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SURFACTANTS AND DETERGENTS TECHNICAL

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Technical

☘ Temperature Dependence of the Solubility Areas for W/O Microemulsions with Nonionic/Anionic Surfactants

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ABSTRACT

The solubitity areas were determined at 30, 50 and 75 C for W/O microemulsions of water and decane stabilized by sodium dodecyl sulfate or hexaethylene glycol dodecyl ether in combination with pentanol. The results showed no pronounced changes when the ionic surfactant was partly replaced with the nonionic one and revealed an excellent temperature stability in the range 30-75 C for the W/O microemulsions.

INTRODUCTION

The research on microemulsions has made pronounced progress during the last 10 years (1,2) both from the theoretical (3-6) and experimental (7-9) points of view. The role of ionic surfactants (10-15), as well as the special characteristics of systems stabilized by hydrophobic nonionic surfactants (16-21), have been clarified.

The temperature stability of the common systems with the ionic surfactant/pentanol combination as stabilizers surprisingly has not been treated. Because this factor is obviously of pronounced importance from a preparative point of view, we judged an investigation into the temperature stability of W/O systems to be of general interest.

Practical applications of microemulsions in liquid cleaners involve the use of ionic/nonionic surfactant combinations. Such combinations are essential to obtain good cleaning of both natural and synthetic fibers. The preparation and properties of such microemulsions have only been given a preliminary description (22).

In the present article, we describe the solubility areas for W/O microemulsions stabilized by pentanol as the cosurfactant and sodium dodecyl sulfate or hexaethylene glycol dodecyl ether as the surfactant combination.

EXPERIMENTAL PROCEDURES

Materials

Sodium dodecyl sulphate was obtained from BDH Chemical Ltd., Poole, England. It was especially pure (>99%), and was recrystallized twice from ethanol. Hexaethylene glycol n-dodecyl ether was from Nikkol Chemicals Ltd. (>98%); the pentanol was from Fisher Scientific Co., Fairlawn, NJ, (Bp 137.3-138.3 C); and n-decane was from Aldrich Chemical Co., Milwaukee, WI, (Bp 174 C) with no further purification. Twice distilled water was used.

Determination of Microemulsion Regions

The microemulsion areas were determined at 30 C by water titration of mixtures of the remaining components, noting points of turbidity and clarity. For some parts of the regions for which the slope of the border line of the solubility region made of determinations difficult, complementary determinations were made using pentanol or pentanol and decane solution as the titrand. The solubility regions were checked by storing for 7 days, samples immediately inside and outside the solubility limit. The phase diagrams are given in percentage of weight compositions.

RESULTS

The influence of partly replacing the anionic surfactant with the nonionic one gave only small changes in the solubility areas in the systems without hydrocarbon (Figs. 1 and 2). The original continuous solubility area, from the cosurfactant corner to the water corner, was interrupted for the SDS/$C_{12}(EO)_6$ ratios 2:1 and 1:1 and the minimum surfactant concentration to achieve high water solubilization was increased, as shown in Figure 3. This minimum surfactant concentration is the maximum value of the surfactant concentration of the 2-phase area along the water-consurfactant (hydrocarbon) axis in Figures 2, 4 and so forth. The necessary surfactant concentration varied to only a small degree when up to 4/5 of the ionic surfactant was replaced with the nonionic one. The increase was found first for extremely high nonionic/anionic ratios.

The pattern for the microemulsions with hydrocarbons, Figures 4-7, is similar. Replacing up to 4/5 of the ionic surfactnat with the nonionic one brings only small changes in the solubility areas. The maximum water content stayed more or less constant and the necessary surfactant concentration increased slightly.

The influence of temperature for the systems without hydrocarbon is revealed by a comparison between Figures 2, 7 and 9. The pattern was identical for the systems with and without nonionic surfactant. The solubility region connecting the W/O and O/W parts of the system became wider and the surfactant concentration to achieve the water solubilization was increased.

The trend for systems containing hydrocarbons is similar as shown by comparing Figures 5, 8 and 9.

