The Correlation Between Phase Behavior And Structure of A Four-Component System, Poly-Ethylene Glycol/Sodium Dodecyl Sulfate/Pentanol/H₂O*

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Synopsis

The change in the concentration of sodium dodecyl sulfate (SDS) can, in fact, affect directly the correlation between phase behavior and structure of a four-component system, polyethylene glycol/sodium dodecyl sulfate/pentanol/H₂O. Experimental results indicate that the phenomena of microemulsion and lamellar liquid crystals can take place at a concentration of SDS greater than 5% and 17% by weight, respectively. In our experiments, these liquid crystals are tested and found to be hydrophilic and their rheological properties to be non-Newtonian as well.

INTRODUCTION

Unlike regular surfactants[1,2] with a long hydrocarbon chain length, low-molecular weight polymer of polyethylene glycol,[2,3] having both hydrophilic and hydrophobic (a short ethylene chain) properties, could be treated as a special kind of polymerlike surfactant. Use of this polymerlike surfactant in the system of sodium dodecyl sulfate/pentanol/H₂O may contribute to increasing the solubility of pentanol in water solution and may interact with sodium dodecyl sulfate (SDS) to form polyelectrolyte-like conformations. The formation of these conformations, depending upon composition, temperature, polymer and surfactant concentration and chain length is responsible for the variation of the surface characteristics, structure, and phase behavior of a polyethylene glycol/sodium dodecyl sulfate/pentanol/H₂O system. The chief aim of this work is to investigate the properties performance of low-molecular weight polyethylene glycol employed in the system and to relate the structure and phase behavior to the composition of this four-component system at room temperature in terms of the surface and interfacial tension, rheologic, and morphologic studies.

EXPERIMENTAL

Materials and Methods

Reagent-grade polyethylene glycol (PEG) with a molecular weight of 400 was purchased from Merck Co. Sodium dodecyl sulfate and pentanol (sup-

plied by Merck Co.) are reported to be 99% pure. All of these chemicals were used in our experiments without further purification.

Samples of solutions were prepared by dissolving sodium dodecyl sulfate in a fixed 50 g of distilled, deionized water, followed by addition of polyethylene glycol and pentanol, respectively. The total amount of a sample was 100 g by weight. These samples containing different amounts of sodium dodecyl sulfate, polyethylene-glycol, and pentanol and with a constant concentration of water (50 g) were used for the structure and phase behavior analysis.

APPARATUS

Du Noüy ring tensiometer was calibrated using water and ethanol, and used to measure the surface and interfacial tension for samples of solutions including liquid crystals at room temperature. The experimental error of surface tension measurements for these solution samples with no liquid crystals was estimated to be approximately ±0.2%, and of solutions with liquid crystals to be greater than ±0.4%. Rheological measurements for samples after one day of preparation were carried out at 25±0.05°C with a Brookfield viscometer. Microscopic examination of all the samples using polarized light was also conducted at 25±0.05°C. Details of Du Noüy ring tensiometer, Brookfield viscometer, and polarized light microscope, are given in Refs. 4–6.

