Determination of the Critical Micelle Concentration of Surfactants and the Partition Coefficient of an Electrochemical Probe by Using Cyclic Voltammetry

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A novel electrochemical technique, viz., cyclic voltammetry, is proposed for determination of the critical micelle concentration (cmc) of various surfactants in aqueous solution with Pt as both working electrode and counterelectrode and a saturated calomel reference electrode. The redox-active electrochemical probe and supporting electrolyte used were $K_4Fe(CN)_6$ and KCl, respectively. The cmc values so obtained (SDS, 8.0×10^{-3} M; Triton X-100, 3.0×10^{-4} M; Tween-80, 2.2×10^{-5} g/mL) were found to be in good agreement with the literature values (SDS, 8.27×10^{-3} M; Triton X-100, 2.8×10^{-4} M; Tween-80, 2.0×10^{-5} g/mL). The peak current, i_p, of each solution was measured, and the partition coefficient, K, of the electrochemical probe between water and surfactants in nonmicellar and micellar states was estimated. The results suggest that the probe is sensitive to the surfactant concentration and can reflect the changes taking place within the structure of the micellar species.

Introduction

Amphiphilic surfactants form micelles at a certain concentration range called the critical micelle concentration (cmc).[1,2] The micelle has important applications in industrial[3] and biological systems.[4] There are several techniques for the determination of the cmc.[2] Some of these methods depend upon the fact that spectroscopic properties of some dyes are altered upon their interaction with micelles as a result of adsorption of the dye to the micellar surface or its incorporation within the relatively apolar micellar interior. Although these spectroscopic methods are easily accessible and rapidly performed, they are not always very exact. The inexactness is a severe problem if a relatively large number of dye molecules must interact with a single micelle to give a detectable signal, as in the case of absorption measurements[2] or measurements involving the formation of excimers and exciplex. Methods based on the increase or decrease of the emission quantum yield of a luminescent dye,[5,6] on the other hand, require the dye–micellar molar ratio to be $\ll 1$.

Metal surfaces in contact with electrolytic solutions tend to adsorb a mixture of species derived from the solvent, supporting electrolyte, and redox-active material.[7] In this paper, we report the results of an attempt to assess the utility of cyclic voltammetry for the determination of the critical micelle concentration of surfactants in aqueous solution. The technique is novel in the sense that it is used to detect exact cmc of surfactants. The surfactants chosen for the study viz., *p*-(*tert*-alkyl)phenoxy poly(oxyethylene) ether (Triton X-100), decaglycerol dioleate (DGD), poly(oxyethylene) sorbitan monooleate (Tween-80), and sodium dodecyl sulfate (SDS), are known to exhibit different molecular structures and aqueous dispersibility.

Experimental Section

Materials. For the grade, purity, and characteristics of the surfactants, refer to our earlier works.[8] Triton X-100 was a pure grade material of Fluka, and the head group of this on the average contained 9.5 oxyethylene units. Tween-80 was a pure grade material of Sigma, containing an average of 20 oxyethylene units. DGD was also a pure grade material of Sigma. $K_4Fe(CN)_6$ and KCl were BDH analar grade. Doubly distilled conductivity water of specific conductance, $(2–3) \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 25 °C, was used as the solvent media throughout the experiment.

Methods. Spectral measurements were made on a Shimadzu spectrophotometer (Model UV-260) using silica cells of 1-cm path length. Spectrophotometric determination of the cmc of DGD was performed by recording its spectra and plotting the absorbance at 287 nm against the concentration of DGD (cf. Figure 1).

In the electrochemical measurements, the solutions were deoxygenated with bubbling nitrogen for at least 10 min. A three-way stopcock permitted pure nitrogen gas to flow over the solution after completion of the deoxygenation process and during the time required for the measurements, thereby preventing oxygen redissolution in the system. A prebubbler containing water was used to minimize compositional changes. The electrochemical measurements were performed by using a cyclic voltammeter (Princeton Applied Research, Model 173 with a PARC Model 175 universal programmer) and a three-compartment electrolytic cell. A saturated calomel reference (SCE) electrode was employed in this study, and all potentials that are quoted are with respect to the SCE. The working electrode was Pt with a Pt counterelectrode. The area of the working electrode is 0.0032 cm². In the electrochemical measurements the potential sweep speed was 100 mV/s. Generally, a 2.5×10^{-2} M $K_4Fe(CN)_6$ solution (fixed) and a 0.5 M KCl (fixed) with varying concentration of surfactants were used. The cleaned electrode was mounted in the cell, and an oxidation–reduction cycle (ORC) was applied to the Pt electrode with a double potential step: −0.1 to +0.4 to −0.1 V. For the determination of the cmc of surfactants by cyclic voltammetry, a series of solutions was prepared at a definite concentration of the redox-active material and supporting electrolyte (2.5×10^{-2} M $K_4Fe(CN)_6$ and 0.5 M KCl); the concentrations of the surfactants were varied. The peak current, i_p, of each solution was measured and plotted against the concentration of surfactant. The abrupt changes in the values of the initial slopes were considered as the cmc points.

