

Molecular aggregation in the ternary system deca glycerol dioleate/heptane/water

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Abstract: The phase diagram for the ternary system deca glycerol dioleate(DGD)/heptane/water was established at 25 °C. In this phase diagram it was seen that the reverse micellar solution phase extends in its area until the water content reaches 35-45 wt %, at which a liquid crystalline phase begins to appear. On the basis of the experimental results of specific conductivity, viscosity, etc. for the samples containing a definite amount of DGD (0,1 M), and varying relative amounts of heptane and water, the mechanism of the transition of reverse micellar structures to liquid crystalline phase is discussed.

Key words: Phase diagram, reverse micelles, liquid crystals, conductivity, viscosity.

Introduction

Deca glycerol dioleate (DGD) is a nonionic surfactant, which is characterized by its favorable hydrophilic and lipophilic balance in its molecular structure. This compound is soluble either in water, a typical polar solvent, or heptane, a typical apolar solvent. It is also interesting to note that DGD forms reverse micelles or swollen micelles in heptane with certain amounts of solubilized water, termed microemulsion, which is considered thermodynamically stable. Although extensive studies on the formation and nature of molecular aggregation in apolar media with AOT as one component, have been carried out by Eicke and his collaborators [1] including the importance of the role of water in forming various structures [2, 3], not much attention has been paid so far to the formation of molecular aggregation in DGD/heptane/water ternary system.

Detailed phase equilibria studies on the binary and ternary systems containing AOT as one component have also been made by Shinoda and his collaborators [4], and by Ekwall, Mandell and Fontell [5].

In the present study, we have attempted to establish the phase diagram for the ternary system: DGD/heptane/water in order to know the extension of phase area of reverse micellar solution as well as that of phase

resembling liquid crystal and also to determine, particularly, the mechanism of the transition from micellar phase to liquid crystalline phase.

In our present study, however, experiments on the phase diagram and conductivity and viscometric measurements of certain phase regions have been performed at 25 °C in order to understand the mechanism of the transition from swollen inverse micellar structures to liquid crystalline phase.

Experimental

Materials

Deca glycerol dioleate (DGD) was a pure grade material from Sigma and was used as received. The chemical formula of DGD is $\text{ROCH}_2(\text{CHOH-CH}_2\text{-O-CH}_2)_9\text{-CHOHCH}_2\text{OR}$, where $\text{R} = \text{C}_8\text{H}_{17}\text{CH}_2\text{CH}(\text{CH}_2)_7\text{CO}$. The HLB value of this surfactant is 10.5. The cmc value of DGD at 25 °C is 3×10^{-5} g/ml [6, 7]. Heptane was analytical grade reagent. Water was twice distilled.

Phase diagrams

These were determined by following procedure: DGD-heptane solutions of various concentrations are prepared and then varying amounts of water are added stepwise to them. The mixtures are sealed in glass tubes and kept in a thermostat at 25 ± 0.2 °C for 24 h. The type of phases and their transitions are detected visually or by using microscope and measuring conductivity.

Conductivity measurements

We measured electrical conductivities of ternary mixtures containing a definite amount of DGD and varying amounts of heptane and water at $25^\circ \pm 0.2^\circ\text{C}$. Starting from DGD-heptane (0.10 M) noted by *a*, we prepared mixtures of DGD/heptane/water of compositions corresponding to: *b, c, d, e, f, g, h, i, j, k, l, m, n, o, p* in the phase diagram and measured their properties. The measurement of direct specific conductance was made by the apparatus of Systronics (Model: 308, India) with a cell of cell constant 1.0 cm^{-1} .

Viscosity measurements

Viscosities of ternary mixtures containing a definite amount of DGD and varying amounts of heptane and water starting from *a* to *p* were measured using a Rotating Cylindrical Viscometer (Brookfield, Model C, Stoughton, Massachusetts, U.S.A.) at the temperature of $25^\circ \pm 0.2^\circ\text{C}$.

