Critical Micelle Concentration of Lauric Acid-Diethanolamine Condensate by Polarographic and Spectrophotometric Methods: A Comparative Study

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Abstract

The critical micelle concentration (cmc) values of surfactants obtained by different physical methods do not show any concordance especially in cases when determinations are made in presence of electrolytes. With lauric acid-diethanolamine condensate, the behavior is altogether different.

A comparison of the spectrophotometric and polarographic determinations, with and without the presence of extraneous electrolytes reveals that the cmc values in both cases are almost similar. The results indicate that the cmc values of nonionic surfactants are not affected by acids, bases and salts when added in low concentrations.

Introduction

NONIONIC SURFACTANTS of the fatty acid-diethanolamine condensate type, particularly lauric acid-diethanolamine condensate, have found wide application in detergent formulations and cosmetics as foam builders (1) for alkylaryl sulfonates, lime soap dispersing agents (2), softening agents (3), and principal ingredients in shampoos for controlling the viscosity, elasticity and stability of the fluid (4). These compounds also find use in industry and technology for the preparation of agricultural emulsions and textile treating compounds (5) and flotation materials (6). The mixtures of lauric acid-diethanol amine condensate with alkylaryl benzene sulfonates also find use in the preparation of liquid household washing compositions (7). In contrast to ionic surfactants, these compounds are indifferent to hard water and to salts, acids and bases (8).

From the purely physicochemical viewpoint, we have shown that the lauric acid-diethanolamine condensate (LDC) can be usefully employed as a suppressor of polarographic maxima (12) of difficult suppressable metal and complex ions with much smaller amounts of LDC than anionic or cationic surfactants.

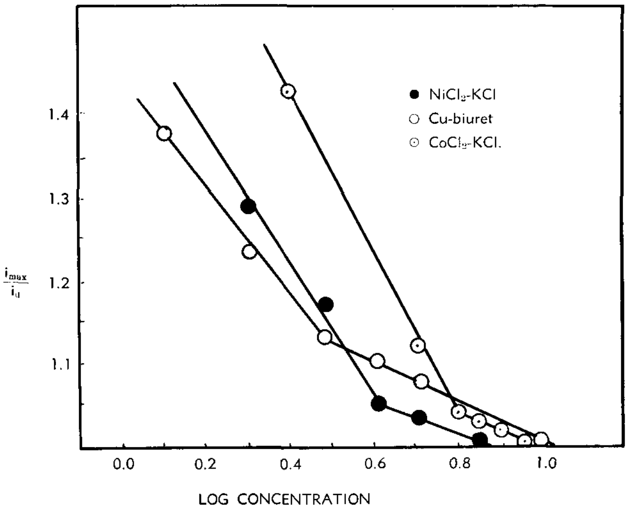

FIG. 1. Plots between log conc. and 'maximum/'diffusion current.

Another interesting aspect of the study on nonionic surfactants can be the determination of critical micelle concentration (cmc) of the surfactants as such and in the presence of extraneous electrolytes. Since nonionic surfactants should be less susceptible to the effect of the foreign ions, there should not be much difference in the cmc values obtained with and without the electrolytes. That is, the cmc values of LDC obtained by the polarographic method in different supportnig electrolytes (used in polarographic reduction) should be comparable among themselves and with the values obtaind by the spectrophotometric method. The work described in this paper was done with this object in view.

Experimental

Materials

LDC (9) was prepared by condensing pure lauric acid (BDH) with diethanolamine. AR and "chemically pure" reagents were used in all the preparations. Biuret (10) and succinamide (11) were also prepared in the laboratory. Double distilled water (all glass) was used in preparing the solutions.

Apparatus and Procedure

The polarographic apparatus and procedure used in this investigation are described in detail elsewhere (12). All the measurements were carried out at 25C ± 0.1C in a thermostated water bath. A Beckman pH meter model H was used for all pH measurements.

