

Critical Micelle Concentration of Nonionic Surfactants in Water and Carbon Tetrachloride

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The critical micelle concentration (CMC) of two nonionic surface-active agents was studied. The micellization properties of polysorbate 80 and sorbitan monooleate were investigated in water and chloroform utilizing iodine as the indicator. Mixtures of polysorbates and sorbitans in various proportions were also tested relative to the CMC for mixed micelles in both solvents. A spectrophotometric method was used to determine the CMC in both solvents; the aqueous systems were also studied by a surface-tension method.

CERTAIN SUBSTANCES have the distinct characteristic of altering the surface properties of liquids and are referred to as surface-active agents or surfactants. Most of these agents exhibit the ability to aggregate in solution into what are called "micelles."

Many theories have been advanced on the size and shape of micelles. Notable among these are the McBain lamellar micelle, the Hartley spherical micelle, and the Debye rod micelle (1-3). These models serve to explain much of the published data on micelle formation, but no one model is sufficient in scope to be generally applicable.

Nonionic surfactants offer an unusual opportunity to study micelle formation. The absence of charged species in solution may facilitate the aggregation phenomenon because charge repulsion is minimized. Generally, their structure may be described as having both a hydrophilic and a hydrophobic group in these molecules. It is the relative balance of these groups which determines their characteristic behavior.

A number of the properties of solutions of surface-active agents exhibit an abrupt discontinuity at the concentration where aggregates or micelles start to form in appreciable numbers. One property that shows a marked change is the ability of the surfactant to solubilize certain dye materials. Harkins *et al.* (4) studied cationic and anionic surface-active agents utilizing this method. At the critical concentration, the dye is thought to be solubilized in the micelle and is in equilibrium with the dye in the bulk solution. This results in a spectral change. Additional work on this method was reported by Corrin (5), Nichols (6), and Sata (7).

Another spectrophotometric technique has

been advanced by the work of Ross and Olivier (8). Their investigations dealt with nonionic surfactants in aqueous and nonaqueous solvents. The method is based on the use of iodine as an indicator; the equilibrium of iodine in the micelle and in solution lent itself well to spectrophotometric analysis.

This method has several absorption advantages. The major one is that the absorption maximum at 360 m μ does not vary from one solvent to another; the small molecular size of iodine compared with surface-active agent or dye molecules probably does not affect micelle formation.

The study reported here dealt with the physical properties of two nonionic surfactants in an aqueous and nonaqueous solvent. The nonionic surfactants selected were polysorbate 80¹ U.S.P. and sorbitan monooleate,² and these compounds were studied as single solutes and mixed in various proportions. Spectrophotometric absorbance and static surface-tension measurements were examined in an attempt to correlate the properties of these nonionic compounds. Measurements were made after various periods of aging to determine any variation in these properties. Specifically, the CMC for these systems was determined so that micelle formation under the conditions of this study might be further elucidated.

EXPERIMENTAL

Materials.—Sorbitan monooleate, lots 585 and 621; polysorbate 80, lots 360 and 678; carbon tetrachloride, analytical grade; iodine crystals, C.P., lot 472610 (Fisher Scientific Co.); and distilled water were used.

Equipment.—Beckman DU and DK-2 spectrophotometers, silica cells, and a Christian Becker laboratory balance, model AB-4, modified for surface-tension measurements were employed.

Methods.—Stock solutions (w/v) of surface-active agents were prepared in water and carbon tetrachloride. These solutions were subsequently

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¹ Marketed as Tween 80 by the Atlas Chemical Industries, Inc., Wilmington, Del.

² Marketed as Span 80 by the Atlas Chemical Industries, Inc., Wilmington, Del.

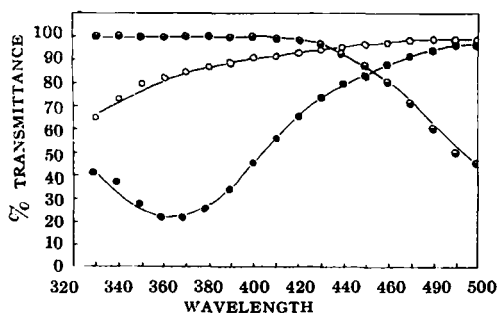


Fig. 1.—The development of the iodine-micelle complex maximum at 360 $m\mu$ and the corresponding isosbestic point at 452 $m\mu$. One per cent polysorbate 80 in carbon tetrachloride (O); iodine in carbon tetrachloride (\ominus); iodine-polysorbate 80-carbon tetrachloride (\bullet).

