Amphiphiles containing aromatic groups in the hydrophobic part
Visscher, Inge

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Chapter 2
Mono-\textit{n}-alkyl phosphates
Single-tailed surfactants containing an aromatic moiety in the tail

The synthesis of three mono-\textit{n}-alkyl phosphate amphiphiles is described. Their aggregation behaviour has been investigated. The critical micelle concentrations (CMC) of \textit{n}-tetradecyl phosphate and 11-phenoxyundecyl phosphate were determined by drop tensiometry and pyrene fluorescence. The large difference between the CMC values of the two compounds in bidistilled water suggests a different ionisation state of the head group in micelles of 11-phenoxyundecyl phosphate. It is suggested that the phenoxy group resides not only in the micellar core, but also to a significant extent at the micellar interface. The latter assumption was confirmed by \textsuperscript{1}H-NMR spectroscopy.

2.1 Introduction

Single-tailed surfactants can display a wide variety of aggregate morphologies, depending on their exact molecular structure. Previously it has been found that the length and branching of the hydrophobic tail has a large influence on the aggregate morphology and properties.\textsuperscript{1-4} Introducing unsaturated bonds in the alkyl chain of an amphiphile generally increases the critical micelle concentration (CMC).\textsuperscript{5-8} The introduction of an acetylenic moiety in the chain also leads to larger CMC values.\textsuperscript{5,9,10} Modification of the hydrophobic part of a single-chain amphiphile with a rigid aromatic segment (e.g. diphenyl-azomethine, biphenyl and azobenzene) changes the aggregate morphology and, depending on the position along the chain and the length of the ethylene chain, disks, rods, tubes and lamellar aggregates have been observed.\textsuperscript{11-14} Also amphiphiles with styrene,\textsuperscript{15,16} phenyl, phenoxy and naphthoxy groups\textsuperscript{17-19} have been investigated. Most of these aromatic moieties have been incorporated in the middle of the hydrophobic chain and not at the end.

Mono-\textit{n}-alkyl phosphates can exist in three protonation states, depending on the pH. At low pH the phosphate head group is fully protonated, increasing the pH results in gradual deprotonation of the head group (Scheme 2.1).

\[ \text{ROPO}_3\text{H}_2 \quad \text{ROPO}_3\text{H}^- \quad \text{ROPO}_3^{2-} \]

\textbf{Scheme 2.1} Successive protonation states of the phosphate head group.
This variable charge can give rise to interesting aggregation behaviour. *N*-dodecylphosphoric acid forms vesicles at low pH. Branched alkyl phosphates form already vesicles at pH 11, at lower pH values the alkyl phosphates form larger vesicles. 

In this chapter the effects of incorporating an aromatic moiety at the end of the hydrophobic chain of a mono-*n*-alkyl phosphate on its aggregate morphology and the properties of the formed aggregates have been investigated. The total chain length was kept approximately equal.

### 2.2 Synthesis

Often mono-*n*-alkyl phosphates are prepared by stirring the corresponding alcohol with pyrophosphoric acid. The phosphate amphiphiles in this chapter were prepared by stirring the alcohol with an excess of phosphoryl chloride and subsequent hydrolysis. The alkyl phosphates were then converted into their sodium salts by adding two equivalents of sodium ethanoate. The synthesis of the derivatised long-chain alcohols used for the synthesis of the mono-*n*-alkyl phosphates will be described in Chapter 5.

![Scheme 2.2 Synthesis of the mono-*n*-alkyl phosphates.](image-url)
2.3 Aggregation behaviour and Krafft temperature

$C_{14}PO_4$, $C_8$ObiphPO$_4$ and $C_8$OnaphtPO$_4$ did not dissolve in water at room temperature. $C_{14}PO_4$ did dissolve upon increasing the temperature. The Krafft temperature was measured by monitoring the temperature dependence of the transmission at 400 nm of a stirred 10 mM aqueous solution. The temperature at which the transmission is 50% upon heating (indicated with the dotted line), was taken as the Krafft temperature and amounts to 45 °C for $C_{14}PO_4$ (Figure 2.1).

$C_8$ObiphPO$_4$ and $C_8$OnaphtPO$_4$ did not dissolve even upon heating. Apparently the Gibbs energy necessary to break down the crystal lattice is too large.

