STUDY OF MICELLIZATION AND MICROEMULSION FORMATION FOR SURFACE ACTIV AGENT IN OCTANOL AND WATER MIXTURE

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Abstract

A mixture of three components having different physical and chemical properties is represented by equilateral triangular diagram. Such a mixture produces various regions on the interior of the triangular diagram. A system in each apex of the triangle consists of two components.

In this work, the effect of surface active agent on the micelle and microemulsion formation in a mixture, of octylphenyloxy-ethylene, octanol and water were studied at 25°C.

This mixture exhibits three regions. The appearance of these regions well fit with approach that surface active agent can take several forms depending on their concentration in any mixture (22). The possible forms are monomer hexagonally ordered molecules or gonfeled micelles.

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دراسة تكوين المايسل والمستحلب الدقيق لمنشط السطح في مزيج الأوكتانول والماء

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الملخص

عند التقاء ثلاث سوائل احدهما يختلف عن الآخر بصفاته الكيميائية والفيزيائية. فتتكون مناطق متعـددة من المزج، وبذلك يرسم مثلث مكونات، وعند كل رأس منه يمثل مكونة نقية. وفي هذا البحث تمت دراسـة تأثير منشط السطح على تكوين المايسل والمستحلب الدقيق *microemulsion* في مناطق مختلفة في نظـام ثلاثي المكونات وهي منشط السطح *octylphenyloxyetheleneglycol* والأوكتانول *octanol* والـذي يطلق عليه بالزيت لصفته الدهنية والماء. حيث تمت هذه الدراسة في درجة حرارة 25°C. ونتيجة لالتقـاء هذه المكونات فان جزيئات منشط السطح أخذت اشكالات مختلفة حسب التراكيز المعطاة. أما بشكل مونمور (*monomer*) أو لها شكل سداسي (*hexagonal*) أو تترتب بشكل صفوف منتظمة أو تتجمع هذه الجزيئات مشكلة المايسل المنتفخ.

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Background

The main point of interest here is that during Hammurabi's period one of the lesser known forms of divination involved pouring oil on water (or water on oil) and observing the types of spreading behavior that occurred (1-5) The following picture seen that portion of clay tablet inscribed in cuneiform, (dealing with the art of lecanomancy). The tablet dates back to the of Hammurabi (18th century b.c.). the omens numbered 1 to 5 deal with the spreading of oil in water.
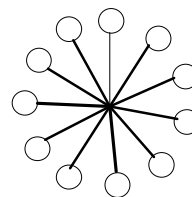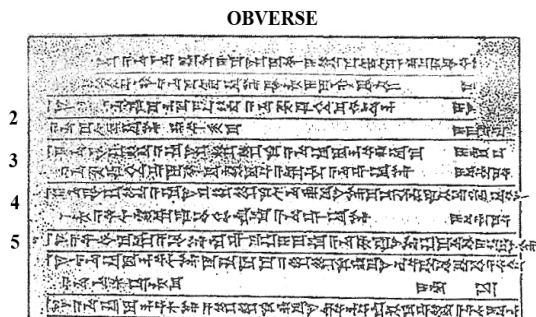
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Introduction

It is known that surface active agent compounds have no ionic structure in their aqueous solution. Their polar part (the hydrophilic) is resembled by R-O-R, R-OH, R-C-R or R-NH-R and the nonpolar part (the lipophilic) resembled by aliphatic chain; mostly, these surface active agents are obtained by the polycondensation of the oxyethylene on lipophil part as shown by the following reaction:

$$R\text{-}H + nCH_2\text{-}CH_2 \longrightarrow R\text{-}(CH_2\text{-}CH_2\text{-})O_n\text{-}H$$
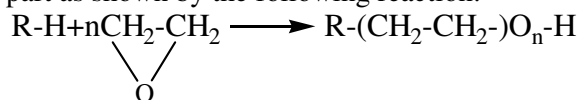
The above reaction is a stepwise reaction, it forms a mixture of ethoxy group (CH$_2$-CH$_2$O) depending on their preparation method(1). The molecule under investigation are consists of a polar part (CH$_2$-CH$_2$O) and a nonpolar aliphatic chain, having different isomers of a formula of $C_8H_{.17}$ $(OCH_2CH_2)_{9-10}OH$. The whole structure can be resembled by the following model.

