〔報 文〕

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

—Dialkylbenzene and Dialkylphenol Hydrophobes—

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계면활성제의 구조가 Microemulsion 형성에 미치는 영향(제II보)

—친유기 Dialkylbenzene과 Dialkylphenol—

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요 약

Microemulsion을 형성하기 위해서는 일반적으로 주계면활성제와 함께 보조계면활성제가 첨가된다. 그러나 보조계면활성제는 이론적으로 반드시 필요한 것은 아니며, 주계면활성제의 친유기 구조를 적절히 변화시킴으로써 보조계면활성제의 필요량을 감소시킬 수 있다. Microemulsion계를 형성하기 위한 최적의 계면활성제구조를 찾기 위하여 twin tail형 계면활성제인 dialkylbenzene과 dialkylphenol 친유기를 갖는 계면활성제를 연구하였다. P-dihexylbenzene sodium sulfonate는 보조계면활성제 없이 microemulsion을 형성하였지만, dialkylphenol sodium sulfates는 젤이나 액정등을 제거하기 위하여 보조계면활성제를 필요로 하였다.

I. INTRODUCTION

Microemulsions are optically transparent or translucent thermodynamically stable mixtures of oil, water and surfactants. Microemulsions can exist in equilibrium with excess oil, water, or both, and Winsor[1] referred to these systems as type I, II and III respectively. Middle phase microemulsions (Winsor type III) from 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*)(Fig. 1).

Early on Schulman and Bowcott[2] found their microemulsions required alcohols (usally mid- or short-chain alcohols) as cosurfactants. The most basic role of a cosurfactant is probably its ability to eliminate rigid structures such as gels, precipitates and liquid crystals, and to improve phase behavior of the system[3,4].

However, no fundamental considerations dictate that a cosurfactant is a necessary requirement for microemulsion formation, but is simply added as a matter of practicality. In a previous paper, we

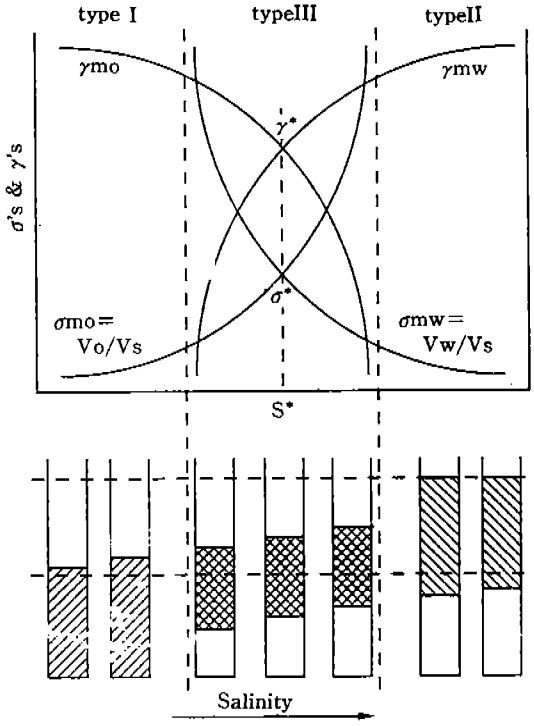


Fig. 1. The optimum salinity (S*) and the phase behavior as a function of salinity.

reported that C_{14} Guerbet alcohol sulfates formed cosurfactant-free microemulsions at low temperatures with acceptable solubilization parameters[5].

The objective of this study is the minimization and possible elimination of cosurfactants from microemulsion formulations by optimizing surfactant structures, since much previous research has found that hydrophobe structure has a significant effect on cosurfactant requirements of the microemulsion systems.

From extensive previous studies[6~14], the following general results are obtained for the extremes in hydrophobe structure.

A) Twin tail surfactants

1) prefer to micellize in the oil phase,
2) produce low values of σ^*,
3) produce high values of γ^*, and
4) have minimal cosurfactant requirements.

