Critical Micelle Concentration of Non-Ionic Surfactants by Polaro-Graphic and Spectrophotometric Methods-A Comparative Study

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Abstract

The polarographic micelle point (PMP) values of non-ionic surfactants, viz., Nonidet P40, Nonidet P42 and Nonex 501 have been determined by a polarographic maximum suppression method in the presence of electrolytes (used for polarographic reduction) and compared with the critical micelle concentration (c.m.c.) values of nonionic surfactants obtained by other methods (spectrophotometric and electrocapillary curves methods). The PMP values are always lower than those obtained by other methods. The difference in c.m.c. values is due to the presence of ions of depolarizer and supporting electrolytes. The presence of electrolytes is likely to influence the water structure, thereby causing a lowering in c.m.c. values.

Introduction

The ionic surfactants have been extensively put to use for suppressing the difficult to suppress maxima of a large number of simple and complex metal ions (1,2). The data obtained from these studies have been put to indirect use for determining the c.m.c. of ionic surfactants in the presence of electrolytes (3,4). Corresponding studies with nonionic surfactants as maxima suppressors have not been extensively taken up as yet although such studies can be of great interest in view of the well-established effect of nonionic surfactants on the water structure. In this communication, the results of the c.m.c. values of Nonidet P40, Nonidet P42 and Nonex 501 in the presence of supporting electrolytes are described. For the sake of comparison, the c.m.c. values of the nonionic surfactants under investigation determined by the electrocapillary curve and spectrophotometric methods are also given in the present communication.

Experimental Procedures

Reagents

Nonionic surfactants, i.e., Nonidet P40 (100% polyethylene oxide condensate), Nonidet P42 (condensation product of dioctyl phenol and ethylene oxide), and Nonex 501 (methoxy polyethylene glycol laurate) were all B.D.H. products and were used without further purification. Analytical reagents and chemically pure reagents were used in all the investigations. Double distilled water (all glass) was used for preparing the solutions.

Polarographic Maximum Suppression Method

Apparatus and procedure. The polarographic apparatus and procedure used in this investigation are described in detail elsewhere (5). All the measurements were carried out at 25 ± 0.1 C in a thermostatic water bath. A Beckman pH-meter model H was used for pH measurements.

The polarographic micelle point (PMP) was obtained by plotting $i_{\text{maximum}}/i_{\text{diffusion}}$ vs. log concentration of the surfactant and taking the point of intersection of two lines representing the pre c.m.c. and post-c.m.c. curves, respectively, and maximum suppression point (MSP) was obtained by extrapolating the post-c.m.c. curve to unity.

Electrocapillary Curves Method

Electrocapillary measurements were carried out with a Heyrovsky polarograph (No. Lp 55A) operated manually in conjunction with a Pye Scalamp galvanometer. A dropping mercury electrode was used as the cathode whereas a saturated calomel electrode was used as the reference electrode.

The solutions of 0.1 M KCl were deaerated by bubbling nitrogen in the polarographic cell (H-cell). At least 20 drops were counted and drop time was measured by means of a stop watch. Each set of measurements at a constant potential was repeated three times. The electrocapillary data were obtained from 0.0 to −1.2 volts (S.C.E.) and they were repeated in the presence of different concentrations of the surfactant.