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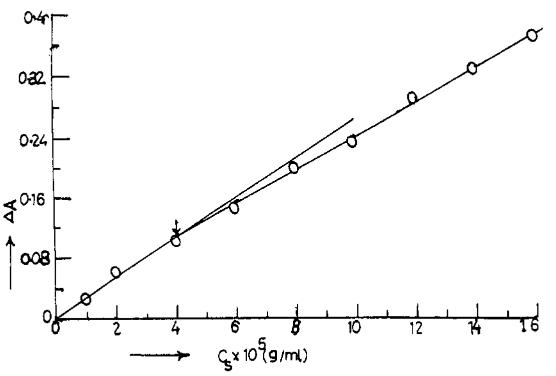

Figure 1. Plot of absorbance vs concentration of DGD in aqueous solution at 287 nm. Temperature = 25 °C.

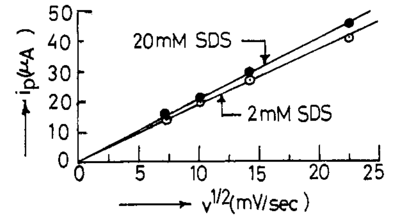

Figure 2. Plot of peak current, i_p, vs square root of sweep rate, $v^{1/2}$, in SDS environment at 25 °C: open circle, 2 mM SDS; closed circle, 20 mM SDS. [$K_4Fe(CN)_6$] = 2.5×10^{-2} M (fixed); [KCl] = 0.5 M (fixed).

The viscosity of the $K_4Fe(CN)_6$ solution (2.5×10^{-2} M, fixed) at various surfactant concentrations was measured by an Ostwald viscometer at 25 °C using 0.5 M KCl as the solvent media. The viscometer was calibrated with 10% and 20% sucrose solution in water, and the results are in good agreement with the values available in the literature. The viscometer gives a flow time of 240 s for water at 25 °C. The temperature of measurement was accurate within ±0.1 °C. Uncertainties in temperature density measurement and the flow detection imparted a maximum error of ±0.7% to the measured viscosity. Details of viscosity measurements are furnished in our earlier publications.[9-11]

Results and Discussion

In cyclic voltammetry the peak current i_p (μA) for a reversible system is given by the following equation:[12]

$$i_p = \frac{0.447F^{3/2}An^{3/2}D^{1/2}Cv^{1/2}}{R^{1/2}T^{1/2}} \qquad (1)$$

where n is the number of electrons involved in oxidation or reduction, A is the area of the electrode (cm^2), D is the diffusion coefficient of the electroactive species (cm^2 s^{-1}), C is the concentration of electroactive species in the solution (mol L^{-1}), v is the sweep rate (V s^{-1}), F is the Faraday constant, R is the gas constant, and T is the absolute temperature.

However, for linear diffusion where a species in solution is reduced or oxidized to a species in solution at 25 °C, eq 1 can be written as

$$i_p = 2.687 \times 10^5 n^{3/2}AD^{1/2}Cv^{1/2} \qquad (2)$$

With micellar systems involving an electrochemical probe completely solubilized in the micelles, the diffusion coefficient D in eq 2 would correspond to the micelle diffusion coefficient D_m since the probe diffuses with the micelle, whereas C would still be the probe concentration. The diffusion-controlled nature of the peak current was verified by performing the experiments at various scan rates in micellar environments (Figure 2). In the case where the probe is distributed between micelles and bulk, it can be readily shown that

$$D^{1/2} = \frac{i_p}{2.687 \times 10^5 n^{3/2}ACv^{1/2}} = \frac{D_m^{1/2}K(C_s - \text{cmc}) + D_p^{1/2}}{1 + K(C_s - \text{cmc})} \qquad (3)$$

