A study on interaction between benzyl alcohol and cationic surfactant micelles by \(^1\text{H} \) NMR

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Received 18 April 2005; revised 20 February 2006

Solubilization of benzyl alcohol in aqueous micellar solution of 3-alkoxy-2-hydroxypropyl trimethyl ammonium bromides \((C_nH_{2n+1}OCH_2CH(OH)CH_2N(CH_3)_3)^+Br^–\), abbreviated as \(C_n\text{NBr}\), \((n=8, 12, 14, 16)\) has been studied by high resolution \(^1\text{H} \) NMR. Results indicate that the alkyl chain length of the surfactant affects the solubility of benzyl alcohol in the micellar solution. The peak of methylenes in long chain surfactant splits into an upfield signal and a downfield signal when the solubilization system is at high molar ratio of benzyl alcohol to surfactant. The solubility of benzyl alcohol in micelle solutions of different surfactants \((n=8, 12, 14, 16)\) at the same concentration \((3.00\times10^{-2}\text{ mol} \cdot \text{L}^{-1})\) are 0.1125, 0.1470, 0.1755 and 0.2100 mol L\(^{-1}\), respectively. The transfer free energy of benzyl alcohol from aqueous phase to micellar phase is \(-18.45, -18.59, -18.72\) and \(-18.80 \text{ kJ} \cdot \text{mol}^{-1}\) for \(n=8, 12, 14\) and 16, respectively.

Solubilization of organics in surfactant micelles after their formation in the solution is of major importance in many applications. Nuclear magnetic resonance spectroscopy can be used to study the microcosmic structure of micelles\(^{1-5}\) because it is a highly differentiating method. The added surfactant molecules can form micelles by self-assembly to provide a more compatible environment for the sparingly soluble molecules increasing their experimental solubility, i.e., the liposome solute is solubilized. Surfactant micelles in aqueous solution can be pictured as having a highly non-polar interior and a relatively polar interfacial region. The interior of the micelles is generally considered to be the locus of solubilization for very weak polar or non-polar solubilize such as alkane. Solubilize molecules of comparatively high polarity such as alcohols are believed to be solubilized in the interfacial region of the micelles, so that their polar functional groups (OH, for example) can retain their contact with water. Polar benzyl alcohol is often chosen as model compound when \(^1\text{H} \) NMR method is utilized to investigate solubilization of micellar solutions, because the benzene ring current of the benzene alcohol molecule can obviously vary the chemical shift of protons in some groups of surfactant molecules. Miyagishi and Li \(^{1,3,6,7}\) carried out the investigation of the solubilization of aromatic compound in surfactant micelles. They reported that alcohol was solubilized with its carbon chains in the region of the middle micelle where methylenes are gathered.

In this note, we have determined the \(^1\text{H} \) NMR spectra of surfactant solution containing benzyl alcohol to investigate the influence of the length of hydrophobic chain of surfactant molecule on the solubility of benzyl alcohol, and also to developed a rather facile method to estimate the transfer free energy of benzyl alcohol from aqueous phase to micellar phase.

Experimental

The surfactant, 3-alkoxy-2-hydroxypropyl trimethyl ammonium bromide, \((C_nH_{2n+1}OCH_2CH(OH)CH_2N(CH_3)_3)^+Br^–\), \(n=8, 12, 14, 16\), abridged to \(C_n\text{NBr}\), was synthesized by an earlier reported method\(^6\). Surface tension of their solutions were determined by drop-volume method, and cmc of every surfactant was read on the curve of surface tension versus the concentration, and the aggregation numbers were determined by an NAES-1100 fluorimeter (Japan) using the method introduced by Zhang et al.\(^5\). Benzyl alcohol (analytical reagent) was purchased from Shanghai Reagents Company (Shanghai, China) and used without further purification. Heavy water (deuterium oxide) was a product of Aldrich with the isotopic purity better than 99.96% (atom D). The \(^1\text{H} \) NMR spectra were obtained on a Varian MP-400 spectrometer\(^4\). All the experiments were conducted at 25 ± 0.1°C.
Results and discussion

Determination of solubility of benzyl alcohol in micellar solution

A typical $^1$H NMR spectrum of micellar solution containing benzyl alcohol is shown in Fig. 1. In the present study, chemical shifts of $\text{-CH}_2$, (CH$_2$)$_n$ and N-CH$_3$ groups in surfactant molecules were chosen to investigate the interaction of surfactant in micelle with the solubilized benzyl alcohol. In $3.00 \times 10^{-2}$ mol L$^{-1}$ C$_{12}$NBr micellar solution (four surfactants solution can form micelles at this concentration), the chemical shifts of $\text{-CH}_2$, (CH$_2$)$_n$, N-CH$_3$ groups were 0.901, 1.320 and 3.170 ppm respectively. In micellar solutions of other surfactants ($3.00 \times 10^{-2}$ mol L$^{-1}$), the chemical shifts were same as the above. When the molar ratio of benzyl alcohol to surfactant was increased, the chemical shifts of these groups varied due to the change in microenvironment caused by ring-current induced effects (Fig. 2). In the presence of benzyl alcohol, the signals of $\text{-CH}_3$ and N-CH$_3$ groups of these surfactants (C$_{12}$NBr) showed an upfield shift and finally attained a constant values (0.866 ppm for $\text{-CH}_2$, 3.00 ppm for N-CH$_3$). The signals of the inner methylene chains also showed an upfield shift, and then split into an upfield signal and a downfield signal with the addition of benzyl alcohol (see Fig. 1), and finally each attained their constant values. The variance of chemical shift ($\Delta$) is about 0.035 ppm for the terminal methyl group, and 0.17 ppm for the N-substituted methyl group. The $\Delta$ of methylene chains ranged from 0.084 to 0.22 ppm. The difference in $\Delta$ values indicates that the benzyl alcohol may be localized in the middle region of micelles with its polar head near to the micelle surface and its phenyl group may be in the region of the middle methylenes of the micelle.

