〔報 文〕

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Optimal Surfactant Structures for Cosurfactant-Free Microemulsion Systems (III)

— Nonylphenol and Tridecyl Alcohol Hydrophobes —

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계면활성제의 구조가 Microemulsion 형성에 미치는 영향(제 III 보)

— 친유기 Nonylpheonl과 Tridecyol alcohol —

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요 약

보조계면활성제 없이 microemulsion을 형성하는 최적의 계면활성제 구조를 찾기 위한 일련의 연구 중 세번째로 propoxylated nonylphenol sulfates와 ethoxylated 혹은 propoxylated highly-branched tridecyl alcohol sulfates를 연구하였다. 온도, NaCl 농도, 보조계면활성제 농도, ethylene oxide 몰수(EON), propylene oxide 몰수(PON) 등을 변인으로 하여 phase behavior 실험을 한 결과 tridecyl alcohol 친유기를 갖는 계면활성제가 보조계면활성제 없이 microemulsion을 형성하였다. $C_{13}O(EO)_m(PO)_nSO_3Na$ 일반식으로부터 m과 n을 변경시킴으로써 제의 다양한 조건을 만족시키는 계면활성제를 디자인할 수 있었다.

I. INTRODUCTION

Middle phase microemulsions, in equilibrium with excess oil and brine, form in a narrow salinity range. The salinity, at which equal volumes of brine and oil are solubilized in the middle phase microemulsion, is termed the optimum salinity (S*). The higher the solubilization of brine or oil in the middle phase microemulsion, the lower the interfacial tension with the excess phases. In most surfactant formulations involving microemulsions, a cosurfactant (usually a mid- or short-chain alcohol) is often required in combination with a primary surfactant for several purposes. However, on a theoretical basis, a cosurfactant is not a necessary requirement for a microemulsion formation. Much previous research has found that surfactant structure has a significant effect on microemulsion formation and twin tail surfactants have inherent low cosurfactant requirements[1~9]. Several surfactants, such as didodecyldimethylammonium bromide ($(C_{12})_2DAB$)[10,11] and Aerosol OT (sodium di-2-ethylhexylsulfosuccinate)[12~14], were long ago repor-

ted to form cosurfactant-free microemulsions. In previous papers, we reported that C_{14} Guerbet alcohol sulfates[15] and p-dihexylbenzene sodium sulfonate[16] formed cosurfactant-free microemulsions at low temperatures.

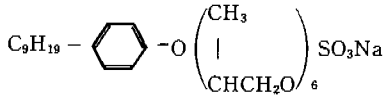
Above mentioned species have twin tail structures. Now, we tried nonylphenol and highly-branched tridecyl (C_{13}) alcohol sulfates which were not twin tail surfactants and were commercially available. In order to find optimal surfactant structures which make microemulsions without cosurfactants at low temperatures with acceptable solubilization parameters, we performed phase behavior experiments using rtemperature, salinity, cosurfactant concentration, ethylene oxide number (EON), and propylene oxide number (PON) as variables. The hydrophobes are the mixtures of several isomers, and EO and PO units were added distributionally.

II. EXPERIMENTAL

1. Materials

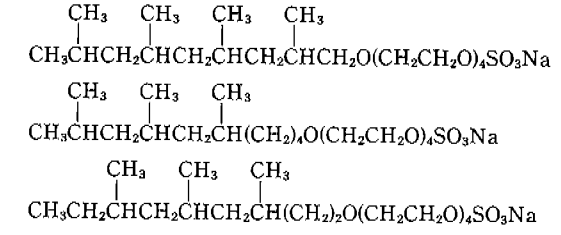
The following surfactants were obtained as ammonium sulfates, purified and ion exchanged to the sodium salt form. Ethylene oxide units (EO's) and propylene oxide units (PO's) have a Gaussian distribution. The major isomers of highly-branched commercial tridecyl alcohol are tetramethyl-1-nonanols, trimethyl-1-decanols and trimethyl-1-nonanols. It contains about 20% C_{12} alcohols.