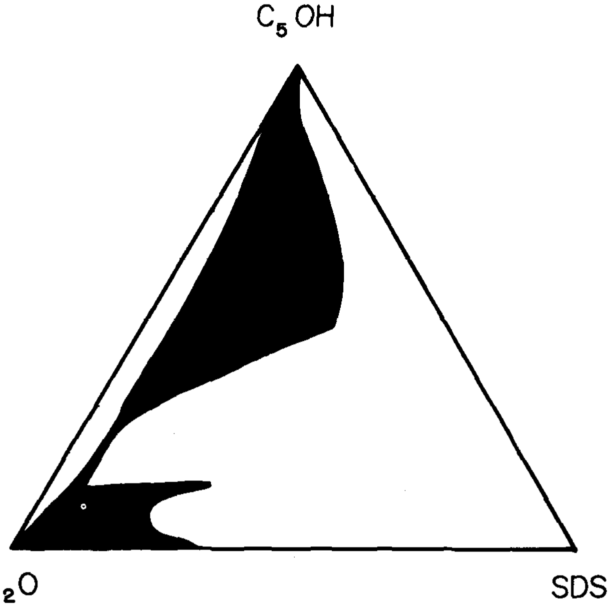

FIG. 1. The isotropic liquid area (black) in the system water (H_2O), pentanol (C_5OH) and sodium dodecyl sulfate (SDS).

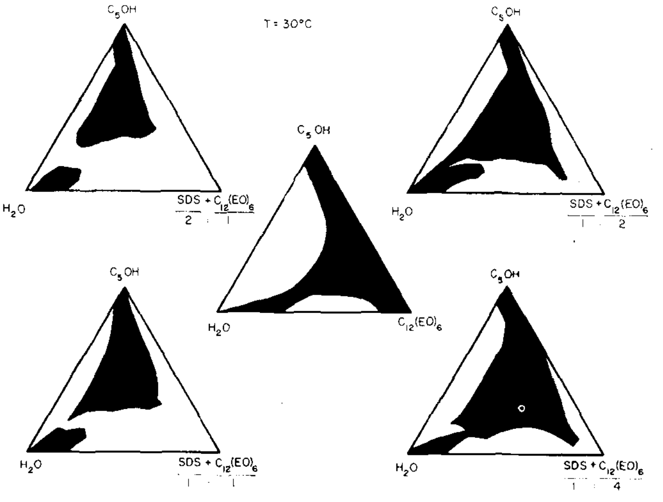

FIG. 2. The isotropic liquid areas (black) in the systems water (H_2O), pentanol (C_5OH) and sodium dodecyl sulfate (SDS)/hexaethylene glycol dodecyl ether ($C_{12}EO_6$) in the weight ratios indicated.

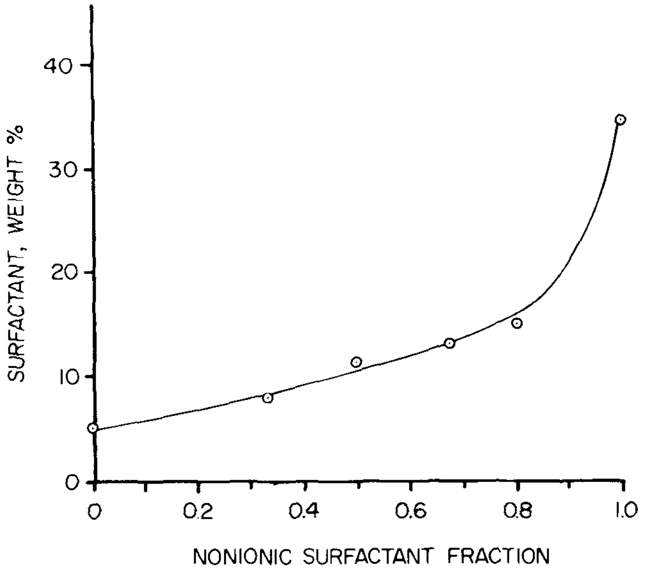

FIG. 3. Maximum surfactant concentration of the 2-phase area to the left in the diagrams of Figures 1 and 2.

