CMC of Polysorbates

LUCY S. C. WAN[x] and PHILIP F. S. LEE

Abstract ☐ The CMC of a series of polysorbates was determined using a surface tension method. The CMC values obtained did not vary to any appreciable extent from those determined by other techniques, indicating that the procedure adopted was reliable, simple, and fast. The application of the usual correction factors was not necessary in the calculation of the CMC values. Deviations for corrected and uncorrected CMC values were considered insignificant.

Keyphrases ☐ Polysorbates—CMC determination using surface tension method, values compared to other techniques ☐ CMC, polysorbates—determined using surface tension method, values compared to other techniques ☐ Surfactants—CMC determination of polysorbates using surface tension method, values compared to other techniques

The fundamental micellar properties of the polysorbate group of nonionic surfactants have been widely investigated. Becher (1) tabulated the critical micelle concentration (CMC) values of some polysorbates in aqueous solutions, as determined by iodine solubilization and light-scattering methods. A differential refractive index method has also been used (2), while Bloor *et al.* (3) and Mittal (4) employed a surface tension method to determine the CMC of polysorbates 40 and 20, respectively. Since the polysorbates are essentially heterodisperse in character (5), any "definite" values assigned to their determined micellar properties must be looked upon with caution, because such values differ among research workers and especially among different batches of the same material. In a study involving polysorbates, in solubilization and emulsification processes, the CMC values were determined by a rapid surface tension method without the need for elaborate experimental details and calculations.

EXPERIMENTAL

Materials—Polysorbates 20 [1], 40 [1], 60 [1], 80 [1], 65 [1], and 85 [1] were used as supplied. Distilled water from an all-glass still was used throughout this study.

Aging Effects on Surface Tension—Nonionic surfactants exhibit marked surface activity at much lower concentrations than ionic surface-active agents with identical hydrophobic groups and, therefore, have lower CMC values (6). The effect has been attributed to a gradual diffusion of solute molecules from the bulk to the surface and orientation of the surface molecules before equilibrium is attained. From a preliminary experiment, an equilibrium of 15 min was found to be sufficient so this period was utilized for subsequent experiments.

Measurement of Surface Tension—An aqueous stock solution of 0.10% (w/v) concentration was prepared for each polysorbate. From each stock solution, appropriate dilutions were made to produce solutions of concentrations ranging from 0.0001 to 0.050% (w/v). Polysorbates 60, 65, and 85 formed hazy solutions at these dilutions. All solutions were allowed to stand overnight in their containers before measurements of their surface tension (γ)

values were made. Surface tension data, as a function of concentration (C), were determined employing the ring-detachment method[2]. An accuracy check on the tensiometer was made by measuring the γ of pure water; γ_{water} = 72.0, 72.1, 72.0, and 72.0 dynes/cm, giving an average γ of 72 dynes/cm at 25 ± 0.5° which is in agreement with the literature value (3, 7).

The following standardized procedures were adopted:

1. All measurements were made at 25 ± 0.5°. All reported values were averaged.

2. All glass apparatus used, as well as the platinum ring, were cleaned with freshly prepared chromic acid and then thoroughly rinsed with distilled water.

3. Each solution contained in the dish was set aside for 10 min prior to the actual measurement of γ. This procedure was to compensate for any adsorption by the glass apparatus. The dish was then thoroughly drained, a fresh volume of the same solution was added, the ring was submerged just below the liquid surface, and the whole was allowed to equilibrate undisturbed for 15 min before measurement of γ. This procedure was to make allowance for aging effects mentioned earlier.

RESULTS AND DISCUSSION

The objective of this investigation was to establish a relatively fast and accurate method for the CMC determination of heterodispersed nonionic surfactants. Figure 1 shows the plot of γ against
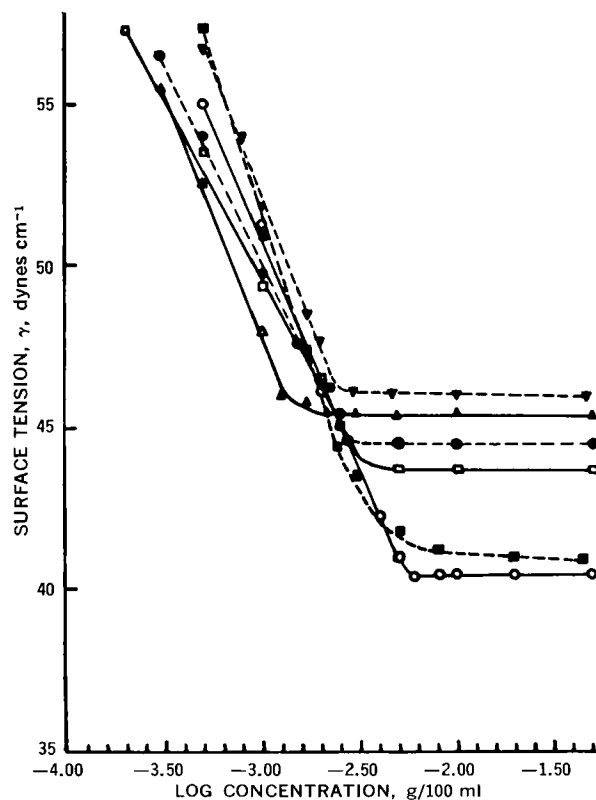

Figure 1—*Change of surface tension with concentration of various polysorbate solutions. Key:* O, *polysorbate 20;* □, *polysorbate 40;* ●, *polysorbate 60;* ▲, *polysorbate 80;* ■, *polysorbate 65;* ▼, *polysorbate 85;* – – –, *turbid solution; and* ——, *clear solution.*

[1] Tween 20, 40, 60, 80, 65, and 85, respectively; Honeywill-Atlas Ltd., London, England.