1) NP(PO)$_6$SO$_4$Na; propoxylated nonylphenol sodium sulfates



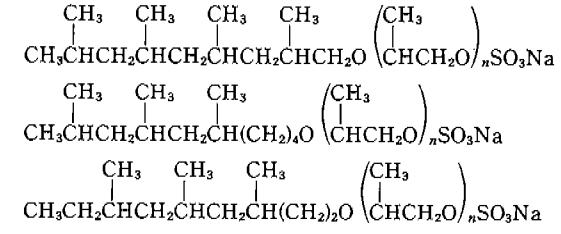
2) C$_{13}$(EO)$_4$SO$_4$Na; ethoxylated commercial tridecyl alcohol sodium sulfates

typical isomers



3) C$_{13}$(PO)$_n$SO$_4$Na; propoxylated commercial tridecyl alcohol sodium sulfates

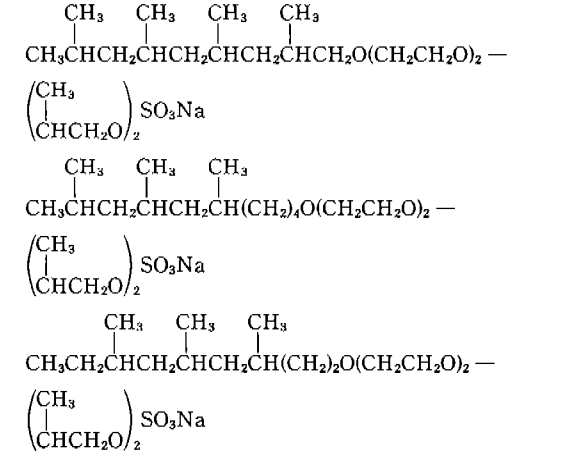
typical isomers (n=4, 6 and 8)



The following surfactants were obtained as corresponding alcohols, sulfated and purified.

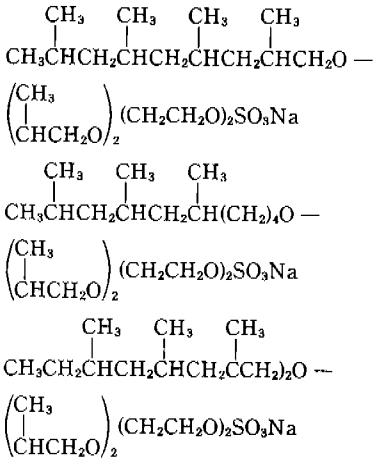
4) C$_{13}$(EO)$_2$(PO)$_2$SO$_4$Na; ethoxylated and propoxylated commercial tridecyl alcohol sodium sulfates

typical isomers



5) C$_{13}$(PO)$_2$(EO)$_2$SO$_4$Na; propoxylated and ethoxylated commercial tridecyl alcohol sodium sulfates.

typical isomers



All the other materials used in this study were the same as the ones reported in previous papers[15,16].

The purification was not performed quantitatively. Some studies were performed on samples as received to verify the effect of impurities, usually unsulfated alcohols. They are designated 'as received', however, most studies were performed on samples whose purity was upgraded by solvent extraction procedures. The % activity of each surfactant was measured by two-phase titration and are shown in Table 1.

Table 1. The % activity values for purified and 'as received' sulfates

		Purified sodium sulfates	'as received' ammonium sulfates (buffered)
$C_{13}(PO)_n$	n=4	91.9	56.2
	n=6	93.0	40.7
	n=8	92.1	79.7
$C_{13}(EO)_4$		78.3	
$C_{13}(EO)_2(PO)_2$		86.6	
$C_{13}(PO)_2(EO)_2$		83.9	
$NP(PO)_n$		82.0	48.8

2. Procedure

The procedure of phase behavior experiments were explained elsewhere[15,16].

