

## Effect of Polar Components on Phase Inversion Temperatures in Systems Containing Nonionic Surfactants and Nonpolar Oils

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비이온성 계면활성제, 비극성 오일을 포함한 계에서의  
극성 성분의 Phase Inversion Temperature에 대한 영향

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**Abstract:** Phase Inversion Temperature (PIT) measurements showed that the addition of polar components such as oleyl alcohol and oleic acid to the system comprising n-dodecylpentaoxyethylene monoether ( $C_{12}E_5$ ), nonpolar oil (n-hexadecane) and water produced large reductions in the PIT. The PIT was lowered as the additive-to-surfactant ratio in the surfactant films in the microemulsion phase was increased. Another dramatic effect of additive was the manner in which it affects the volume of the microemulsion phase at the PIT or the oil and water solubilization characteristics. Microemulsion phase volume was increased rapidly with decreasing PIT, i.e., with increasing amounts of additive in the system. Also with a decrease in PIT, the solubilization parameters of both oil and water in the microemulsion phase were strikingly increased. Even though soil removal data were not available for the conditions where our results obtained, PIT measurement seems a useful starting point for estimating conditions when middle-phase microemulsion formation and its associated high solubilization of oil can be expected.

**요 약:** 비이온성 계면활성제  $C_{12}E_5$ , 비극성 오일 n-hexadecane, 물을 포함한 계에 oleyl alcohol 혹은 oleic acid 같은 극성 성분을 첨가했을 때의 Phase Inversion Temperature (PIT)를 측정된 결과, 첨가한 극성성분은 친유성 첨가제와 같이 PIT를 급격히 감소시킴을 알 수 있었다. PIT에서의 microemulsion phase의 surfactant film 조성 계산에 의하면 surfactant film에서의 극성 성분/계면활성제 비율이 증가할수록 PIT는 감소하였다. 또한 극성 성분의 첨가는 PIT에서의 microemulsion phase의 부피와 오일, 물의 solubilization parameter에도 큰 영향이 있었다. PIT의 감소에 따라, 예를 들면 극성 성분의 첨가량을 증가시킴에 따라, microemulsion phase의 부피는 급격히 증가하였으며 아울러 오일, 물 모두의 microemulsion phase에 대한 solubilization parameter가 급격히 증가하였다. 본 연구 결과를 비교할 수 있는 세척력 실험 결과는 현재 없지만 PIT의 측정은 middle-phase microemulsion phase가 형성되는, 즉 많은 양의 오일을 제거할 수 있는 조건을 예측할 수 있는 유용한 방법임을 알 수 있었다.

## 1. Introduction

Detergency is among the oldest applications of surfactants and remains the largest in terms of surfactant usage. Although much is known about the detergency [1,2], mechanisms are still not completely understood. For instance, the current widespread use of synthetic fabrics and the associated use of lower washing temperatures have been the main cause of a substantial increase in recent years in the amount of nonionic surfactants used in household laundry products.

The removal of oily liquid soils from cotton fabrics during washing processes is considered to occur primarily by rollback mechanism. During rollback adsorption of surfactant on the fabric increases the contact angle as measured through the oil and causes thin layers of the oil to retract into drops which are broken off by agitation in the washing bath. For synthetic fabrics greater adhesion between fabric and soil makes this mechanism relatively ineffective, and removal occurs mainly by a solubilization-emulsification mechanism. Previous studies for various systems with pure nonionic surfactants where the oils were pure hydrocarbons, pure triglycerides, and pure polar soils have shown that a central feature of soil removal in many such cases is formation of intermediate phases such as middle-phase microemulsions or liquid crystals at the surface of contact between surfactant solution and soil [3-6]. Results of a similar study were presented where mixtures of nonionic surfactants or mixtures of anionic and nonionic surfactants were used instead of pure nonionic surfactants [7,8]. Here, too, intermediate phases were frequently observed.

These papers also addressed the relationship between the observed dynamic behavior and the removal of the same oils from polyester/cotton fabric by the same surfactants during washing. Basically, it was found that detergency was best when the oil was solubilized most rapidly into intermediate phases

and/or rather concentrated phases such as liquid crystals initially present in the washing bath [4-8]. For instance, it was found that the maximum removal of hydrocarbons occurred near the Phase Inversion Temperature (PIT) or Hydrophilic-Lipophilic Balance (HLB) Temperature [4,7]. The PIT or HLB temperature is the one at which a nonionic surfactant-oil-water system forms a middle-phase microemulsion containing equal volumes of oil and water which coexists with excess oil and water phases. For ternary nonionic surfactant-oil-water systems, optimum detergency occurs near the PIT of the system due to the existence of high oil solubilization and ultralow interfacial tensions [9]. The latter would facilitate emulsification of microemulsions formed during washing.

