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Surface Activity of Separated Phases of the Surfactant/Water/Corn Oil System

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ABSTRACT

Aqueous solutions of octyl phenoxy polyethoxy ethanol (Triton X-114) show phase separation on standing and also in the presence of corn oil. The surface tension of varying concentrations of the upper phase of these systems decreases markedly at lower concentrations, tending to become constant at higher concentrations. The surface activity of this phase as observed from surface tension/concentration curves may be greater, less than or about the same as that of the corresponding upper phase concentration of the control which is a surfactant solution without the oil. Results of this study indicate that the surface activity of the upper phase of Triton X-114 solutions is not affected so much by the solubilization of corn oil but by the limit to which solubilization has occurred. The surface activity of this phase is much less than that of the lower phase of corresponding systems. However, the surface activity of the lower phase is not influenced by the solubilizate or solubilization of the oil.

INTRODUCTION

When a solution of nonionic surfactant is heated to a particular temperature, it suddenly becomes cloudy. This occurs within a narrow temperature range and is termed the cloud point. Above the cloud point, there is a tendency for the solution to separate into two phases. This is believed to be associated with the solubility of nonionic surfactants, which increases by virtue of the power of the ether oxygen to hydrate (1, 2). Hydration is sensitive to temperature. Elevated temperature causes dehydration. Consequently, nonionic surfactants of the polyoxyethylene type become markedly less soluble at elevated temperature, the surfactant solution turns turbid and eventually phases separate out.

Debye (3) has shown that the micellar weight of a nonionic surfactant increases rapidly when the temperature of the solution approaches the cloud point. It will appear, therefore, that the micelle becomes much larger with rise in temperature and finally separates from the water phase. This means that the clouding phenomenon and the subsequent phase separation takes place as a result of the formation of very large aggregates. This is yet another interpretation of the mechanism of phase separation.

The cloud point of aqueous solutions of nonionic surfactants may be affected by the incorporation of coexisting substances. It would seem that a coexisting substance may affect the cloud point of a nonionic surfactant in one of two ways, either by changing the structure of the micelle by penetration of the coexisting substance or by dissolving in the water phase and thereby changing the environment of the micelle (4).

Two-phase liquid systems of Triton X-114 and corn oil as a solubilizate have not been studied previously, as evidenced by the lack of references in the literature. The purpose of the present investigation is to examine the surface activity of the phases resulting from the phase separation of Triton X-114 solutions to which corn oil has been added. It represents a logical sequence to the attempts made previously to solubilize corn oil with various surfactants (5, 6). In the study of the solubilization of corn oil with Triton X-114 solutions (6), it was found that the solubilization of this oil did not follow the usual behavior of most other solubilized systems in that the amount of solubilizate taken into the micelle did not increase with surfactant concentration; much higher concentrations than normal were required to solubilize the oil and the process took several days instead of the usual, almost spontaneous, taking in of the solubilizate into the micelles.

EXPERIMENTAL

Materials

Corn oil (Mazola, Best Foods Div., CPC International Inc., NJ) of commercial grade was used. The surfactant employed was octyl phenoxy polyethoxy ethanol (marketed as Triton X-114 by Rohm and Haas, Philadelphia, PA).

Method

Corn oil was added dropwise from the same microsyringe to the selected concentration of Triton X-114 in 25 cm^3 graduated stoppered cylinders and then made up to 20 cm^3. The number of drops of oil added to each surfactant concentration ranged from 1 to 9 drops. The average weights of 2, 4, 6 and 8 drops of oil were found to be 6.30 mg, 6.15 mg, 6.18 mg, 6.17 mg/drop, respectively. There is no appreciable difference between these values, and hence the mean weight of a drop of corn oil was taken as the average of these four values, i.e., 6.20 mg. From this value, the percentage concentration of oil in the system was calculated. The surfactant concentrations of the systems studied were 1%, 2%, 3% and 4%. This was based on a previous study (6) which showed that corn oil could be solubilized in 3% and 4% surfactant solutions of Triton X-114 but not in the 1% and 2% surfactant solutions.

The graduated cylinders were rotated in a thermostatically controlled water-bath at 25 ± 0.5 C for 6 hr and then allowed to stand overnight, after which they were rotated for a further 6 hr to provide adequate time for the oil to be solubilized. A control consisting of the corresponding amount of Triton X-114 in water was also included. The systems were allowed to stand over a period of time for phase separation to occur and to attain equilibrium which is achieved when the volume of the lower phase becomes constant.

