INTERACTIONS BETWEEN SURFACTANTS AND HYDROPHOBICALLY MODIFIED POLYMERS STUDIED BY SIZE EXCLUSION CHROMATOGRAPHY.

Michèle MILLEQUANT, Ilias ILIOPoulos and James LESEC.

Laboratoire de Physico-chimie Macromoléculaire, Université Pierre et Marie CURIE - CNRS URA 278, ESPCI, 10 rue Vauquelin, 75231 PARIS cedex 05 - FRANCE.

INTRODUCTION

Complex aqueous fluids containing polymers and surfactants find important practical applications in various domains such as detergency, paints, cosmetics, oil recovery, etc... The polymer/surfactant interactions govern the macroscopic behavior of these mixed systems (rheology, phase diagram). Of special interest are systems containing hydrophobically modified polymers. These polymers are based on a water soluble backbone and contain a low fraction of hydrophobic side groups (for instance, long alkyl chains). In the presence of surfactants, they can form mixed micellar-type aggregates in which the alkyl groups of the polymer are involved. The association influences dramatically the rheological behavior of the system as shown schematically in Figure 1.

THE SYSTEM

We study the association between a non-ionic surfactant, Triton-X100 and hydrophobically modified derivatives of poly(sodium acrylate) (HMPA). They are random copolymers with the following structure:

\[
\begin{align*}
\text{C}=\text{O} & \quad \text{C}=\text{O} \\
\text{O}^+\text{Na}^+ & \quad \text{HN}-\text{C}_n\text{H}_{2n+1}
\end{align*}
\]

where \(x\) is the molar content in hydrophobic units (modification degree), with \(0 < x < 20\) and \(1 \leq n \leq 18\).
Figure 1: Schematic illustration of the association between hydrophobically modified polymer and surfactant and the resulting influence on viscosity.

The modified polymers are denoted, for instance, PA-150-xCn when obtained from a precursor poly(sodium acrylate) PA-150. Two precursors are used PA-150 and PA-5 of a molecular weight 150 000 and 5000 respectively. 

The precursor does not associate with the non-ionic surfactant.

SIZE EXCLUSION CHROMATOGRAPHY (SEC)

A Waters chromatograph, equipped with a differential refractometer as concentration detector, was used for SEC experiments. The columns set was composed of a series of 4 Shodex OH-pak B803, B804, B805, B806. The eluent was an aqueous solution containing either 0.1M LiNO₃ or 0.1M LiNO₃ + 10⁻³M Triton-X100. The flow rate was 1 ml/min and all the experiments were run at 40°C. The eluent is used as solvent for the preparation of the polymer solutions.
DETERMINATION OF THE BOUND SURFACTANT

In a typical SEC experiment, when there is no interaction between the injected polymer and the stationary phase (column) leading to some adsorption, the surface area of the peak, \( S_p \), is proportional to the polymer concentration, \( C_p^0 \):

\[
S_p = K \left( \frac{dn}{dc} \right)_p C_p^0
\]  

(1)

where \( K \) is a constant depending on the SEC instrument and \( \left( \frac{dn}{dc} \right)_p \) the refractive index increment for the polymer in the eluent. If a surfactant is injected instead of polymer, the same relationship holds true:

\[
S_s = K \left( \frac{dn}{dc} \right)_s C_s^0
\]  

(2)

where the index \( s \) refers to the surfactant.

When the eluent contains surfactant at constant concentration and the injected polymer associates with the surfactant, the surface area of the polymer peak, \( S_t \), increases:

\[
S_t = K \left( \frac{dn}{dc} \right)_p C_p + K \left( \frac{dn}{dc} \right)_s C_s
\]  

(3)

where the meaning of the symbols is the same as in equations (1) and (2). Equation (3) gives directly the ratio of surfactant bound to the polymer \( C_s/C_p \). At the same time a negative peak appears at the elution volume of the solvent, the surface of which is equal to the second term of the right part of equation (3):

\[
S_s^- = K \left( \frac{dn}{dc} \right)_s C_s
\]  

(4)

Equation (4) can also be used to estimate \( C_s/C_p \).

Therefore, SEC is used here as kind of dynamic dialysis technique.

RESULTS AND DISCUSSION

Figures 2 and 3 show the chromatograms for two series of PA modified with C12 groups. The eluent is 0.1M LiNO\(_3\). By increasing the polymer hydrophobicity, the area of the peak decreases and moves to higher elution volumes. The most modified PA-150 derivatives are totally retained by the
columns. Qualitatively similar results are obtained when increased the length of the alkyl side groups. This behavior has been attributed to the polymer adsorption on the stationary phase which obviously exhibits an affinity towards hydrophobic compounds. As expected, the highest molecular weight derivatives adsorb more efficiently.

