}\) values were calculated at different concentrations (1, 3 and 6 mM initial concentrations). The results are reported in Figure 6.

The relative stability of the paste air voids, as reflected by the magnitude of the \(t_{1/2}\) values, follows trends similar to those observed in the initial air volume entrained. As noted above, maximum air entrainment was observed with C₁₀ surfactants, and the later also appear to yield more stable air voids (longer \(t_{1/2}\) values). A notable exception is the behaviour of the carboxylate surfactants; recalling that, for example, the C₉ carboxylate entrained rather little air (Figures 2-4); the air entrained is quite stable. This observation lends support to the earlier suggestion that the insoluble Ca-salts of fatty acids can still contribute to air entrainment². Indeed, insoluble Ca-salts of n-alkylcarboxylic acids prepared separately could entrain significant levels of air when introduced in a cement paste; such salts would not, by themselves, support the formation of stable air bubbles, and were instead reported to act as potential defoamers¹³,¹⁴.
Figure 6: Effect of surfactant type, chain length and concentration on the time to attain 50% air loss (based on initial air).

Phenomenology of air void formation/dispersion promoted by anionic surfactants

In accordance with the results and observations discussed above, the formation of stable microscopic air voids in a cement paste may be described as the result of two equilibrating processes: air entrapment/dispersion and air void stabilization.

First, the air entrapment normally observed when mixing a cement paste is promoted by the surfactant; the amount of air which can be entrapped and dispersed in the paste will depend on the surface activity of the AEA, i.e., its ability to reduce the surface tension of water. The initial air entrainment process thus relies on the available surfactant molecules (soluble in the paste solution); the latter are most effective in reducing water surface tension and they can diffuse rapidly to the air/paste interfaces to generate the surfactant films. The insoluble Ca-salts of anionic surfactants should contribute only marginally to the initial air entrainment process.

Second, the stabilization of the air voids formed towards shear forces, coalescence into larger voids, or outwards diffusion of the air (re-dissolving into the solution) relies on a combination of effects. The elasticity and robustness of the surfactant film at the air void interface depend on:

- Interaction between the ordered hydrocarbon chains in the surfactant film, the interactions being stronger for the longer chain surfactants.
- Incorporation of insoluble surfactant molecules, i.e., in the form of Ca-salt, in the interfacial film. The Ca-salt being electrically neutral, the electrostatic repulsion normally operating between the head groups of anionic surfactants is absent, so the cohesion of the film is enhanced\textsuperscript{1,2}. This stabilization process is analogous to that produced by long chain fatty alcohols\textsuperscript{17}.

- Incorporation of colloidal particles (cement or other) in the interfacial film, a well-known phenomenon in other colloidal systems\textsuperscript{19,20}.

- Interaction of the air void with a neighbouring surface (e.g. surfactant-coated cement particle or aggregate) providing a protecting 'wall' against shear forces, thus enhancing the air void stability.

The air void stabilization mechanisms invoked here, although difficult to assess individually, are most likely responsible for the relative performance of different surfactants (or mixtures) in promoting stable air void network.

**Air entrainment in Fly Ash-cement pastes and mortars**

The influence of residual FA-carbon on air entrainment in FA-cement (30-70) mortars is illustrated in Figure 7; the latter shows the air entrained (vol\%) with a fixed dosage of two common air-entraining agents, a Tall oil fatty acid salt and Sodium dodecylbenzene sulfonate (DDBS), plotted against the LOI values of the fly ash. As expected from countless other observations\textsuperscript{8,22}, the volume of air entrained is strongly depressed by the presence of residual FA-carbon. The effect increases with carbon content (LOI), though clearly not in a linear fashion; the specific properties of the residual carbon (surface area, porosity, surface functionality) also play a role in the carbon-AEA interactions and air entrainment. This is now acknowledged as a fundamental problem for predicting air entrainment behaviour in FA-cement concrete\textsuperscript{8}.

A similar situation is illustrated in Figure 8 for air entrainment by DDBS at three dosages in cementitious pastes containing 50wt\% FA from different sources (the FA materials are different from those referred to in Figure 6 and their composition and properties can be found in ref.6). As noted with mortar data, the entrained air level decreases in relation to the amount of residual carbon, though not linearly with increasing LOI. To further illustrate the FA-carbon effects, two FA materials having different LOI values were selected for a detailed investigation using the homologous surfactants of the earlier study.

**Air entrainment in FA-cement pastes with n-alkylsulfate surfactants**

The paste air entrainment data obtained with the C\textsubscript{8}SO\textsubscript{4} surfactant are given in Figure 9 as function of concentration in the cement and FA-cement pastes; corresponding data are reported in Figure 10 for C\textsubscript{10}SO\textsubscript{4}, the latter being one of the most effective AEA examined in this work.
Figure 7: Air entrained (vol%) in cement and in (30:70) fly ash:cement mortars by DDBS (0.002%) and a tall oil fatty acid salt (0.005%).