TABLE I.—ABSORPTION PEAKS AND CONCURRENT ISOSBESTIC POINT OF VARIOUS SYSTEMS EXPRESSED IN MILLIMICRONS

System	Peak	Isosbestic Point
Iodine in water	450	...
Iodine with sorbitan monooleate in water	350 ^a	390
Iodine with polysorbate 80 U.S.P. in water	360	428
Iodine in carbon tetrachloride	510	...
Iodine in sorbitan monooleate and carbon tetrachloride	360	440
Iodine in polysorbate 80 U.S.P. and carbon tetrachloride	360	452

^a Broad peak.

bureted into a solution of iodine in the solvents studied; a sufficient amount was added so that the surfactant concentration with respect to the final volume was incrementally increased. The solvents used were saturated with iodine, and a 1:10 dilution with the appropriate solvent was made just prior to use. These samples were assayed spectrophotometrically at the appropriate wavelength (360 $m\mu$) for a given system.

Surface-tension measurements were carried out on the samples described above, the determinations were made at 5-minute intervals for 30 minutes. These results were averaged and used directly in the determination of the CMC.

Samples prepared for both methods were carried out at ambient temperatures (25°) and stored for a 1-week period and a 30-day period at the same temperature. At the end of each aging period, the samples were analyzed by the previously indicated methods.

RESULTS AND DISCUSSION

The absorption spectra of iodine in water and iodine in carbon tetrachloride were obtained on the Beckman DK-2 recording spectrophotometer. Peaks for these systems occurred at 450 $m\mu$ for iodine in water and at 510 $m\mu$ for iodine in carbon tetrachloride. The spectra of 1% solutions of sorbitan monooleate and polysorbate 80 were determined by the DK-2; they have relatively low absorption values in the 500 to 330- $m\mu$ range. The

spectrum of polysorbate 80 in carbon tetrachloride is illustrated in Fig. 1. Since the concentration of most sample solutions was about 1% or less in the water and carbon tetrachloride systems, it was felt that a correction for the colored constituents of these surfactants need not be applied.

When the absorption spectra of solutions containing iodine alone and solutions containing the surfactants and iodine were plotted, an isosbestic point was found between the two absorption maxima. This was done for both solvents studied in this work. The results are recorded in Table I. Figure 1 shows the iodine-carbon tetrachloride peak and the corresponding isosbestic point for iodine-polysorbate 80-carbon tetrachloride system.

The isosbestic point which developed between the two absorption maxima of the solutions containing iodine alone and solutions containing surfactants and iodine may indicate that a simple equilibrium exists between the iodine molecules in the solution and the iodine in the micelles. It may also indicate that one type of iodine-micelle complex existed in the solution which has an absorption maximum at 360 $m\mu$.

Figure 2 shows that the iodine-polysorbate 80-water system had an increased absorption up to the CMC, followed by a change in slope. After the CMC had been reached, the absorption of the iodine-micelle complex decreased upon the addition of polysorbate 80. Although the concentrations of polysorbate 80 were low, the concentration of the polyglycol contaminant (approximately 5% of the total surfactant) became sig-

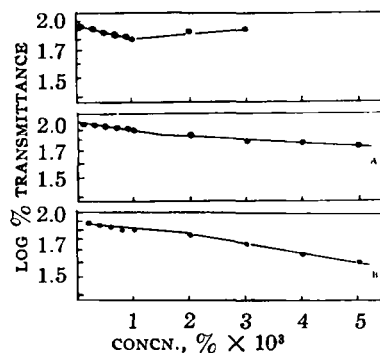


Fig. 2.—Log per cent transmittance versus concentration of polysorbate 80 in iodine-water system. A, Log per cent transmittance versus concentration of 1:1 mixture of sorbitan monooleate-polysorbate 80 in iodine-water system. B, Log per cent transmittance versus concentration of 2:1 mixture of sorbitan monooleate-polysorbate 80 in iodine-water system.

