January, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *31—34 (1983)* 31

Phase Diagrams and Association Structures of Combined Surfactants–Water Systems

Hiromichi Sagitani[†] and Stig E. Friberg*
Chemistry Department, University of Missouri-Rolla, Rolla, MO., 65401, U.S.A.

(Received May 8, 1982)

Phase regions were determined in systems with water and sodium dodecyl sulfate combined with a series of nonionic surfactants of the structure di-, tetra-, hexa-, and octaoxyethylene dodecyl ethers. The results showed the more hydrophobic members to act as cosurfactants, stabilizing the lamellar structure at high water contents. The more hydrophilic members of the nonionic series acted in a manner similar to ionic surfactants with a slight tendency to stabilization of the lamellar phase for 1:1 combinations of the surfactants.

Modern formulations for use in the laundry process use a combination of nonionic and anionic surfactants, a necessity in order to obtain optimum removal of soil from different kinds of fabric.

The nonionic/ionic surfactant combinations are also of importance for emulsion stability; the well known combination of a long-chain alcohol plus a long-chain ionic surfactant has been extensively discussed.[1–4]) Similar surfactant combinations using medium-chain alcohols are well known for their use in microemulsion systems; the literature in that field is as rich as it is varied.[5–11])

These investigations have been confined to essential but limited parts of the total systems, and we found an investigation of the systematic changes in the general features of surfactant combination systems to be desirable in order better to understand their behavior.

The combination chosen was water and sodium dodecyl sulfate with a series of polyoxyethylene dodecyl ethers. The latter were varied from the most hydrophobic one, the alcohol, to a member with distinctly hydrophilic properties, the octaoxyethylene homologue.

Experimental

Materials. Sodium dodecyl sulfate ($C_{12}SO_4Na$), specially pure grade, BDH Chemicals, Ltd., was recrystallized twice from ethanol. Di-, tetra-, hexa-, and octaoxyethylene dodecyl ether ($C_{12}(EO)_n$) were 98% from Nikko Chemical Co.; 1-decanol ($C_{10}H_{21}OH$) was practical grade from Eastman Kodak Co.

Phase Diagrams. The solubility regions were determined by titration of water to a mixture of the other components. The liquid crystalline and crystalline regions were analyzed by visual observation between polarized films and in a microscope with polarized light. The measurements and determinations were made at 30±0.1 °C.

Light Scattering Measurements. The light scattering measurements were done on a Sofica Photo Gonio Diffusometer, Model 42000, at 30 °C and 546 nm. The reported $I_{90°}$ values were scaled to the value of pure benzene, put a 100. The cells were immersed in a chromosulfuric acid solution for 15 h and rinsed several times with twice distilled water. The benzene and the distilled water were filtered through a Millipore filter, 0.22 μm prior to use. Dust particles were finally removed from the solutions by centrifugation at 25000 g for 3 h immediately before the determinations.

X-Ray Measurements. The interlayer spacings of lamellar phases were determined by low angle diffraction X-ray (Siemens Crystalloflex 4) with an X-ray detector (Tennelec, PSD-100) and a multichannel analyzer (Packard, Model 901). The measurements were done at 40 KV, 30 mA, and room temperature (24 °C).

Results

The results have a bearing on both the extension of the phase regions and the structure of the associations. They will be reported in order.

Phase Regions. The combination with 1-decanol, Fig. 1, has the expected phase regions: two isotropic liquid phases, A and B in the figure. A emanating from the pure water corner is an aqueous micellar solution solubilized 1-decanol. B emanating from the 1-decanol is an alcoholic solution solubilized water. This alcoholic solution of water and surfactant will contain inverse micelles.[12]) In addition, 2 liquid crystals are found. One has a structure of close-packed cylinders with the amphiphiles radially packed (C), while the other is the well known lamellar structure (D).[13]) Observation under polarized light confirmed