The optimum solubilization parameter (σ^*) was defined as follows:

$$\sigma^* = \frac{V_O \text{ or } V_W (V_O = V_W)}{g_{\text{pure surf.}}} = \frac{V_O \text{ or } V_W (V_O = V_W)}{g_{\text{surf.}} \times \text{Activity}} \left(\frac{\text{ml}}{\text{g}}\right)$$

III. RESULTS AND DISCUSSION

1. $C_{13}(PO)_nSO_4Na$ and $NP(PO)_6SO_4Na$

Fig. 1, 2, and 3 show optimum phase behavior for C_{13} (PO)n (n=4, 6, and 8) and NP $(PO)_6$, with 2.0 gpdl sec-butanol. Optimum salinity (S*) decreases and optimum solubilization parameter (σ^*) increases with increasing PO, indicating that PO units function as a hydrophobic part and increase the structural length of molecules. The S* decreases with increasing temperature indicating the nonionic character dominance of these molecules. It is well known that the S* increases with increasing temperature for anionic surfactants because of increas-

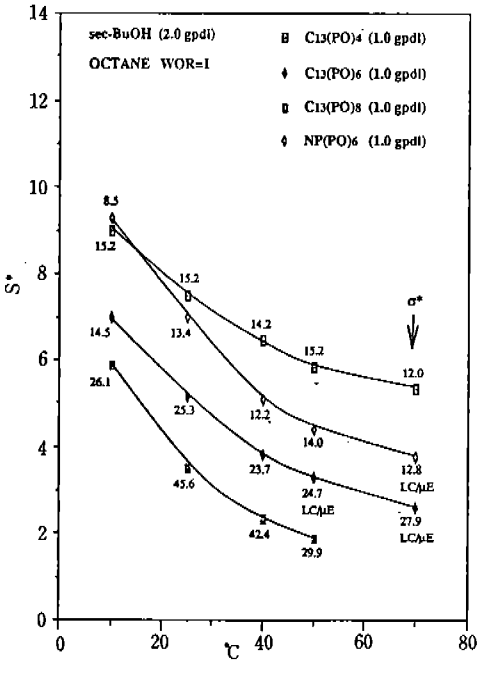


Fig. 1. The optimum phase behavior for purified C_{13} $(PO)_nSO_4Na$ and $NP(PO)_6SO_4Na$ with 2.0 gpdl sec-butanol.

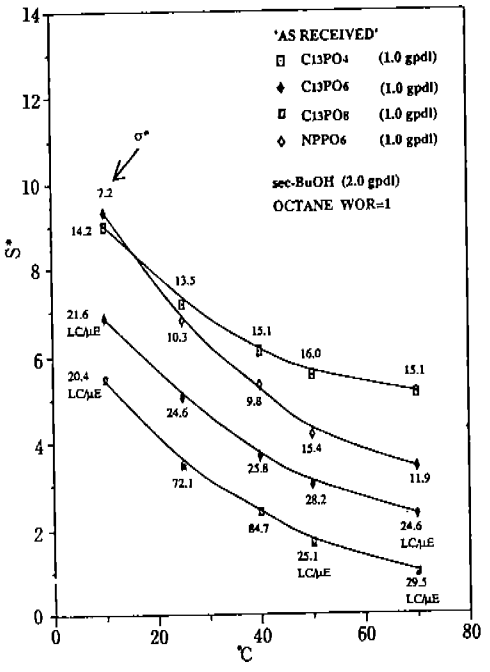


Fig. 2. The optimum phase behavior for 'as received' $C_{13}(PO)_nSO_4NH_4$ and $NP(PO)_6SO_4NH_4$ with 2.0 gpdl sec-butanol.