where D is the experimental value of the apparent diffusion coefficient of the partitioned probe in the micellar system, D_p the probe diffusion coefficient in the bulk, K the partition coefficient of the probe between micelle and bulk, and C_s the surfactant concentration. Equation 3 assumes that the peak currents due to the free probe and micellized probe are independent. Equations 2 and 3 predict that i_p will increase linearly with the probe concentration whether the probe is partitioned or not. Regarding details in utilizing eq 3, we refer to a recent publication, ref 13. Squaring and rearranging eq 3, we can write

$$(D - D_m)\Delta C^2K^2 + (D - D_m^{1/2}D_p^{1/2})2\Delta CK + D = 0 \qquad (4)$$

where $\Delta C = C_s - \text{cmc}$. After the quadratic eq 4 was solved, the K value was readily calculated.

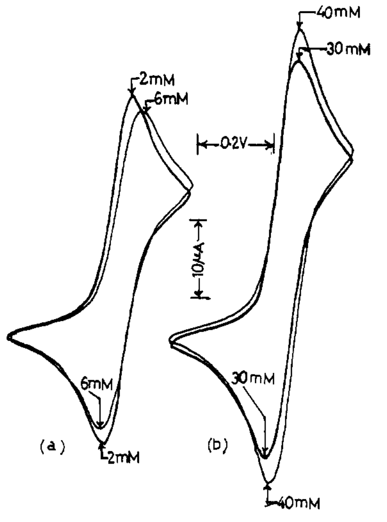

Figure 3. Cyclic voltammogram of $K_4Fe(CN)_6$ solution (2.5×10^{-2} M, fixed) in various concentrations of SDS at 25 °C: (a) below cmc of SDS; (b) above cmc of SDS. [KCl] = 0.5 M (fixed); sweep rate = 100 mV/s.

Figure 3 shows some typical cyclic voltammetric curves (i_t vs the voltage E between the working electrode and SCE) for various concentrations of SDS solutions (below and above its cmc) with the $K_4Fe(CN)_6$ probe and KCl supporting electrolyte. Similar ORC curves were obtained for a variety of nonionic surfactants also.

We have also attempted to get ORC curves for the cationic surfactant cetyltrimethylammonium bromide (CTAB) by using the $K_4Fe(CN)_6$ probe. For CTAB, however, the peak current was found to be extremely small, and the results suggest that the anionic probe used in this work is no longer accessible to the electrons once they are incorporated into CTAB micelles, which results in the observed effect of obtaining precipitation due to the interaction between oppositely charged ions. An electroac-

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Table I. Critical Micelle Concentrations[a]

surfactant	cmc this work	 lit value	ref
SDS	8.0×10^{-3} M	8.27×10^{-3} M	2, 16
Triton X-100	3.0×10^{-4} M	2.8×10^{-4} M	16
Tween-80	2.2×10^{-5} g/mL	2.0×10^{-5} g/mL	8, 15
DGD	3.0×10^{-5} g/mL	4.0×10^{-5} g/mL	this work

[a] $K_4Fe(CN)_6$ was used as a probe.

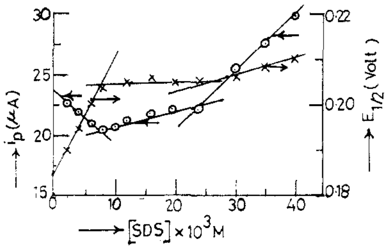

Figure 4. Plot of i_p and $E_{1/2}$ vs concentration of SDS. [$K_4Fe(CN)_6$] = 2.5×10^{-2} M (fixed); [KCl] = 0.5 M (fixed); temperature = 25 °C.

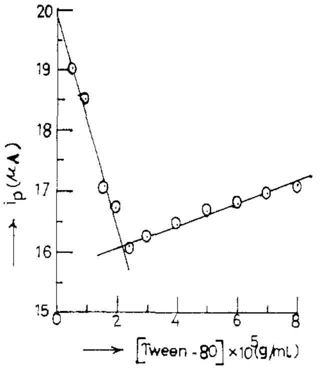

Figure 5. Plot of i_p vs concentration of Tween-80. [$K_4Fe(CN)_6$] = 2.5×10^{-2} M (fixed); [KCl] = 0.5 M (fixed); temperature = 25 °C.