Figure 8: Air entrained (vol%) in (50:50) fly ash:cement pastes by various dosages DDBS; note the FA materials of Figs 7 and 8 are different.
Figure 9: Air entrainment in FA-cement paste by n-octyl sulfate (C₈SO₄).

Figure 10: Air entrainment in FA-cement paste by n-decyl sulfate (C₁₀SO₄).
With both surfactants, the presence of the fly ash labeled ‘C’ (FA-C) had little influence on the entrained air volumes. On the other hand, in the presence of fly ash-B, much higher surfactant dosages were required to achieve a given air entrainment level.

The higher LOI and carbon content is qualitatively consistent with the higher air depressing ability of the B fly ash.

Measurement of residual surfactant concentrations in these pastes yielded the results shown in Figure 11 and Figure 12. With both surfactants, the residual concentration in the paste extracts was found to be lower in pastes containing fly ash, compared to cement-only pastes.

While both FA decrease the concentration of residual surfactant, the effect is greater for FA-B (higher LOI). Since carbonaceous materials similar to the carbon found in fly ash (e.g. activated carbon, carbon black) were shown to adsorb AEA surfactants\(^6\), it is safe to conclude that the \(\text{C}_8\text{SO}_4\) and \(\text{C}_{10}\text{SO}_4\) surfactants are partly adsorbed by the FA-carbon. However, the relative difference between the effects of FA-B and FA-C is much greater on the air entrained values than on the surfactant adsorption; hence, it can be anticipated that effects other than surfactant adsorption contribute to the air entrainment reduction. Other contributing mechanisms are discussed in a separate paper\(^{21}\).

**Mitigating FA-carbon effects with sacrificial agents**

Various approaches have been proposed to neutralize, or compensate for, the residual carbon present in fly ash materials\(^6,22\). One such approach, which has found broad industrial application, is the introduction of ‘sacrificial’ admixtures\(^22\). The latter designate a class of chemical compounds which are not air-entraining by themselves, but can interact with the FA-carbon to mitigate its effect on air entrainment.

The influence of a model sacrificial admixture, in this case ethyleneglycol-phenylether (EGPE), on air entrainment by \(\text{C}_8\text{SO}_4\) in FA-cement pastes is illustrated in Figure 13. In the absence of the sacrificial agent (SA), the B fly ash exerts a strong deleterious effect on air entrainment. Addition of low dosages of the SA in the FA-cement pastes (0.025%-0.05%) largely neutralizes the FA-carbon effect. Interestingly, beyond a minimum dosage, the air recovery effect induced by the SA reaches a saturation, with no deleterious effect upon further addition, i.e., allowing for substantial overdosage. Since EGPE is not significantly air-entraining by itself, it may be viewed as adsorbing preferentially onto the FA-carbon, releasing the surfactant molecules to perform their air-entraining function. While this provides a simple explanation for the mode of action of the sacrificial admixtures, more recent work shows that other mechanisms contribute to the benefits derived from these admixtures. The mode of action of sacrificial admixtures and their application in mortar and concrete will be discussed in a following paper\(^{21}\).
Figure 11: Residual n-octyl sulphate ($C_8SO_4$) surfactant in FA-cement paste solution.

Figure 12: Residual n-decyl sulphate ($C_{10}SO_4$) surfactant in FA-cement paste solution.
CONCLUSION

The simple paste air entrainment protocol developed recently was found most adequate for fundamental investigations on air entrainment in cementitious pastes. Measurements performed with three series of anionic surfactants, as model air-entraining agents in cement pastes, have identified the key surfactant features which determine their performance as air-entraining agents (AEA).

The optimal performance of an anionic AEA is achieved as a compromise between the surface activity (sometimes referred to as 'surfactancy') of the surfactants and their solubility in cement paste solution. Within a homologous series of surfactants, the two features vary in opposite directions as function of the surfactant’s hydrocarbon chain length; hence, maximum air entrainment is obtained with intermediate chain length surfactants. Comparing surfactants having different functional groups at a given chain length, the air entrainment decreases in the order sulphate > sulfonate > carboxylate, in line with the respective solubility of these compounds.

These observations, coupled to the results of paste air stability measurements, provide reliable insight into the phenomenology of air void formation in cement paste as...
promoted by anionic surfactants. The suggested mechanism proposes that the volume of entrained air depends on the amount and surface activity (amount x activity) of the surfactant solubilized in the paste solution; on the other hand, stabilization of the finely dispersed air voids is assisted by the insoluble Ca-salts of the surfactant and other colloidal and interfacial effects.

Air entrainment data collected on FA-cement pastes confirm the usefulness of the paste air protocol for systematic studies of the role of residual FA-carbon on air entrainment. The deleterious effect of FA-carbon on air entrainment could be traced, in part, to the adsorption of the AEA surfactant by the carbon particles and, in part to other effects to be discussed later. These effects can be largely neutralized through the addition of 'sacrificial' admixtures (SA).

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