The polarographic micelle concentration (pmp) (13) obtained by plotting $i_{maximum}/i_{diffusion}$ vs. log concentration of LDC and taking the point where first sharp discontinuity appears and the maximum suppression point (MSP) (14) obtained by plotting $i_{maximum}/i_{diffusion}$ vs. log concentration of LDC and extrapolating to unity are shown in Figure 1.

For determining cmc by the iodine solubilization method of Ross and Olivier (15), absorption measurements were made by a Bausch and Lomb Spectronic-20.

The stock solution of iodine (A) was prepared of concentration 10^{-3} M. The stock solution of the nonionic surfactant (B) whose cmc was to be determined, contained a known concentration 10^{-3} M) of the surfactant well above its cmc. By diluting the solution (B) with solution (A), a wide range of concentrations of surfactant could be obtained containing a fixed concentration of iodine. The mixture thus comprised solutions of concentration above and below the cmc to be determined. The spectrophotometer readings are best made with solution A as the standard for 100% transmittance, although the pure solvent (distilled water) could be used.

The spectrophotometric measurements were made at a wavelength of 360 mμ (iodine-micelle complex

TABLE I

Comparative Values (Order 10^{-5}M) of MSP and PMP for LDC, SPSA, STSA and SXSA

Ions or complexes	pH	LDC		SPSA		STSA		SXSA	
		MSP	PMP	MSP	PMP	MSP	PMP	MSP	PMP
Pb^{+2} in KNO_3	5.15	1.99	1.00	17.38	9.80	5.62	2.18	3.80	1.29
Co^{+2} in KCl	2.95	8.99	5.99	17.38	4.90	120.20	34.67	83.18	10.47
Ni^{+2} in KCl	4.92	6.99	3.98	43.65	8.20	50.12	48.98	50.12	36.31
$Co^{+2}Ni^{+2}$ in pyridine	......	175.00	100.00	363.10	121.00	20.89	4.89	20.89	4.78
CdI_2 —KI complex	6.03	9.26	2.50	169.80	12.10	15.85	7.94	15.85	5.37
Cu-Glycinate	10.50	9.12	2.00	16.80	4.90	5.11	4.26	5.11	3.98
Cu-biuret	12.04	9.80	3.00	83.30	13.20	12.02	2.39	2.81	1.95
Cu-succinimide	11.50	12.50	4.99	....	....	....	....	....	....

LDC = Lauric acid —diethanol amine condensate.
SPSA = Sulfonated phenyl stearic acid.
STSA = Sulfonated tolyl stearic acid.
SXSA =Sulfonated xylyl stearic acid.

maximum). It was always found important to take the reading within an hour of the preparation of solutions, because of a slow fading of the color of iodine-micelle complex.

Results and Discussion

The results of the polarographic micelle concentration (pmp) and the maximum suppression point (MSP) values of LDC are given in Table I (Fig. 1).

The MSP values are almost of the same order (10^{-5}M) except for the Ni^{+2} $-Co^{+2}$ mixture in pyridine where a very high concentration of the LDC (10^{-4}M) is required to suppress the polarographic maxima. A similar discrepancy is observed in the case of PMP values for the Ni^{+2} $-Co^{+2}$ mixture in pyridine, otherwise the PMP values for other ions lie in the same concentration range, viz., 10^{-5}M. Although the order of the MSP and PMP values in the presence of different supporting electrolytes is $Cl^- > I^- > NO_3^-$, the values do not differ much from each other as observed in the case of ionic surfactants (Table I). Our results are in agreement with those of Hsiao and co-workers (16) and also of Schick (17) on polyoxyethylated nonionic compounds who showed that the cmc values of ionic surface active agents are lowered to a greater extent in presence of electrolytes than that of nonionic compounds.