With the widespread use of synthetic fabrics and the desire to conserve energy, it is desirable to find a means for obtaining optimum detergency performance at low temperatures. The PIT of a system can be reduced by making the surfactant less hydrophilic or more lipophilic, e. g., by decreasing the hydrophilic chain length or increasing the lipophilic hydrocarbon chain length of a nonionic surfactant. Another way of reducing the PIT without changing surfactant structure is to add a small quantity of a lipophilic amphiphile. Indeed, Raney and Miller [7] showed that a lipophilic additive such as *n*-dodecanol can reduce the PIT of a nonionic surfactant-oil-water system.

For a ternary nonionic surfactant-oil-water system, the PIT is a system property independent of system composition. However, in quaternary nonionic surfactant-additive-water-oil system, the PIT is dependent on the relative amounts of the various species present. Even if the ratio of additive to surfactant is fixed, the different solubilities of additive and surfactant in the oil cause the PIT to depend on the surfactant-to-oil ratio [10-11].

In practical washing processes removal of oily soils which are mixtures of nonpolar compound such as hydrocarbons or triglycerides and polar

compound such as long-chain alcohols or fatty acids is of great interest. For example, the synthetic sebum developed and used at Shell Development Company for detergency testing consists of 25% mineral oil, 30% triglycerides, and 45% long-chain alcohols or fatty acids [12]. The synthetic sebum is a model of natural fatty soil which has to be removed during washing processes.

In this paper, measurements of the PIT as a function of composition in systems containing water,  $C_{12}E_5$ , *n*-hexadecane, and polar components are reported. Of particular interest is the effect of the polar components on the PIT. Oleyl alcohol and oleic acid, often used as model fatty alcohols and fatty acids for detergency studies, are chosen as polar components. The equilibrium phase compositions in a three-phase region at the PIT, determined by phase volume measurements, are presented. The implications of the results for detergency processes are also briefly discussed.

## 2. Experimental

### 2.1. Materials

The nonionic surfactant *n*-dodecyl pentaoxyethylene monoether ( $C_{12}E_5$ ), which is the pure component analog of some of the most widely used commercial ethoxylated alcohol surfactants, was obtained from Nikko Chemical Company, Tokyo, Japan, and was used as received. The purity of the neat surfactant was typically greater than 97%. Oleyl alcohol and oleic acid were purchased from Sigma and had a reported purity of 99%. The NaCl and *n*-hexadecane used were obtained from Humphrey Chemical Co. and were of analytical grade. The water used for solution preparation was deionized and doubly distilled.

### 2.2. Methods

Solutions for phase behavior studies were prepared in Teflon-capped, 13 mm I. D., flat-bottomed test tubes and mixed for 20 seconds by vortex mix-

ing. Typically, sample volume was about 10mL with comparable volumes of the initial oil phase and the aqueous surfactant solution. All surfactant solutions were blanketed with nitrogen.

The polarized light screening (PLS) system described previously [13] was used for determining macroscopic phase behavior. This technique provides information about the isotropy, anisotropy, and scattering of solutions. The test tubes were calibrated, and the phase volumes were measured with an accuracy of 1% of the test tube volume.

PIT measurements were made using the emulsion stability [14], which is based on the fact that equilibration is more rapid at the PIT than at higher and lower temperatures. While periodically being shaken by hand, the samples were observed at increasing temperatures in a thermostatically-controlled water bath. The temperature at which the most rapid separation into three phases (excess water, excess oil, and a middle microemulsion phase) occurred was taken to be the PIT.

## 3. Results and Discussions

### 3.1. Determination of PIT for Systems Containing Oleyl Alcohol

The PIT measurements as a function of the amount of oleyl alcohol added were performed to determine the effect of oleyl alcohol on a system containing  $C_{12}E_5$ , water, and *n*-hexadecane. In these experiments, the amount of *n*-hexadecane and the water-to-oil ratio were kept constant while both surfactant and oleyl alcohol concentrations were varied.

The PIT curves, as shown in Figure 1, exhibit trends similar to those found with the lipophilic additive, *n*-dodecanol [7]. That is, the PIT has lower values when more alcohol is present. In other words, the PIT is lower for higher oleyl alcohol-to-*n*-hexadecane ratios as well as for lower surfactant-to-alcohol ratios. However, because of high solubility of oleyl alcohol, the oleyl alcohol's effectiveness

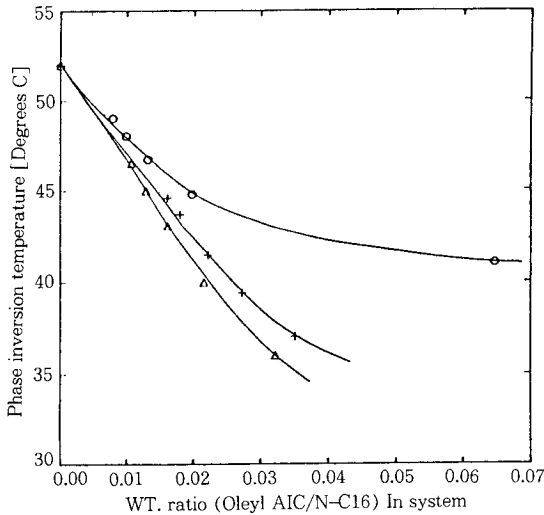


Fig. 1. PIT of the  $C_{12}E_5$ -oleyl alcohol-water-n-hexadecane system as a function of amount of oleyl alcohol added to the system.