TABLE II.—CMC OF NONIONICS EXPRESSED AS PER CENT W/V IN WATER-IODINE SYSTEMS

Surfactant	Spectrophotometric Data, %	Surface-Tension Data, %
Sorbitan monooleate	0.0020	0.002
Sorbitan monooleate, 2/3	0.0020	0.001
Polysorbate 80 U.S.P., 1/3		
Sorbitan monooleate, 1/2	0.0015	0.001
Polysorbate 80 U.S.P., 1/2		
Sorbitan monooleate, 1/3	0.0013	0.001
Polysorbate 80 U.S.P., 2/3		
Polysorbate 80 U.S.P.	0.0010	0.001

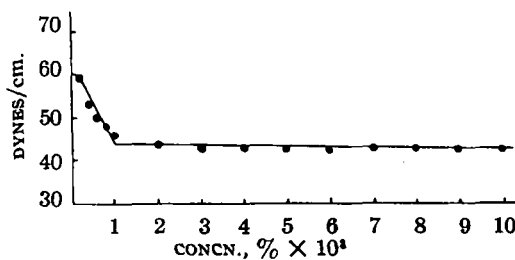


Fig. 3.—Surface tension *versus* concentration of a 1:1 mixture of sorbitan monooleate-polysorbate 80 in water.

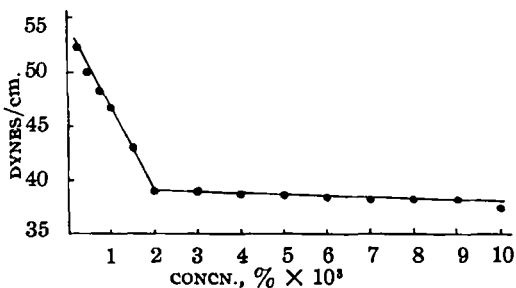


Fig. 4.—Surface tension *versus* concentration of sorbitan monooleate in water.

nificant in relation to the iodine concentration which remained constant. Therefore, it may be postulated that the polyglycol-iodine complex formed, disturbing the equilibrium and showing an apparent micelle decrease at the higher concentrations of polysorbate 80.

The data obtained from the spectrophotometric determinations were plotted in several fashions relative to the values of the abscissa. A plot of the log per cent transmittance *versus* concentration illustrated the CMC "break" in the clearest fashion. Thus, all the representative plots utilizing spectrophotometric data were illustrated in this manner.

To determine micelle formation for mixed surfactants, polysorbate 80 and sorbitan monooleate were mixed in various proportions and tested. The ratios of polysorbate 80 to sorbitan monooleate tested were 2:1, 1:1, and 1:2. The results for two of these systems were plotted and are illustrated in Fig. 2A and B. The CMC's for the aqueous systems are recorded in Table II. The data showed values of the CMC for the mixed solutes intermediate between the CMC value of the single solutes.

It was then felt necessary to attempt the possible correlation of the determined CMC's using a surface-tension method. This was done for single and mixed solutes. Data for two of these systems were plotted and are illustrated in Figs. 3 and 4. The CMC's determined by the surface-tension method for these systems are also included in Table II.

It is interesting to note that the CMC's for the mixed solutes showed no apparent correlation with composition for the surface-tension method. The CMC's for the spectrophotometric method were approximately proportional to composition. This is illustrated in Fig. 5.

Aging for 30 days showed the same CMC's but with a slight decrease in the absorption of the iodine-micelle complex. This may be explained by the reaction of the iodine with the double bond of oleate in the polysorbate 80 and the formation of the polyglycol-iodine complex (12). These two effects may have disturbed the iodine-iodine-micelle complex equilibrium, and a consequent decrease in absorption would be expected. Experimentally, this was the case.

The CMC's in carbon tetrachloride were also determined for the single and mixed solutes. The CMC's for polysorbate 80 and sorbitan monooleate resulted in values of 0.07% and 0.025% in the iodine-carbon tetrachloride mixtures. The data for polysorbate 80 have been plotted and are illustrated in Fig. 6. Again, the absorption increased up to the CMC; after this point, the absorption remained fairly constant, an implication of virtually complete micelle formation at the break.

It is interesting that the shapes of the curves of systems containing single solutes were different from the mixtures, but the CMC's were in the same range.