B) Single tail surfactants

1) prefer to micellize in the aqueous phase,
2) produce high values of σ^*,
3) produce low values of γ^*, and
4) have high cosurfactant requirements.

C) Mixtures of above the two species or intermediately branched single species have intermediate properties

In a present study, dialkylbenzene sulfonates and dialkylphenol sulfates were investigated, because twin tail surfactants have inherent low cosurfactant requirements. P-dihexylbenzene sodium sulfonate, ethoxylated dihexylphenol sodium sulfates, and ethoxylated 2-hexyl-4-octylphenol sodium sulfates were synthesized. Next, we could obtain commercially available surfactants with dioctylphenol and dinonylphenol hydrophobes.

The optimum phase behavior of each surfactants were examined with oil phase composition, temperature, salinity, cosurfactant concentration and ethylene oxide number (EON) as variables. For commercial surfactants, the hydrophobes are the mixtures of several isomers and ethylene oxide (EO) units are added distributionally.

II. EXPERIMENTAL

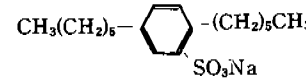
1. Materials

n-Octane, n-decane, and n-dodecane were technical grade (95 Mol % minimum purity). Singly distilled water was used. NaCl, reagent grade, was obtained from Baker Analyzed.

The following surfactants and cosurfactants were used in this study.

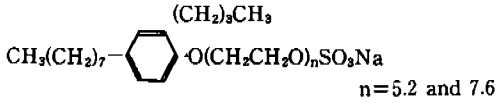
1) $C_6\phi C_6SO_3Na$: p-dihexylbenzene sodium sulfonates

They were synthesized and have the following structure.



2) $C_6\phi_8$(EO)nSO_4Na: ethoxylated 2-hexyl-4-octyl-phenol sodium sulfates

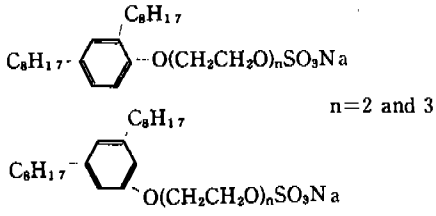
The hydrophobes of these molecules were synthesized and distributional ethylene oxide additions were performed.



$C_6\phi C_8$(EO)n sodium sulfates were synthesized and examined. The NMR spectra show that C-6 and C-8 chains are attached in the meta position to each other and that EO chains are attached to ortho and para positions with respect to C-6 and C-8 chains, respectively. Fig. 2 and 3 show Gaussian distributions of EO chains. The average molecular weight and further average EO numbers (EON's) are calculated by a weight averaged molecular weight equation: $Mw=\Sigma Ni\ Mi^2/\Sigma Ni\ Mi$ where Ni is the intensity and Mi is the mass of the componenti. The EON's are found to be 5.0 and 7.5, and in good accordance with EON's alternately determined by gas chromatography (5.2 and 7.6).

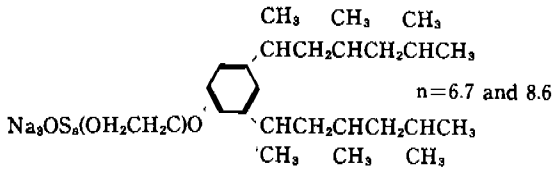
3) $C_8\phi C_8$(EO)nSO_4Na: ethoxylated dioctyl phenol sodium sulfates

They were obtained as ammonium sulfates, purified and ion exchanged to the sodium salts form. They have distributionally added EO's and have the following structure.



4) $C_9\phi C_9$(EO)nSO_4Na: ethoxylated dinonylphenol sodium sulfates

They were made by sulfating the corresponding alcohols, which have commercial names of DM 430 and DM 530 respectively.



5) 99.6 Mol % sec-butanol obtained from Fisher Scientific Company was used as a cosurfactant.