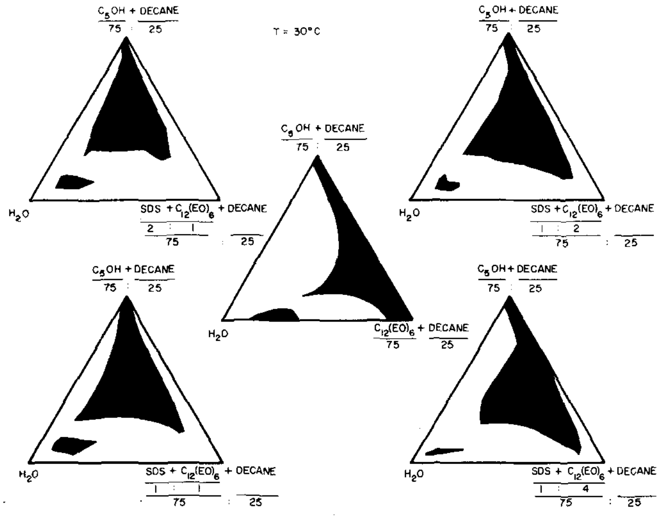

FIG. 4. The isotropic liquid areas (black) in the systems water (H_2O), pentanol (C_5OH)/decane and sodium dodecyl sulfate (SDS)/hexaethylene glycol dodecyl ether ($C_{12}EO_6$)/decane in the weight ratios indicated.

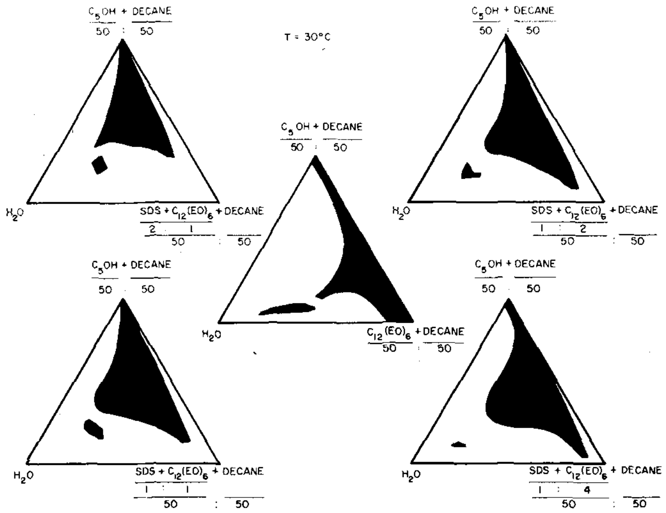

FIG. 5. The isotropic liquid areas (black) in the systems water (H_2O), pentanol (C_5OH)/decane and sodium dodecyl sulfate (SDS)/hexaethylene glycol dodecyl ether ($C_{12}EO_6$)/decane in the weight ratios indicated.

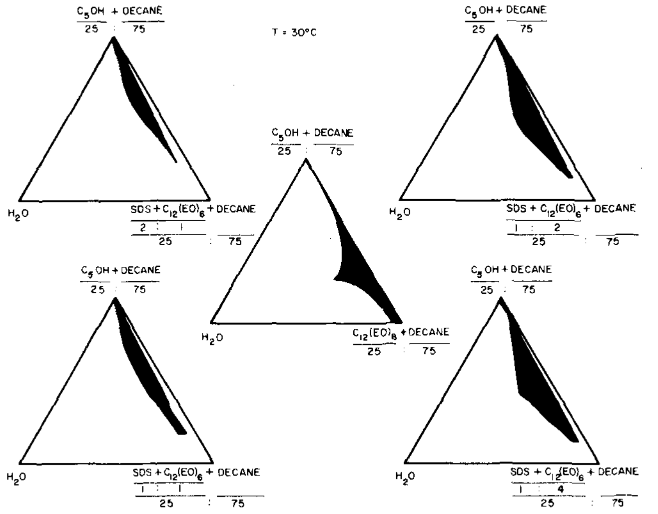

FIG. 6. The isotropic liquid areas (black) in the systems water (H_2O), pentanol (C_5OH)/decane and sodium dodecyl sulfate (SDS)/hexaethylene glycol dodecyl ether ($C_{12}EO_6$)/decane in the weight ratios indicated.