When only a little amount of benzyl alcohol was added to micellar solution, there was little change in the chemical shifts of the protons in the core region of the micelles. With increase in molar ratio of benzyl alcohol to surfactant, a turning point was observed in the chemical shift curve for a certain functional group (Fig. 2). This is due to the saturation of benzyl alcohol in the interfacial region of the micelle with the alcohol.
molecules oriented along the hydrophobic chain. If the molar ratio was increased further, some alcohol molecule will be solubilized in the interior part of the micelle. When the benzyl alcohol reached its saturation value in these micellar solutions, the chemical shifts of various radicals of surfactants became constant. The molar ratios of benzyl alcohol to surfactants at the turning points in the chemical shift curves for all radicals (shown in Fig. 2) were 3.75, 4.90, 5.85 and 7.00 corresponding to \( \text{C}_9\text{NBr}, \text{C}_{12}\text{NBr}, \text{C}_{14}\text{NBr} \) and \( \text{C}_{16}\text{NBr} \), respectively. The largest dissolved amounts of benzyl alcohol in one liter 3.00×10^{-2} \text{ mol·L}^{-1} \) (5) micellar solution were 0.1125, 0.1470, 0.1755 and 0.2100 mol for \( \text{C}_9\text{NBr}, \text{C}_{12}\text{NBr}, \text{C}_{14}\text{NBr} \) and \( \text{C}_{16}\text{NBr} \), respectively.

In Fig. 2, we can see that the solubilized concentration for benzyl alcohol increases with elongation of hydrophobic chains of \( \text{C}_n\text{NBr} \). This is due to the size of micelle which may increase with increase in carbolic atomic (n) in the derivatives of the surfactants, i.e., the longer a hydrophobic chain of \( \text{C}_n\text{NBr} \) is, stronger will be its hydrophobic property and higher the aggregation number of the formed micelle (Table 1), better will be the surface activity of surfactant \( ^9 \). Therefore, at the same molar concentration of \( \text{C}_n\text{NBr} \), larger the value of n, larger will be the capacity of micelle, and the larger will be the amount of benzyl alcohol solubilized in the micelles.

The transfer free energy of benzyl alcohol from \( \text{D}_2\text{O} \) to micelle

In the micellar solution containing benzyl alcohol, the total concentration of surfactant, the concentrations of monomer-surfactant molecules and those in composite form are defined respectively as: \( S_n, S_n \), \( (S) \) equal to cmc and \( S_m \), respectively, the total concentration of benzyl alcohol as solubilize, \( B_n \), and that of the singly dispersed benzyl alcohol molecules and that in micellar phase are defined respectively as \( B_n \) and \( B_m \). Thus, \( S_n = S_n + S_m \) and \( B_n = B_n + B_m \). The mole fraction of benzyl alcohol in aqueous phase \( (X_n) \) and in micellar phase \( (X_m) \) are given respectively by Eqs 1 and 2.

\[
X_n = \frac{B_n}{B_n + 55.26 + S}
\]  
\[
X_m = \frac{B_m}{S_m + B_m}
\]

Table 1 — Total solubility of benzyl alcohol \( (B_n) \) in 3.00×10^{-2} \text{ mol·L}^{-1} \( \text{C}_n\text{NBr} \) solution, transfer free energy \( (\Delta G^T) \) for benzyl alcohol from continuous \( \text{D}_2\text{O} \) phase to micelle and corresponding ratio of mole fraction of benzyl alcohol in aqueous phase \( (X_n) \) to that in micellar phase \( (X_m) \) along with cmc and aggregation number of surfactant in the micelle.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>emc (mol·L^{-1})</th>
<th>Aggregation number</th>
<th>( B_n ) (mol·L^{-1})</th>
<th>( X_n/X_m )</th>
<th>( -\Delta G^T ) (kJ·mol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_9\text{NBr} )</td>
<td>1.05×10^{-2}</td>
<td>45.2</td>
<td>0.1125</td>
<td>5.57×10^{-5}</td>
<td>24.28</td>
</tr>
<tr>
<td>( \text{C}_{12}\text{NBr} )</td>
<td>3.47×10^{-2}</td>
<td>52.3</td>
<td>0.1470</td>
<td>5.28×10^{-5}</td>
<td>24.41</td>
</tr>
<tr>
<td>( \text{C}_{14}\text{NBr} )</td>
<td>1.91×10^{-2}</td>
<td>66.5</td>
<td>0.1755</td>
<td>5.14×10^{-5}</td>
<td>24.48</td>
</tr>
<tr>
<td>( \text{C}_{16}\text{NBr} )</td>
<td>5.25×10^{-2}</td>
<td>79.6</td>
<td>0.2100</td>
<td>5.01×10^{-5}</td>
<td>24.54</td>
</tr>
</tbody>
</table>
>C_{12}NBr>C_{14}NBr>C_{16}NBr. We can, thus, conclude that the length of hydrophobic chains of C_{n}NBr has a significant effect on the transfer free energy of the solubilizate from aqueous phase to micellar phase. The longer the hydrophobic chain of C_{n}NBr, stronger is the tendency of benzyl alcohol to transfer from D_2O to micelle phase and easier is the solubilization of benzyl alcohol in its micelles.

Acknowledgement
The authors are grateful to the Science Research Developed Foundation of Liaocheng University, PR China, and the Natural Science Foundation of Shandong Province, PR China (Grant No. 2004ZX15).

References