Results

Phase diagrams

The phase diagram of DGD/heptane/water system obtained is illustrated in Fig. 1, where L_1 is the aqueous micellar solution, $2L$ the emulsion, L_2 reverse micellar solution, LC liquid crystal. $L + LC$ is the phase region where liquid crystal exists in equilibrium with solution (chiefly L_2 and LC). In Fig. 1, it can be observed that the region of reverse micellar solution (L_2) extends widely in the phase diagram over about 35–45 % water

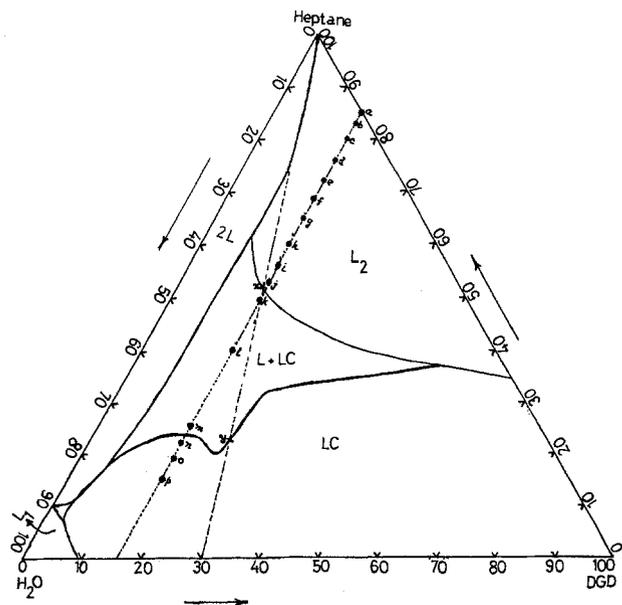


Fig. 1. Phase diagram of deca glycerol dioleate/heptane/water system at $25^\circ \pm 0.2^\circ\text{C}$

content and that also the liquid crystal phase (LC) covers a wide area along water-DGD axis.

Conductivity

Figure 2 shows the relation of specific conductivity (k) vs. W_0 which means water content, in moles per mole of DGD (i. e. $W_0 = [\text{H}_2\text{O}]/[\text{DGD}] = \text{mol/mol}$). The phase transition from L_2 to $L + LC$ takes place between points *j* and *k* and the transition from $L + LC$ to LC occurs between points *m* and *n*.

Viscosity

Figure 3 shows the relation of relative viscosity (η_r) vs. W_0 . The flow of microemulsion corresponding to the point *j* in Fig. 2, and that for liquid crystal corresponding to the point *l*, were determined by the rotati-

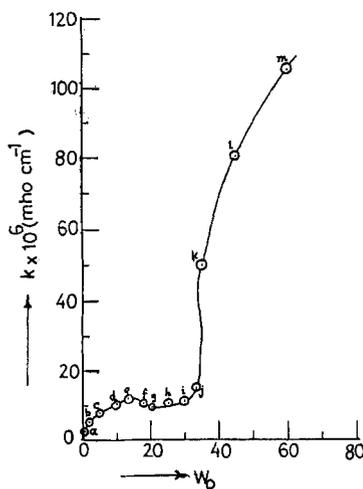


Fig. 2. Specific conductivity (k) and water content for microemulsion at 25°C

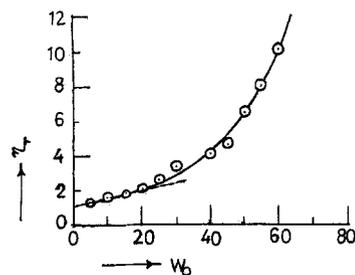


Fig. 3. Relative viscosity (η_r) vs. water content for microemulsion at $25^\circ \pm 0.2^\circ\text{C}$

onal viscometer. It was found that the flow type of microemulsion is Newtonian, having viscosity of less than 10 cp, whereas the flow type of liquid crystal is non-Newtonian, having apparent viscosity of about 80 cp. The value of the viscosity of liquid crystal is thus about 8–10 times greater than that of microemulsion.

