

Determination of Critical Micelle Concentration (CMC) of Nonionic Surfactants by Donor–Acceptor Interaction with Iodine and Correlation of CMC with Hydrophile–Lipophile Balance and Other Parameters of the Surfactants

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ABSTRACT: The nonionic surfactants form donor–acceptor complexes with iodine in aqueous medium. The spectral absorption and the shift in the λ_{max} of I_2 upon complexation have been exploited to determine the critical micelle concentration (CMC) of Tweens, Brijis, and Triton X-100. The CMC values obtained closely agree with those determined by other methods, including measurements of static surface tension, differential refractive index, and iodine solubilization. The spectral characteristics of the complex salt KI_3 can be utilized as well to derive similar information. The CMC and the spectral shift can be correlated with the weight fraction of the polyoxyethylene groups and the hydrophile–lipophile balance (HLB) in various ways, with the parameters in these relationships depending on the series to which the surfactant belong. Because both CMC and HLB depend on temperature, the results and the relations obtained are temperature-dependent; those presented are with reference to 298 K.

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KEY WORDS: CMC, Donor–acceptor complex, CMC, HLB, iodine, nonionic surfactants.

Amphiphiles consisting of nonpolar and polar sections in their molecules have dual affinity for water and oil (1). Under specific environmental conditions, they may self-organize or associate to form “micelles.” Nonionic amphiphiles (surfactants), *viz.*, Tweens, Brijis, Spans, Myrjls, and Triton Xs, have a vast array of chemical, biochemical, and pharmaceutical applications. With the exception of the Spans, they usually have a distinct hydrophobic (HP) tail consisting of a polymethylene chain and a hydrophilic (HF) head consisting of varying numbers of polyoxyethylene (POE) groups. Depending on the molecular structure and type, a balance between hydrophilicity and hydrophobicity exists in surfactant molecules. This is called the hydrophile–lipophile balance or HLB, which is important in categorizing surfactants as emulsifiers, detergents, etc. (2) (Table 1).

Surfactants having greater hydrophobicity are more surface-active and vice versa. With increasing hydrophobicity in a homologous series, micelle formation becomes easier. Thus, HLB may be one of the fundamental properties of surfactants, especially of nonionic surfactants, in relation to their self-association. HLB was estimated from the chemical formulas of surfactants by Griffin (3). Hydrophilic surfactants having high water solubility are good stabilizers for oil-in-water (o/w) emulsions and have higher HLB values. Those with low water solubility have lower HLB and they are good stabilizers for water-in-oil (w/o) emulsions. For nonionic surfactants with polyoxyethylene groups, the HLB can be obtained from Equation 1 (3):

$$\text{HLB} = (\text{mol\% of hydrophilic group})/5 \quad [1]$$

In such a scheme, the maximum HLB of an unsubstituted nonionic surfactant would be 20. Semiempirical ways of determining HLB (4) have shown that $\ln C_0$ [C_0 is the critical micelle concentration (CMC) of a nonionic surfactant, expressed in $\text{g/dL} \times 10^4$] is linearly related to the number of carbon atoms in the surfactant molecule.

The CMC of surfactants can be determined by a number of methods, including tensiometry, conductometry, viscometry, light scattering, fluorimetry, calorimetry, spectrophotometry, and nuclear magnetic resonance (NMR) spectroscopy (1). The most frequently used methods are tensiometry, fluorimetry, and spectrophotometry. When the

TABLE 1
Uses of Surfactants in Terms of the Range of Hydrophile–Lipophile Balance (HLB) Values^a

HLB ranges	Uses
3 – 6	Water-in-oil emulsions
7 – 9	Wetting agents
8 – 15	Oil-in-water emulsions
13 – 15	Detergents
15 – 18	Solubilizers

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values of the measured physical properties are plotted against concentration, there are usually breaks in the plots, which are considered as the CMC points for the surfactants under investigation. Plotting the derivatives of the values may also be a convenient way of precisely locating the CMC (5).