RESULTS AND DISCUSSION

The phase diagram of a four-component system, PEG/SDS/pentanol/H_2O, is presented in Figure 1. Notations given in this phase diagram represent different phases in which 2L means a mixture of two liquid phases; L_1 the microemulsion-like phase (in which pentanol is being solubilized) or aqueous micellar solution; LC the liquid crystalline phase; L the liquid phase or solution; L_2 the aqueous micellar phase; $L_2 + L$ the aqueous micellar phase in equilibrium with liquids or solutions, and $L + LC + S$ a mixture of solid crystals in equilibrium with liquid crystals and solutions. The oil-water interfacial tensions for samples labeled with a, b, c, d, and e, given in the region of 2L, with a constant ratio of pentanol and PEG equal to 9:1 and with various concentrations of SDS, were measured at 25±0.05°C, and are shown in Figure 2. It is noticed that interfacial tensions between oil and water for these five samples decrease drastically, as the SDS concentration is gradually increased. This is mainly due to increased adsorption of SDS molecules (SDS concentration greater than 5% by weight) at the oil-water interface causing large amounts of pentanol to diffuse into PEG aqueous solutions to form the oil in water transparent microemulsion-like phase. In Figure 3, it appears that, for samples given in the region of L_1 containing SDS and pentanol in a weight ratio of 1:3 (represented by ○) and with various concentrations of PEG, the surface tension at 25±0.05°C is seen to be constant, almost independent of the concentrations of PEG employed in the composition. Under the same experimental conditions, the surface tensions for these samples with the ratios of SDS/PEG and PEG/pentanol equal to
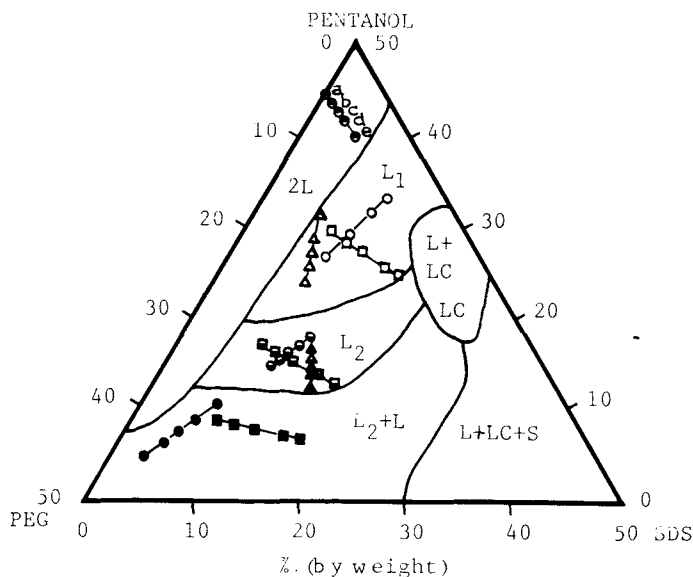
Fig. 1. Phase diagram for a four-component system, PEG/SDS/pentanol/H_2O (the amount of H_2O used in the system was fixed at 50% by weight; $\bigcirc$, $\triangle$, $\square$, $\mathbf{0}$, $\blacktriangle$, $\blacksquare$, $\bullet$, and $\blacksquare$ represent samples taken from different regions).

1:2 (represented by $\triangle$) and 2:5 are observed to be independent of the amounts of SDS and pentanol used, respectively, as shown in Figures 4 and 5. Obviously, our results given in Figures 3 through 5 illustrate that the change in compositions for these samples has almost no effect on their surface characteristics. We then studied the rheological properties of these samples in the same region given above. It was found that a linear relationship between apparent viscosity and shear rate at $25 \pm 0.05°C$ for a sample com-
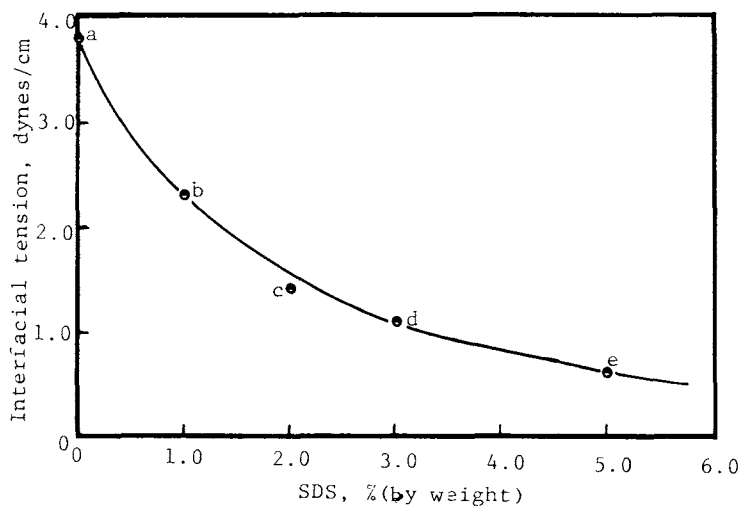