The equilibrated systems containing surfactant and corn oil consist of a clear, aqueous upper phase and a clear but gel-like lower phase. A 50% w/v solution of the upper phase in water was prepared and appropriate dilutions were made to give a series of solutions of varying concentrations. These solutions were allowed to stand for ca. 4 hr before surface tension measurements were made using the drop-weight method and using the Agla micrometer syringe (Burroughs Wellcome, London) at 25 ± 1 C. For the lower gel-like phase, a 1% w/v solution was prepared and the surface tension of the appropriately diluted solutions measured in a similar manner. Duplicate measurements were made for each concentration. The results differed from the average by less than 0.9%. Hence the average surface tension values were used.

RESULTS AND DISCUSSION

In solutions of Triton X-114, the phases which separate on standing are definite, as the demarcation between the upper phase and lower phase is distinct. The lower phase is richer in surfactant compared with the upper phase. Maclay (4) and Nakagawa (7) have also found that the concentration of nonionic surfactants in the upper phase is lower and that in the lower phase is higher in similar systems which show phase separation.

Figure 1 shows the surface activity of the upper phase of systems containing 4% Triton X-114 and different quantities of corn oil. Three types of surface tension/concentration curves are obtained. Type I curves are demonstrated by upper phase solutions of systems containing 0.031%, 0.062%, 0.093% and 0.124% oil. The surface tensions of these solutions do not differ much from that of the control which contains only the surfactant in water without the oil. Type II curves are shown by upper phase solutions of systems which contain 0.155% and 0.186% oil. In these solutions, the surface tension is higher than that of corresponding concentrations of solutions which exhibit type I curves. It is noted that the inflection is not as sharp as that seen in type I and III curves. Type III curves are given by upper phase solutions of systems containing 0.217% and 0.248% oil. In these solutions, the surface tension is lower than that of solutions which produce type I and II curves. Similar types I, II and III curves are also found for the upper phase of systems containing 3% Triton X-114 and similar amounts of corn oil.

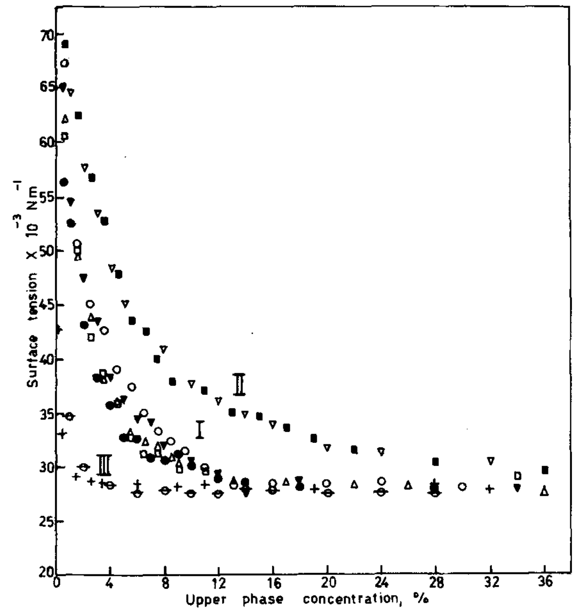

FIG. 1. Surface activity of various concentrations of the upper phase of systems containing 4% Triton X-114 and different amounts of corn oil at 25 ± 1 C. Corn oil concentration (%): ▼ control; □ 0.031; ● 0.062; △ 0.093; ○ 0.124; ▽ 0.155; ■ 0.186; ⊖ 0.248.

The pattern of behavior of all the surface tension/concentration curves is similar to that shown generally by aqueous solutions of surfactants, except that the break in the curve is not sharp.Hence the critical micelle concentration (cmc) cannot be determined accurately. Estimations of the cmc from the plots may lead to erroneous conclusions regarding monomer concentration/activity or thermodynamics of monomer-micelle equilibrium. The curves all appear to flatten out. The surface tension of the upper phase concentrations in which this flattening occurs is ca. 27–28 × 10^{-3} Nm^{-1} and that of corresponding concentrations of the lower phase is almost 29–30 × 10^{-3} Nm^{-1}. The difference between the two is small. It indicates that both phases when diluted appropriately can attain almost the same surface tension values and at sufficiently high concentrations of both these phases, the surface activity does not differ much. At concentrations below the cmc, there exists a dynamic equilibrium between monomers and micelles (8, 9). The reduction in surface tension is due to surfactant monomers and, since micelles are not surface active, the surface tension remains approximately constant.