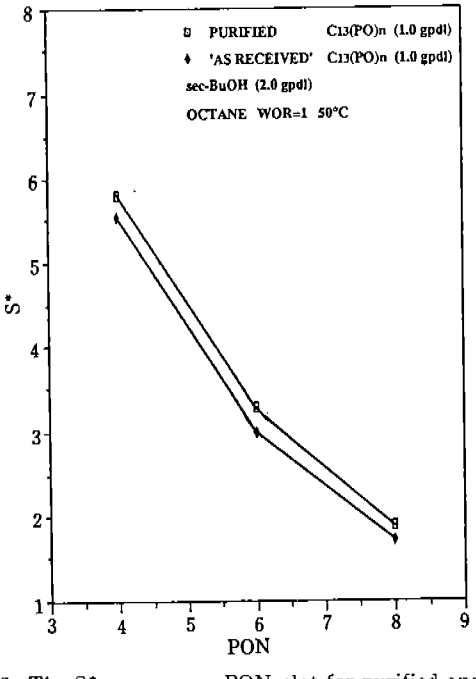


Fig. 3. The S* vs. average PON plot for purified and 'as received' $C_{13}(PO)_n$ sulfates with 2.0 gpdl sec-butanol at 50 ℃.

ing relative solubility in water; however, increased temperature causes dehydration around the EO or PO chains in nonionic surfactants, which causes S* to decrease with increasing temperature.

The σ^* increases with decreasing temperatures due to the decrease of molecular mobility. However, the σ^* slightly decreases at 10 ℃ again. The C_{13} alcohol structure gives much higher σ^* than nonylphenol structure.

'As received' ammonium sulfates show the same trend of phase behavior as purified sodium sulfates. S* and σ^* are reduced in ammonium sulfates because unsulfated alcohols function as cosurfactants. 'As received' C_{13} $(PO)_8$ molecules require extremely long equilibrium period, and final results are obtained after four months of equilibration. Table 2 shows the results of two weeks and four months of equilibration for this molecule. The σ^* decreases and liquid crystals (LC's) are formed after longer equilibration. Thus, the results for C_{13} $(PO)_8$ in Fig. 2 are not the equilibrated ones, even though the data are taken after two weeks. Therefore, it can be concluded that high propoxylation generally causes rigid structures due to van der Waals interactions between PO groups; requires extremely long equilibrium periods; and should be avoided.

Table 2. The effect of equilibration periods on the optimum phase behavior for $C_{13}(PO)_8SO_4NH_4$

T (℃)	2 weeks (S* : σ^*)	4 months (S* : σ^*)
70	LC/μE (1.0 : 29.5)	LC/gel/μE (1.0 : 18.6)
50	LC/μE (1.7 : 25.1)	LC/μE (1.7 : 21.9)
40	(2.4 : 84.7)	LC/μE (2.4 : 25.7)
25	(3.5 : 72.1)	LC/gel/μE (3.5 : 18.4)
10	LC/μE (5.5 : 20.4)	not working

Fig. 4 shows the influence of cosurfactant concentration on the phase behavior for 2.0 gpdl C_{13} $(PO)_6$. As expected, a high cosurfactant concentra-

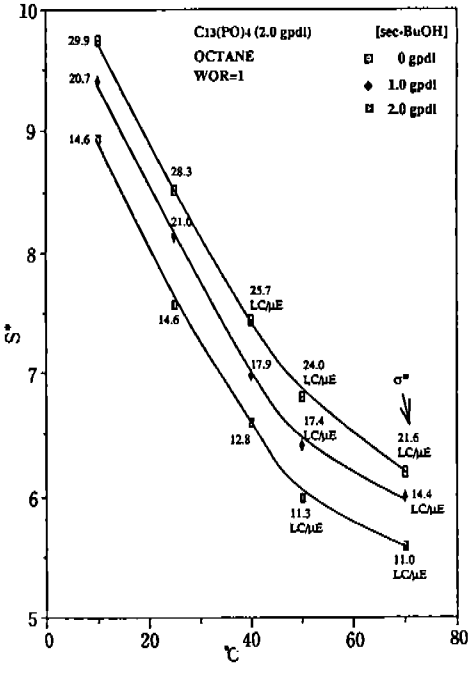


Fig. 4. The effect of cosurfactant concentration on the optimum phase behavior for purified $C_{13}(PO)_4SO_4Na$ with sec-butanol.