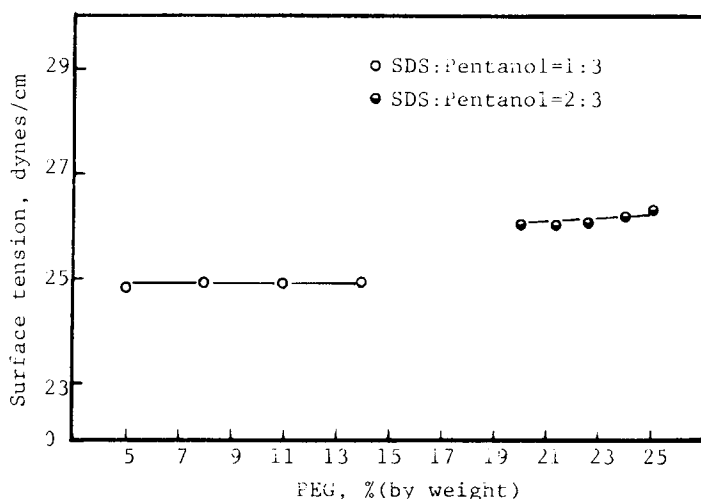Fig. 2. Interfacial tension between pentanol and PEG aqueous solution vs. SDS concentration at $25 \pm 0.05°C$.

Fig. 3. Surface tension vs. the concentration of PEG at $25 \pm 0.05°C$ for samples given in the regions of L_1 and L_2.
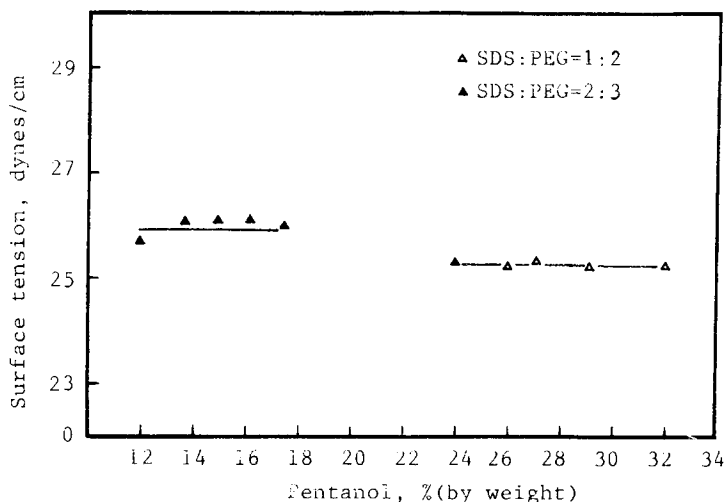

Fig. 4. Surface tension vs. the amount of pentanol at $25 \pm 0.05°C$ for samples given in the regions of L_1 and L_2.

prising 10% PEG, 15% SDS, 25% pentanol, and 50% H_2O (shown in Fig. 6), represented Newtonian flow behavior. By combining the evidences described above, they suggest that the O/W transparent microemulsion-like structures are likely to be formed.

In Figures 3 and 5, it seems that the surface tensions at $25 \pm 0.05°C$ for samples given in the region of L_2 with the ratios of PEG/pentanol and SDS/pentanol equal to 3:2 and 2:3 (represented by ◓) and with various amounts of SDS and PEG increase slightly with increasing SDS and PEG concentrations, respectively. This is because the interaction of SDS with PEG may lead to formation of polyelectrolyte-like structures which reduce the ad-
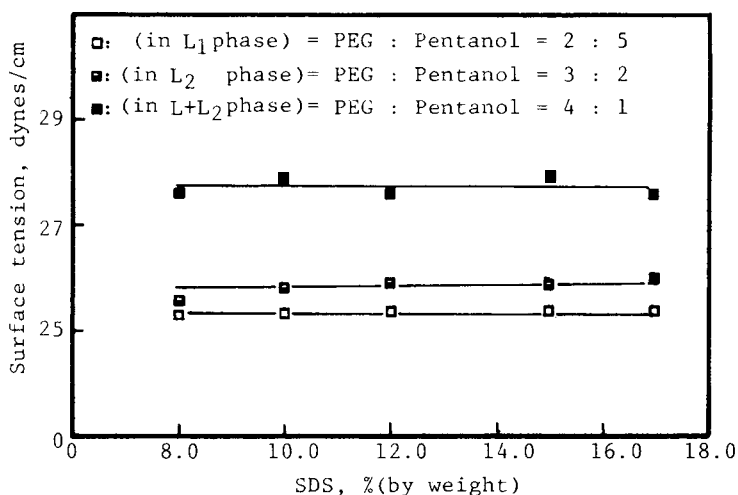
Fig. 5. Surface tension of L_1, L_2 and $L + L_2$ phases vs. the concentration of SDS at $25 \pm 0.05°C$.