The purity of samples was upgraded by solvent extraction procedures. As previously found, it is very difficult to obtain high purity surfactants when there is a distribution of EO's or PO's.

The % activity of each surfactant is measured by two-phase titration[15~18] and is shown in Table 1. One determination in Table 1 (*) is greater than 100%. As discussed in a previous paper[5], this error can be attributed to imperfectly defined surfactant structures with incorrect molecular weight. The % activity was not measured for $C_6\phi C_6$ sodium sulfonate and considered to be 100%.

Table 1. The % activity values for purified sulfates.

		purified sodium sulfates
$C_6\phi C_8$(EO)n	n=5.2	79.6
	n=7.6	89.1
$C_8\phi C_8$(EO)n	n=2.0	84.3
	n=3.0	86.1
$C_9\phi C_9$(EO)n	n=6.7	101.2*
	n=8.6	99.3

2. Procedure

All concentrations were given in grams per deciliter (gpdl) of either the aqueous or oil phase prior to contacting each other. The surfactant concentrations were 1.0 gpdl.

Oil, brine, and surfactnat (and cosurfactant if needed) were mixed in 5.0 ml disposable graduated pipettes. After gentle shaking three times over a 24-hour period, they were equilibrated at constant temperature until the phase volumes became

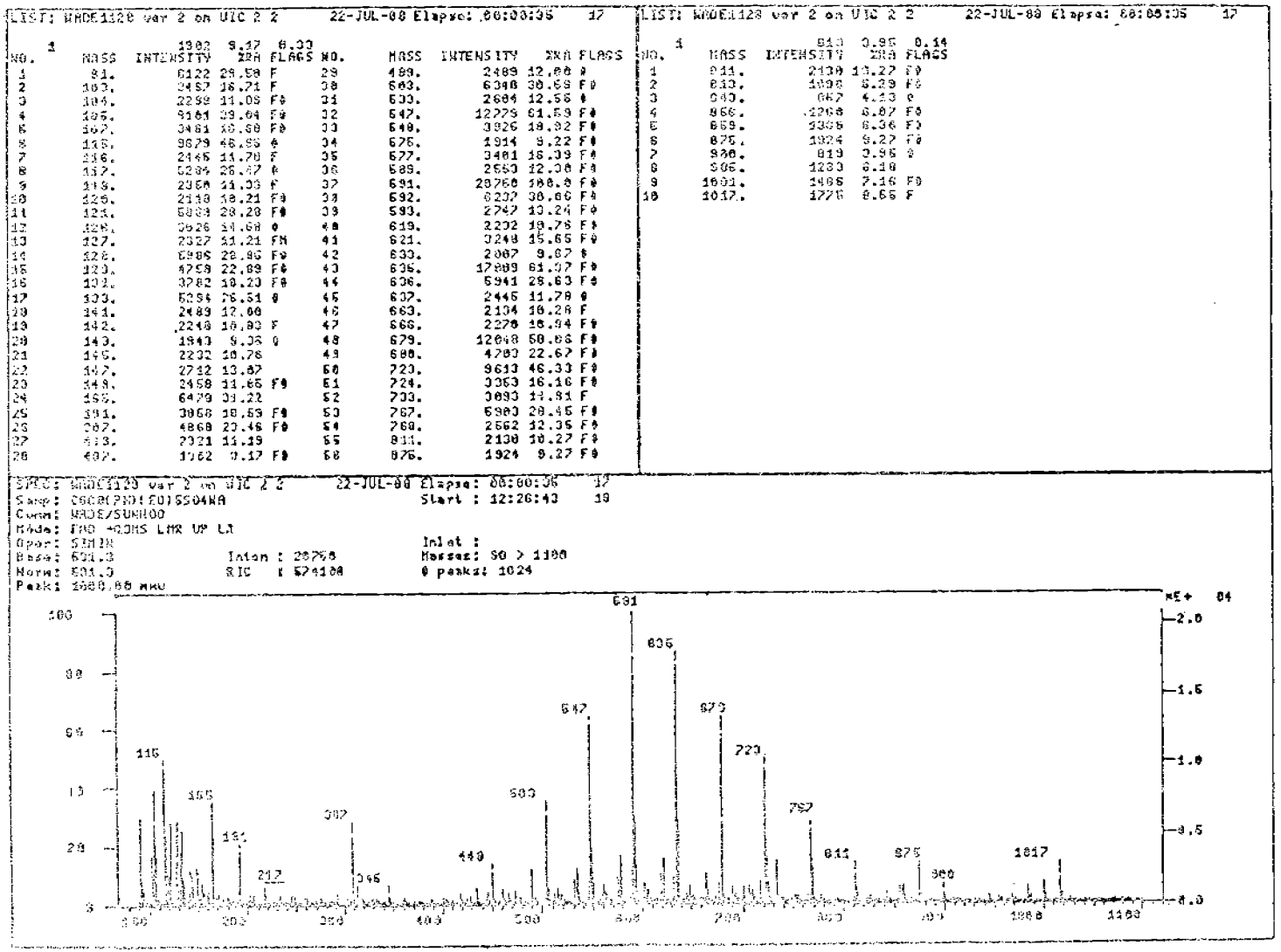


Fig. 2. Mass spectrum for $C_6\emptyset C_8$ $(EO)_{5.2}SO_4Na$ without matrix.