$C_{11}$OphenPO$_4$ dissolves at room temperature; this could be an indication that the phenoxy group disturbs the packing in the lattice as compared to $C_{14}PO_4$. This reduction of the Krafft point may be compared to the reduction of the Krafft point upon branching of the alkyl chain.23

Figure 2.1 Transmission plotted against the temperature of a 10 mM aqueous solution of $C_{14}PO_4$. 

$C_8$ObiphPO$_4$ and $C_8$OnaphtPO$_4$ did not dissolve even upon heating. Apparently the Gibbs energy necessary to break down the crystal lattice is too large.

$C_{11}$OphenPO$_4$ dissolves at room temperature; this could be an indication that the phenoxy group disturbs the packing in the lattice as compared to $C_{14}PO_4$. This reduction of the Krafft point may be compared to the reduction of the Krafft point upon branching of the alkyl chain.23
2.4 Pyrene fluorescence spectroscopy

The critical micelle concentrations (CMC) of C\textsubscript{14}PO\textsubscript{4} and C\textsubscript{11}OphenPO\textsubscript{4} in pure water were determined by pyrene fluorescence. Previous work has established that the ratio of the intensity of the first (I\textsubscript{1}) and third peak (I\textsubscript{3}) in the fluorescence spectrum of the probe reflects the medium polarity experienced by the probe at its binding site.\textsuperscript{24,25} The results are shown in Table 2.1.

The CMC of C\textsubscript{11}OphenPO\textsubscript{4} is much higher (ca. 5 times) than that of C\textsubscript{14}PO\textsubscript{4}. The CMC that was found for C\textsubscript{14}PO\textsubscript{4} differs from the literature value obtained by surface tension (17 mM).\textsuperscript{26} However the surface tension measurements were performed in 0.01 M NaOH, whereas the fluorescence measurements were carried out in bidistilled water. It is likely that in distilled water the phosphate group in the micelle is partially monoanionic, whereas in 0.01 M NaOH it is completely dianionic. The increased head group size and the higher head group charge cause the higher CMC value. The polarity of micelles composed of C\textsubscript{11}OphenPO\textsubscript{4} as reflected by the value of I\textsubscript{1}/I\textsubscript{3} (1.2), seems to be slightly higher than the polarity of micelles composed of C\textsubscript{14}PO\textsubscript{4} (I\textsubscript{1}/I\textsubscript{3} = 1.1). This could mean that in micelles composed of C\textsubscript{11}OphenPO\textsubscript{4} at the location of the pyrene molecule, more water is present than in micelles formed from C\textsubscript{14}PO\textsubscript{4}.

<table>
<thead>
<tr>
<th></th>
<th>CMC (mM)</th>
<th>I\textsubscript{1}/I\textsubscript{3} above CMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{14}PO\textsubscript{4}</td>
<td>5.1</td>
<td>1.1</td>
</tr>
<tr>
<td>C\textsubscript{11}OphenPO\textsubscript{4}</td>
<td>25</td>
<td>1.2</td>
</tr>
</tbody>
</table>

2.5 Surface tension and head group size

The surfactant-concentration dependence of the surface tension was measured to determine the CMC values and the head group area. In Figure 2.2 the surface tensions are plotted against the logarithm of the concentration in bidistilled water. The CMC corresponds to the break in the plot and is 4 mM for C\textsubscript{14}PO\textsubscript{4} and 30 mM for C\textsubscript{11}OphenPO\textsubscript{4} which is in reasonable agreement with the results of the pyrene fluorescence measurements.
The surface tension at the CMC ($\gamma_{\text{CMC}}$) of C$_{14}$PO$_4$ is 28.4 mN/m. This is much lower than the $\gamma_{\text{CMC}}$ of C$_{11}$OphenPO$_4$ (48.5 mN/m) and correlates with the difference in CMC. The correlation between CMC and $\gamma_{\text{CMC}}$ has been found before. A low surface tension means that the aqueous surface is well covered with alkane-like materials. The increase of $\gamma_{\text{CMC}}$ means that in the case of C$_{11}$OphenPO$_4$, the density of the alkyl chains at the air-water interface has been decreased compared to that of C$_{14}$PO$_4$. The area per molecule ($A_0$), calculated from the Gibbs equation, is consistent with this situation. If the ratio of the surfactant to counter ion is assumed to be 1:1, $A_0$ is 39 Å$^2$ for C$_{14}$PO$_4$ and 119 Å$^2$ for C$_{11}$OphenPO$_4$. If we assume that three species are present at the interface whose concentration changes with surfactant concentration, $A_0$ is 58 Å$^2$ for C$_{14}$PO$_4$ and 178 Å$^2$ for C$_{11}$OphenPO$_4$ (Table 2.2). So the area occupied by a C$_{11}$OphenPO$_4$ molecule at the air-water interface is about three times larger than the area occupied by C$_{14}$PO$_4$. This difference can be explained by assuming that the less hydrophobic phenoxy group on average resides more in the region near the head group and the chain bends more towards the micellar interface compared to an unsubstituted alkyl chain.