As shown in Fig. 6A and B, the carbon tetrachloride systems showed the same shaped curves in all cases. It is proposed that the general shape of the curve was due to the following. The absorption increased up to the CMC; a subsequent decrease in absorption was due to the polyglycol-iodine and the oleate-iodine reactions for a certain concentration

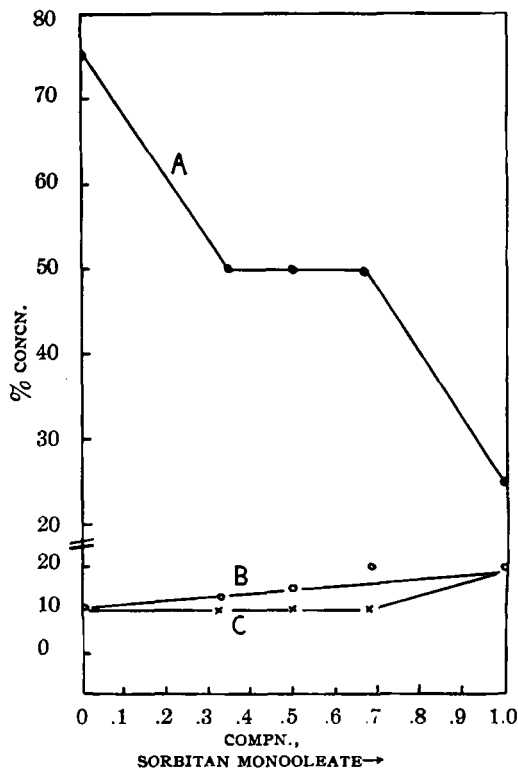


Fig. 5.—Variation of the CMC as a function of composition. Curve A is for carbon tetrachloride systems ($10^{-3}\%$). Curves B and C are the spectrophotometric and surface-tension data for the aqueous systems ($10^{-4}\%$).

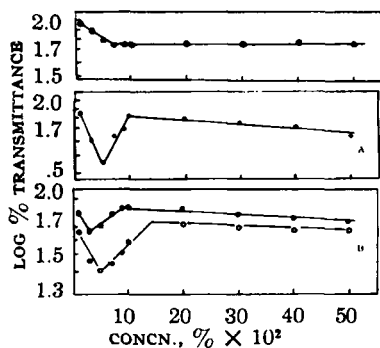


Fig. 6.—Log per cent transmittance versus concentration of polysorbate 80 in iodine-carbon tetrachloride system. *A*, Log per cent transmittance versus concentration of 2:1 mixture of sorbitan monooleate-polysorbate 80 in iodine-carbon tetrachloride systems. *B*, Log per cent transmittance versus concentration of 1:1 mixture of sorbitan monooleate-polysorbate 80 in iodine-carbon tetrachloride systems. Data shown for 1 week (●) and for 30 days (○).

TABLE III.—CMC OF NONIONICS EXPRESSED AS PER CENT W/V IN CARBON TETRACHLORIDE-IODINE SYSTEM

Surfactant	Spectrophotometric Data—		
	1 Hr., %	1 Wk., %	30 Days, %
Sorbitan monooleate	0.025	0.020	0.020
Sorbitan monooleate, 2/3 U.S.P., 1/3	0.050	0.050	0.050
Sorbitan monooleate, 1/2 U.S.P., 1/2	0.050	0.050	0.030
Polysorbate 80 U.S.P., 2/3	0.050	0.040	0.040
Polysorbate 80 U.S.P.	0.075	0.065	0.060

range. After this point, due to the relatively high concentrations of surfactants and the partial consumption of iodine in the system, the absorption was essentially due to the surfactants.

The samples for a given run were stored at 25° in a dark place for 1-week and a 30-day period. Upon aging, the above reactions would tend to be favored, and a general decrease in absorption would be expected; but the shape of the curve should remain unchanged. Experimentally, this was the case, and the absorption essentially due to the surfactant remained relatively constant.

However, it was also found that the CMC's in these systems decreased upon aging to various degrees. This observation is illustrated in Fig. 6*A*. All the results have been summarized in Table III.

The CMC's in the iodine-carbon tetrachloride systems showed higher values than the CMC's in the aqueous systems. Approximately a tenfold increase was noted for sorbitan monooleate in carbon tetrachloride relative to water, whereas polysorbate 80 gave a thirty-fivefold increase. These values may be explained on the basis of decreased solubility in carbon tetrachloride requiring higher concentrations for micelle formation. The CMC's for single solutes and mixed solutes have been plotted and are also illustrated in Fig. 5 as a function of composition. From the values for the mixed solutes it seems that polysorbate 80 had a more pronounced contribution to the formation of micelles than sorbitan monooleate.

The nonionic surfactants used in this study are known to be heterogenous mixtures of compounds of differing physical properties. It is important to note, however, that batch variation for both single and mixed solutes showed no apparent differences in the CMC's for the systems studied. Therefore, it can be assumed that the average physical properties of these heterogenous mixtures are relatively reproducible.

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