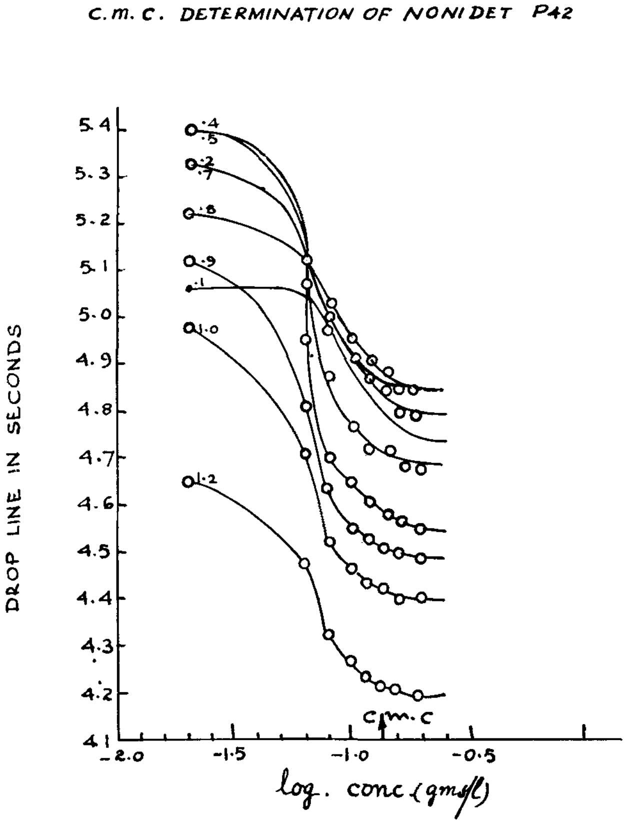

FIG. 1. Determination of c.m.c. of Nonidet P42 by electrocapillary curve method. Curves plotted between long conc. of Nonidet P42 and drop time (seconds) at different potentials, e.g., 0.1, 0.2, 0.4, 0.5, 0.7, 0.8, 0.9, 1.0 and 1.2 volts (−c ve).

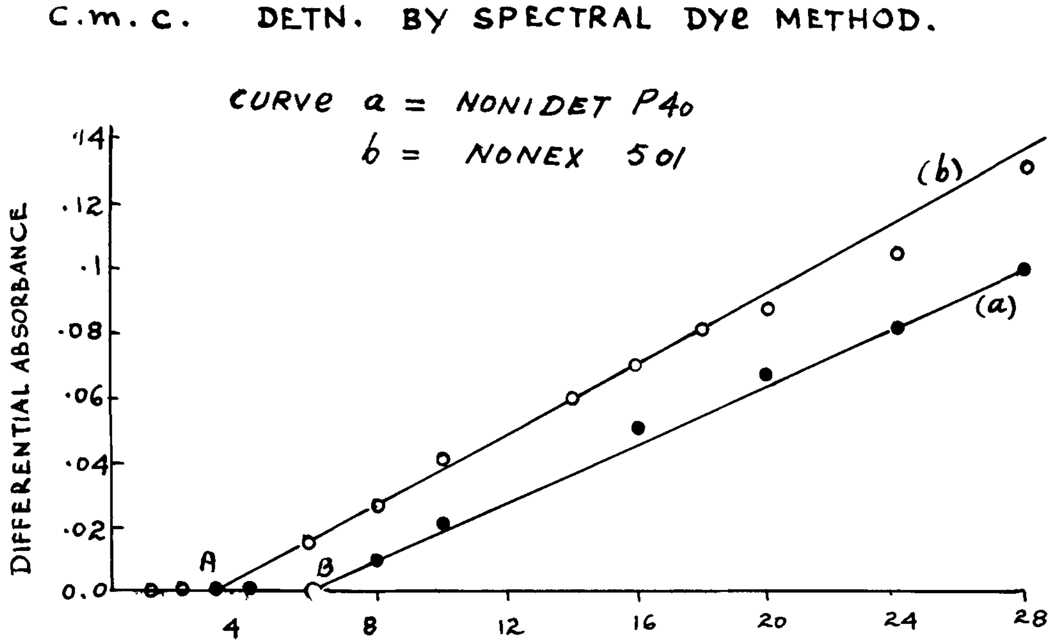

FIG. 2. Determination of c.m.c. by the spectral dye method. Curves plotted between surfactant concentration ($\times 10^{-2}$ g/liter) and differential absorbance.

The drop time was plotted against log concentration of the surfactant at various potentials. In order to locate the c.m.c. point, the portion of the curves showing a sharp fall in drop time with the increase in surfactant concentration was extrapolated downwards while the flat portion was extrapolated backwards. The concentration of the surfactant corresponding to the point of intersection of the extrapolated portions of the curve was taken as the c.m.c. value (Figure 1).

Spectrophotometric Methods

Iodine Solubilization Method. For determining the c.m.c. by the iodine solubilization method of Ross and Olivier (6), the apparatus and procedure are described in detail elsewhere (7).