In this work, a detailed investigation of the spectral behavior of nonionic surfactant/iodine system has been made. The surfactants employed in this study include Tweens, Brijs, and Triton X-100 (TX-100). The spectral shifts of I_2 and the KI_3 complex in the surfactant solutions have been exploited to derive information on the CMC. The possible correlations among the CMC, HLB, and other useful physicochemical parameters, relevant to the systems, have been investigated. Although studies dealing with I_2 /nonionic surfactant systems have been reported in the literature (6–10), there has been only limited investigation of the determination of CMC by the method described here.

MATERIALS AND METHODS

The iodine used was the resublimed product of May and Baker Ltd. (Dagenham, England). The nonionic surfactants Tween-20, -40, -60, -80, and Triton X-100 were products of Sigma Chemical Co. (St. Louis, MO), Brij-35 and -56 of E. Merck (Darmstadt, Germany), and Brij-76 of Aldrich Chemical Co. (Milwaukee, WI). Triply distilled water was employed in the preparation of solutions.

Spectral measurements were taken with a temperature-compensated ultraviolet (UV)-visible recording spectrophotometer (UV-160A; Shimadzu, Kyoto, Japan) using a matched pair of quartz cells having a pathlength of 1 cm.

In one set of experiments, 2.5 mL of a saturated aqueous solution of iodine was placed in each of a number of stoppered and calibrated test tubes, and varying amounts of surfactant solution were added. The solutions were made up to a volume of 10 mL by adding water. Their spectra were recorded after temperature equilibration at 298 K, and the absorbances at 286, 346, and 460 nm were measured. The absorbance maximum (λ_{max}) of I_2 in each solution, which showed a blue shift from 460 nm with increasing concentration of the nonionic surfactant, was also measured.

In another set of experiments, 0.5 mL of 0.01 M KI_3 solution (prepared by adding KI to a saturated iodine solution) was placed in several graduated test tubes and the volume was brought to 10 mL by addition of both surfactant solution and water in requisite amounts. The absorbances of each solution at 286, 320, 346, and 460 nm were measured. All measurements were taken at a temperature of 298 ± 0.2 K.

RESULTS AND DISCUSSION

The critical micellar concentration. Figure 1 shows plots of absorbance at different wavelengths vs. surfactant concentration for TX-100 solutions containing both I_2 and KI_3 . The

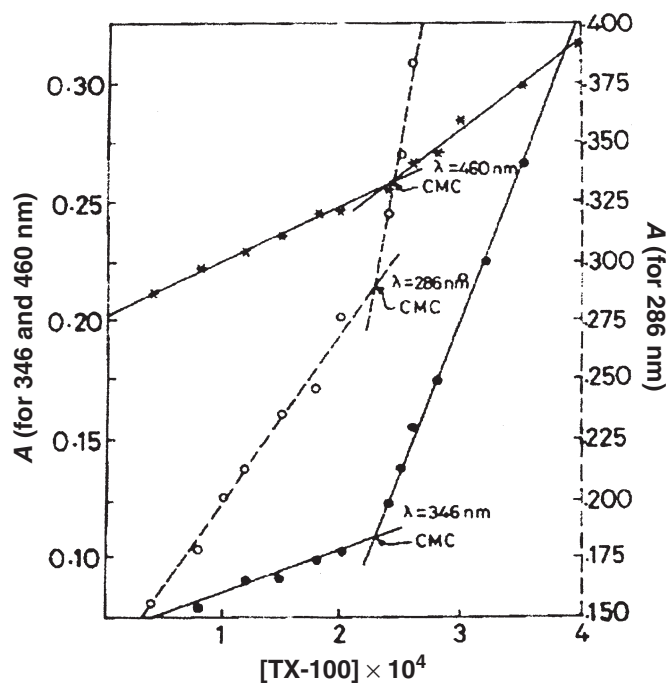


FIG. 1. Absorbance vs. concentration plot for Triton X-100 (TX-100) and I_2 (33.46×10^{-5} M) at 286, 346, and 460 nm at 298 K. The break in each plot is the critical micelle concentration (CMC) point.

containing both I_2 and KI_3 . It has similarity with the plots reported by Ross and Oliver (11).