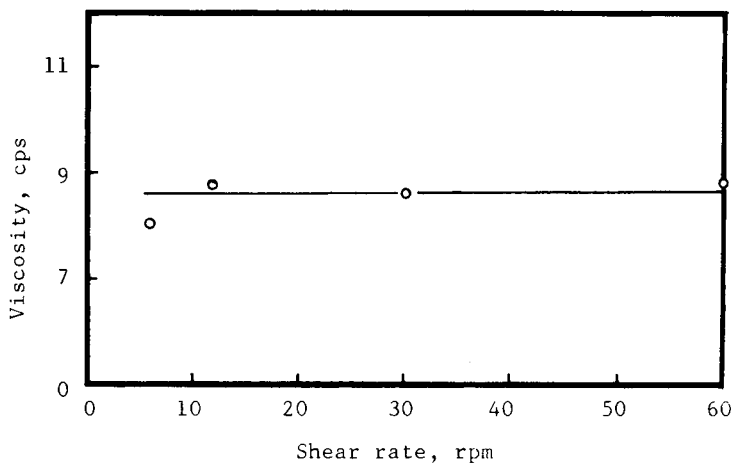

Fig. 6. Viscosity vs. shear rate at $25 \pm 0.05°C$ for a sample containing 10% PEG, 15% SDS, 25% pentanol, and 50% H_2O given in the region of L_1.

sorption of SDS molecules at the interface, and therefore, the surface tension increases slightly. In the same region described above, the surface tension for samples with the ratio of SDS/PEG equal to 2:3 (represented by ▲) is seen to be independent of the amounts of pentanol used, as shown in Figure 4. It may be explained that, since the saturation adsorption of SDS and pentanol and, possibly, PEG molecules at the interface has been reached, therefore, the surface concentration associated with the surface tension of solutions does not change significantly on further addition of pentanol. Figure 7 shows that surface tensions for samples selected from the region of $L_2 + L$ containing the ratio of SDS/pentanol equal to 2:3 largely increase as the concentration of PEG is gradually increased. This is possibly due to the formation of polyelectrolyte-like structures resulting from the interaction between
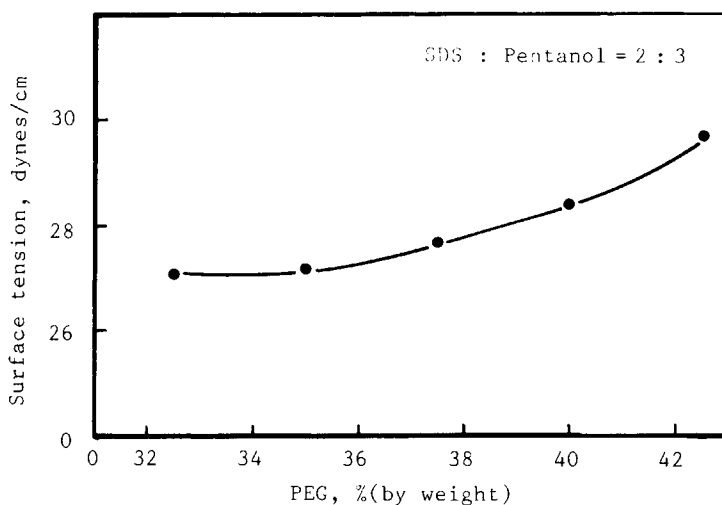
Fig. 7.   Surface tension vs. the concentration of PEG at $25 \pm 0.05°C$ for samples given in the region of $L_2 + L$.

SDS and PEG molecules strongly decreasing the adsorption of SDS molecules at the oil-water interface. A comparison of Figures 3, 5, and 7 shows the values of surface tensions for samples given in the region of $L_2 + L$ are larger than those of samples in the region of L_2, indicating that more polyelectrolyte-like structures formed in the $L_2 + L$ region are responsible for increased surface tension of solutions. Additionally, Figure 5 also points out that the surface tension for samples of the $L_2 + L$ region with a ratio of PEG/pentanol equal to 4:1 increases with increasing concentration of SDS and is seen to be higher than that of samples with a ratio of PEG/pentanol equal to 3:2 given in the region of L_2. The explanation of this behavior is the same as described above. However, the formation of large amounts of polyelectrolyte-like structures in the region of $L_2 + L$ turns out to be true.