![Figure 2.2](image_url)  

**Figure 2.2** Concentration-dependence of the surface tension of solutions of C$_{14}$PO$_4$ (□) and C$_{11}$OphenPO$_4$ (●) at 40 °C.

This bending towards the micellar interface will increase the distance between the head groups. Another effect of this bending will be that the pKa of the phosphate changes in the micelle and that in double-distilled water the micelle composed of C$_{11}$OphenPO$_4$ contains more dianionic phosphate groups than C$_{14}$PO$_4$. 

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To compare the CMC to literature values, the measurements were repeated in 0.01 M NaOH (Figure 2.3, Table 2.2). The CMC found for C$_{14}$PO$_4$ was 30.5 mM at 40 °C and is different from the literature value of 17 mM at 25 °C.\textsuperscript{26} The difference could be due to the temperature difference (15 degrees higher in our measurements because we observed precipitation of C$_{14}$PO$_4$ at room temperature). $A_0$ increased to 69 Å$^2$ for C$_{14}$PO$_4$ if the ratio of the surfactant to counter ion is taken as 1:1. If we assume that three species are present at the interface whose concentration changes with surfactant concentration, $A_0$ increases to 104 Å$^2$ for C$_{14}$PO$_4$. The $\gamma_{\text{CMC}}$ increases to 39.1 mN/m, which is what one would expect when the head group increases in size.

The CMC (38.5 mM) and $\gamma_{\text{CMC}}$ (47.8 mN/m) values found for C$_{11}$OphenPO$_4$ differ little from the values obtained in bidistilled water. This supports our hypothesis that the pKa of C$_{11}$OphenPO$_4$ in a micelle differs from the pKa of C$_{14}$PO$_4$ in a micelle. Apparently, both in bidistilled water and in 0.01 M NaOH solution the head groups are mostly doubly deprotonated. The CMC of C$_{11}$OphenPO$_4$ in 0.01 M NaOH is higher, because more phosphates are doubly deprotonated than in bidistilled water. The values obtained for $A_0$ ($n=2$, 92 Å$^2$, $n=3$, 138 Å$^2$) are smaller than those in bidistilled water, probably due to the increased ionic strength of the solution. Compared to the CMC of C$_{14}$PO$_4$ in 0.01 M NaOH the CMC of
C\textsubscript{11}OphenPO\textsubscript{4} is larger. The CMC is an indication of the hydrophobicity of the amphiphile chain and the increased CMC of C\textsubscript{11}OphenPO\textsubscript{4} shows the decreased hydrophobicity of the tails of C\textsubscript{11}OphenPO\textsubscript{4} compared to those of C\textsubscript{14}PO\textsubscript{4}.

Table 2.2 Surface tension results

<table>
<thead>
<tr>
<th></th>
<th>CMC (mM)</th>
<th>(A_0), (n=2) (Å(^2))</th>
<th>(A_0), (n=3) (Å(^2))</th>
<th>(\gamma_{CMC}) (mN/m)</th>
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</thead>
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<tr>
<td>C\textsubscript{14}PO\textsubscript{4}</td>
<td>4</td>
<td>39</td>
<td>58</td>
<td>28.4</td>
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<tr>
<td>C\textsubscript{11}OphenPO\textsubscript{4}</td>
<td>30</td>
<td>119</td>
<td>178</td>
<td>48.5</td>
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<tr>
<td>C\textsubscript{14}PO\textsubscript{4a}</td>
<td>30.5</td>
<td>69</td>
<td>104</td>
<td>39.1</td>
</tr>
<tr>
<td>C\textsubscript{11}OphenPO\textsubscript{4a}</td>
<td>38.5</td>
<td>92</td>
<td>138</td>
<td>47.8</td>
</tr>
</tbody>
</table>

(a) In 0.01M NaOH.