The PMP values obtained in the higher pH range (pH 12.00) in the case of the polarograms for copper biuret and copper succinamide complexes also do not exhibit any appreciable deviation from the values obtained in the lower pH range (the pH in presence of the salts used as supporting electrolytes are in the range of pH 2.92 – 6.03). It may thus be concluded that like the salts, the pH also does not affect the cmc values of LDC. On the other hand, there is a large effect of pH on the PMP values in the case of ionic surface active agents (Table I).

Malik and co-workers (18,19) explained the results on the MSP and PMP values of alkylaryl sulfonates in the higher pH range on the basis of enhanced dissociation of the soap resulting in increased repulsion at dropping mercury electrode (dme). Such factors, however, cannot be operative in nonionic surfactants.

TABLE II

Comparative cmc Values of LDC, SPSA, STSA and SXSA by Different Methods

Method	cmc values (order 10^{-5}M)			
	Without electrolyte	KCl	KNO_3	KI
Polarographic				
LDC	......	3.98	1.00	2.50
SPSA	......	8.20	9.80	12.10
STSA	......	48.98	2.19	7.94
SXSA	......	36.31	1.29	5.37
Spectrophotometric				
LDC	4.0	4.0	4.0	4.0
SPSA[a]	8.0	......	......	......
STSA[a]	10.0	......	......	. ....
SXSA[a]	12.0	......	......	......

[a] The cmc values have been taken from the PhD thesis of S. P. Verma.

TABLE III

Relative Effectiveness of Anionic and Nonionic Surfactants

Surfactant	Molecular Weight	Concentration to suppress the polarographic maximax 10^{-5}M		
		Pb $^{+2}$ in KNO_3	CdI_2 — KI complex	Cu-biuret
LDC	290	2.0	10.0	6.0
SPSA	441	23.5	238.0	83.3
STSA	454	23.8	23.8	60.5
SXSA	469	12.1	23.8	4.9

There are several factors which may be responsible for the lower cmc values of LDC as compared to the alkylaryl sulfonates: (i) the amido (−CON <) group is less hydrophilic than the sulfonate group ($x - SO_3^-$); (ii) it has a greater tendency to associate more strongly than the ionic ones because of lack of electrical charge; (iii) the latter factor is supported by the statement of Fowkes (20) that the tendency to form micelles is proportional to the square of the concentration of ionic detergents but only to the first power of the concentration of nonionic material. Another interesting fact emerges from these studies. Unlike ionic surfactants, the nonionic ones, even of low molecular weight suppress the polarographic maxima at much lower concentration. This is evident from the comparison of their molecular weights (Table III).

It has been found that the cmc value (4.0×10^{-5}M) of LDC obtained by the iodine solubilization method is of the same order as obtained by the polarographic method (Table II). It is also observed that the cmc value is not at all affected by the presence of different electrolytes viz., KCl, KNO_3 and KI by the solubilization method. The results on the cmc values of LDC described here go to show that unlike the ionic surfactants, the concentration for micelle formation is not affected by the changes in pH or by the presence of extraneous electrolytes. The concordance between

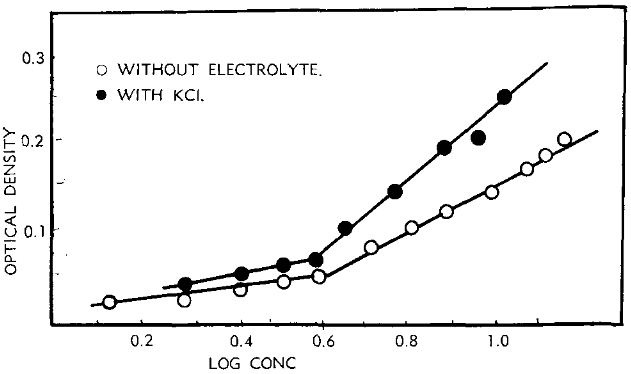

FIG. 2. Plots between log conc. and optical density.

the polarographic and spectrophotometric methods in this case is also very significant.

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