Both liquid phase (L) and liquid crystalline phases (LC) were separated from samples of solutions taken from the region of L + LC by a centrifuge at a rate of 500 rpm for 30 minutes. Surface tension, interfacial tension, and viscosity measurements at $25 \pm 0.05°C$ for L, LC, and L + LC phases given in a phase diagram of Figure 1 are shown in Table II. It seems that the surface tension of L phase for samples with a fixed concentration of PEG (1% by weight), which is almost equivalent to that of pentanol (see Table I)

TABLE I
Surface Tension of Substances at $25 \pm 0.05°C$

Substance	Surface tension (dynes/cm)
Pentanol	27.6
SDS	40.1
PEG	47.7
H_2O	72.3

and smaller than that of LC phase, does not depend upon the concentration of SDS and pentanol used in the compositions, while the surface tension of LC phase changing with the compositions increases with increasing amounts of SDS and with decreasing amounts of pentanol. It can be considered that lamellar liquid crystals, due to their parallel-oriented hydrocarbon chains of SDS molecules adsorbed at the interface, are more ordered than pure pentanol in the surface layer. Furthermore, under the influence of the dispersion force, the interaction between parallel-ordered molecules in LC phase is much stronger than that of disordered molecules present in L phase. This interaction makes molecules become even more ordered, and therefore, the surface tension of LC phase increases. Table II illustrates that the L–LC interfacial tension for samples containing the ratio of pentanol/PEG approximately equal to 29:1 increases with increased concentration of SDS, and for samples with the ratio of pentanol/SDS nearly equal to 26:20 it increases as the concentration of PEG is increased. This can be explained by the interaction between SDS and PEG molecules which tends to form polyelectrolyte-like structures, thus greatly reducing the adsorption of SDS molecules at the interface and resulting in increased oil-water interfacial tension.

Table II clearly indicates that apparent viscosities for all the phases tend to increase when the concentration of SDS is increased. This is because the strong interaction between planner micelles themselves and between planner micelles and PEG molecules yielding large effective phase volume, coupled with the steric hindrance experienced, causes the viscosity to be higher. It is also noteworthy that apparent viscosities of LC phase, having large amounts of lamellar liquid crystals, are much higher than those of L and L+LC phases, as a result of much stronger interaction between ordered molecules. To further explore the structures of liquid crystals, the rheological properties of these liquid crystals were examined and presented in Figure 10. It shows that the apparent viscosity decreases with an increase in the shear rate for a liquid crystal consisting of 0% PEG, 20% SDS, 30% pentanol, and 50% H_2O, as shown in Figure 8. Since the planner micelles are large in two dimensions and restrict each other's rotational degree of

TABLE II.
Surface Tension, Interfacial Tension, and Viscosity for L, LC, and L+LC Phases in a PEG/SDS/Pentanol/H_2O System at $25 \pm 0.05°C$

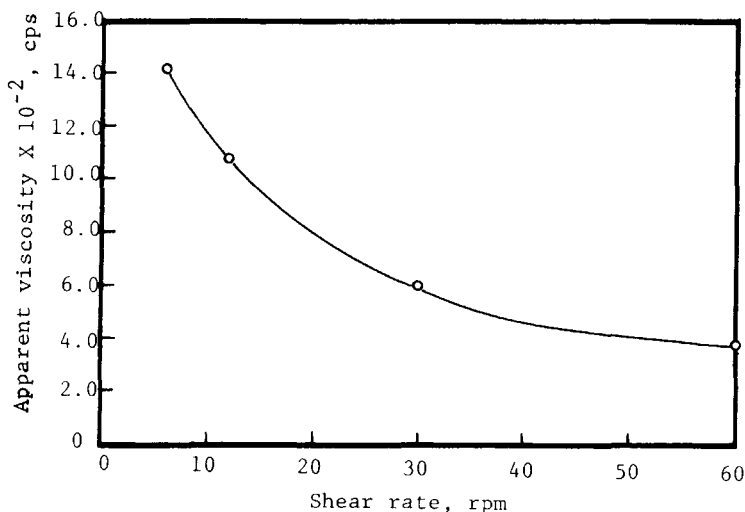| Composition % (by weight) (PEG/SDS/pentanol/H_2O)	Surface tension for LC phase dynes/cm	Surface tension for L phase dynes/cm	Interfacial tension dynes/cm	Viscosity cps		
				η_{LC}	η_{L+LC}	η_{L}
1/18.5/30.5/50	30.0	27.1	1.1	287	18.3	10.3
1/19/30/50	29.5	27.2	1.6	296	18.9	11.3
1/20/29/50	32.0	27.1	1.8	442	77.4	12.2
1/21/28/50	32.6	27.6	2.3	513	175.5	13.0
0/20/30/50			1.0			
1/20/29/50			1.8			
3/20/27/50			2.1			
5/20/25/50			3.3			