- :  $C_{12}E_5/O.A. = 10.0$ ,
- :  $C_{12}E_5/O.A. = 5.25$
- △---△ :  $C_{12}E_5/O.A. = 4.0$

in lowering the PIT is reduced in the presence of large amounts of n-hexadecane. In this case, most of the oleyl alcohol partitions into the oil and the PIT approaches the alcohol-free value of 52°C.

Since only small amounts of oil are present in detergency processes, the optimum detergency is expected to correspond to the PIT of a system where most of the surfactant and additive remain in the interfacial films of the phases present [7]. That is, the surfactant films in the middle-phase microemulsions have the same composition as the initial oil-free surfactant solution. The composition of the surfactant films at the PIT can be calculated using a method introduced by Raney et al. for quaternary systems consisting of surfactant-lipophilic additive-water-oil [7]. It is based on the assumptions that

① the aqueous phase in equilibrium with the middle-phase microemulsion and excess oil phase contains only water,

② the oil solubilized in the middle-phase microemulsion has the same concentrations of surfactant and additive as the excess oil phase.

These assumptions have been found to be reasonable for similar nonionic surfactant systems [15].

At a given temperature and pressure, a three-phase, four-component system is left only one degree of freedom according to Gibbs' phase rule. If one more restriction is imposed such as equal solubilization of oil and water in the middle-phase microemulsion at the PIT, the compositions of not only all the individual phases but also of the surfactant films in the microemulsion are completely fixed.

At a given PIT, the following mass balance equation based on the above assumptions yields [7] :

$$(A/O)_i = (A/S)_i (S/A)_i (A/O)_i + [(A/O)_o - (S/O)_o (A/S)_i] = (A/S)_i (S/O)_i + [(A/O)_o - (S/O)_o (A/S)_i] \quad (1)$$

where  $(A/S)_i$  is the additive-to-surfactant weight ratio in the surfactant films in the microemulsion,  $(A/O)_i$  and  $(S/O)_i$  are the ratios of additive and surfactant to oil in the total system,  $(A/O)_o$  and  $(S/O)_o$  are the corresponding ratios for the oil phase, and  $(S/A)_i$  is the ratio of surfactant to additive in the total system. Because the compositions of phases are fixed at a particular PIT,  $(A/O)_o$ ,  $(S/O)_o$ , and  $(A/S)_i$  are constants and the PIT-composition relationship can be given in terms of  $(A/O)_i$  and  $(S/O)_i$ . From the slope of the line obtained by plotting  $(A/O)_i$  as a function of  $(S/O)_i$  at a given PIT,  $(A/S)_i$  can be found.

Such a plot in Figure 2 shows the result, utilizing the results of the PIT measurements for three different surfactant concentrations. As expected, the PIT is lowered as the alcohol-to-surfactant ratio in the film,  $(A/S)_i$ , is increased. Therefore, when the additive, namely oleyl alcohol, is present in the washing solution, the additive-to-surfactant ratio in the overall system determines the PIT, which can be used to predict optimal conditions for detergency.

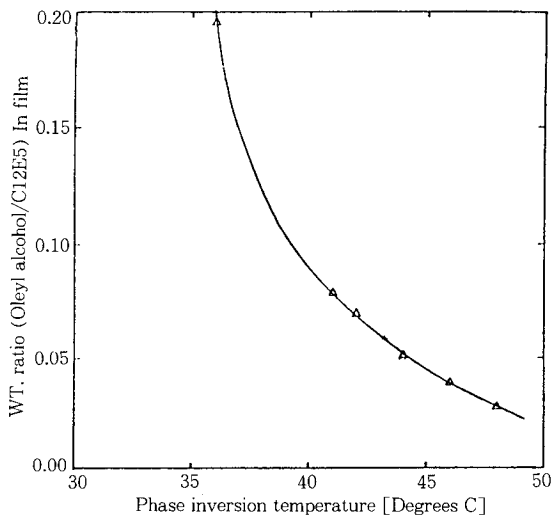


Fig. 2. Composition of surfactant films in microemulsion phase for the  $C_{12}E_5$ -oleyl alcohol-water-n-hexadecane system as a function of PIT.