A blue shift of the λ_{max} of I_2 from 460 nm was observed in nonionic surfactant medium. Fluorescence measurements in micellar media of certain dyes also show blue shifts (12). The observed blue shift is attributed to the ability of the ether oxygen of the POE groups in the surfactant molecules to donate electrons to the vacant σ^* orbital of I_2 (13), resulting in the formation of a surfactant-iodine donor-acceptor type complex. The extent of the blue shift depends on the nature of the nonionic surfactant. The spectra of I_2 between 300 and 600 nm in the absence and in the presence of TX-100 are presented in Figure 2. With increasing

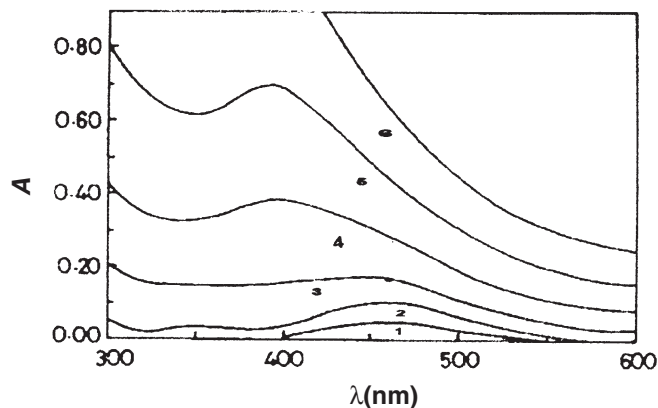


FIG. 2. Absorption spectra of TX-100 and I_2 (33.46×10^{-5} M) at 298 K. Curve 1 I_2 ; curves 2–4, [TX-100] = 5×10^{-5} , 10×10^{-5} , and 20×10^{-5} M, respectively (below CMC); curve 5, [TX-100] = 25×10^{-5} M (around CMC); curve 6, [TX-100] = 30×10^{-5} M (above CMC). See Figure 1 for

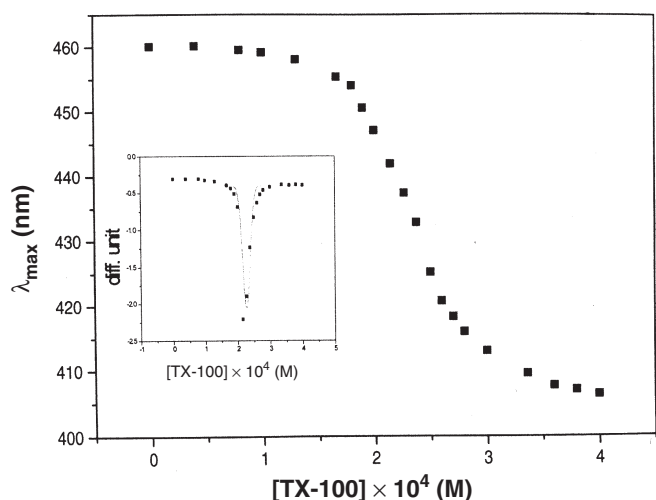


FIG. 3. Dependence of λ_{\max} of TX-100- I_2 system on [TX-100] at 298 K. Inset: Second degree differential plot of the variation of λ_{\max} with [TX-100]; Gaussian fit, showing the minimum as CMC. See Figure 1 for abbreviations.

concentration of TX-100, the 460-nm peak of I_2 is increasingly blue-shifted and the absorbance increases. A plot of λ_{\max} vs. surfactant concentration shows a sharp decline in the CMC region. When the derivative of a function consisting of two different linear segments is plotted, a step function is obtained. The second derivative (5) of the original function would show a positive or negative peak, the position of which corresponds to the intersection point of the two nearly linear segments of the original function. The estimation of the break, herein the CMC, thus becomes less ambiguous. The blue shift of the λ_{\max} of I_2 from 460 nm and the second-degree differential plots for TX-100 and Tween-20 are presented in Figures 3 and 4, respectively. The second-degree differential plots exhibit sharp minima at concentrations of 22.5×10^{-5} and 5.57×10^{-5} mol