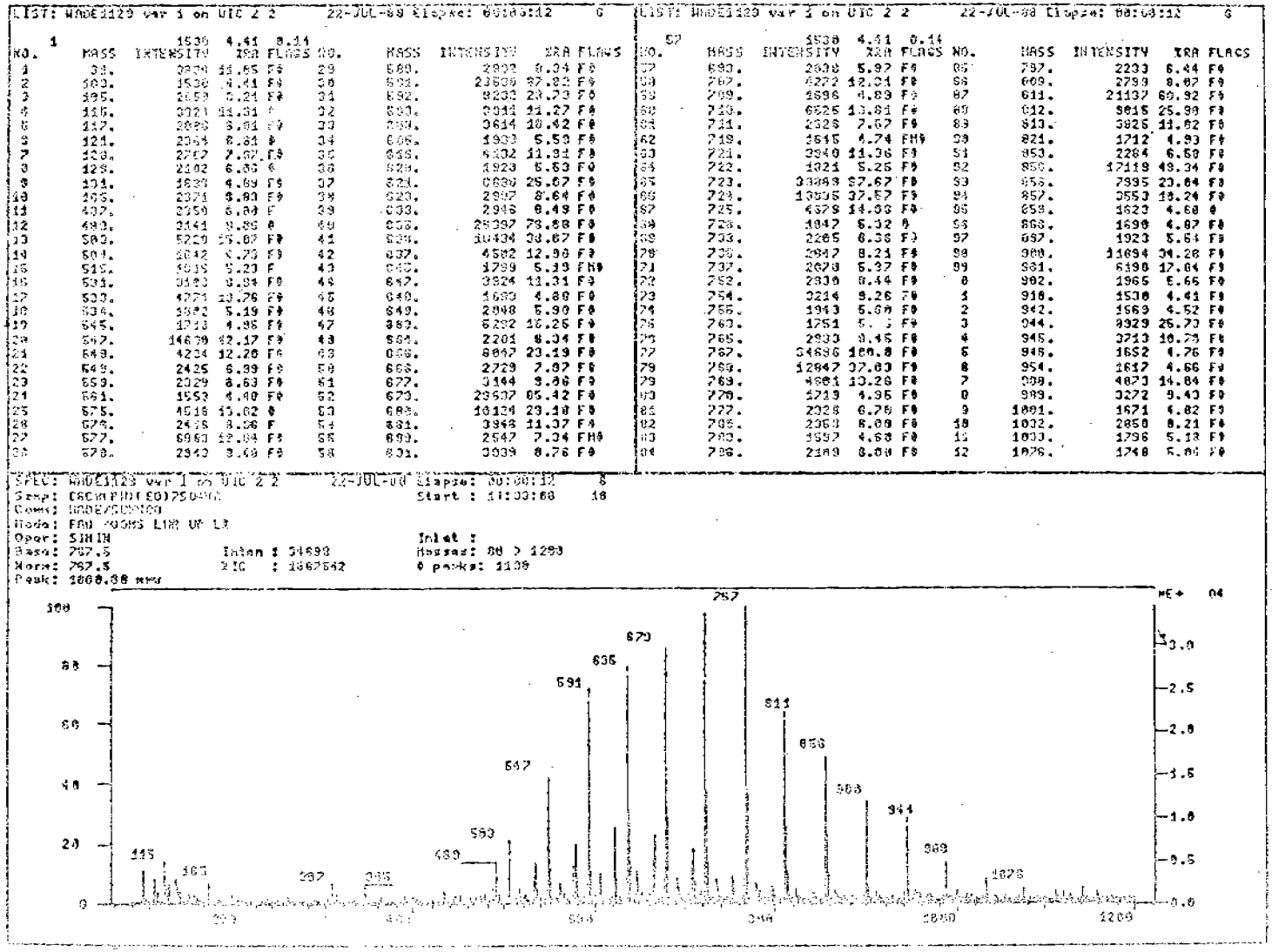


Fig. 3. Mass spectrum for $C_6\phi C_8$ $(EO)_{7.6}SO_4Na$ without matrix.

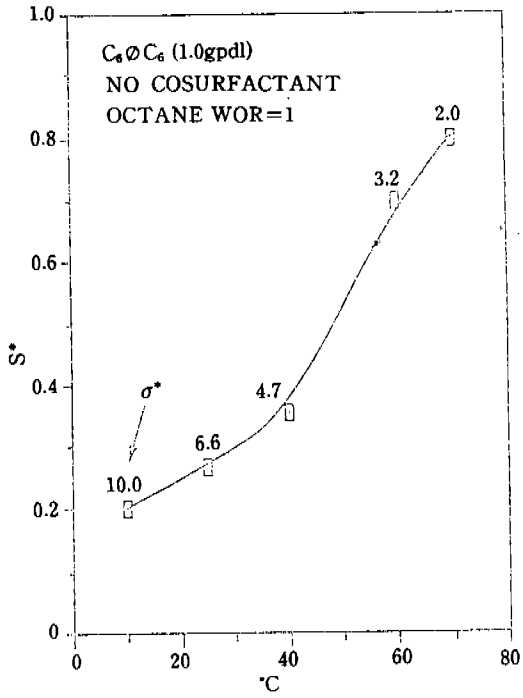


Fig. 4. The optimum phase behavior for $C_6ØC_6SO_3Na$ without cosurfactants.

constant with time (usually one week). The volume ratio of aqueous to oil phase (WOR) was always one.

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

$$\sigma^* = \frac{\text{Vo or Vw (Vo=Vw)}}{g_{\text{pure surf.}}}$$

$$= \frac{\text{Vo or Vw (Vo=Vw)}}{g_{\text{surf.}} \times \text{Activity}} \left(\frac{\text{ml}}{\text{g}}\right)$$

III. RESULTS AND DISCUSSION

1. $C_6ØC_6SO_3Na$

$C_6ØC_6$ sodium sulfonate was synthesized and examined. Fig. 4 shows optimum phase behavior (Winsor type III) for $C_6ØC_6SO_3Na$ without cosurfactant.