### 3. 2. Determination of PIT for Systems Containing Oleic Acid

To determine the effect of added oleic acid on the PIT, the measured values of the PIT were plotted as a function of the acid-to-oil and surfactant-to-acid ratios in the overall system. In these experiments, the water-to-oil ratio was kept constant at one and 0.1 N NaCl was used instead of water. The salt was added to suppress electrical double layer effects which might be present because of dissociation of oleic acid molecules.

The results of PIT measurements as a function of the amount of oleic acid added to the systems containing different concentrations of  $C_{12}E_5$  are shown in Figure 3. The corresponding results for a salt-free system are also given for comparison. Figure 3 indicates that the effect of oleic acid is similar to that of oleyl alcohol, that is, both additives produce large reductions in the PIT. This behavior confirms that some oleic acid is incorporated into the surfactant films of the microemulsion phase. Comparing the middle solid curve with that for the salt-free system which has the same surfactant

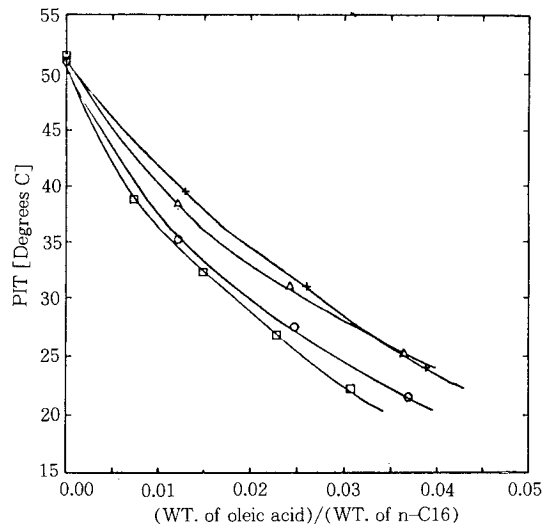


Fig. 3. PIT of the  $C_{12}E_5$ -oleic acid-0.1N NaCl-n-hexadecane system as a function of amount of oleic acid added to the system.

- +---+ :  $C_{12}E_5/nC_{16}=0.05$ (no salt),
- $\triangle$ --- $\triangle$  :  $C_{12}E_5/nC_{16}=0.0775$
- $\circ$ --- $\circ$  :  $C_{12}E_5/nC_{16}=0.0512$ ,
- $\square$ --- $\square$  :  $C_{12}E_5/nC_{16}=0.0272$

content, one sees that PIT values in the former case are about 5°C lower except at very small concentrations of oleic acid. Thus electrical effects, while not negligible, do not change the conclusion that oleic acid acts as a lipophilic additive.

The composition of the surfactant films at the PIT can be calculated using equation (1). However, besides the assumptions used in oleyl alcohol system, the additional assumption that brine behaves as a pseudo-component is needed. The validity of this assumption has been found for other surfactant systems [1, ].

The result is given in Figure 4. As expected, one finds that the more oleic acid is incorporated into the surfactant film, the more lipophilic the system becomes.

Besides the composition of the surfactant film, one can also calculate the compositions of the individual phases at the PIT by making use of phase volume measurements. With no volume change on

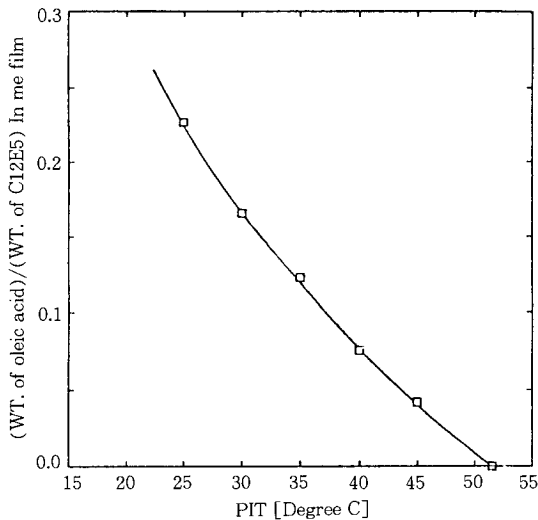


Fig. 4. Composition of surfactant films in microemulsion phase for the  $C_{12}E_5$ -oleic acid-0.1N NaCl-n-hexadecane system as a function of PIT.

mixing, the following set of equations can be constructed based on component mass balance equations :

$$\begin{aligned} S_t &= \phi_O^S V_O + \phi_{ME}^S V_{ME} \\ A_t &= \phi_O^A V_O + \phi_{ME}^A V_{ME} \\ O_t &= \phi_O^O V_O + \phi_{ME}^O V_{ME} \\ W_t &= V_W + \phi_{ME}^W V_{ME} \end{aligned} \quad (2)$$

where  $S_t$ ,  $A_t$ ,  $O_t$ , and  $W_t$  are total volumes of surfactant, additive, oil, and brine present in the system,  $\phi_i^j$  ( $i=S, A, O, W, j=O, ME, W$ ) denotes the volume fraction of component  $i$  in phase  $j$ , and  $V_j$  is the volume of phase  $j$ .