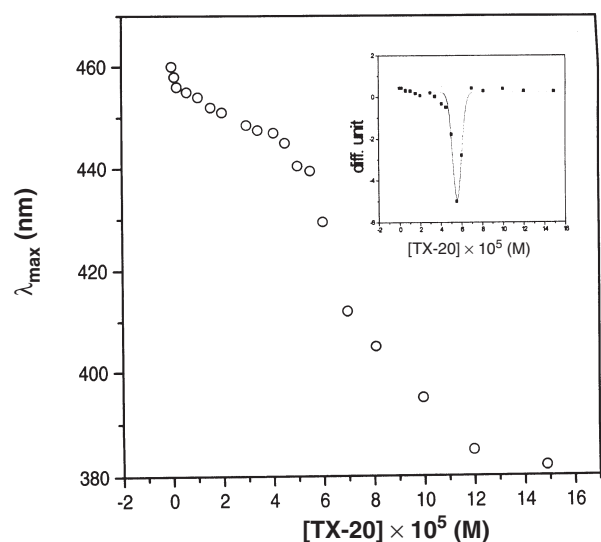


FIG. 4. Dependence of λ_{\max} of Tween-20- I_2 system on [Tween-20] at 298 K. Inset: Second degree differential plot of the variation of λ_{\max} with [Tween-20]; Gaussian fit, showing the minimum as CMC is shown

TABLE 2
Critical Micelle Concentration (CMC) of Nonionic Surfactants Obtained by Surface Tension (ST) and Spectral Measurements in the Presence of I_2 at 298 K

Surfactant	CMC $\times 10^5$ (mol dm $^{-3}$)		
	ST ^a	Absorbance ^b	Shift in λ_{\max} ^b
Tween 20	4.88	5.50	5.57
Tween 40	2.26	2.30	2.10
Tween 60	2.06	2.09	1.96
Tween 80	0.99	1.05	1.15
Brij 35	6.00	3.80	4.75
Brij 56	0.20	0.40	0.43
Brij 76	0.30	0.38	0.38
Triton X-100	24.0	24.0	22.5

^aReference 3.

^bThis study.

dm $^{-3}$ at 298 K for TX-100 and Tween-20, respectively. These minima are considered to correspond to the respective CMC. The CMC of the nonionic surfactants determined by spectral measurements of their interaction with I_2 are listed in Table 2, together with tensiometric literature data (6). The results obtained in this study closely agree with the data available in the literature.

The characteristic plots of absorbance (A) vs. [TX-100] at 286, 346, and 460 nm (Fig. 1) have crossing points at 23×10^{-5} , 23×10^{-5} , and 24×10^{-5} mol dm $^{-3}$, respectively. These CMC values agree nicely with the literature value of 24×10^{-5} mol dm $^{-3}$ (6). The spectra of I_2 at [TX-100] > CMC become symmetrical, with no further shift of λ_{\max} at 280 nm (Fig. 5). Plots of the absorbance of KI_3 at 286 and 346 nm against concentration of nonionic surfactants show distinct intersection points that are considered to correspond to their CMC. A representative plot is shown in Figure 6. The derivative plots to determine the CMC (inset, Figs. 3 and 4) are according to Zhao *et al.* (14).

Rationalization of spectral observations. The nonionic surfactants are referred to as iodophores or I_2 carriers and re-

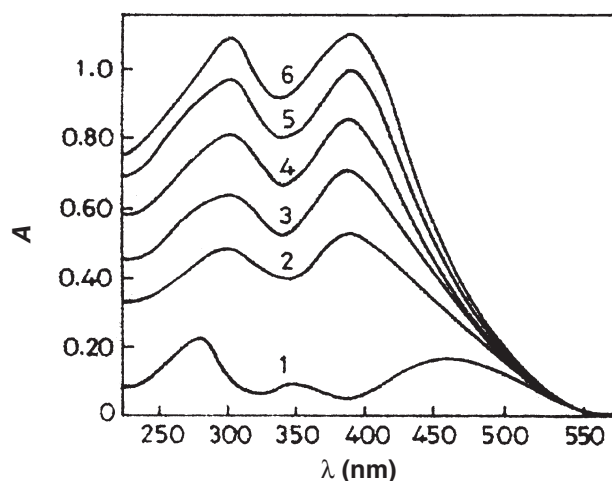


FIG. 5. Absorption spectra of TX-100 solutions treated with I_2 at 298 K. Curves 1–6 represent [TX-100] = 0.0, 50×10^{-5} , 75×10^{-5} , 100×10^{-5} , 125×10^{-5} , and 150×10^{-5} M, respectively. All the concentrations are