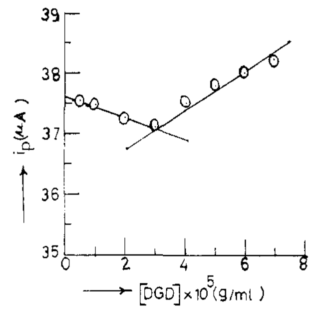

Figure 6. Plot of i_p vs concentration of DGD. [$K_4Fe(CN)_6$] = 2.5×10^{-2} M (fixed); [KCl] = 0.5 M (fixed); temperature = 25 °C.

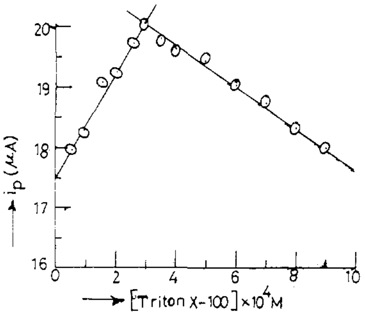

Figure 7. Plot of i_p vs concentration of Triton X-100. [$K_4Fe(CN)_6$] = 2.5×10^{-2} M (fixed); [KCl] = 0.5 M (fixed); temperature = 25 °C.

tive cationic or neutral probe should be used for CTAB and other cationic surfactants as suggested recently by Zana and Mackay.[13]

As is to be expected from eq 2, i_p increases linearly with the probe concentration C in the whole concentration range. Such a proportionality between i_p and C has been observed for all the surfactants investigated. Although at the highest probe concentration employed the [probe]/[micelle] molar concentration ratio was greater than 1, it does not affect the absolute cmc values of the surfactants. The cmc values determined by this CV method are in good agreement with the literature values as depicted in Table I.

The results of Figure 4 show the changes of i_p and $E_{1/2}$ upon increasing surfactant concentration C_s at constant C, in 0.5 M KCl. $E_{1/2}$ becomes increasingly positive, whereas i_p shows a very large decrease as C_s increases, and this is valid up to the cmc of SDS; beyond cmc the increase of i_p with the increase of C_s was observed (see Figure 4). Again, these changes are predictable from eq 3. It is also seen from Figure 4 that there are two breaks in the i_p vs C_s plot (or $E_{1/2}$ vs C_s plot) which correspond to the first and second cmc of SDS. That means primary micelles of SDS can aggregate to form secondary micelles.[14]

Like SDS, the sharp decrease of i_p with the increase of C_s was observed in the case of Tween-80 and DGD up to their respective cmc, whereas above their cmc increase of i_p with the increase of C_s (see Figures 5 and 6) was obtained. However, in the case of Triton X-100, the completely opposite trend of i_p vs C_s was observed (see Figure 7). Basically, Triton X-100 is a polydisperse nonionic surfactant with homogeneous character in the Poisson–Boltzmann distribution, and it differs from those of Tween-80 and DGD. Although Tween-80 and DGD are nonionic surfactants, both of them are heterodisperse[15] in character.

According to Zana and Mackay,[13] when $C \gg C_s$, K becomes a function of C and decreases as C increases, at constant C_s. We have found that K is also a function of surfactant concentration and decreases as C_s increases, at constant C. Because of this reason, the K values at below and above cmc regions, namely, K_b and K_m, were calculated. The calculated K values for the surfactants investigated are depicted in Table II. According to Zana and Mackay,[13] for cationic surfactants, as C_s increases, more and more probe is solubilized in the micelles because of the mixed micelle formation by two cationic surfactants of differing chain length, namely, the probe and the investigated surfactant. However, in our present case of anionic and nonionic surfactants, as C_s increases the anionic probe is less solubilized in the micelles. It is seen from Table II that the K_b values are always greater than that of K_m for the investigated surfactants. It is interesting to note that for the second cmc region of SDS the value of K_m is negative, which indicates that at that concentration range our electrochemical probe is hardly solubilized in the SDS micelles. In fact, at concentrations much above the second cmc, some turbidity (with precipitate) was observed. Becausae of this complicated behavior we were not able to get the suitable CV at high concentration of

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Table II. Diffusion Coefficient of the Micelles, D_m, and Partition Coefficient of the Electrochemical Probe between Surfactant and Water in Bulk (K_b) and Micellar Phases (K_m)[a]

$D_m \times 10^6$, cm^2 s^{-1}			K of surfactants, M^{-1} [f]						
			SDS[e]			Triton X-100		Tween-80	
SDS[b]	Triton X-100[c]	Tween-80[d]	K_b	$K_m^{(1)}$	$K_m^{(2)}$	K_b	K_m	K_b	K_m
1.2	0.62	0.678	500 ± 250	5 ± 3	−8 ± 4	698 ± 40	185 ± 88	5190 ± 460	3607 ± 197