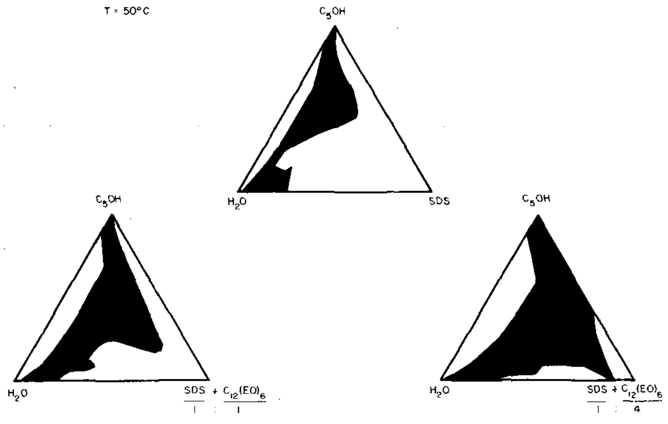

FIG. 7. The isotropic liquid areas (black) in the systems water (H_2O), pentanol (C_5OH) and sodium dodecyl sulfate (SDS)/hexaethylene glycol dodecyl ether ($C_{12}EO_6$) in the weight ratios indicated.

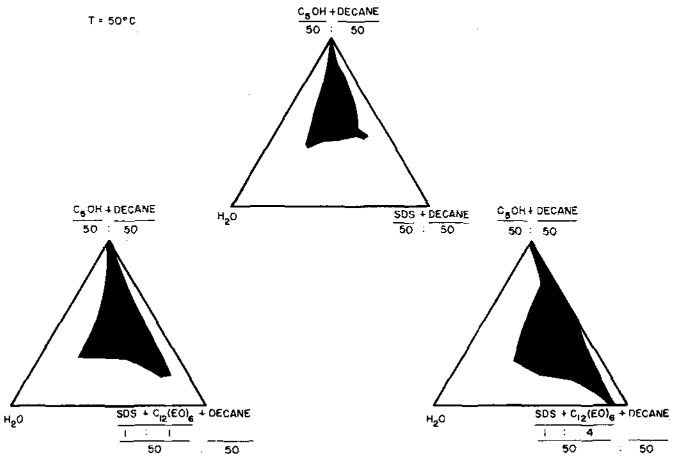

FIG. 8. The isotropic liquid areas (black) in the systems water (H_2O), pentanol (C_5OH)/decane and sodium dodecyl sulfate (SDS)/hexaethylene glycol dodecyl ether ($C_{12}EO_6$)/decane in the weight ratios indicated.

DISCUSSION

The results contain pertinent information about the preparation of microemulsions for application as liquid cleaners and also about the temperature stability for such compositions.

The results show that the microemulsion preparation with mixtures of nonionic and ionic surfactant present no serious problems once the simple relations for microemulsions with ionic surfactants have been mastered. Evidently, the nonionic surfactant, with its extended hydrophilic chain, encounters little difficulty when mixed into the micellar structure of the ionic surfactant/consurfactant combination, even at very high nonionic/anionic surfactnat ratios.

The loss of the continuous solubility area at the initial addition of nonionic surfactant (Fig. 2; SDS/$C_{12}[EO]_6$ ratios 2:1 and 1:1) may be understood when compared with the behavior of nonionic/anionic surfactant combinations (23). Such mixtures show the lamellar liquid-crystalline phase to be strongly stabilized against high water concentrations for certain combinations of the two.

Because the W/O and O/W microemulsions in general are separated by a lamellar liquid-crystalline phase [10], any ratio of the nonionic/anionic surfactants that cause stabilization of the liquid-crystalline phase toward high water contents will separate the W/O and O/W regions. This result is found for SDS/$C_{12}(EO)_6$ ratios 2:1 and 1:1 in Figure 2.

The addition of hydrocarbon also caused a separation of the W/O and O/W systems (Figs. 4 and 5) and the O/W part did not reach the water corner in the diagram but formed an isolated area. These changes are not related to the enhanced stability of the liquid-crystalline phase; on the contrary, the addition of a hydrocarbon usually causes destabilization of the lamellar structure.