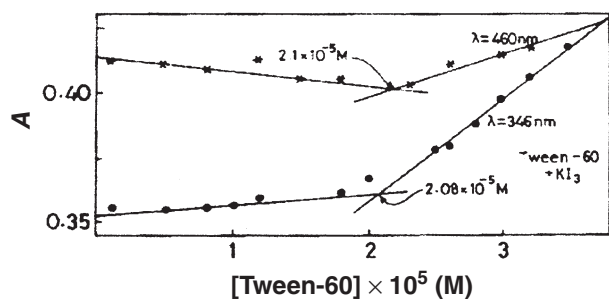


FIG. 6. Absorbance at 346 and 460 nm of Tween-60 and KI_3 ($19.7 \times 10^{-5} \text{ M}$) vs. [Tween 60] at 298 K. The break points in each plot are the CMC point. See Figure 1 for abbreviation.

tain their surfactant properties when complexed with I_2 . The nature of the nonionic surfactant–iodine bond is not completely understood. Complexation by POE oxygen has been considered to be a plausible mechanism (15–18), which is supported by the failure of solvents such as CCl_4 to extract I_2 from the complex. In solution, the dissolved I_2 is in equilibrium with I_2 in micelles or I_2 -micelle complexes. An NMR study in CCl_4 provided evidence that a donor–acceptor type complex is formed between TX-100 and I_2 (19). In a nonaqueous medium such as CCl_4 , a charge-transfer type complex between TX-100 and I_2 has been reported (13). A distinct isosbestic point corresponding to the formation of a 1:1 complex was observed. Such complexes with the ether oxygen as electron donor and I_2 as electron acceptor are also formed by other nonionic surfactants. In our laboratory, a solid donor–acceptor complex between Brij –35 and I_2 has been isolated and spectroscopically characterized. The results of this work are not presented for here because they are not in line with the objectives of this paper.

CMC, HLB, and $\Delta\lambda$ data correlation. The general formulas of the nonionic surfactants of the Tween, Span, Brij, and TX-series are presented in Figure 7. It has been shown (6) that the weight fraction (W) of POE groups in the molecule is directly proportional to the HLB of nonionic surfactants. We have found that the following relationship holds:

$$\frac{\text{HLB}}{W} \approx 20.00 \quad [2]$$

where W is given by the relation (3)

$$W = \frac{44R}{44R + M_1} = \frac{44R}{M_0} \quad [3]$$

where M_1 , M_0 , and R are, respectively, the molecular weight of the lipophilic moiety, the molecular weight of the surfactant, and the polyoxyethylene mole ratio in the molecule. On the basis of this rationale, the HLB value of Myrj 59 is 18.8. We have observed that, for the nonionic surfactants, plots of $\ln C_0$ (where C_0 is the CMC of the surfactant, in units of $\text{g/dL} \times 10^4$) vs. HLB are linear,