Fig. 8. Apparent viscosity vs. Shear rate at $25 \pm 0.05°C$ for a liquid crystal containing 0% PEG, 20% SDS, 30% pentanol, and 50% H_2O chosen from the region of $L + LC$.

freedom to a very marked extent, ordering of these planner micelles creates lamellar liquid crystals. The interaction between lamellar liquid crystals are strong and a network-like structure created in solutions is readily broken down by shear stress. This results in reduced viscosity.

In order to examine in detail structures present in this four-component system, microscopic examination of samples of solutions chosen from L_2 phase under polarized light at $25 \pm 0.05°C$ exhibited dark between crossed polarizers, indicative of isotropic aqueous micellar phases. Under the same experimental condition, it showed the presence of liquid crystalline phases with anisotropic structures for samples of solutions given in the region of $L + LC$. These structured solutions with unique structural direction exhibited liquid crystals with circular shapes to be known as lamellar liquid crystals,[7,8] given in Figure 9. These liquid crystals appeared initially at the concentration of SDS equal to and greater than 17% by weight, and increased as the concentration of SDS was further increased. Similarly, microscopic analysis of samples given in the region of $L + LC + S$ was done at $25 \pm 0.05°C$ and is presented in Figure 10. In Figure 10, it appears that the sizes of lamellar liquid crystals become much smaller in comparison to that of the liquid crystals shown in Figure 9 and that large amounts of solid crystals appear, as the SDS concentration is increased appreciably.

