A nuclear magnetic resonance study of solubilization of aromatic alcohols and phenols by a surfactant

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With 3 figures and 3 tables

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Introduction

In recent years a number of papers have appeared dealing with the use of nuclear magnetic resonance (NMR) technique for the studies of the nature of surfactant micelles and their interaction with the surrounding solution, and also for the determination of critical micelle concentration (CMC). However, papers on the solubilization of organic materials in micellar solutions with the use of NMR technique have been limited (1–3). Although the solubilization of organic materials which are insoluble or slightly soluble in water by surfactants is a familiar phenomenon (4), this subject is not necessarily well understood. The NMR technique is thought to be a potentially useful tool to investigate the solubilization of materials having a benzene ring in the molecule, and it will provide some important information of this solubilization which may not be obtained by means of other techniques.

In the present work, the NMR spectra of aromatic alcohols and phenols solubilized by a surfactant, sodium dodecyl sulfate, have been measured to discuss the mode of solubilization of these materials and the locus of their solubilization in the micelle. The alcohols and phenols used as solubilizates have the chemical structures of

\[
\begin{align*}
\text{CH}_3\text{-} \bigcirc \text{-} \text{(CH}_2)\!_n\text{OH}, & \quad n = 1 \sim 3 \\
\text{CH}_3\text{-} \bigcirc \text{-} \text{(CH}_2)\!_n\text{OH}, & \quad n = 1 \text{ or } 2 \\
\text{H(} \text{CH}_3\text{)_n-} \bigcirc \text{-} \text{OH}, & \quad n = 1 \sim 3
\end{align*}
\]

Attention has been paid mainly to the chemical shifts of their phenyl protons. The phenyl protons in a micellar environment are expected to have different chemical shifts from the phenyl protons in a water environment.

Experimental

Materials

Sodium dodecyl sulfate (NaC\(_{12}\)S) was the same sample as that used in a previous work (5). This sample showed no minimum in the surface tension-concentration curve. p-Cresol (C\(_1\)PhOH), p-ethylphenol (C\(_2\)PhOH), benzyl alcohol (PhC\(_2\)OH), p-methyl benzyl alcohol (C\(_1\)PhC\(_1\)OH), 2-phenyl ethanol (PhC\(_2\)OH) and 3-phenyl propanol (PhC\(_3\)OH), which were of guaranteed reagent grade, were obtained from Wako Pure Chemicals Co., Japan. Further purifications of these samples were made by fractional distillation or recrystallization from n-hexane. p-n-Propylphenol (C\(_3\)PhOH) was prepared from p-hydroxypropiophenone by the Clemmensen method (6) of reduction and purified by fractional distillation. 2-p-Tolyl ethanol (C\(_2\)PhC\(_1\)OH) was synthesized by the Grignard reaction (7) of p-bromotoluene with ethylene oxide and purified by a preparative vapor phase chromatograph. The element-analytical values of these two samples agreed with their theoretical values. High purities of these phenols and alcohols used as solubilizates were verified by vapor phase chromatography and NMR spectral measurement.

Solubilization and sample solutions

The solubilization limit of each solubilize in the solution of NaC\(_{12}\)S was determined as follows. A series of different amounts of a solubilize were added to the surfactant solution of a definite concentration. The solution was then automatically shaken at 20 ± 0.1 °C for 50 h by the method described in a previous paper (5, 8), and the turbidity of the solution shaken was measured with a turbidimeter to determine the solubilization limit of this solubilize. A sample solution was prepared by dissolving a solubilize, the amount of which was at or below its solubilization limit, in the surfactant solution of a known concentration containing a small amount of 1,4-dioxane as an internal standard. The solution thus prepared was thoroughly
shaken, as described above, to make the solubilize completely dissolved.

**NMR spectral measurements**

The NMR spectra were obtained with a Japan Electron Optics JNM-3H-60 spectrometer (60 mcs) operating at 20-21 °C. Chemical shifts were measured in cycles per second from an internal standard, 1,4-dioxane. The use of an internal standard eliminates the need for corrections due to differences on the bulk diamagnetic susceptibilities of the solutions being investigated (9). The precision of measurements of the distance between the dioxane peak and the phenyl peak(s) of a solubilize was about ± 0.5 cps.

**Results and discussion**

In the present experiment the concentration of the surfactant (NaC₁₂S) was kept constant at 5.0% by weight/volume. At this concentration, most of the surfactant molecules are dissolved in the form of micelles because the concentration is sufficiently high as compared to the critical micelle concentration (CMC, 0.15–0.20% in the presence of solubilize). The typical NMR spectra of phenyl protons for C₂PhOH, C₃PhOH, C₃PhC₁OH and PhC₂OH saturated in water and in the surfactant solution are given in table 1. In the surfactant solution, the signals of their phenyl protons shift to higher magnetic fields owing to the solubilization of these materials in the micellar medium which is a different environment from the aqueous medium. The pattern of phenyl proton signals and the extent of their shifts to higher fields depend on the chemical structure of solubilizes and the number of n, i.e., the number of methylene units in the molecule. For all the solubilizes examined, they can be classified into four types of patterns as shown in table 1.

Table 1. NMR spectra of phenyl groups of C₃PhOH, C₃PhOH, C₃PhC₁OH and PhC₂OH saturated in water and in 5.0% NaC₁₂S solution

<table>
<thead>
<tr>
<th>Type</th>
<th>Solubilize</th>
<th>Spectra of phenyl protons in water</th>
<th>Spectra of phenyl protons in NaC₁₂S soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>C₃H₅OH</td>
<td><img src="https://example.com/diagram1.png" alt="Diagram" /></td>
<td><img src="https://example.com/diagram2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>II</td>
<td>CH₃OH</td>
<td><img src="https://example.com/diagram3.png" alt="Diagram" /></td>
<td><img src="https://example.com/diagram4.png" alt="Diagram" /></td>
</tr>
<tr>
<td>III</td>
<td>CH₃OH</td>
<td><img src="https://example.com/diagram5.png" alt="Diagram" /></td>
<td><img src="https://example.com/diagram6.png" alt="Diagram" /></td>
</tr>
<tr>
<td>VIb</td>
<td>Ph₄OH</td>
<td><img src="https://example.com/diagram7.png" alt="Diagram" /></td>
<td><img src="https://example.com/diagram8.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

a C₃PhOH shows a spectrum similar to the type I; b PhC₁OH, PhC₂OH and C₃PhC₂OH similar to the type IV; c cps from the dioxane peak.