$$\ln C_0 = A + B(\text{HLB}) \quad [4]$$

When the CMC values are in units of mole dm^{-3} , similar lin-

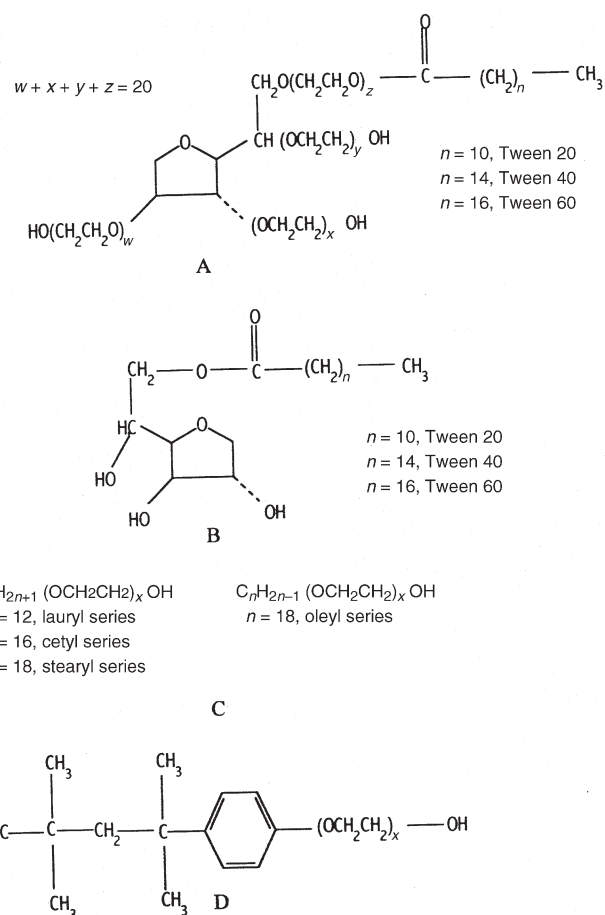


FIG. 7. Structural formulas of nonionic surfactants: A, Tween; B, Span; C, Brij; D, Triton X.

the constants A and B. The values of W , HLB, HLB/W , and CMC for four series of nonionic surfactants are presented in Table 3. The values of the constants A and B are given in Table 4. The maximum HLB value of nonionic surfactants is 20 (3). The results in Table 3 show that all the HLB/W values are also around 20 except in the case of Tweens, for which the average value is 23. The W value of a nonionic surfactant is therefore related to its HLB. Low values of HLB, as in the case of Triton X-15 and Triton X-35, correspond to low values of W . Values of HLB close to 20 correspond to values of W close to unity.

By using the above relation, the CMC of the nonionic surfactants can be predicted. Thus, the CMC of Triton X-15, Triton X-35, and Triton X-705 at 298 K [not available in the literature (20)] are predicted to be 0.015, 0.048, and 1.04 mM, respectively. In Table 3, the CMC values normally unavailable in the literature are enclosed in parentheses. We are not aware of any report of the self-aggregation behavior of Myrjs in aqueous solution except for that of Sultana *et al.* (21) on Myrj 45. The CMC at 298 K obtained by extrapolation of the results at different temperatures reported by Sultana *et al.* (21) is presented in Table 3. Because CMC values for one or two other Myrjs are not available, evaluation of CMC values for Myrjs using Equation 4 has not been possible. Because Spans have a sorbitan head group,