This molecule has distinctive properties, such as a good temperature tolerance and no alcohol requirement. The limiting molecular area of the molecule at the water/air interface at 25℃ was found to be 57.9 Å[2,19]. The molecule is isomerically pure and can be used for academic studies; however, the low value of optimum solubilization paramenter ($\sigma^*=2 \sim 10$) and the low optimum salinity ($S^*=0 \sim 1$ gpdl) made the molecule difficult to use as a primary surfactant for microemulsion formulations.

Dihexylphenol was ethoxylated with 1, 2, and 3 molar equivalents of gaseous EO in an attempt to increase both σ^* and S^*. Inexplicitly, these species failed to make microemulsions. However, this can be explained due to the negative S^* of the systems. Skauge et al.[20] reported that the S^* decreases at low degrees of ethoxylation and explained the phenomenon as a minor contribution of 1 EO group to the effective size of the head group. Therefore, we realized the need to add more EO units to the surfactants or to increase the side alkyl chain length.

2. $C_6ØC_8$ (EO)nSO_4Na

Adding a different length of side chains to phenol is based on chain length compatibility effects[21], expecting low cosurfactant requirements due to the bigger molecular area. The chain length compatibility effects are explained as follows: The equal chain length surfactant molecules form a condensed mixed monolayer as compared to the dissimilar chain length molecules. In mixed monolayers of different chain lengths, it is very likely that the portion of the molecule above the height of the adjacent molecules exhibits thermal motion, such as oscillational, vibrational, and rotational modes. Moreover, if these thermal disturbances are limited to the portion above the height of the adjacent molecules, it would not expand the mixed monolayer and the molecular area would remain the same. However, the thermal motion most probably propagates along the chain toward the polar group of the molecule, which in trun causes the expansion

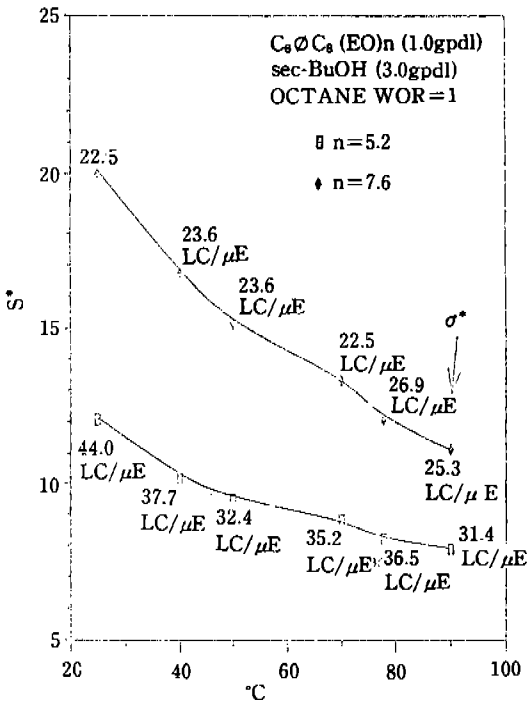


Fig. 5. The optimum phase behavior for $C_6ØC_8$(EO)nSO$_4$Na with 3.0 gpdl sec-butanol.

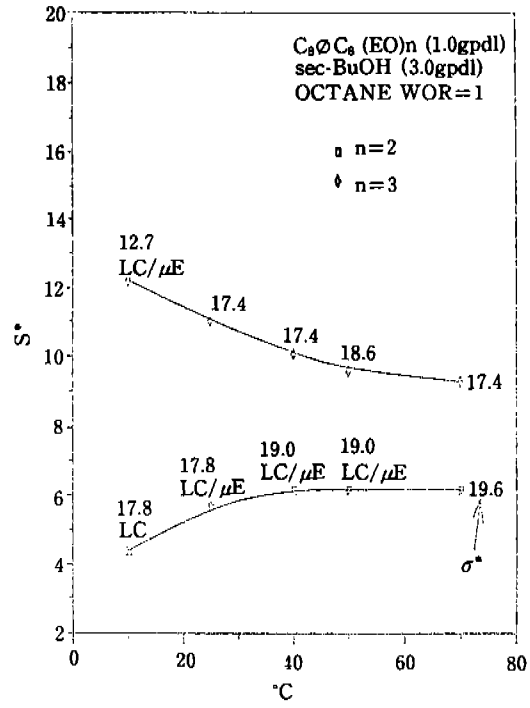


Fig. 6. The optimum phase ehavior for $C_6ØC_8$(EO)nSO$_4$Na with 3.0 gpdl sec-butanol.