Discussion

In Fig. 2, the relationship between specific conductivity (k) and water content (W_0) demonstrates that k rises gradually with W_0 in the range of 0–14 and also that k marginally decreases with W_0 in the range of 14–20. However, in the range of W_0 : 20–30, k is almost constant in the present case. For samples of $W_0 > 35$ it was found that the value of k increases abruptly due to the occurrence of a liquid crystalline phase. In our case, the liquid crystalline phase (LC) separates out from the microemulsion (L_2) at $W_0 \approx 40$.

Figure 3 shows the relation between the relative viscosity (η_r) and water content (W_0) at a DGD concentration of 0.1M. It has been found that η_r increases almost linearly with W_0 in the range 5–20 and then increases exponentially in the range 20–60.

Our experimental results, given in Figs. 2 and 3, can be interpreted to reflect the change of molecular aggregations at different regions of water content. The increase of specific conductivity in the range of W_0 : 0–14 probably corresponds to the formation of hydrated reverse micelles, and the gradual decrease of k after passing the maximum in the range of W_0 : 14–20 is likely to correspond to the coalescence of micelles, i.e. the decrease in the number of micelles. The constancy of k in the range of W_0 : 20–30 is considered due to the swelling process of micelles with the increase of water, during which the number of micelles are apparently kept constant. The increase of η_r in the range of W_0 : 20–40 is attributable to the increase of micelle sizes due to the swelling process. The fact that the relative viscosity increases first linearly with W_0 for 5–20 and then exponentially for 20–60 is also consistent with the change of molecular aggregations, as assumed above. Furthermore, it should be noticed that at $W_0 \approx 40$, liquid crystal separates out from the microemulsion to form the phase area $L + LC$ as shown in the phase diagram (see Fig. 1) and it is interesting to note that at this point both conductivity and viscosity exhibit an abrupt change.

In the phase region of $L + LC$, microemulsion is in equilibrium with liquid crystal, the chemical compositions of which are different. For example, at the point l

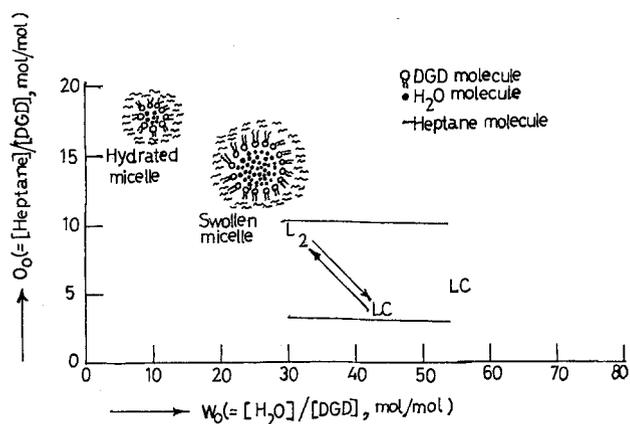


Fig. 4. Schematic illustration of the phase transitions in the deca glycerol dioleate/heptane/water system at 25 °C

in the phase diagram (cf. Fig. 1), the sample has a total chemical composition (DGD 15 %, heptane 40 %, water 45 %). This will be separated into two parts, $x(L_2)$ and $y(LC)$, having compositions (DGD 14 %, heptane 52 %, water 34 %) and (DGD 20 %, heptane 20 %, water 60 %), respectively, which exist in equilibrium. Comparing the values of molar ratios: $[H_2O]/[DGD]$ and $[heptane]/[DGD]$ for L_2 (x) and LC (y) which are in equilibrium, it has been found that the water content in LC is about 1.25 times richer per mole of DGD than that in L_2 , and LC is about 2.5 times poorer in heptane per mole of DGD than L_2 in equilibrium. These results show that there is a certain limit to the number of water molecules that can be accommodated in the inner core of a micelle formed by a definite amount of DGD molecules in a stable microemulsion. When the relative number of water molecules exceeds such a limit, reverse micelles will collapse and, consequently, it will be transformed into a liquid crystalline structure. On the basis of our experimental results, a schematic illustration for the phase transition is given (Fig. 4).

Our present results do not indicate whether the liquid crystal is lamellar, or hexagonal or both. Further experiments to characterize it by NMR and X-ray diffraction are in progress.

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