Spectral dye method. The c.m.c. determination was made by Becher's spectral dye method (8). Absorption measurements were carried out by a Bausch and Lomb Spectronic-20′.

The fixed amount (0.5 ml) of benzopur-purin 4B

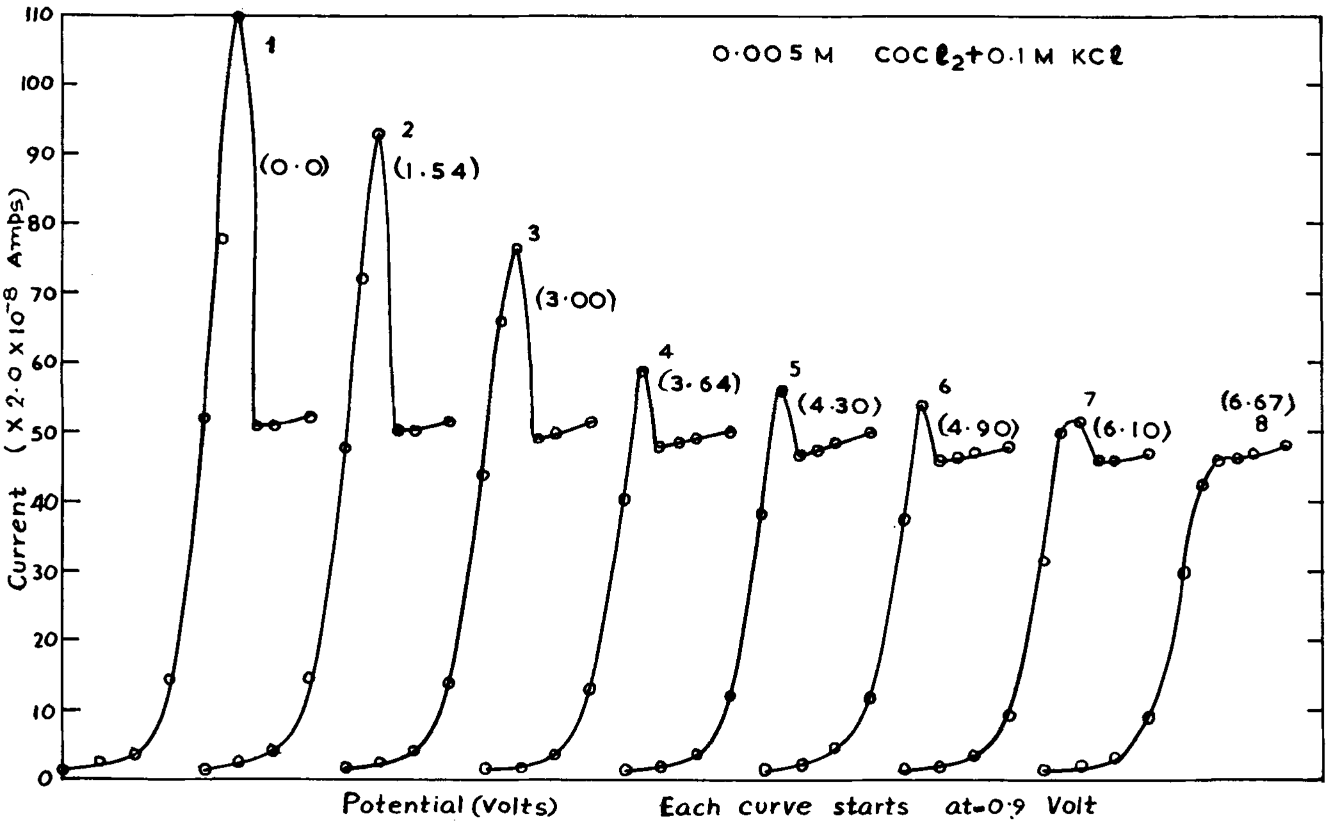

FIG. 3. Polarograms of Co^{2+} (0.005 M) in 0.1 M KCl in varying amounts of Nonidet P40. Curve: 1 = 0.0, 2 = 1.54, 3 = 3.00, 4 = 3.64, 5 = 4.30, 6 = 4.90, 7 = 6.10 and 8 = 6.67 ($\times 10^{+3}$ g/liter) of Nonidet P40.