on the mixed monolayers and exhibitis a greater molecular area.

Fig. 5 shows the optimum phase behavior for $C_6Ø$-C_8(EO)nSO$_4$Na with 3.0 gpdl sec-butanol. Contrary to expectations, these species require a higher cosurfactant concentration than the $C_9ØC_9$(EO)n species, presumably because the difference between the two chains is not big enough to exhibit chain length compatibility effects. Moreover, the phenol ring already separates the side chains and the molecular area of surfactants may be determined by the phenol ring.

Both surfactants make liquid crystals with 3.0 gpdl sec-butanol in the temperature range from 25℃ to 90℃. The temperature dependence of S* shows predominant nonionic character due to high ethoxylation. It is well known that the S* increases with increasing temperature for anionic surfactants because of increasing relative solubility in water; however, increased temperature causes dehydration around the EO chains in nonionic surfactants, which causes S* to decrease with increasing temperature. Higher ethoxylation increases S* itself and thus decreases σ^*, since it is universally observed that σ^* decreases with increasing S*.

The exclusion of the liquid crystals at 25℃ with n =7.6 species indicates again nonionic character. It is well known that anionic surfactants have a tendency to form rigid structures at low temperatures due to the decrease of molecular mobility; however, nonionics have a tendency to form rigid structures at high temperatures due to the dehydration of EO chains and increased van der Waals interactions between the molecules.

3. $C_8ØC_8$(EO)nSO$_4$Na

$C_6ØC_8$(EO)n sodium sulfates (n=2 and 3) were examined (Fig. 6). The NMR spectra show that they

are equimolar mixtures of ortho-para and meta-meta EO chain position sepcies with respect to the two octyl chains. EO units are added as Gaussian distributions with average numbers of 2 and 3.

The n=2 species form liquid crystals with 3.0 gpdl sec-butanol in the temperature range of 10~50℃. The S* decreases as temperature decreases. Both phenomena indicate that anionic character prevails in these low ethoxylated species.

As expected, the n=3 species have generally higher S*'s and require less cosurfactant than the n =2 species. S* increases with decreasing temperature, indicating the predominance of nonionic character.

4. $C_9\phi C_9(EO)nSO_4Na$

$C_9\phi C_9$ (EO)n sodium sulfates (n=6.7 and 8.6) were synthesized and phase behavior for these species

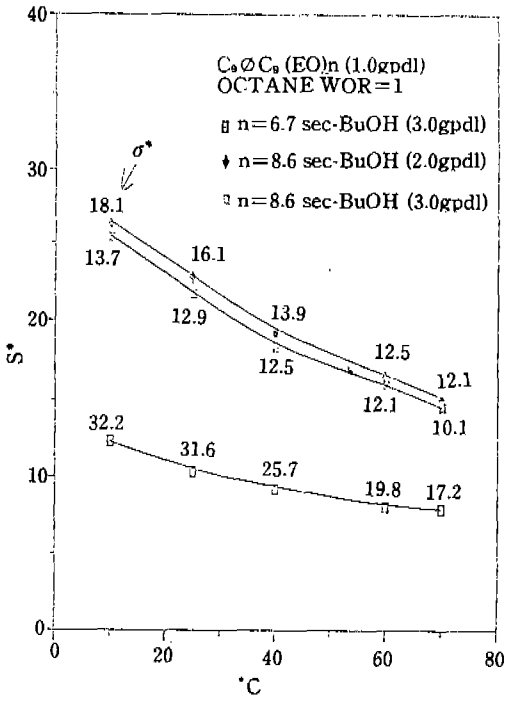


Fig. 7. The optimum phase behavior for $C_9\phi C_9$(EO) nSO_4Na with 3.0 gpdl sec-butanol.