CONCLUSIONS

1. Experimental results on the surface tension and viscosity studied at $25 \pm 0.05°C$ suggest that sufficient amounts of SDS molecules (5% by weight) adsorbed at the oil-water interface may lead to form the O/W transparent microemulsion-like phase.
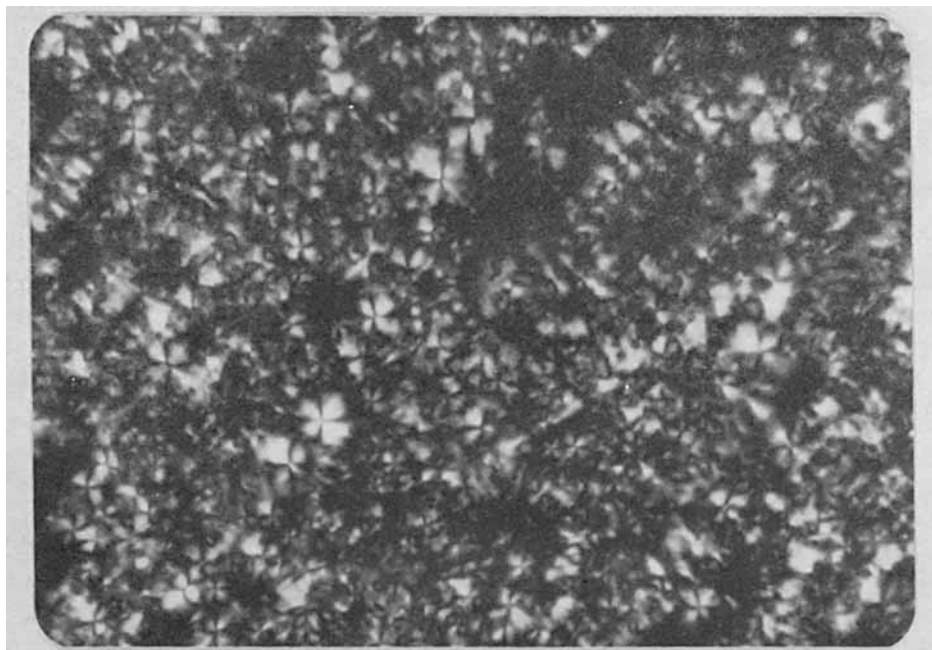
Fig. 9.   Optical microscopy of crossed polarizers for dispersed structure containing 0% PEG/ 20% SDS/30% pentanol/50% H_2O (X125).
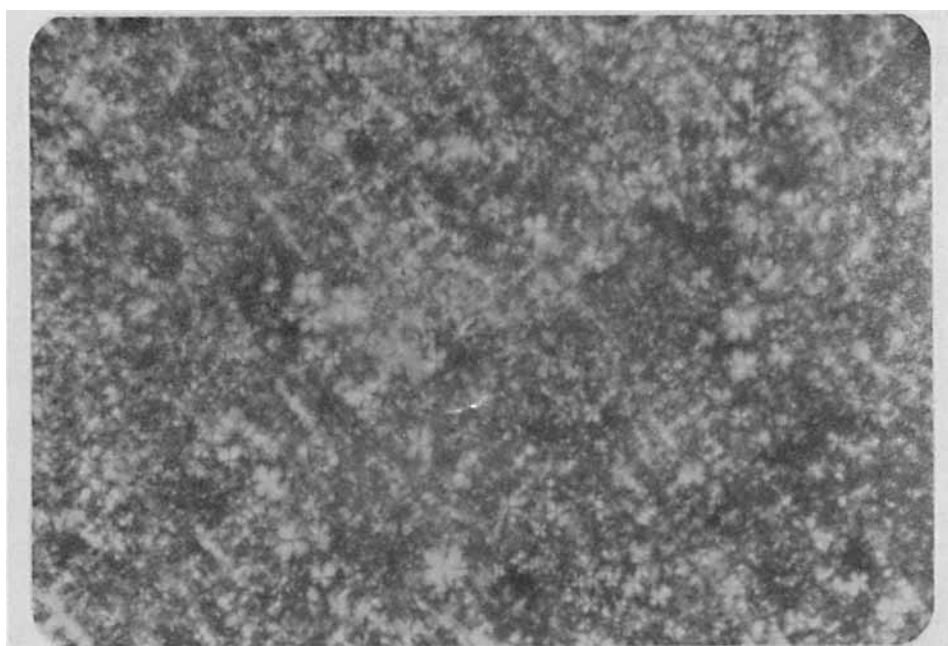

Fig. 10.   Optical microscopy of crossed polarizers for dispersed structure containing 0% PEG/ 25% SDS/25% pentanol/50% H_2O (X125).

    2. Microscopic examination of samples using polarized light at $25 \pm 0.05°C$ exhibits circular-shaped liquid crystals known as lamellar liquid crystals. These lamellar liquid crystals appear initially at the concentration of SDS equal to and greater than 17% by weight, and increase as the concentration of SDS is further increased. The rheological properties of these liquid crystals are tested to be non-Newtonian.

    3. Under polarized light, the phenomenon of solid crystals in equilibrium with liquid crystals and/or solutions can take place at the concentration of SDS equal to and greater than 25% by weight. These mixed phases tend to form gel-like structures with high viscosities.

References

    1. P. Mukerjee, *Adv. Colloid Interface Sci.*, **1**, 241 (1967).

    2. D. Attwood and A. T. Florence (eds.), *Surfactant Systems*, Chapman and Hall Ltd., New York, 1983.

    3. A. F. Gallaugher and H. Hibbert, *J. Am. Chem. Soc.*, **59**, 2514 (1973).

    4. Harkins, *Physical Methods of Organic Chemistry*, Vol 1., A. Weissberger, Ed., Interscience, New York 1959.

    5. J. R. Van Wazer, J. W. Lyon, K. Y. Kim, and R. E. Colwell, *Viscosity and Flow Measurement, A Laboratory Handbook of Rheology*, Interscience, New York, 1963.

    6. N. H. Hartshorne and A. Stuart, *Crystals and the Polarizing Microscope*, Edward Arnold (Publishers) LTD, London, 1960.

    7. F. B. Rosevear, *J. Am. Oil Soc.*, **31**, 628 (1954).

    8. W. J. Benton, T. Fort, Jr., and C. A. Miller, *SPE* (Society of Petroleum Engineers of Aime) 7579 (1978).