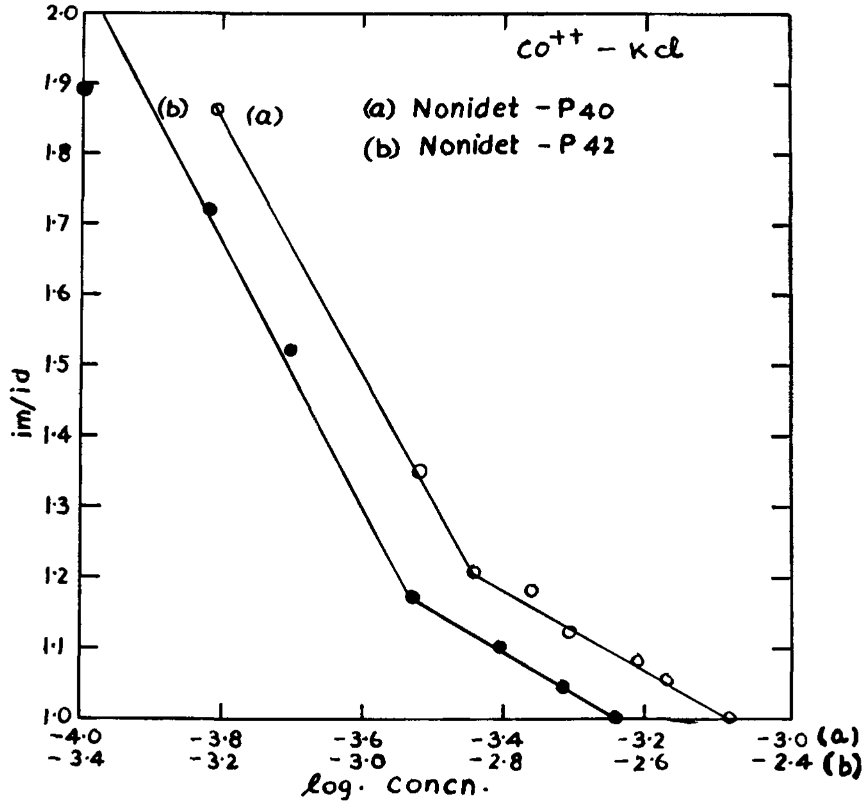

FIG. 4. Determination of c.m.c. by polarographic method. Plots between log concentration of the surfactants and $i_{maximun}/i_{diffusion}$.

(10^{-3} M) was mixed with the different amounts of the nonionic surfactant solution whose c.m.c. was to be determined and the total volume (10.0 ml) was made up with water. A series of the solutions having a fixed concentration of the dye and different concentrations of surface active agent above and below the c.m.c. were obtained.

The absorption measurements were made at a wavelength of 510 mμ (maximum of surfactant-dye complex) after half an hour's mixing of the mixture.

The differential absorption of surfactant dye mixtures was plotted against the surfactant concentration. The point at which a sharp increase in differential absorption (Figure 2, Points A and B) was observed was taken as the c.m.c. value.

Results and Discussion

Typical polarograms of Co^{2+} having 0.1 N KCl in the presence of varying amounts of Nonidet P40 (x10^{-3} g/liter) are shown in Figure 3. The values of $i_{maximum}/i_{diffusion}$ obtained by these polarograms were used to determine PMP and MSP values of surfactant (Figure 4).

TABLE I

Polarographic Micelle Point (P.M.P.) Values of Nonidet P40, Nonidet P42 and Nonex 501 in the Presence of Different Supporting Electrolytes

Ion or complexes	pH	PMP ($\times10^{-3}$ g/liter)		
		Nonidet P40	Nonidet P42	Nonex 501
Pb^{2+}-KNO_3	5.15	1.90	7.84	2.32
Ni^{2+}-KCl	4.92	2.32	15.40	2.32
Co^{2+}-KCl	2.95	3.64	11.00	2.32
CdI_2-KI complex	6.03	3.00	11.60	2.32
Ni^{2+}-Co^{2+} mixture in pyridine and KCl	....	8.60	30.00	3.89
Cu-biuret	12.04	1.60	11.60	3.08
Cu-glycine	10.50	3.80	15.40	2.70
U^{6+} $KClO_3$ and phosphoric acid	....	3.80	7.84	0.80

The results of PMP values of nonionic surfactants, i.e., Nonidet P40, Nonidet P42 and Nonex 501 are given in Table I. The PMP and MSP values can both be correlated to the c.m.c. of the surfactants although it is usual to relate it with the former. For this reason only PMP values are shown in the Table.