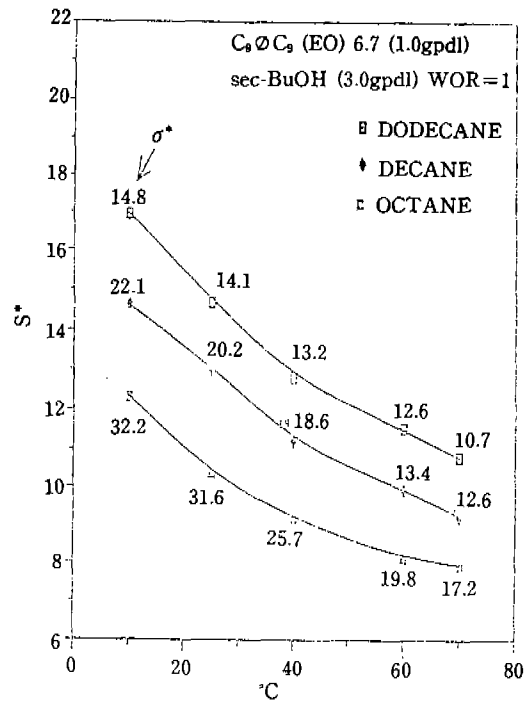


Fig. 8. The effect of oil phase on the optimum phase behavior for $C_9\phi C_9(EO)_{6.7}SO_4Na$ wtih 3.0 gpdl sec-butanol.

was examined (Fig. 7). The n=6.7 species require at least 3.0 gpdl sec-butanol and the n=8.6 species require 2.0 gpdl sec-butanol to exclude all extended rigid structures.

For these surfactants having both anionic and nonionic hydrophiles, the temperature dependence of S* is controlled by nonionic segments. Higher ethoxylation increases S* and decreases σ^*.

The system with higher cosurfactant concentrations has a lower S* and a lower σ^* possibly because of the lower surfactant concentrations at the interface, since cosurfactants compete with surfactants for the adsorption sites. The σ^* increases with decreasing temperature simply because molecules are less mobile at low temperature.

Fig. 8 shows the effect of oil chain length (alkane carbon number: ACN) on the phase behavior of the

n=6.7 species. The S* increases and the σ^* decreases with increasing ACN.

IV. CONCLUSIONS

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

1. $C_6\Phi C_6$ sodium sulfonate

This molecule form microemulsions without cosurfactants at low temperatures; however, it has low values of optimum solubilization parameter (σ^*) and optimum salinity (S*).

2. All of ethoxylated dialkylphenol sulfates require cosurfactants to exclude rigid structures.

3. $C_6\Phi C_8$ (EO)n sodium sulfates (n=5.2 and 7.6)

These surfactants require higher cosurfactant concentrations than $C_9\Phi C_9$ (EO)n species.

Nonionic character dominates for both these molecules.

4. $C_8\Phi C_8$ (EO)n sodium sulfates (n=2 and 3)

The n=2 species show anionic character dominance and the n=3 species have nonionic character prevalence. The n=3 species require less cosurfactant.

5. $C_9\Phi C_9$ (EO)n (n=6.7 and 8.6) sodium sulfates

The temperature dependence of S* is controlled by nonionic character due to high ethoxylation. The n=8.6 species have a higher S* and a lower σ^* and require less cosurfactants, presumably because the bulkiness and hydration of EO chains physically separate molecules and reduce van der Waals interactions between the molecules. The σ^* increases with decreasing temperature.

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