2.6 \(^{1}\)H-NMR investigations

In the previous paragraph the larger head group cross-sectional surface area \((A_0)\) found for C\textsubscript{11}OphenPO\textsubscript{4} compared to the value found for C\textsubscript{14}PO\textsubscript{4} was explained by assuming that the polarisable and less hydrophobic phenoxy group bends back towards the micellar interface. \(^{1}\)H-NMR measurements were performed on surfactant solutions of C\textsubscript{14}PO\textsubscript{4} and C\textsubscript{11}OphenPO\textsubscript{4} below and above their CMC to find further evidence for this assumption. The results are summarised in Table 2.3.

Micellisation of C\textsubscript{14}PO\textsubscript{4} induces a downfield shift for all proton resonances. The protons in the tail near the head group exhibit the largest shift. The downfield shift can be attributed to the change from water to the less polar micellar environment.\textsuperscript{28,29} Similar behaviour has been observed for the cationic surfactant \(n\)-hexadecyltrimethylammonium bromide.\textsuperscript{28}

All proton resonances of C\textsubscript{11}OphenPO\textsubscript{4} exhibit an upfield shift upon micellisation, in contrast to the downfield shift observed for all proton resonances of C\textsubscript{14}PO\textsubscript{4} upon micellisation. The upfield shift of the aromatic proton resonances is due to the transfer from a polar to less polar environment.\textsuperscript{28,31} The chemical shift of the aliphatic protons results from a combination of the reduced polarity of the environment of the protons upon micellisation (downfield shift) and the influence of the magnetic anisotropy of the aromatic ring (upfield shift). All aliphatic proton resonances are shifted upfield, so apparently all protons are experiencing an influence of the magnetic anisotropy of the aromatic ring, even the protons near the micellar interface. This means that the location of the aromatic ring is not exclusively confined to the micellar core, but that the phenoxy group can also be
found at the interfacial region to a significant extent. Cationic surfactants containing an aromatic moiety in the tails display similar behaviour.\textsuperscript{18,29}

Table 2.3 \textsuperscript{1}H-NMR chemical shifts in micellar and non-micellar D\textsubscript{2}O solutions of C\textsubscript{14}PO\textsubscript{4} and C\textsubscript{11}OphenPO\textsubscript{4}. $\Delta \delta = \delta_{\text{conc. > CMC}} - \delta_{\text{conc. < CMC}}$

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (1mM)</th>
<th>$\delta$ (20 mM)</th>
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<th>$\delta$ (10 mM)</th>
<th>$\delta$ (40 mM)</th>
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<td>3.883</td>
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<tr>
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<td>1.384</td>
<td>0.025</td>
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</tr>
<tr>
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<td>1.794</td>
<td>-0.041</td>
</tr>
<tr>
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<td></td>
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<td>4.17</td>
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</tr>
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<td></td>
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<td>7.425</td>
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<tr>
<td>14</td>
<td>0.936</td>
<td>0.959</td>
<td>0.023</td>
<td>7.125</td>
<td>7.098</td>
<td>-0.027</td>
</tr>
</tbody>
</table>