From the first three of equations (2), the following equations can be derived :

$$\begin{aligned} S_t &= [\phi_{ME}^S - \phi_{ME}^O (\phi_O^S / \phi_O^O)] V_{ME} + (\phi_O^S / \phi_O^O) O_t \\ A_t &= [\phi_{ME}^A - \phi_{ME}^O (\phi_O^A / \phi_O^O)] V_{ME} + (\phi_O^A / \phi_O^O) O_t \end{aligned} \quad (3)$$

According to equations (3), if  $O_t$  is kept constant, the slopes and intercepts of plots of  $S_t$  and  $A_t$  as a function of  $V_{ME}$  give four independent relationships among the seven  $\phi_i^j$ 's. The following restrictions also apply :

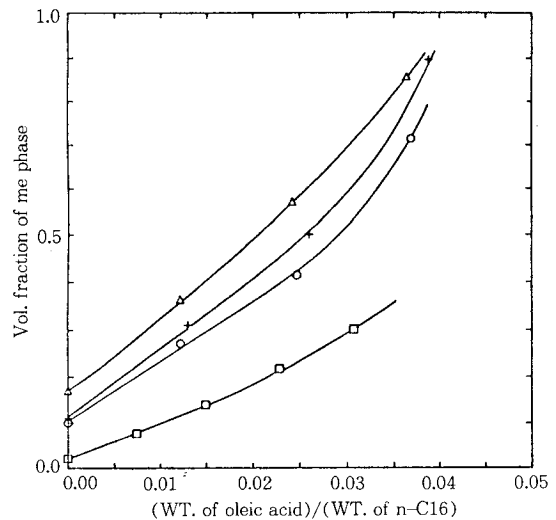


Fig. 5. Volume fraction of microemulsion phase for the  $C_{12}E_5$ -oleic acid-0.1N NaCl-n-hexadecane system as a function of amount of oleic acid added to the system.

+---+ :  $C_{12}E_5/nC_{16}=0.05$ (no salt),

Δ---Δ :  $C_{12}E_5/nC_{16}=0.0775$

○---○ :  $C_{12}E_5/nC_{16}=0.0512$ ,

□---□ :  $C_{12}E_5/nC_{16}=0.0272$

$$\begin{aligned} \phi_{ME}^S + \phi_{ME}^A + \phi_{ME}^O + \phi_{ME}^W &= 1 \\ \phi_O^S + \phi_O^A + \phi_O^O &= 1 \end{aligned} \quad (4)$$

From these six relationships and the last of the equations (2), all of the  $\phi_i^j$ 's can be determined.

The results of the phase volume measurements are illustrated in Figures 5-8. Figure 5 shows the relationship between the phase volume of the microemulsion phase and the oleic acid content. As before the result for the salt-free system is also plotted. Note that the microemulsion phase volume with 0.1 N NaCl present is slightly smaller than that of the salt-free system. This slight difference may be the result of compression of the electrical double layer by the added salt. In all cases, however, microemulsion phase volume increases with increasing oleic acid content.

Figures 6-8 illustrate the phase volume changes as a function of PIT for three different surfactant concentrations. Microemulsion phase volume de-

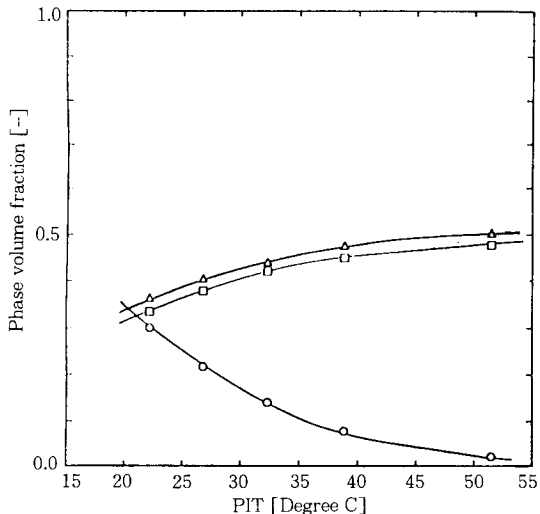


Fig. 6. Phase volumes for the  $C_{12}E_5$ -oleic acid-0.1N NaCl-n-hexadecane system as a function of PIT where a weight ratio of  $C_{12}E_5$  to n-hexadecane is equal to 0.0272.