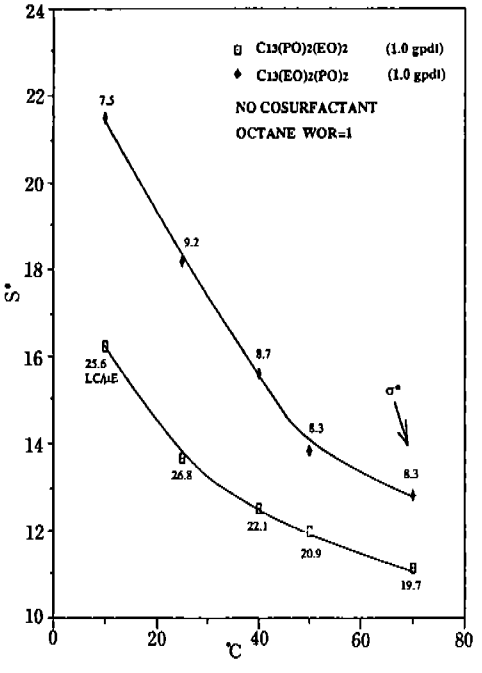


Fig. 5. The optimum phase behavior for $C_{13}(PO)_2(EO)_2SO_4Na$ and $C_{13}(EO)_2(PO)_2SO_4Na$ without cosurfactants.

tion reduces the S*, the σ^*, and the liquid crystal forming tendency.

2. $C_{13}(EO)_2(PO)_2SO_4Na$ and $C_{13}(PO)_2(EO)_2$-SO_4Na

$C_{13}(EO)_2(PO)_2$ and $C_{13}(PO)_2(EO)_2$ sulfates are examined and found to form cosurfactant-free microemulsion systems (Fig. 5). As expected, nonionic characters prevail for both molecules. A high S* of this molecule can be explained as follows: $(PO)_2$ groups in $C_{13}(EO)_2(PO)_2$ have more hydrophilic character than those in $C_{13}(PO)_2(EO)_2$; thus, whole $-(EO)_2(PO)_2SO_4Na$ may function as a hydrophile. On the other hand, $(PO)_2$ groups in $C_{13}(PO)_2(EO)_2$ may have more hydrophobic tendency; thus, the molecule has a longer hydrophobe and is more surface active. This results in a lower γ^* and a bigger σ^* partly by Traube's Rule, which states that "in dilute aqueous solutions of surfactants belonging to any one homo-

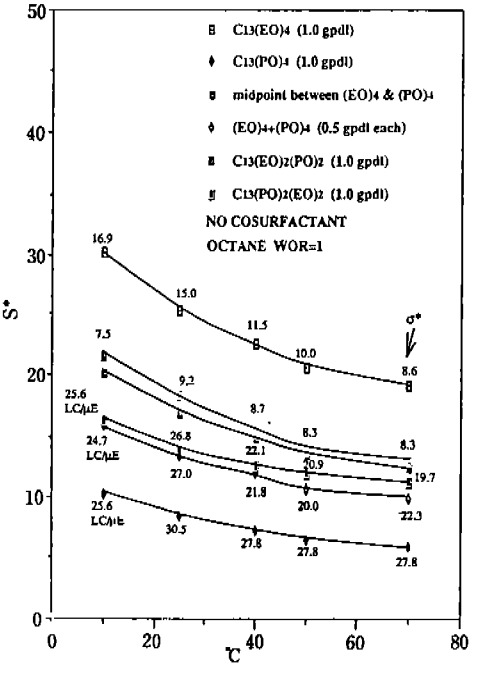


Fig. 6. The optimum phase behavior for the C_{13} alcohol surfactant series without cosurfactants.

logous series, the molar concentrations required to produce equal lowering of the surface or interfacial tension decrease three fold for each additional -CH_2- group in the hydrocarbon chain of the solute"[17,18]. In this molecule, only -$(EO)_2SO_4Na$ plays a role as a hydrophile.