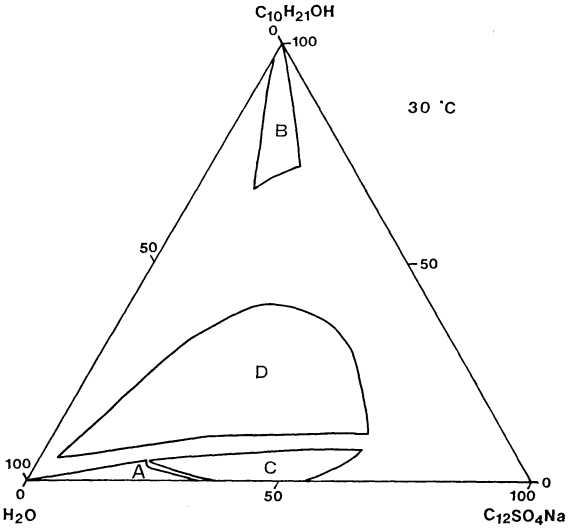

Fig. 1. The phase regions in the system water, sodium dodecyl sulfate ($C_{12}SO_4Na$) and 1-decanol ($C_{10}H_{21}OH$).
The concentrations are given in weight per cent. A: Isotropic aqueous solution, B: isotropic decanol solution, C: liquid crystal with a structure of cylinders in a hexagonal array, D: liquid crystal with lamellar structure.

[†] Present address: Pola Laboratories, 27-1, Takashimadai, Kanagawa-ku, Yokohama 222.

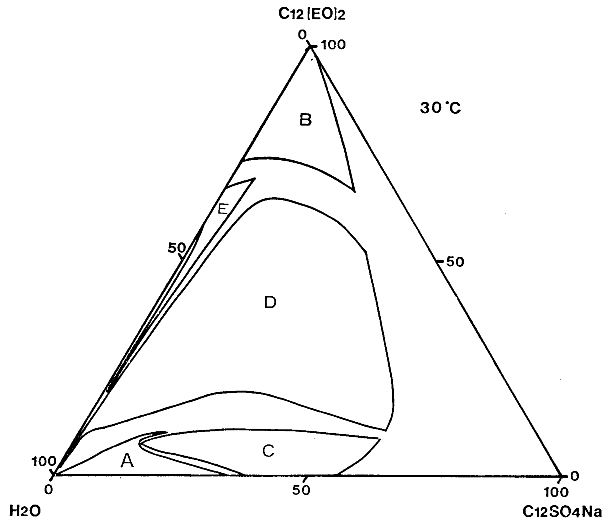

Fig. 2. The phase regions in the system water, sodium dodecyl sulfate ($C_{12}SO_4Na$) and dioxyethylene dodecyl ether ($C_{12}(EO)_2$).
A: Isotropic aqueous solution, B: isotropic ether solution, C: liquid crystal with a structure of cylinders in a hexagonal array, D: liquid crystal with lamellar structure, E: liquid crystal with isotropic structure.

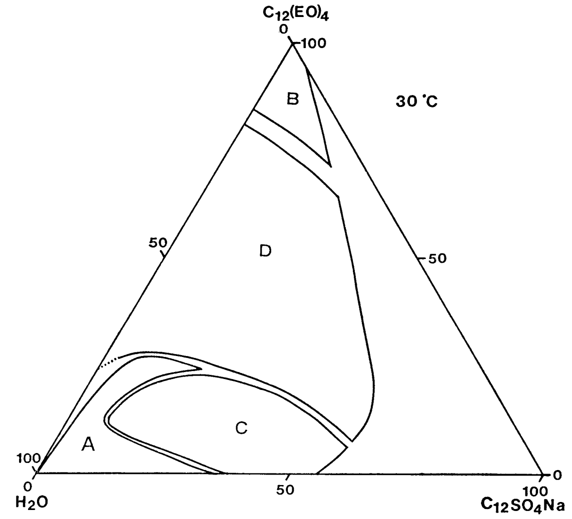

Fig. 3. The phase regions in the system water, sodium dodecyl sulfate ($C_{12}SO_4Na$) and tetraoxyethylene dodecyl ether ($C_{12}(EO)_4$).
A: Isotropic aqueous solution, B: isotropic ether solution, C: liquid crystal with a structure of cylinders in a hexagonal array, D: liquid crystal with lamellar structure.