TABLE 3
Physicochemical Parameters of Nonionic Surfactant Series

Chemical name ^b	Trade name	Molecular weight	W	HLB	HLB/W	CMC ^a (mM)
Tween series						
POE(20) sorbitan monolaurate	Tween 20	1227.54	0.7168	16.7	23.29	0.050
POE(20) sorbitan monopalmitate	Tween 40	1283.65	0.6855	15.6	22.75	0.023
POE(20) sorbitan monostearate	Tween 60	1311.70	0.6708	14.9	22.21	0.021
POE(20) sorbitan monooleate	Tween 80	1309.68	0.6719	15.0	22.32	0.010
POE(20) sorbitan tristearate	Tween 65	1899.54	0.4632	10.5	22.66	(0.00018)
POE(20) sorbitan trioleate	Tween 85	1838.60	0.4786	11.0	22.98	(0.00029)
Myrj series						
POE(8) stearate	Myrj 45	635	0.5543	11.1	20.024	0.373
POE(40) stearate	Myrj 52	2043	0.8614	16.9	19.617	
POE(50) stearate	Myrj 53	2483	0.8860	17.9	20.202	
POE(100) stearate	Myrj 59	4683	0.9395	18.8	20.011	
Triton X (TX) series						
<i>p</i> -t-O-P-POE(1)E	TX-15	250	0.1761	3.6	20.45	(0.0145)
<i>p</i> -t-O-P-POE(3)E	TX-35	338	0.3905	7.8	19.97	(0.047)
<i>p</i> -t-O-P-POE(5)E	TX-45	426	0.5164	10.4	20.14	0.100
<i>p</i> -t-O-P-POE(7.5)E	TX-114	536	0.6156	12.4	20.14	0.168
<i>p</i> -t-O-P-POE(9.5)E	TX-100	625	0.6688	13.5	20.19	0.240
<i>p</i> -t-O-P-POE(12.5)E	TX-102	756	0.7275	14.6	20.06	0.350
<i>p</i> -t-O-P-POE(16)E	TX-165	910	0.7736	15.8	20.42	0.439
<i>p</i> -t-O-P-POE(30)E	TX-305	1526	0.8650	17.3	20.00	0.720
<i>p</i> -t-O-P-POE(40)E	TX-405	1966	0.8952	17.9	20.00	0.810
<i>p</i> -t-O-P-POE(70)E	TX-705	3286	0.9373	18.7	19.95	(1.0413)
Brij series						
POE(4) lauryl ether	Brij 30	362	0.4862	9.7	19.95	0.004
POE(23) lauryl ether	Brij 35	1198	0.8447	16.9	20.01	0.060
POE(2) cetyl ether	Brij 52	330	0.2666	5.3	19.88	(0.000067)
POE(10) cetyl ether	Brij 56	682	0.6452	12.9	20.00	0.002
POE(20) cetyl ether	Brij 58	1120	0.7857	15.7	19.98	0.007
POE(2) stearyl ether	Brij 72	358	0.2458	4.9	19.93	(0.00025)
POE(10) stearyl ether	Brij 76	710	0.6197	12.4	20.01	0.003
POE(20) stearyl ether	Brij 78	1096	0.8029	15.3	19.01	(0.0057)
POE(2) oleyl ether	Brij 92	356	0.2472	4.9	19.82	(24.845)
POE(10) oleyl ether	Brij 97	710	0.6197	12.4	20.01	0.940
POE(20) oleyl ether	Brij 99	1094	0.8043	15.3	19.02	0.265
POE(100) stearyl ether	Brij 700	4670	0.9421	18.8	19.95	0.020
POE(21) stearyl ether	Brij 721	1194	0.7738	15.5	20.03	0.0039

^aCMC at 298 K; values in parentheses are normally unavailable in the literature.

^bPOE, polyoxyethylene; *p*-t-O-P-POE(*x*)E = *p*-tert-octyl phenoxy polyoxy(*x*) ether; where *x* is the number of POE groups. W, weight fraction; for other abbreviations see Tables 1 and 2.

tion in Equation 2 is not applicable to them. They have very low solubility in water and do not form normal micelles. Consequently, the parameters *W* and HLB/*W* are not meaningful in their case.

The CMC values of nonionic surfactants depend on the length of both the lipophilic and hydrophilic parts of their

molecules. The CMC decreases with increasing length of the hydrophobic moiety for a fixed hydrophilic group. The CMC of nonionic surfactant decreases with decreasing POE content in the molecule. These results may be correlated by plotting $\ln \Delta\lambda$ vs. HLB, where $\Delta\lambda$ is the shift in the λ_{\max} of I_2 in the surfactant solution in the CMC region for the different surfactant series. Thus,

$$\ln \Delta\lambda = C + D \ln (\text{HLB}) \quad [5]$$

where *C* and *D* values are appropriate constants given in Table 5. The plots of $\ln \Delta\lambda$ vs. \ln HLB are shown in Figure 8.

In a nonionic surfactant series, the number of carbon atoms in the lyophilic and lyophobic parts of the molecule may essentially control its physicochemical nature, which is reflected in the spectral behavior of the complex with I_2 . A relation of the form

TABLE 4
The Values of the Constants A and B in Equation 4 for the Tween, Brij, and Triton X Series at 298 K

Series	A	B	<i>r</i> ^a
Tween	-10.49	0.88	0.9804
Brij (lauryl)	-14.10	0.54	0.9990
Brij (cetyl)	-16.96	0.625	0.9990
Brij (xtearyl)	-16.18	0.59	0.9528
Brij (oleyl)	0.86	-0.29	0.9990
Triton X	-10.65	0.48	0.9945

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