2.7 Discussion and conclusions

The CMC values of C\textsubscript{14}PO\textsubscript{4} and C\textsubscript{11}OphenPO\textsubscript{4} show a remarkable difference in bidistilled water. The values obtained by pyrene fluorescence and surface tension measurements coincide within a reasonable margin (Table 2.4). \textsuperscript{1}H-NMR measurements showed that even protons in the tail near the head group in the micelle experience the anisotropy of the phenyl ring. This indicates that the phenyl ring is not only situated in the micellar core, but tends to bend back toward the micellar interface. The reason for this is that the phenoxy group is more polar than an alkyl group. Therefore the phenoxy group can interact with and be hydrated by water molecules. The presence of the phenoxy group at the micellar interface alone
cannot increase the $A_0$ with a factor three. The difference can be rationalised by assuming that the presence of the phenoxy group at the micellar surface changes the $pK_a$ of the phosphate in the micelle and that in $C_{11}$OphenPO$_4$ micelles, more phosphate groups are dianionic compared to the phosphate groups in $C_{14}$PO$_4$ micelles. A larger hydrated head group size increases both the CMC and the $A_0$. This explanation is consistent with the CMC and $A_0$ values found for micelles of $C_{14}$PO$_4$ and $C_{11}$OphenPO$_4$ in 0.01M NaOH. The $A_0$ and CMC values of $C_{14}$PO$_4$ and $C_{11}$OphenPO$_4$ in micelles in 0.01M NaOH, where we assume that all phosphates are dianionic, do not differ much. The $A_0$ value of $C_{11}$OphenPO$_4$ in 0.01M NaOH is smaller than that in bidistilled water, this probably has to do with the increased ionic strength of the micellar solution which increases the counterion binding and decreases the electrostatic head group repulsions. The decrease in head group repulsions allows the amphiphile molecules to come closer together, resulting in a smaller $A_0$ and a decreased $\gamma_{\text{cmc}}$.

<table>
<thead>
<tr>
<th>Table 2.4</th>
<th>Comparison of CMC values obtained with different methods.</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>CMC$^a$ (pyrene)</td>
</tr>
<tr>
<td>$C_{14}$PO$_4$</td>
<td>5.1</td>
</tr>
<tr>
<td>$C_{11}$OphenPO$_4$</td>
<td>25</td>
</tr>
</tbody>
</table>

(a) In mM. (b) In 0.01M NaOH. (c) $n$ is 3, $A_0$ in Å$^2$.

2.8 Experimental

**11-Phenoxyundecyl dihydrogen phosphate (1)**

A mixture of 11-phenoxyundecanol (0.500 g, 1.9 mmol) and 2 ml POCl$_3$ was stirred at room temperature in a closed flask for two days. The stopper was periodically removed to allow the HCl gas to escape. Water was added and the product extracted with ether ($3 \times 30$ ml). The combined organic layers were dried on MgSO$_4$ and the ether was evaporated. The resulting solid was crystallised from ether/hexane (1:1). Yield: 0.366 g, 1.1 mmol, 56%; mp. 73.5-75 °C; $^1$H-NMR (200 MHz,CDCl$_3$) δ 7.30-7.22 (m, 3H), 6.95-6.86 (m, 2H), 4.04-3.90 (m, 4H), 1.80-1.66 (m, 4H), 1.28 (bs, 14H); $^{13}$C-NMR (50 MHz, CDCl$_3$) δ 159.69, 130.03, 121.09, 115.10, 68.78(d, $J_{CP} = 3.4$ Hz), 68.50, 30.63, 30.12, 30.03, 29.92, 29.78, 26.69, 25.96, 25.96; $^{31}$P-NMR (81 MHz,CDCl$_3$) δ 1.00; Anal. Calcd. for C$_{17}$H$_{27}$O$_4$PNa$_2$: C, 52.6; H, 7.0. Found C, 52.7; H, 7.3.
N-tetradecyl dihydrogen phosphate (2)

N-tetradecyl dihydrogen phosphate was synthesised analogously to 11-phenoxyundecyl dihydrogen phosphate. The solid was recrystallised from petroleum ether (40-60). Yield 1.351 g, 4.6 mmol, 48 % mp. 65-67 °C (lit. 69 °C)\(^2\); \(^1\)H-NMR(200 MHz,CDCl\(_3\)) \(\delta\) 4.01, (m, 2H), 1.66 (bs, 2H), 1.25 (bs, 2H), 0.88 (t, \(J=6.4\) Hz, 3H); \(^13\)C-NMR(50 MHz,CDCl\(_3\), CD\(_3\)OD) \(\delta\) 66.63 (d, \(J_{CP} = 5.7\) Hz), 31.59, 30.08, 29.94, 29.02, 28.91, 25.16, 22.34, 13.64; \(^31\)P-NMR(200 MHz,CDCl\(_3\), CD\(_3\)OD) \(\delta\) 0.624.