△---△ : Excess Oil, □---□ : Excess Water  
○---○ : Middle-phase Microemulsion

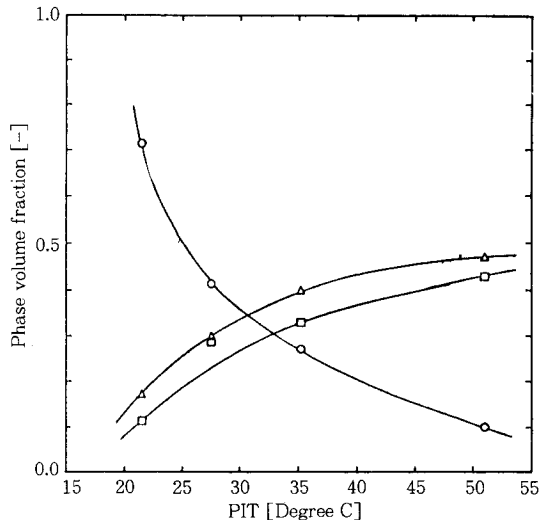


Fig. 8. Phase volumes for the  $C_{12}E_5$ -oleic acid-0.1N NaCl-n-hexadecane system as a function of PIT where a weight ratio of  $C_{12}E_5$  to n-hexadecane is equal to 0.0775.

△---△ : Excess Oil, □---□ : Excess Water  
○---○ : Middle-phase Microemulsion

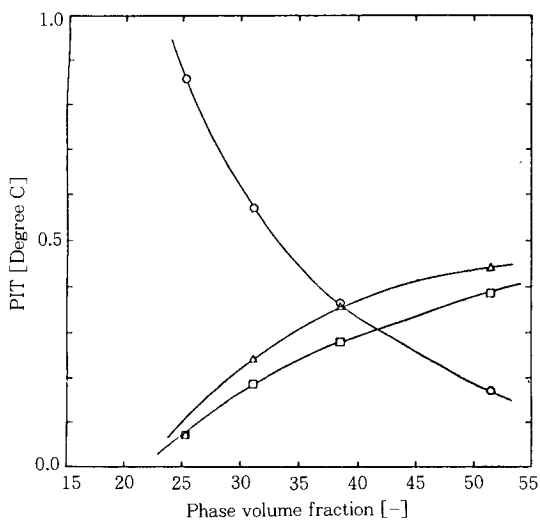


Fig. 7. Phase volumes for the  $C_{12}E_5$ -oleic acid-0.1N NaCl-n-hexadecane system as a function of PIT where a weight ratio of  $C_{12}E_5$  to n-hexadecane is equal to 0.0512.

△---△ : Excess Oil, □---□ : Excess Water  
○---○ : Middle-phase Microemulsion

creases rapidly with increasing PIT, i.e., with decreasing amounts of oleic acid in the system. Also shown in Figures 6-8, microemulsion phase volume increases with increasing amounts of surfactant in the system.

Using the data in Figures 3 and 6-8, and following the calculation method described above, the composition of each phase at several PITs were determined. Results are shown in Table 1 and Figure 9. Note that the volume fractions of brine and n-hexadecane in the microemulsion shown in Table 1 are approximately equal. This result confirms the basic validity of the procedure used here to determine the PIT, viz., the condition where the phases separated most rapidly.

Figure 9 shows the changes in surfactant and oleic acid content of the microemulsion and oil phases with changing PIT. With a decrease in PIT, the volume fraction of surfactant in the microemulsion phases decreases substantially, while the volume fraction of surfactant in the oil phase

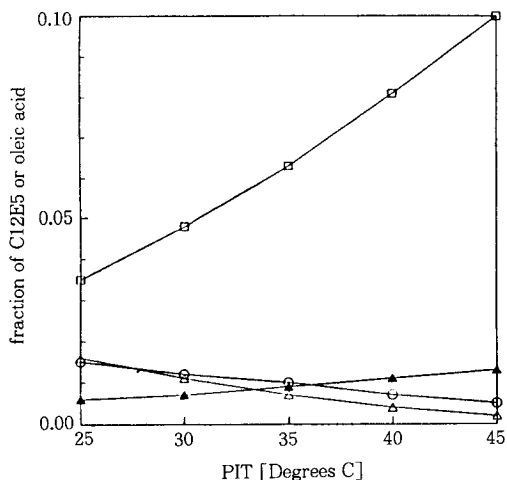


Fig. 9. C<sub>12</sub>E<sub>5</sub> and oleic acid contents in microemulsion phase and excess oil phase for the C<sub>12</sub>E<sub>5</sub>-oleic acid-0.1N NaCl-n-hexadecane system as a function of PIT.

- : C<sub>12</sub>E<sub>5</sub> in Microemulsion Phase
- ▲---▲ : C<sub>12</sub>E<sub>5</sub> in Excess Oil Phase
- : Oleic Acid in Microemulsion Phase
- △---△ : Oleic Acid in Excess Oil Phase

Table 1. Phase Compositions as Functions of PIT in the C<sub>12</sub>E<sub>5</sub>, Oleic Acid, 0.1N NaCl Brine, and N-Hexadecane System

PIT, °C	Microemulsion phase				Excess oil phase		
	S	A	B	O	S	A	O
45	0.103	0.005	0.416	0.476	0.013	0.002	0.985
40	0.081	0.007	0.433	0.478	0.011	0.004	0.985
35	0.063	0.010	0.429	0.498	0.009	0.007	0.985
30	0.048	0.012	0.447	0.493	0.007	0.011	0.982
25	0.035	0.015	0.464	0.487	0.006	0.016	0.978

diminishes only slightly. The latter behavior can be explained as a decrease of surfactant solubility in oil phase with decreasing temperatures.