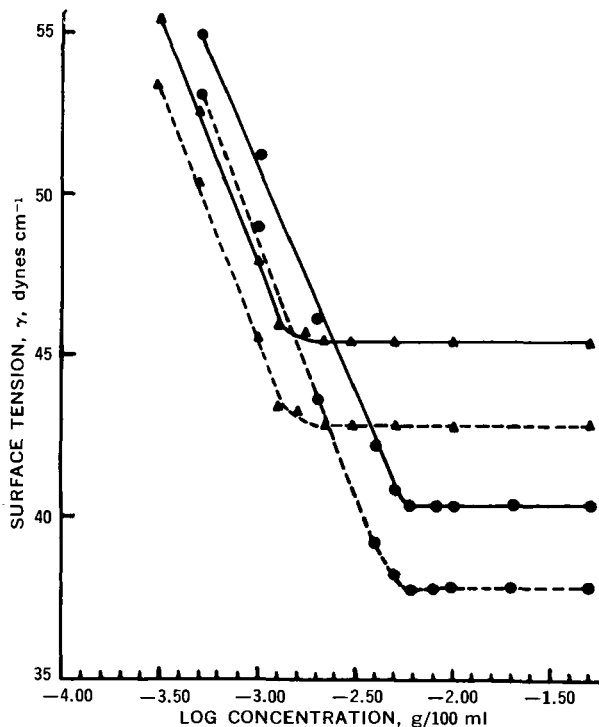[2] Du Nouy tensiometer, Cambridge Instrument Co.

Figure 2—*Comparison between plots of surface tension versus log concentration for polysorbate 20 and 80 solutions, with and without correction factor. Key: ●, polysorbate 20; ▲, polysorbate 80; - - - -, with correction factor; and —, without correction factor.*

log C where γ values were obtained without using the correction factor as suggested previously (8).

All plots show that γ varies linearly with log C up to a certain concentration characteristic of each compound, when γ remains essentially constant with further increases in concentration. The CMC of each compound is determined graphically from the intersection of the extrapolated linear portions of each plot. The results can be seen in column A of Table I. For comparison, the CMC values determined by light-scattering and iodine solubilization techniques stated by Becher (1) are shown in column B. The CMC of polysorbate 65 is given as a concentration range because there is no sharp break in its γ versus log C plot.

Figure 2 compares the plot obtained by employing the correction factor of Harkins and Jordan (8) in the calculation of γ with those calculated without it. The results indicate that although there is an expected shift toward a lower γ value for each concentration plotted, the break in the γ versus log C curve and, therefore, the CMC does not vary. This is also true for the other polysorbates studied.

An interesting observation can be related to the data obtained. Since all of the polysorbates used were soluble in water beyond their CMC's, a CMC–HLB (hydrophilic–lipophilic balance) relationship, as stated by Schott (9), can be empirically established. Since the CMC is a function of composition within a homologous series of surfactants, the more hydrophilic a surfactant is, the larger its HLB value and, therefore, the higher its CMC due to its lower tendency to form micelles.

Table I—CMC of Aqueous Solutions of Various Polysorbates at 25 ± 0.5°

Surfactant	CMC, g/100 ml	
	A	B[a]
Polysorbate 20	0.0060	0.0060
Polysorbate 40	0.0031	0.0029
Polysorbate 60	0.0028	0.0027
Polysorbate 80	0.0014	0.0013
Polysorbate 65	0.0040–0.0060	—
Polysorbate 85	0.0023	—

[a] Values taken from Ref. 1.

These results are also related to the fact that increasing the length of the hydrophobic chain for the same number of ethylene oxide units produces a shift of the γ curve and of the CMC to the lower concentration. The data obtained are consistent with this general behavior of nonionic surfactants. However, a reversal in the order seems to occur with polysorbates 65 and 85. This reversal may be attributed to the much slower attainment of equilibrium surface tension with long-chain members of the same homologous series (10).

From the findings and the data available so far, it appears that the CMC value of each polysorbate does not deviate widely despite the variety of physical methods employed for its determination. However, due to the heterodisperse nature of these compounds and the fact that they are often used as the unpurified, commercially available grade, no definite CMC value ought to be assigned with any degree of certainty to any member of the series. Even among chemically pure compounds, errors and limitations inherent in the method chosen will contribute to variations of the same determination. Nevertheless, a prior knowledge of the CMC of any polysorbate compound will be of immense help in elucidating some of their micellar characteristics.

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