It was mentioned earlier that corn oil was a difficult substance to solubilize and, of the several surfactants studied previously, Triton X-114 was able to solubilize this oil in surfactant concentrations of 3%, 4% and 5% (6). However, the maximum amount of oil taken into the micelles was found to be about the same for all these Triton X-114 concentrations, this amount being 0.185% w/v oil, for 2% and 1% Triton X-114 solutions practically no oil was solubilized.

Aqueous solutions of 4% Triton X-114 containing corn oil, 0.031–0.124%, are not saturated with the oil, and the upper phase of these systems produce type I curves; those with oil concentrations of 0.155% and 0.186% are almost saturated and saturated, respectively, and they give rise to type II curves. Those with concentrations greater than 0.186% are oversaturated and they exhibit type III curves.

In Triton X-114 systems which are not saturated with respect to the solubilizate, there is probably sufficient monomeric surfactant in the upper phase to bring about a reduction of the surface tension to the level of that of the control. Whereas in similar systems but which are saturated with corn oil, most of the surfactant is in micellar form necessary to take up the maximum amount of the solubilizate; consequently, less monomeric surfactant is available and hence the surface tension is not decreased to the same degree as demonstrated by those producing type I curves.

Systems whose upper phase solutions give rise to type III curves contain corn oil in excess of the amount that can be solubilized. Emulsified droplets are readily seen, in particular on the surface of the upper phase. Surfactant is needed to emulsify this excess oil and it is likely that there is a tendency for more monomeric surfactant to remain in the upper phase. Consequently, their presence lowers the surface tension even further.

In systems containing 2% Triton X-114 and different quantities of corn oil (Fig. 2), the surface tension/concentration curves of the upper phase do not show the same pattern of behavior as that observed with the upper phase of corresponding systems of 3% and 4% Triton X-114 and corn oil. This difference in surface activity behavior may be attributed to the fact that no solubilization of the oil occurs in this surfactant concentration (6), the oil is present as droplets on the surface of the upper phase. This behavior supports the finding of those upper phase solutions which exhibit type III curves, as discussed above. A similar behavior was observed with systems containing 1% Triton X-114 and oil concentrations ranging from 0.031 to 0.093%; these systems are oversaturated with the oil and no solubulization takes place (6).

With the lower phase, the surface tension/concentration curves are almost the same for all the systems studies (Fig. 3). This is also true for corresponding systems containing 4% Triton X-114 and corn oil. The results show that the surface activity of the lower phase is not appreciably affected by either the solubilization of the oil or saturation of the system with the solubilizate. In this lower phase the concentration of surfactant is high, both micellar and monomeric forms being present. Though the solubilizate is very hydrophobic and distributes in favor of micelles, the high surfactant concentration here provides the necessary micelles for solubilization. This would explain the very small change in surface activity of the systems studied (Fig. 3) in spite of the different amounts of corn oil included. In like manner, when 2% Triton X-114 systems containing varying quantities of corn oil (Fig. 4) were studied, the surface activity of the lower phase does not differ appreciably with corn oil concentration. The lower phase contained a much greater proportion of surfactant than the upper phase and hence sufficient micelles were available to take up the oil. The cmc of Triton X-114 as determined from surface tension measurements using the drop-weight method was 0.015% w/v.

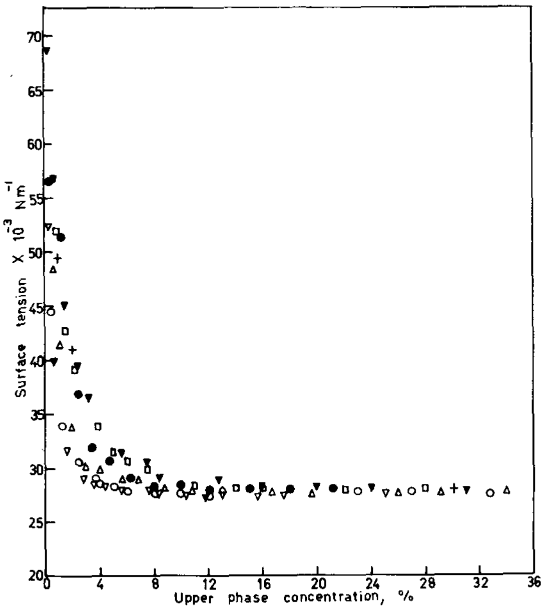

FIG. 2. Surface activity of various concentrations of the upper phase of systems containing 2% Triton X-114 and different amounts of corn oil at 25 ± 1 C. Corn oil concentration (%): ▼ control; □ 0.031; ● 0.062; △ 0.093; ○ 0.124; ▽ 0.155.