Aliphatic chain   Polar part

The usefulness of these compounds is their adsorption onto the solid surfaces from their dilute solutions which have different forms into the interface[6,7]. These kinds of adsorptions possessing the following specific characters:

1. Stability of emulsion and microemulsion (liquid- liquid interface).
2. Their uses as a wetting agent such as a detergent (solid - liquid interfaces).
3. Bulb and foams formation.

Micelle is formed by the aggregating of number of molecules shape (Figure 1), and it can be given by the following equation:

$$mS \rightleftharpoons Sm \qquad \dots\dots\dots\dots\dots\dots\dots(1)$$

Figure 1

S represents a molecule of the surface active. m represents a number of aggregating molecules as spherelike (Number of monomer of each Sm micelle).

The micellary aqueous is considered as pseudobiphasic, in which the lipophiles links with each other to form the micelle. It represents the polar center at which the aggregation occurred[8, 9].

These compounds are capable to dissolve the organic compounds which are insoluble in water. Funidler and Kshindo's[10,11], have shown that these compounds have a wide range of applications in different fields.

The following relation has been derived between CMC (Critical Micelle Concentra-tion) and the number of carbon atoms in the hydrophilic chain[12,13] is:

$$\text{Log CMC} = a + bNc \quad \dots\dots\dots\dots\dots\dots\dots (2)$$

Where a and b are constants, Nc is number of carbon in the hydrophilic part.

It is possible to determine the stability constant of the micelle formation by using the[14] following equation:

$$k = \frac{[Sm]}{[S]^m} = \frac{C\phi}{m[C(1-\phi)]^m} \quad \dots\dots\dots\dots\dots(3)$$

Where:
C = concentration of surface active agent,
ϕ = percentage of linked in the micelle.

From equation (3) the value of ϕ is small in comparing with the concentration of surface active agent, Thus

$$C = CMC = \left[\frac{1}{k_m}\right]^{1/(m-1)} \quad \dots\dots\dots\dots\dots\dots..(4)$$

The free energy of micelle formation can be found by the following relationship

$$\Delta G^\circ = \frac{-RT}{m}\log K \dots\dots\dots\dots\dots\dots\dots\dots(5)$$

Where m is the molality. Shaw [14] found an entropy increase in micelle formation. Cobb[15] described the effect of emulsion and found that there are two ways for obtaining the emulsion, first by searching on a surface active agent which mostly possess a HLB (Haydrophobic Liophobic Balance) by using a strong mixer, and

second to get a surface active agent that has a value of HLB in which the emulsion of water in oil (W/O) can be obtained[16]. When the value of HLB in a range between 8 to 16, it produces an emulsion of oil in water (O/W). It is possible experimentally to determine the value of HLB which produces the exact and most stable emulsion by mixing non-ionic surface active agent have HLB related to their ratios. Shinada [17, l8] study the temperature effects on the value HLB of the non-ionic surface active agent. In water-oil system, non ionic surface active agent-produces emulsion of oil in water [19]. On the other hand when the temperature of this system increases more than that of the room temperature, the emulsion will be water in oil [20].

Experimental Part

The octylphenylpoly (oxy ethylene) glycol ether was supplied by Rohm and Hass Co., France., and it's purity more than 98%, Octanol was supplied by Fluka Co., and it's purity more than 98%, the distilled water have been used in all experiments, In ten test tubes two times (10_{ml}) contain different volumes of water and octanol, the surface active agent was added to each tube. The percentage of mole fraction for each ether are illustrated in (Figure 2).
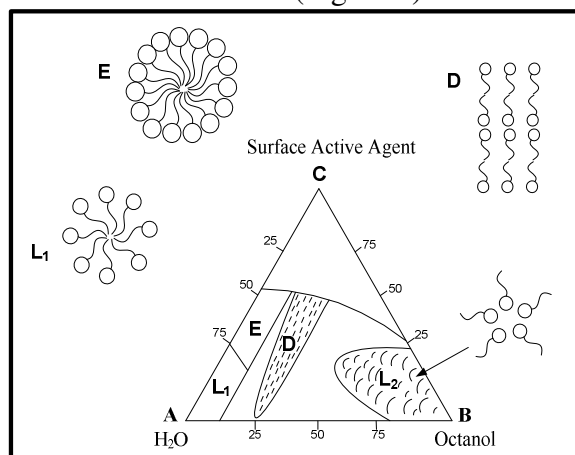

Figure 2: Ternary Diagram of the (Water, Octanol and Surface Active Agent) System at 25°C

The following table represent percentage of each component. A, B and C.