A completely different behavior is found when a low amount of Triton-X100 is added in the eluent (0.1M LiNO₃+10⁻³M Triton X-100). The area of the peak increases substantially with the polymer hydrophobicity and an equivalent negative peak appears at the elution volume of the solvent (figures 4 and 5). Even the most hydrophobic high molecular weight derivatives are now eluted. Obviously surfactant adsorbs on the stationary phase and competes with the modified polymer. In the same time it binds on the hydrophobic parts of the polymer resulting in an increasing surfactant concentration at the elution volume of the polymer and a decreasing one at the elution volume of the solvent.

The ratio of bound surfactant per side alkyl group, \( R = \frac{[\text{surfactant}]}{[\text{alkyl}]} \) and the average number of surfactants per macromolecule, for all the modified polymers used in this study, are summarized in Tables I and II.

### TABLE I

Ratio of bound surfactant per alkyl group and average number of surfactants per macromolecule for the hydrophobic derivatives of high molecular weight poly(sodium acrylate) PA-150

<table>
<thead>
<tr>
<th>Polymer</th>
<th>([\text{surfactant}])</th>
<th>([\text{surfactant}]) [macromolecule]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>([\text{alkyl}])</td>
<td>([\text{macromolecule}])</td>
</tr>
<tr>
<td>PA-150-1C12</td>
<td>4.8</td>
<td>170</td>
</tr>
<tr>
<td>3C12</td>
<td>9.4</td>
<td>990</td>
</tr>
<tr>
<td>7C12</td>
<td>8.6</td>
<td>2100</td>
</tr>
<tr>
<td>10C12</td>
<td>7.1</td>
<td>2500</td>
</tr>
<tr>
<td>PA-150-1C18</td>
<td>27.7</td>
<td>970</td>
</tr>
<tr>
<td>3C18</td>
<td>11.8</td>
<td>1240</td>
</tr>
<tr>
<td>5C18</td>
<td>13.4</td>
<td>2350</td>
</tr>
<tr>
<td>PA-150-3C8</td>
<td>0</td>
<td>170</td>
</tr>
<tr>
<td>5C8</td>
<td>1</td>
<td>870</td>
</tr>
<tr>
<td>10C8</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>
TABLE II
Ratio of bound surfactant per alkyl group and average number of surfactants per macromolecule for the hydrophobic derivatives of low molecular weight poly(sodium acrylate) PA- 5

<table>
<thead>
<tr>
<th>Polymer</th>
<th>[surfactant]</th>
<th>[surfactant]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[alkyl]</td>
<td>[macromolecule]</td>
</tr>
<tr>
<td>PA-5-5C12</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>10C12</td>
<td>21</td>
<td>150</td>
</tr>
<tr>
<td>15C12</td>
<td>16</td>
<td>165</td>
</tr>
<tr>
<td>PA-5-5C18</td>
<td>41</td>
<td>145</td>
</tr>
</tbody>
</table>

For a given value of the modification degree x, the ratio R increases with the alkyl chain length n. On the other hand, for a given n, R seems to pass a maximum as a function of x. The value of x corresponding to $R_{\text{maximum}}$ seems to decrease when n increases. The actual variation of R as a function of x and n is the result of a balance between increased tendency of the polymer to form mixed aggregates with the surfactant and increased constraints due to the confinement of the polymer backbone around the aggregate.

The importance of the backbone confinement is lower for the low molecular weight samples. Presumably, that explains the higher values of R obtained with the PA-5 derivatives. In the latter case the average number of surfactants per macromolecule is low (~ 150) and maybe only one or two aggregates per macromolecule are formed. On the other hand, with the PA-150 derivatives several aggregates per macromolecule are formed, which implies increased confinement constraints.

CONCLUSION

Size Exclusion Chromatography was used as a kind of dynamic dialysis technique to study the association between hydrophobically modified polymers and a non ionic surfactant. The surfactant is introduced in the eluent at constant concentration, above its critical miscellar concentration.

The ratio R of bound surfactant per alkyl group can be easily determined. There is an optimum in R as a function of the modification degree, presumably because of the increasing constraints due to the backbone confinement around the mixed aggregate.
Finally, this type of mixed eluent containing surfactant could be used advantageously for the characterization of amphiphilic polymers by SEC. In the absence of surfactant these polymers are partly or totally adsorbed on the stationary phase of the column.

Figure 2: Chromatograms of PA-150 and its hydrophobic C12 derivatives. Eluent: LiNO3 0.1M - PA-150-7C12 and PA-150-10C12 are totally retained by the columns.
Figure 4: Chromatograms of PA-150 and its hydrophobic C12 derivatives. Eluent: LiNO₃ 0.1M + Triton X-100 10⁻³M
Figure 3: Chromatograms of PA-5 and its hydrophobic C12 derivatives. 
Eluent: LiNO3 0.1M
Figure 5: Chromatograms of PA-5 and its hydrophobic C12 derivatives. Eluent: LiNO₃ 0.1M + Triton X-100 10⁻³M