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Determination of CMC of Polysorbate 20 in Aqueous Solution by Surface Tension Method

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Abstract □ The CMC of polysorbate 20 was determined using a surface tension method; the concentration (C) of polysorbate 20 studied varied from 0.001 to 10.000 mg./ml. The results show clearly that the surface tension (γ) decreases linearly with $\log C$ up to a concentration of 0.06 mg./ml. and is practically constant for more concentrated solutions. This suggests that the CMC of polysorbate 20 is in the vicinity of 0.06 mg./ml., which is in excellent agreement with the values obtained by other methods.

Keyphrases □ CMC—polysorbate 20, surface tension method □ Polysorbate 20—determination of CMC by surface tension method □ Surface tension method—determination of CMC for polysorbate 20

Among other methods, the surface tension method has been widely used to determine the CMC of a variety of nonionic surfactants (1), and the validity of this technique has been well established (2). However, the surface tension method has not been used to determine the CMC of the polysorbate family of surfactants, probably because of their alleged heterodisperse nature. Becher (1) cataloged the CMC values of polysorbate surfactants as determined by light-scattering and iodine solubilization methods, but no application of the surface tension method was mentioned. The surface tension method for the determination of CMC is more accurate than the light-scattering technique; with solubilization methods, one is always doubtful whether or not the solubilized material lowered the actual CMC.

Phares (3) studied the surface and interfacial behavior of polysorbate 20 and tabulated the values of surface tension (γ) as a function of concentration (C), but he did not discuss the CMC. His data did not yield a definite value of the CMC because of the difficulties outlined later. In the present article, results are reported on the surface tension behavior of polysorbate 20 and the value of the CMC derived from the plot γ versus $\log C$.

EXPERIMENTAL

The label of the polysorbate 20¹ sample used read polyoxyethylene (20) sorbitan monolaurate, HLB, 16.7. A stock solution containing 10.0 mg./ml. of polysorbate 20 was prepared using distilled water; from this stock solution, solutions of varying concentrations in the range 10.0–0.001 mg./ml. were prepared by dilution. As the molecular weights of such nonionics is not known with certitude, the concentrations are expressed in milligrams per milliliter. Surface tension (γ) values were obtained using an interfacial tensiometer²; the correction factor was calculated as suggested by Harkins and Jordan (4). The measured values of γ for toluene and water were in good agreement with literature values. The following important points concerning the actual experimental conditions and the mode of measuring γ for polysorbate 20 solutions should be mentioned.

1. All measurements were made at 28°.
2. The solutions used were 9–10 hr. old, *i.e.*, 9–10 hr. elapsed after the dilution and before the measurement of γ .
3. The fresh solution–air interface was left undisturbed for 3–5 min. before measurement of γ ; this procedure was necessary to obtain reliable and constant values of γ . During this interval (3–5 min.), γ decreased quite appreciably (in some cases by 5–6 dynes/cm.); after that time, γ values were quite concordant. The change of γ during this initial period could be attributed to the diffusion of surfactant molecules from the bulk to the interface.

RESULTS AND DISCUSSION

The plot of γ versus $\log C$ is shown in Fig. 1. It is clear that initially γ varies linearly with $\log C$ up to a concentration of 0.06 mg./ml. and then stays practically constant for more concentrated solutions, *i.e.*, up to 10.0 mg./ml. (which is 160 times 0.06 mg./ml.). To be precise, γ decreases slightly (1.0 dyne/cm.) in the concentration range from 0.06 to 1.00 mg./ml. and is essentially constant for higher concentrations. Furthermore, the break in the plot of γ versus $\log C$ is quite sharp considering the broad molecular distribution of the nonionic, which suggests that the CMC value for polysorbate 20 is in the vicinity of 0.06 mg./ml. If the two straight-line portions in Fig. 1 are extended, they cross at a concentration of 0.05 mg./ml.; this indicates that the CMC of polysorbate 20 determined by the extrapolation procedure is 0.05 mg./ml. In any case, the present results suggest clearly that the CMC of polysorbate 20 lies

¹ Tween 20, Atlas Chemical Industries, Wilmington, Del.