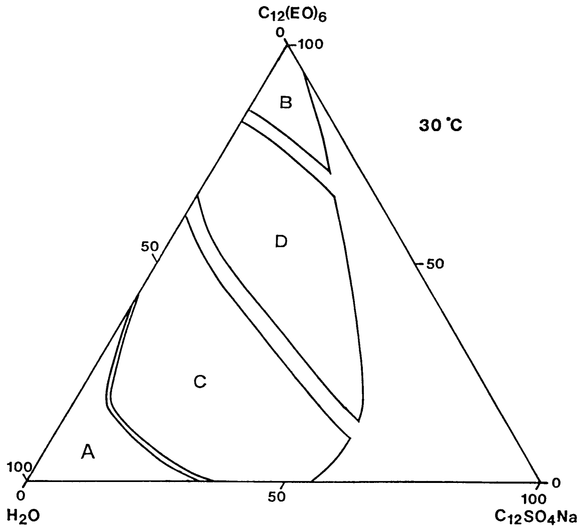

Fig. 4. The phase regions in the system water, sodium dodecyl sulfate ($C_{12}SO_4Na$) and hexaoxyethylene dodecyl ether ($C_{12}(EO)_6$).
A: Isotropic aqueous solution, B: isotropic ether solution, C: liquid crystal with a structure of cylinders in a hexagonal array, D: liquid crystal with lamellar structure.

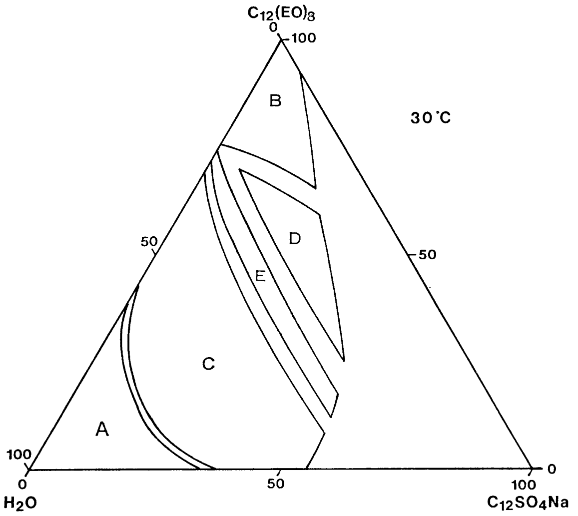

Fig. 5. The phase regions in the system water, sodium dodecyl sulfate ($C_{12}SO_4Na$) and octaoxyethylene dodecyl ether ($C_{12}(EO)_8$).
A: Isotropic aqueous solution, B: isotropic ether solution, C: liquid crystal with a structure of cylinders in a hexagonal array, D: liquid crystal with isotropic structure, E: liquid crystal with isotropic structure.

the structures of C and D phase; the pattern of "Oily streaks" and "Angular texture" for the lamellar and the hexagonal liquid crystals, respectively.[14] The structure and extension of these phases is exactly what would be expected, considering earlier material in this area.[12]

The replacement of 1-decanol with dioxyethylene dodecyl ether led to a series of modifications (Fig. 2). The solubilization of the ether in the aqueous micellar solution was increased, and the lamellar liquid crystalline required a higher content of the nonionic surfactant. The upper limit with a 10:1 weight ratio of the nonionic to anionic surfactant gave a lamellar liquid crystal with a pronounced stability with high contents of water. Its phase region actually reached to 98% water. The third liquid crystalline phase showed a cubic structure (E). The nonionic surfactant solution did not show the typical water solubilization maximum found for alcohols.[12]

With the tetraoxyethylene dodecyl ether (Fig. 3), the cloud point is still below 30 °C, and its lamellar liquid crystal is in equilibrium with pure water. The