On the other hand, the volume fractions of oleic acid in both microemulsion and oil phases are somewhat increased with decreasing PIT. These increases stem from the increase in oleic acid content of the system.

With the data in Figure 4 and Table 1, one can calculate the solubilization parameters of the sur-

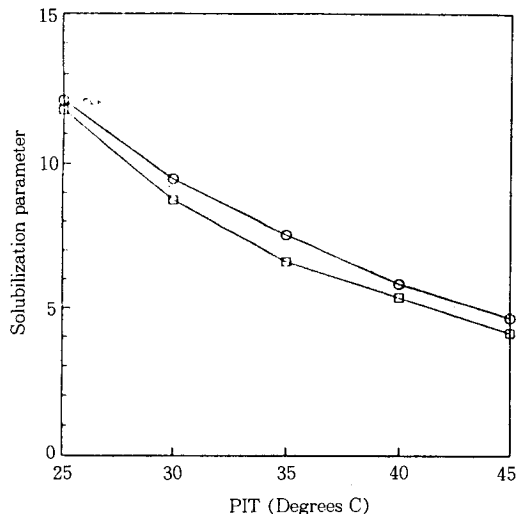


Fig. 10. Solubilization parameters of microemulsion phase for the C<sub>12</sub>E<sub>5</sub>-oleic acid-0.1N NaCl-n-hexadecane system.

- :  $\frac{\text{Volume of Water Solubilized}}{\text{Volume of Surfactant Films in Microemulsion Phase}}$
- :  $\frac{\text{Volume of Oil Solubilized}}{\text{Volume of Surfactant Films in Microemulsion Phase}}$

factant film, defined as the volume ratio of brine or oil solubilized in the microemulsion to that of the surfactant films. The solubilized oil includes dissolving surfactant and additive.

The results are shown in Figure 10 as a function of PIT. The solubilization parameters are strikingly increased with decreasing PIT, reaching a value of about 12 at 25°C. This dramatic increase in solubilization parameters is produced by the addition of oleic acid and the increase in hydration of the ethylene oxide groups of the surfactant with decreasing temperature. The increase in solubilization at the PIT should be accompanied by a decrease in interfacial tensions between microemulsion and excess phases if trends reported in the literature for other microemulsion systems are followed [5,8,16].

### 3. 3. Implications for Detergency Processes

Ultimately, applications of these results to



detergency processes are desirable. In practical washing situations the water-to-oil ratio is usually extremely large so that only small fractions of surfactant and additive partition into the oil. Therefore, the effective ratio of additive to surfactant in the films at this limiting condition would be virtually the same as that present in the initial washing solution [7]. The corresponding PIT can then be easily determined from curves such as those in Figures 2 and 4 to give the temperatures at which the maximum removal of soil by solubilization and/or emulsification into the washing solution can be expected.

Even though small amounts of soil are usually present in practical situations, it is also interesting to speculate the cases where various amounts of soil are present. For this purpose, one can treat the additive as being present in the soil. For example, for the  $C_{12}E_5$ -oleyl alcohol-water-n-hexadecane system, using the data of Figure 1 and equation (1), the surfactant-to-alcohol ratios,  $(S/A)_i$ , can be calculated at the PIT for various alcohol-to-oil ratios,  $(A/O)_i$ , or soil compositions. Two PIT-composition curves (the PIT plotted versus  $(A/O)_i$  at a fixed  $(S/A)_i$  value) are sufficient to plot the corresponding curve for any other  $(S/A)_i$ . The results are shown in Table 2 and typical values of these ratios that would be expected in detergency applications are also indicated in Table 3. Therefore, for example, if 10% alcohol is present in 56 mg total soil, the calculated values of these ratios are  $(A/O)_i = 0.10$  and  $(S/A)_i = 49.1$ . Using Table 3, one would expect a PIT or optimum detergency around 49°C. If the total amount of soil were fixed at 56 mg but the ratio of alcohol to n-hexadecane in the soil doubled, then the PIT would be lowered from 49°C to 46°C. With equal amounts of alcohol and n-hexadecane the PIT would be further lowered to around 35°C. Now, at the same alcohol-to-oil ratio of one, if the total amount of soil were halved, the PIT would be expected to increase from 35°C to 44°C. Therefore, the composition of the soil, that is the alcohol-to-n-hexadecane ratio does not in itself