² Cenco Du Nouy.

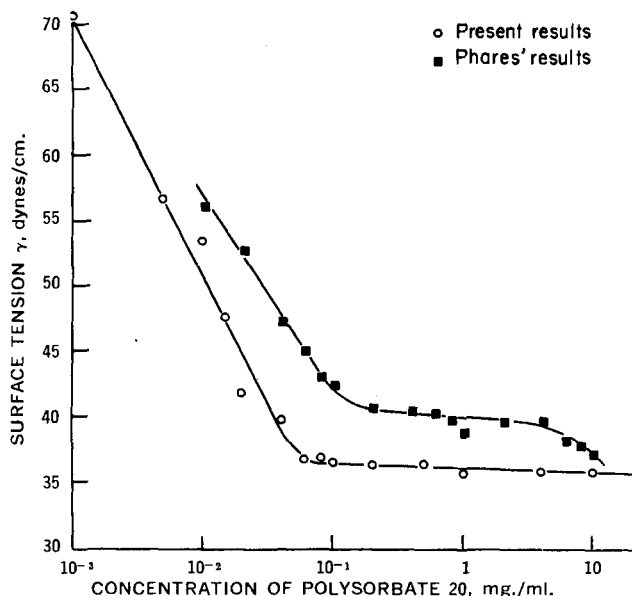


Figure 1—Plot of surface tension versus log concentration for polysorbate 20 aqueous solutions.

between 0.05 and 0.06 mg./ml., which is in excellent agreement with the values quoted by Becher (1) as determined by light-scattering and iodine solubilization techniques.

For comparative purposes, the surface tension results obtained by Phares (3) on polysorbate 20 are also plotted in Fig. 1. Evidently, the γ values recorded by Phares are consistently higher than those observed in the present investigation. The higher values of γ could be attributed to not allowing enough time for the equilibrium to establish between the surface and the bulk. Phares' results show a linear portion up to a concentration of 0.08 mg./ml.; after that concentration, a broad break or bend appears in the curve of γ versus log C . The results of Phares are not easily amenable to quantification because of the following associated difficulties:

1. As the break in the curve is quite broad, its position cannot be defined unambiguously.

2. The values of γ at higher concentrations do not show a regular trend because of large fluctuations, but it is not too unreasonable to say that γ stays practically constant over a concentration range from 0.20 to 4.0 mg./ml.

3. The γ values drop again at higher concentrations (after 5.0 mg./ml.), in discordance with the present findings; furthermore, the decreasing of γ at higher concentrations is difficult to explain. It might be concluded that the results of Phares are incapable of providing definite information relative to the CMC and the surface tension behavior of polysorbate 20 at higher concentrations.

It is clear that the results reported in this article lead to a definite value of the CMC of polysorbate 20, but these results also lead to the

additional following conclusions: (a) the surface tension value for polysorbate 20 solutions of concentration 0.001 mg./ml. is not different from that of pure water, and (b) the linear relation between γ and log C suggests the applicability of Gibb's adsorption isotherm to such solutions. The value of the surface excess, Γ , calculated using:

$$\Gamma = - \frac{1}{2.303RT} \left(\frac{\partial \gamma}{\partial \log C} \right) \quad (\text{Eq. 1})$$

is 3.44×10^{-10} mole/cm.², with a corresponding area per molecule of 48.4 Å².

The CMC values for polysorbate 20 as determined by different methods (all values being in the vicinity of 0.06 mg./ml.) are in excellent agreement with each other, whereas the CMC values for other nonionic surfactants show much variation. For example, CMC values for octoxynol³ vary from 0.10 to 4.00 mg./ml. (5-8), depending upon the researcher, the sample used, and the method applied.

Finally, the following general conclusions based on the present study can be made:

1. The results certainly engender confidence in the study of other members of the polysorbate family and should be extended to other heterogeneous nonionics.

2. The surface tension method is quick, reliable, and accurate for the determination of the CMC of alleged heterodisperse nonionics.

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³ Triton X-100.