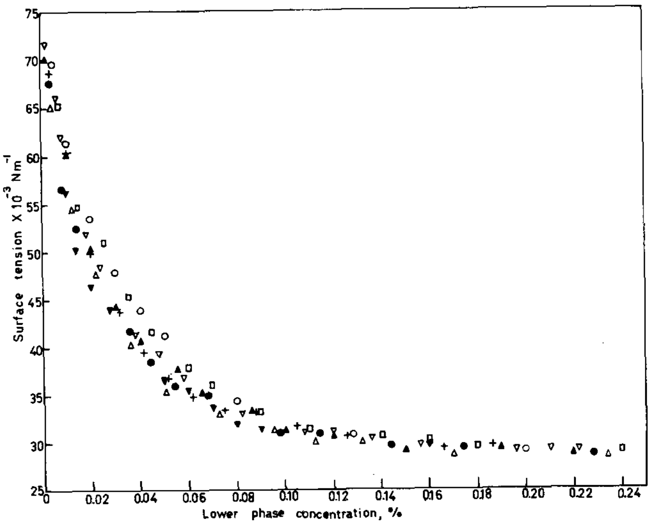

FIG. 3. Surface activity of various concentrations of the lower phase of systems containing 3% Triton X-114 and different amounts of corn oil at 25 ± 1 C. Corn oil concentration (%): ○ control; □ 0.031; + 0.062; ▽ 0.093; ● 0.124; △ 0.155; ▼ 0.186; ▲ 0.248.

Solubilization is a dynamic equilibrium process. It depends on factors such as temperature, nature of solute, surfactant concentration and type of micellar system employed. It is important to note that there can be observed changes in the properties of solutes as a function of surfactant concentration. The changes of properties usually seen at higher surfactant concentration, that is, greater than the cmc, are due to micelle formation and the solubilization of the solute. When a solute is solubilized in a micellar system, the microenvironment about it can be quite different compared to that in the bulk solvent. The nature of solubilization in micellar solutions and the effects of solubilized species on monomer-micelle equilibrium depend on the nature of the interaction of the solubilized species with the monomers and the micelles (10–13).

Further investigation is currently being pursued in an attempt to gain more insight into the monomer-micelle equilibrium of the systems. This probably is the major factor governing the behavior of the surface activity of the upper phase. In addition, other solubilizates are being studied in Triton X-114 systems.

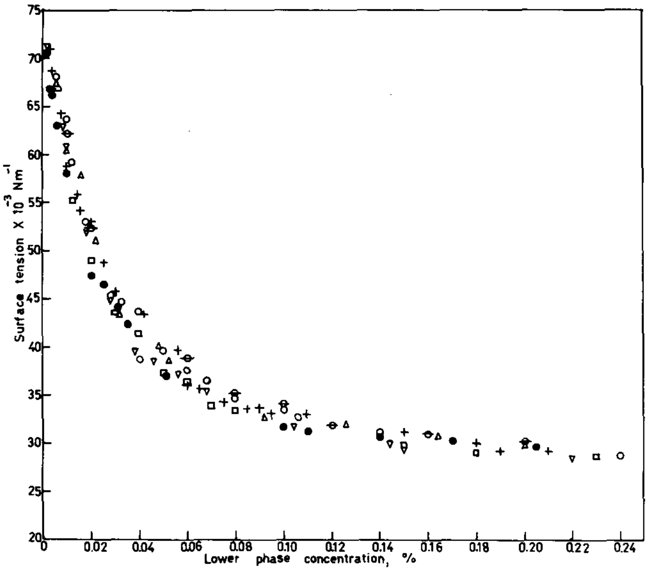

FIG. 4. Surface activity of various concentrations of the lower phase of systems containing 2% Triton X-114 and different amounts of corn oil at 25 ± 1 C. Corn oil concentration (%): ○ control; □ 0.031; + 0.062; ▽ 0.093; ● 0.124; △ 0.155; ⊖ 0.217.

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