[a] Diffusion coefficient of the probe, $D_p = 11.83 \times 10^{-6}$ cm^{-} s^{-1}. Temperature is 25 °C. [b] Diffusion coefficient of SDS micelle was taken after extrapolating to its zero concentration of NaCl (Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1976**, *80*, 1075. [c] Reference 9. [d] Reference 10. [e] $K_m^{(1)}$ and $K_m^{(2)}$ are the partition coefficients of the probe in SDS at its first and second cmc region. [f] In computing the K values, viscosity or other contributing effects were not taken into account.

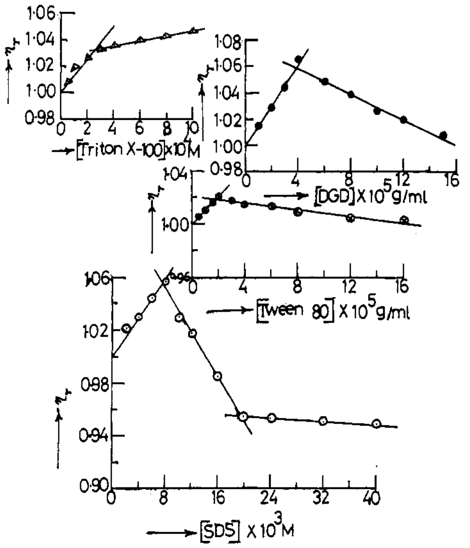

Figure 8. Plot of relative viscosity, η_γ, vs concentration of surfactants at 25 °C. Solution: $K_4Fe(CN)_6$ (2.5×10^{-2} M, fixed) + KCl (0.5 M, fixed) + surfactant (variable). Solvent media is 0.5 M KCl in water: open circle, SDS; crossed circle, Tween-80; closed circle, DGD; triangle, Triton X-100.

SDS (results were rather unreliable due to phase separation). As seen from the K_m values of different surfactants, the probe is practically insoluble in SDS micelles, whereas in the case of Triton X-100 and Tween-80 the probe has some solubility in the respective micelles, even though this solubility is far less compared to its solubility in the bulk. Since D_m is used to calculate the partition coefficient of the probe below its cmc (K_b), the values may not be very accurate. Nevertheless, it shows the trend of solubility of the probe in the bulk and the micellar phase.

It may be possible that $E_{1/2}$ is also being affected by surfactant adsorption on the electrode. In Figure 4, since the SDS surfactant is negatively charged it might be expected that the adsorption increases with increasing positive potential. For SDS, the cmc values determined by i_p vs C_s and $E_{1/2}$ vs C_s are the same. Therefore, it should be emphasized that the process of adsorption does not affect the value of i_p, and thus the values of D are less likely to be affected. The adsorption behavior could be controlled by the cmc, e.g., hemimicelle formation on the electrode surface above the cmc. However, a more likely explanation is that the viscosity of the solution, and thus the diffusion coefficient (and thus i_p), is what is being followed. The viscosity profile of all the surfactants studied (Figure 8) matches with their respective peak current profile except in the case of Triton X-100. Even in the case of Triton X-100, above its cmc, the viscosity profile matches with the peak current profile. The odd behavior of Triton X-100 when compared to Tween-80, which is also a nonionic surfactant, may be due to the difference in their hydrodynamic radius. According to the Stoke–Einstein equation, the diffusion coefficient is inversely proportional to the hydrodynamic radius, R_h. The R_h values[9,10] for Triton X-100 and Tween-80 at 25 °C is 39.62 Å and 31.21 Å, respectively. In other words, Triton X-100 micelles give more obstruction toward transportation of electroactive probe as compared to Tween-80 micelles. In order to identify and quantify other factors influencing the partition coefficient values, work with other electroactive probes is being carried out.

Conclusions

The results reported in this paper show that cyclic voltammetry can be used to investigate the diffusion of various electroactive species in a micellar solution. It is also one of the novel techniques for the determination of the critical micelle concentration of the surfactants. This method is sensitive to the probe partition between bulk and the micelles. The results of decrease or increase of peak current with increasing surfactant concentration as observed depend on the nature of the surfactant used in the experiment. Like polarography, it is noteworthy that this CV method is less sophisticated and generally less time consuming than other techniques presently used to measure micelle diffusion and represents an additional complementary and readily available technique.

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