A = Water, B = Octanol, C = Surface active agent.

Table 1: represent percentage of each component. A, B and C. A = Water, B = Octanol, C = Surface active agent.

A	B	C
28.5	42.8	28.5
23.25	46.5	35.23
45.5	45.2	9
33.3	33.1	3.3
50	25	25
68	10.3	27.8
90.9	4.5	4.5
62.5	41	4.16
68.9	6.9	24
80	8	12
58.2	29.4	11.7
45.5	18.2	36.4

Results and Discussion

The ternary system of (surface active agent-water-octanol) at limited ratio's. We obtain a stable monophase on the addition of these components at different concentrations. This mostly forms a microemulsion called swallen micelles [21]. Ekwal [22] studied the ternary system of (water-hexanol-cetytrimethy-lammonium bromide) and showed that this system represents the best example for microemulsion formation. It was also shown [21] that hexanol has a parallel role like surface active agent.

In (Figure 2) Regions distributed and the microemulsion was found it formed of microdroplet (L_1) of Octanol in aqueous phase. This part of the diagram is representing the O/W which is rich with water. While L_2 represents the part which is rich with Octanol (W/O), when the surface active agent increases, it shows the appearance of a new region (D) which is celled gonfeled Lamellair micelles.

The region (E) of the diagram is a hexagond structure of reticulate form in which the hydrocarbon parts of molecular are directed toward the center. While the polar parts are directed upwards, the structure of (D) is different from L_1, L_2 and E, through which the surface active agents are ordering themselves in a uniform lineup, and the polar parts of the molecular are directed toward water molecules forming hydrogen bonds while, the aliphatic parts tangled with the aliphatic part of Octanol Therefore the polar directed toward up in the uniform lineup and the aliphatic part meet of surface active agent. In 1950 Winsor put the idea of classification which related to number of

phases of liquid after mixing of the components and stability of the solution.

Region I (according to Winsor) which contains two solutions in an equilibrium state with the microemulsion, comprising oil and water (the greatest part of the above solution (microemulsion) are surface active agent + oil) (Figure 3).
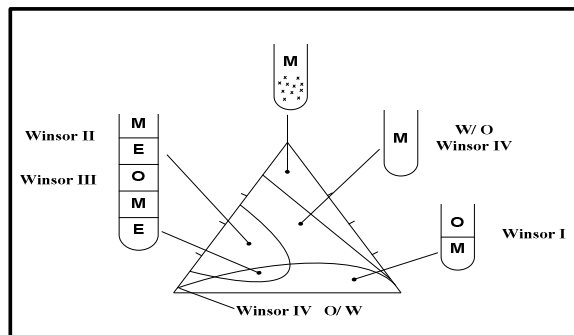

Figure 3: Represents WINSOR Zones

Region II (according to Winsor) consists of two layers. This region represents the microemulsion that equal to monoaqueous phase.

Region III (Winsor) comprises three layer where microeomulsion in the middle of oil and aqueous solution layer. Similarly, various regions formed on the interior of the triangle on mixing Octonal, water, and surface active agent depending on the arrangement of the surface active agent with the participations of water and Octanol molecuis.

Conclusion

In this work the ternary system of surface active agent, Octanol, and water have been studied at 25°C. This study shows the formation of different zones on the interior of triangle by changing the concentration of the components in the mixture. Consequently, the surface active agent play an important role in the formation of these regions, as it contains the polar part contributing in the formation of Hydrogen bonding with water molecules and non polar part which evolves an aliphatic part of the Octanol.

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