3. C_{13} Alcohol Sodium Sulfate Series

Fig. 6 shows the optimum phase behavior for C_{13} alcohol sulfate series. The purpose of this experiment is to find the impact of EO and PO groups on the optimum phase behavior for C_{13} alcohol sulfate series. All surfactant systems have a nonionic character dominance and make cosurfactant-free microemulsions. $C_{13}(EO)_4$ molecules also form cosurfactant-free microemulsions at 10 ℃; however, the σ^* is low. $C_{13}(EO)_4$ molecules are extremely salt-tolerant due to the rather short hydrophobe and long EO chains.

Angstadt[19] reported that the S* of a 50-50 weight percent surfactant mixture of $C_{13}(EO)_4$ and $C_{13}(PO)_4$ was almost exactly mid-way between those of the two components and that this S* was, again, almost exactly the same as that of $C_{13}(EO)_2(PO)_2$ at 60 ℃. He concluded as follows: "The important implication is that one may be able to obtain a desired salt tolerance within a single molecule by adjusting the internal EO/PO ratio rather than by mixing two different surfactants according to a calculated mole-fraction ratio."

Similar but slightly different results are obtained, probably due to the differences in the purity of surfactants, cosurfactant effects, or temperature effects. The S* of $C_{13}(EO)_2(PO)_2$ is similar (slightly higher), to the mean behavior of the S* of $C_{13}(EO)_4$ and that of $C_{13}(PO)_4$ molecules. However, 50-50 weight percent binary surfactant mixtures display a similar optimum phase behavior with $C_{13}(PO)_2(EO)_2$ rather than with $C_{13}(EO)_2(PO)_2$.

From these results, we conclude that this hydrophobe is a good structure for a cosurfactant-free microemulsion formulation. A general surfactant structure of $C_{13}O(EO)_m(PO)_nSO_3Na$ is developed. By adding different molar contents and the sequences of EO's, PO's, or both, we can design a surfactant which has the desired properties over a wide salinity range.

IV. CONCLUSIONS

The phase behavior was investigated for several series of industrially feasible surfactants to optimize surfactant structures for cosurfactant-free microemulsion systems. The following conclusions were drawn from the results:

1. $C_{13}(PO)_n$ sodium sulfates and $NP(PO)_6$ sodium sulfates

For $C_{13}(PO)_n$ sodium sulfates (n=4, 6, and 8) and nonylphenol $(PO)_6$ sodium sulfates, the optimum salinity (S*) decreases and the optimum solubilization parameter (σ^*) increases with increasing PO numbers, indicating that PO groups function as a hydrophobic part and increase the structural length of molecules. All these molecules show nonionic character dominance. 'As received' ammonium sulfates have a lower S* and σ^* values than purified sodium sulfates.

2. $C_{13}(EO)_2(PO)_2$ sodium sulfates and $C_{13}(PO)_2(EO)_2$ sodium sulfates

These surfactants form cosurfactant-free microemulsions. $C_{13}(EO)_2(PO)_2$ has a lower σ^* and a higher S* than $C_{13}(PO)_2(EO)_2$. These molecules show nonionic character dominance.

3. C_{13} alcohol sodium sulfate series

$C_{13}(EO)_4$ and $C_{13}(PO)_4$ molecules form microemulsions without cosurfactants. The S* of $C_{13}(EO)_2(PO)_2$ is similar to the midpoint between the S* of $C_{13}(EO)_4$ and $C_{13}(PO)_4$ molecules. 50-50 weight percent binary surfactant mixtures display similar optimum phase behavior with $C_{13}(PO)_2(EO)_2$ molecule. All these

molecules show nonionic character dominance.

Highly-branched tridecyl (C_{13}) alcohol hydrophobe is a good structure for cosurfactant-free microemulsion formulations, and a general surfactant structure of $C_{13}O(EO)_m(PO)_nSO_3Na$ is developed for cosurfactant-free microemulsion systems. When m becomes larger, the molecule becomes more hydrophilic. Therefore, we can design a molecule which has a desired salt tolerance by adjusting the m/n ratio.

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