From the data given in Table I, it may be seen that the PMP values differ very little from each other irrespective of the cations used. With the exception of the Ni^{2+}-Co^{2+} mixture in pyridine and KCl, where a large amount of the surfactants is required to suppress the maximum the PMP values range within narrow limits. The values range between 0.8 to 3.08 x10^{-3} g/liter, 1.60 to 3.80 x10^{-3} g/liter and 7.84 to 15.4 x10^{-3} g/liter for Nonex 501, Nonidet P40 and Nonidet P42, respectively. The anions of the supporting electrolytes do not affect the PMP values of the nonionic surfactants.

Unlike the ionic surfactants, the pH of the medium does not markedly influence the PMP values. It is thus seen from Table I that the PMP values obtained in the higher pH range, 10.0 and 12.0 for Cu-glycine and Cu-biuret complexes respectively, are not far

TABLE II

C.m.c. Values of Nonidet P40, Nonidet P42 and Nonex 501 by *Different Methods*

Method	C.m.c. $\times10^{-2}$ g/liter)		
	Nonidet P40	Nonex 501	Nonidet P42
Electrocapillary curves in 0.1 N KCl	7.60	4.70	13.8
Surface tension[a] (without electrolyte)	12.50	6.20	39.80
(With 0.1 N KCl)	10.0	3.5	35.00
Iodine solubilization	12.00	4.80	35.00
Spectral dye	12.50	3.00	36.00
Polarographic maximum suppression			
(Ni^{2+} in 0.1 N KCl)	0.23	0.23	1.54
(Co^{2+} in 0.1 N KCl)	0.36	0.23	1.10

[a] From Reference 9.

TABLE III[a]

Comparative c.m.c. Values of Anionic Surfactants from Different Electrochemical Methods

Method	$(\times 10^{-2}$ g/liter)		
	SPSA	STSA	SXSA
Polarographic method (Ni^{2+} in 0.1 N KCl)	3.60	21.20	17.00
pH-metric method (Without electrolyte)	6.10	7.10	9.40
Conductometric method (Without electrolyte)	18.90	22.68	25.10

[a] C.m.c. values $(\times 10^{-5}$ M) given in reference 11) were converted to $(\times 10^{-2}$ g/liter).

removed from the PMP values obtained with Ni^{2+} and Co^{2+} in 0.1 N KCl in the lower pH range (4.92 and 2.95). These results are in good agreement with our earlier work on lauric acid diethanolamine condensate (5). The PMP values of anionic surfactants are, however, greatly influenced by pH of the medium as observed by Malik et al. (2) in the case of alkyl aryl sulphonates.

Since the values determined by the polarographic method give the c.m.c. values in the presence of electrolytes (used for polarographic reduction), it was considered necessary to compare the values with those obtained by other methods. In Table II, the c.m.c. values obtained in this laboratory by various methods are summarized. From these results, it is evident that the PMP and MSP values obtained by the polarographic maximum suppression method are always lower than those obtained by spectral dye, iodine solubilization, surface tension and electrocapillary curve methods which compare favorably with each other. This difference is obviously due to the presence of the ions of depolarizer and the supporting electrolytes in the surfactant solution. Since the presence of electrolytes is likely to influence the water structure (9), the lowering in c.m.c. values is understandable.

A comparison of the c.m.c. values of nonionic surfactants with those of ionic surfactants in Table III (reported earlier) reveal that the former have smaller c.m.c. values than the latter.

This difference may be attributed to several factors: (a) greater hydration of the nonionized polar groups, (b) greater tendency of nonionic groups to associate because of lack of electrical charge, and (c) absence of gegenions in nonionic surfactants.

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