LETTER

An Unusual Behavior in Cloud Points of New Surface Active Crown Ethers in the Presence of Alkali Metal Chlorides

Effect of Terminal Hydroxyl Group in Sidearm

Yohji NAKATSUJI, Kohichi IWAISAKO, Isao IKEDA, and Mitsuo OKAHARA
Department of Applied Chemistry, Faculty of Engineering, Osaka University
(Yamada-oka, Suita, Osaka 565)

The structure of the terminal group of the electron-donating sidearm of 18-crown-6 ether derivatives was found to remarkably affect the change in the cloud points in the presence of alkali metal chlorides.

The cloud points of non-ionic surfactants are usually discussed in terms of the hydration of their hydrophilic groups in water. Generally speaking, cloud points decrease markedly by the addition of alkali metal or alkaline earth metal salts because of the salting-out effect, except for cases using special counter anions. On the other hand, the cloud points of long chain alkyl crown ethers or the corresponding aza crown ethers have been found to display characteristic complexation behaviors in the presence of a variety of cations.

Recently, the complexation properties of the crown ethers have been modified by the introduction of a side-chain containing a secondary donating site. The series of the crown ethers possessing an electron-donating sidearm and the corresponding aza crown ethers are called C-pivot lariat ethers and N-pivot lariat ethers, respectively. These lariat ethers having a terminal long chain alkoxy group on the sidearm are a type of non-ionic surfactant. The relationship between the cloud point and the stability constant measured in methanol has been determined for some lariat ethers and for some normal lipophilic crown ethers and aza crown ethers. However, the structure of the terminal group of these surfactants seems to be relatively limited.

We report here an interesting effect on the cloud point of the terminal group on the sidearm of a new type of lariat ether.

Lariat ethers (1a and 1b) were prepared from decanal via six steps according to the reported method. The structures of 1a and 1b were characterized by MS, NMR, IR, and elemental analyses. The cloud points of these new lariat ethers and their changes upon the addition of alkali metal chlorides are summarized in Table-1 along with the data for octyl 18-crown-6 (2).

Table-1 shows two important facts. First, compound 1b bearing a terminal methoxy group displayed almost the same behavior as compound 2 regarding changes in cloud points in the presence of alkali metal chlorides. Second, the differences in the change in cloud points between compounds 1a and 1b were...
Table-1 Effect of alkali metal chlorides on cloud points of new surfactants.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{ep}$ (°C)</th>
<th>LiCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>RbCl</th>
<th>CsCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>39.8</td>
<td>-4.9</td>
<td>-6.2</td>
<td>+10.6</td>
<td>+3.4</td>
<td>-3.0</td>
</tr>
<tr>
<td>1 b</td>
<td>30.8</td>
<td>-3.0</td>
<td>+10.2</td>
<td>+40.3</td>
<td>+27.2</td>
<td>+12.5</td>
</tr>
<tr>
<td>2 b)</td>
<td>28.5</td>
<td>-2.5</td>
<td>+12.5</td>
<td>+43.0</td>
<td>+26.5</td>
<td>+11.5</td>
</tr>
</tbody>
</table>

a) 1 molar salt solutions including 1 wt% of sample  
b) ref. 1

...extremely large in spite of the similarity of the structure except for the terminal group. Lariat ethers having the 15-crown-5 ring, and which have a methyl group attached to the ring carbon containing the C-pivot group, possessed a higher complexing ability than the corresponding non-methyl-substituted lariat ethers. On the other hand, the corresponding methyl-substituted 18-crown-6 lariat ethers complexed about the same as the unsubstituted 18-crown-6 lariat ethers. Thus, the stability constants of 1 b and 2 would not be expected to be different. The similarity of the change of cloud points upon addition of alkali metal chlorides between 1 b and 2 is readily understood and is consistent with the results previously obtained. The stability constants of the complexes formed from N-pivot lariat ethers bearing a terminal hydroxyl group and K+ and Na+ in methanol were similar to those of the corresponding N-pivot lariat ethers bearing a terminal methoxy group. The same trend was observed in the measurement of the stability constants of C-pivot 15-crown-5 lariat ethers in methanol. Consequently, we expected that the usual increase in hydrophilicity of long chain alkyl-containing crown ethers could easily be attained by simply introducing a terminal hydroxy group in the electron-donating sidearm of the lariat ethers, and that this would not change their characteristic complexation properties. The cloud point, which is considered to be a measure of hydrophilicity, of 1 a clearly increased compared with that of 1 b or 2. However, the behavior of the change of cloud points for 1 a caused by the presence of alkali metal chlorides was remarkably different from that for 1 b or 2. Although we cannot only draw any conclusions concerning this phenomenon, from only this one example, it should be stressed that the molecular design of the hydrophilic part of the surfactants is very important. We will attempt to clarify the cause of this phenomenon by using a variety of approaches from the standpoint of surface chemistry.

Finally, the authors thank Professor Jerald S. Bradshaw, Brigham Young University (U.S.A.), for helpful comments in preparing the manuscript.

(Received June 28, 1986)

References
7) M. Okahara et al., unpublished results.