**Table 2.** PIT as a Function of Composition in the  $C_{12}E_5$ , Oleyl Alcohol, Water, and n-Hexadecane System. Obtained from Equation (1) :  $(A/O)_i = (A/S)_i(S/A)_i(A/O)_i + [(A/O)_o - (S/O)_o(A/S)_i]$

PIT, °C	$(A/O)_i=0.1$	$(A/O)_i=0.2$	$(A/O)_i=1.0$
	$(S/A)_i$	$(S/A)_i$	$(S/A)_i$
36.0	8.50	9.58	10.45
37.0	9.44	10.58	11.49
39.0	10.98	12.09	12.99
41.0	11.38	12.29	13.01
43.0	14.44	15.44	16.24
45.0	20.53	21.76	22.75
48.0	30.36	31.43	32.29
48.5	41.28	42.64	43.73
49.0	57.98	59.70	61.08

**Table 3.** Calculations for Various Amounts of Soil and Soil Composition  
0.05% wt% Surfactant in 500ml Water is Used ( $S=250$ mg)

Soil(A+O), mg	$(A/O)_i=0.1$	$(A/O)_i=0.2$	$(A/O)_i=1.0$
	$(S/A)_i$	$(S/A)_i$	$(S/A)_i$
28.0	98.2	53.6	17.8
56.0	49.1	26.8	8.9
112.0	24.5	13.4	4.45

determine the PIT. Both the amount of the soil and the surfactant concentration in the washing solution can also have large effects on the PIT.

Benson and Raney [12] presented quantitative information on removal of mixed n-hexadecane-oleyl alcohol and n-hexadecane-oleic acid soils by three different nonionic surfactants ( $C_{12}E_6$ ,  $C_{12}E_7$ , and  $C_{12}E_8$ ) below their cloud points. They found that the PIT is typically below the cloud point for these soils, and the highest level of soil removal is obtained between the PIT and cloud point rather than only at the PIT. This behavior contrasts sharply with the results for nonpolar oily soils where maximum soil removal occurs only at the PIT, as discussed above. Later, using a newly developed oil drop contacting technique Lim and Miller [17] showed that for the above lipophilic systems which exhibit good soil removal, i.e., those above the PIT, an intermediate lamellar liquid crystalline phase de<sub>2</sub>

velops as myelinic figures, beginning at a definite time after initial contact. They also showed that when the alcohol or acid content of the oil is low and the temperature is near or only slightly above the PIT, which corresponds to systems of interest here, the first intermediate phase formed is a middle-phase microemulsion which later becomes again a lamellar liquid crystalline phase as the surfactant content in the oil phase continues to increase. Since nonequilibrium data are not available for the conditions where our results obtained, it is not clear that the same transition from a middle-phase microemulsion to a lamellar liquid crystalline phase would also occur near the PIT in our systems. Nevertheless, PIT measurement seems a useful starting point for estimating conditions when middle-phase microemulsion formation and its associated high solubilization of oil can be expected.

It is noteworthy that the behavior of *n*-hexadecane-oleic acid soils is similar to that observed for *n*-hexadecane-oleyl alcohol mixtures, provided that the pH is neutral or acidic. For high pH conditions, conversion of acid to soap would produce additional effects, which needs to be further investigated.

#### 4. Conclusions

The effects of soils containing mixtures of the nonpolar hydrocarbons and more polar components which better simulate soils typically present in laundry have been investigated. Of particular interest was the effect of the polar components on the PIT in systems containing water, the nonionic surfactant,  $C_{12}E_5$ , and *n*-hexadecane. Oleyl alcohol and oleic acid, often used as model fatty alcohols and fatty acids for detergency studies, have been chosen as polar components. The following results are obtained in this work.

1. The effect of the polar components is similar to that of the lipophilic additive, that is, both oleyl alcohol and oleic acid present in soil produce large reductions in the PIT. Also, the PIT is lowered for higher additive-to-*n*-hexadecane ratios as well as

for lower surfactant-to-additive ratios.

2. Microemulsion phase volume increases rapidly with decreasing PIT, i.e., with increasing amounts of additive in the system. Also with a decrease in PIT, the volume fraction of surfactant in the microemulsion phase decreases substantially, while the volume fraction of surfactant in the oil phase diminishes slightly. On the other hand, the volume fractions of lipophilic additive in both microemulsion and oil phases are somewhat increased with decreasing PIT.

3. The solubilization parameters of oil and water in the microemulsion phase are strikingly increased with decreasing PIT.

4. Due to the different partitioning of additive and surfactant in the oil phase, the composition of the soil, that is the additive-to-*n*-hexadecane ratio does not in itself determine the PIT. Both the amount of the soil and the surfactant concentration in the washing solution can also have large effects on the PIT.

5. In practical washing situations, where the water-to-oil ratio is usually extremely large, the PIT of interest is actually that corresponding to a ratio of additive to surfactant in the surfactant films in the microemulsion phase is virtually the same as that present in the initial washing solution.

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