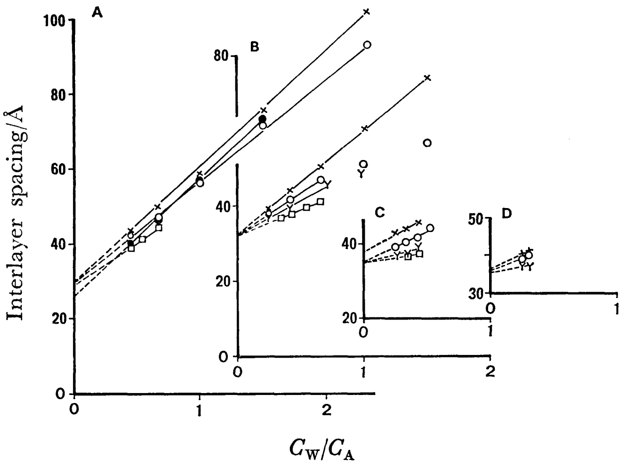

Fig. 6. Interlayer spacing as a function of water/amphiphile mass ratio (C_w/C_a).
From left to right, sodium dodecyl sulfate and:
A. Dioxyethylene dodecyl ether, or 1-decanol: $C_{12}SO_4Na/C_{12}(EO)_2$; x: 0.15/0.85, ○: 0.3/0.7, □: 0.665/0.335, $C_{12}SO_4Na/C_{10}H_{21}OH$; ●: 0.5/0.5.
B. Tetraoxyethylene dodecyl ether: $C_{12}SO_4Na/C_{12}(EO)_4$; x: 0/1, ○: 0.3/0.7, y: 0.5/0.5, □: 0.7/0.3.
C. Hexaoxyethylene dodecyl ether: $C_{12}SO_4Na/C_{12}(EO)_6$; x: 0/1, ○: 0.3/0.7, y: 0.5/0.5, □: 0.7/0.3.
D. Octaoxyethylene dodecyl ether: $C_{12}SO_4Na/C_{12}(EO)_8$; +: 0.2/0.8, ○: 0.3/0.7, y: 0.5/0.5.

changes in the region of the water and continuous phases are a direct continuation and further extension of those found at the shift from 1-decanol to the dioxyethylene ether. The solubilization of the ether in the aqueous micellar solution was very much enchanced, reaching an ether/sulfate weight ratio of 10:1. The extension of the lamellar phase toward the aqueous corner disappeared.

The hexa- and octaoxyethylene ethers both have cloud points in excess of 30 °C, and the diagrams contain only minor details of interest (Figs. 4 and 5). For both compounds the liquid crystal with a hexagonal arrangement showed higher maximum water content for mixtures than for the individual surfactant.[3] Combinations with the octaoxyethylene ether formed an isotropic liquid crystalline between the region of the lamellar and the hexagonal structure.

X-Ray Diffraction Patterns. The X-ray data is plotted in the usual manner as interlayer distance *versus* amphiphilic weight fraction in Fig. 6. The data, with few exceptions, were suited for extrapolation to water content equal to zero. The results show a reduction of interlayer distance with increased content of the ionic surfactant. This is true also for the extrapolated values, although the difference in this case was smaller. The extrapolated value is increased with increased polar chain length of the nonionic surfactant.

Light Scattering. The light scattering of samples in the isotropic liquid of the sample, dioxyethylene dodecyl ether, showed small values (Fig. 7). The values are given as fractions of the scale value for a pure liquid, benzene. The values are approximately unity, showing the scattering to be similar to that from a pure liquid.

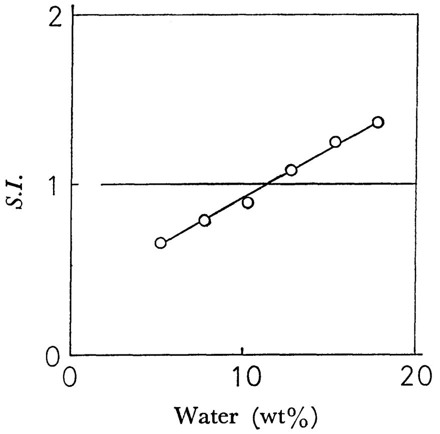

Fig. 7. Light scattering intensity for the dioxyethylene dodecyl ether ($C_{12}(EO)_2$) solution of water and sodium sulfate ($C_{12}SO_4Na$).
$C_{12}(EO)_2/C_{12}SO_4Na$ weight ratio=9:1. The scattering intensity (*S.I.*) is given relative to the value for pure benzene ($S.I._{\text{benzene}}=1$).

Discussion

The experiments gave general trends for the phase behavior of the mixed surfactants; the lower homologues performed as hydrophobic cosurfactants enhancing the stability of the liquid crystalline phases. This is most remarkable for the case of the dioxyethylene ether. Its combination gave a liquid crystalline phase with extremely high tolerance toward water. This behavior should indicate this combination to be good as emulsion stabilizers.[15] Subsequent experiments[16] have confirmed this assumption.