The reason for the separation of the W/O region is instead found in the fact that the consurfactant is soluble in the hydrocarbon. Added hydrocarbon means a reduced chemical potential for the cosurfactant and less tendency to associate with the water and the surfactant and hence, less stability for the liquid crystalline phase (11).

The isolated O/W region is a consequence of the general shape of these regions (14,24). The extension of the microemulsion region from the aqueous micellar solution does not emanate from the water corner but from a point with a certain surfactant concentration in the micellar area (24).

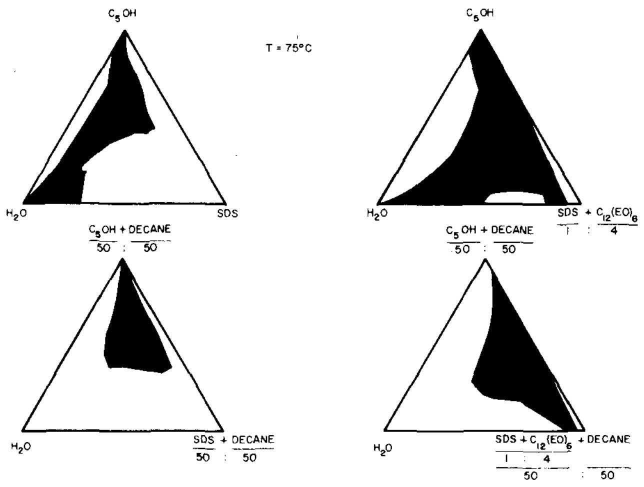

FIG. 9. The isotropic liquid areas (black) in the systems water (H_2O), pentanol (C_5OH)/decane and sodium dodecyl sulfate (SDS)/hexaethylene glycol dodecyl ether ($C_{12}EO_6$)/decane in the weight ratios indicated.

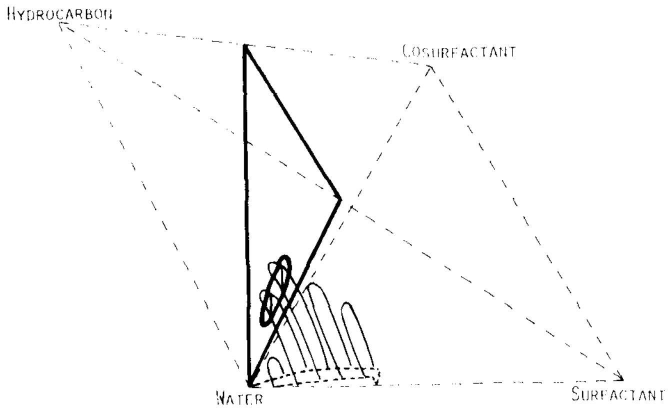

FIG. 10. The shape of the O/W microemulsion region makes it appear as an isolated area in a plane with a certain hydrocarbon/cosurfactant and dydrocarbon/surfactant ratio in spite of the fact that it forms a continuous region to the aqueous corner.

Hence, a plane including a certain ratio of hydrocarbon will intersect the O/W microemulsion region at a certain distance from the water corner as illustrated in Figure 10.

These mechanisms also form the basis for the temperature dependent changes (Figs. 2, 7 and 9). These, in general, consist of a widening of the region joining the W/O and O/W areas. An increase in temperature will cause a destabilization of the liquid crystalline phase and an increase of the microemulsion region at water/cosurfactant ratios characteristic of the lamellar liquid-crystalline phase in the system.

A reduction of the stability of the liquid-crystalline phase should also lead to a reduction of the stability of the W/O microemulsion phase, e.g., the left boundary of the region should be moved to the right with increasing temperature. This change did not take place.

This fact indicates a connection between the microemulsion concept and the critical mixing of water with polar organic solvents. In many such systems, mutual solubility is enhanced by an increase in temperature. If such a mechanism is the operational factor controlling the location of the left border in the present case, the invariance of its location may be explained by a reduction of the stability of the micellar structure with temperature being countered by an increase in mutual solubility of the components. This hypothesis requires further testing.

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