8-(2-Naphthyloxy)octyl dihydrogen phosphate (3)

8-(2-Naphthyloxy)octyl dihydrogen phosphate was synthesized analogously to 11-phenoxyundecyl dihydrogen phosphate, except after addition of water, the precipitate was filtered off and the obtained material was crystallised from ethanol. Yield: 0.747 g, 2.1 mmol, 58%. The product displayed liquid crystalline behaviour from 127 °C to 151-154 °C where it melts to an isotropic fluid state. \(^1\)H-NMR (200 MHz,CDCl\(_3\), CD\(_3\)OD) \(\delta\) 7.77-7.70 (m, 3H), 7.68-7.24 (m, 2H), 7.16-7.07 (m, 2H), 4.07 (t, \(J= 6.4\) Hz, 2H), 3.91 (dt, 2H), 1.86-1.26 (m, 12H); \(^31\)P-NMR (81 MHz, CDCl\(_3\), CD\(_3\)OD) \(\delta\) 0.404.

8-(1,1'-Biphenyl-4-yloxy)octyl dihydrogen phosphate (4)

8-(1,1'-Biphenyl-4-yloxy)-1-octanol (1.000 g, 3.35 mmol) was added to an excess of POCl\(_3\) (559 \(\mu\)l, 6 mmol) and pyridine (0.338 g., 3.35 mmol) in dry THF under a nitrogen atmosphere. After stirring for a day the mixture was poured into water and the precipitate was filtered off and washed with 5% HCl and water. The filter cake was suspended in ethanol, stirred for an hour and filtered. The solid was then suspended in dichloromethane and heated to reflux for two hours. After cooling and filtration a white solid was obtained. (0.5055 g, 1.34 mmol, 40%); \(^1\)H-NMR (200 MHz,CDCl\(_3\)) \(\delta\) 7.40-7.19 (m, 7H), 6.85-6.81 (m, 2H), 3.99-3.86 (m, 4H), 1.66-1.24 (m, 12H); \(^13\)C-NMR (50 MHz,CDCl\(_3\)) \(\delta\) 157.93, 140.00, 132.67, 127.59, 126.85, 125.41, 113.69 , 66.91 , 65.42 (d, \(J = 5.3\) Hz), 29.45 , 29.30, 28.28, 28.13, 24.98, 24.48; \(^31\)P-NMR (81 MHz, CDCl\(_3\)) \(\delta\) -0.06.

Disodium alkyl phosphates

All di-sodium phosphate salts were prepared by adding 2.1 equiv. of sodium ethanoate solution to a solution of the \(n\)-alkyl phosphate in ethanol. The di-sodium salt precipitated from the solution.

Pyrene fluorescence spectroscopy

The pyrene solution was prepared by adding 0.5 mg pyrene to 50 ml of bidistilled water. After standing overnight the undissolved pyrene was filtered off and the
solution was diluted with an equal part of bidistilled water. Pyrene fluorescence spectra were measured on an SLM-Aminco SPF-500C spectrofluorometer equipped with a thermostatted cell holder and magnetic stirring at 45 °C. The excitation wavelength was 335 nm, bandpass 5 nm. The emission was monitored from 370 to 390 nm (bandwidth 2 nm, stepsize 0.2 nm).

Surface tension measurements
Surface tensions were measured on a Lauda TVT1 drop tensiometer equipped with a Lauda RM6 temperature controller at 40 °C. A surface tension value of bidistilled water of 68.85 ± 0.4 mN m⁻¹ (literature value at 40 °C = 69.56 mN/m) was taken as an internal standard before starting measurements on surfactant solutions. The area per molecule was calculated using the Gibbs adsorption equations (1) and (2):

\[ \Gamma_{\text{max}} = -1/(2.303nRT) \left( \frac{\partial \gamma}{\partial \log C} \right)_T \]  
\[ A_0 = \left( N_A \Gamma_{\text{max}} \right)^{-1} \times 10^{16} \]  

where \( \gamma \) is the surface tension in mN/m, \( T \) is the absolute temperature, \( R = 8.31 \) J/(mol K), \( N_A \) = Avogadro’s number, \( \Gamma_{\text{max}} \) is in moles per square centimeter, \( A_0 \) is in Å² and \( n \) is the number of ionic species whose concentration at the interface varies with a change in the surfactant concentration.

NMR measurements
The surfactants were dissolved in D₂O by heating to 50°C. The ¹H-NMR spectra were recorded using a 300 MHz Varian spectrometer at 40 ± 1 °C. The HDO signal was used as chemical shift reference and was set to 4.70 ppm.

2.9 References


Chapter 2