The liquid crystalline region C and D in Figs. 4 and 5 do not remarkably change with the ratio of sodium dodecyl sulfate/cosurfactant. This is interpreted that nonionics with long polar chain lengths (hexa- and octaoxyethylene ethers) have hydrophilic properties and behave in a similar manner as the ionic surfactant.

A minimum amount of water was necessary in order to bring the ionic surfactant into solution, which is shown by the right hand solubility limit in Figs. 1—5. The amount of water was identical for all the nonionic surfactants, from the most hydrophilic to the most hydrophobic one. A calculation shows a need of eight water molecules in order to dissolve one molecule of soap. It appears evident that the ether groups do not partake in the polar interactions[17] that lead to the ionic surfactant being dissolved. The ether bridge of the polyoxyethylene compounds obviously do not form sufficiently strong ligands with the metal ion to solubilize the surfactant.

The results also gave information about the structure of the liquid crystalline phase and indirectly about the order of the polar chain of the nonionic surfactant. The extrapolated values (Fig. 6) show a value of 26 Å for the 1-decanol/surfactant combination. A comparison with the corresponding values for the ethers (Fig. 6) shows all values to be larger. The slope of interlayer spacing/(C_w/C_a) for the 1-decanol/surfactant combination is steeper than that for the others. Furthermore, a tendency of lower values with enhanced content of ionic compound is also found. We interpret these results in the form of the following model. The nonionic surfactant allows water to penetrate between the polar layers in accordance with results from NMR spectroscopy.[18,19] The addition of the ionic surfactant causes two changes: the presence of the polar group allows more water to penetrate between the polar chains of the nonionic surfactant and causes an enhanced disorder of its polar part.

This interpretation also accommodates itself to the values for variation of interlayer spacing with water content. The increase of spacing with water content was less for samples which contained also the ionic surfactant, an indication of enhanced disorder and increased water penetration between the molecules.

It is interesting to observe the extremely small values for the light scattering from solutions in the dioxyethylene dodecyl ether solution of water and surfactant. The scattering is similar to the one from a pure liquid. A reasonable interpretation is absence of colloidal aggregates.

References

1) J. T. Davies and G. R. A. Mayers, *Trans. Faraday Soc.*, **56**, 69 (1960).

2) B. C. Blakey and A. C. S. Lawrence, *Discuss. Faraday Soc.*, **18**, 268 (1954).

3) R. D. Vold and K. D. Mittal, *J. Colloid Interface Sci.*, **38**, 541 (1972).

4) S. Friberg, *Kolloid Z. Z. Polym.*, **244**, 333 (1971).

5) D. O. Shah and R. M. Hamlin, *Science*, **171**, 483 (1971).

6) A. W. Adamson, *J. Colloid Interface Sci.*, **29**, 261 (1969).

7) G. Gillberg, H. Lehtinen, and S. Friberg, *J. Colloid Interface Sci.*, **33**, 40 (1970).

8) K. Shinoda and H. Kunieda, *J. Colloid Interface Sci.*, **42**, 381 (1973).

9) H. L. Rosano, *J. Soc. Cosmetic Chem.*, **25**, 609 (1974).

10) H. F. Eicke and H. Christen, *J. Colloid Interface Sci.*, **46**, 417 (1974).

11) E. Ruckenstein and J. C. Chi, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1690 (1975).

12) P. Ekwall, "Advances in Liquid Crystals," ed by G. H. Brown, Academic Press, N.Y. (1975), Vol. 1, p. 1.

13) K. Fontell, "Liquid Crystals and Plastic Crystals," ed by G. W. Gray and W. S. Winsor, Academic Press, N.Y. (1975), p. 80.

14) F. B. Rosevear, *J. Soc. Cosmet. Chem.*, **19**, 581 (1968).

15) S. Friberg, P. O. Jansson, and E. Cederberg, *J. Colloid Interface Sci.*, **55**, 614 (1976).

16) L. Ganzuo and S. Friberg, *J. Am. Oil Chem. Soc.*, in press.

17) B. Bendiksen, S. E. Friberg, and P. L. M. Plummer, *J. Colloid Interface Sci.*, **72**, 495 (1979).

18) H. Christenson and S. E. Friberg, *J. Colloid Interface Sci.*, **75**, 276 (1980).

19) H. Christenson, S. E. Friberg, and D. W. Larsen, *J. Phys. Chem.*, **84**, 3633 (1980).