Effect of Nonionic Surfactants on the Polarographic Maximum and Electrocapillary Curves: A Comparative Study

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ABSTRACT

The polarographic and electrocapillary curve methods have been used to determine the maximum suppression point (MSP), polarographic micelle point (PMP) and critical micelle concentration (cmc) of some polyoxyethylated nonionic surfactants, viz., Tween 20, Tween 40 and Tween 80. The cmc values thus obtained have been compared with the values obtained by surface tension, iodine solubilization, spectral dye and radiometric methods.

TABLE I

Polarographic Micelle Point (pmp) and Maximum Suppression Point (msp) Values of Nonionic Surfactants in Presence of Cd Ions in 0.1M Potassium Iodide

Surfactant	pmp (x 10^{-3} g/liter)	smp (x 10^{-3} g/liter)
Tween 20	12.0	14.0
Tween 40	8.0	12.5
Tween 80	12.0	21.2
Nonidet P40[a]	3.0	4.3
Nonidet P42[a]	11.6	12.3
Nonex 501[a]	2.3	3.6
LDC[a]	7.2	14.1

[a]Data from Malik and Chand (2): Nonidet P40, octyl phenolethylene oxide condensate (100% active constituent); Nonidet P42, octyl phenolexylene oxide condensate; Nonex 501, methoxy polyethylene glycol laurage/(27% active constituent); LDC, lauric acid-diethanol amine condensate. All four surfactants are British Drug House products.

TABLE II

Comparative Critical Micelle Concentration (cmc) Values of Nonionic Surfactants From Different Electro-Chemical Methods

Method employed	Tween 20	Tween 40	Tween 80
	cmc (x 10^{-2} g/liter)		
Radiotracer technique	10.00	6.31	5.01
Surface tension	10.59	7.08	5.31
Iodine solubilization method	10.20	6.80	5.00
Spectral dye method	10.00	6.40	5.00
Polarographic method (Cd^{++} in 0.1M KCl)	1.20	0.80	1.20
Electrocapillary curves method in 0.1M KCl	7.00	4.47	4.00

TABLE III

Comparative Critical Micelle Concentration (cmc) Values of Anionic Surfactants From Different Electro-Chemical Methods

Method	SPSA[b]	STSA[b]	SXSA[b]
	cmc[a] (x 10^{-2} g/liter)		
Polarographic method Ni^{++} in 0.1M 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]The cmc values (x 10^{-5}M) given in (3) were converted in (x 10^{-2} g/liter).

[b]SPSA = sulphonated phenyl stearic acid; STSA = sulphonated tolyl stearic acid; SXSA = sulphonated xylyl stearic acid.

INTRODUCTION

The method of determining critical micelle concentration (cmc) of soaps and surfactants based on suppression of the polarographic maxima has been criticized since the cmc thus obtained is not the true value but the one obtained in the presence of electrolytes. Nevertheless the method has its own significance since it is one of the few methods that can provide cmc data in the presence of various electrolytes. Another method that can be used for this purpose is the electrocapillary curve method.

In this communication the results on the cmc of some polyoxyethylated nonionic surfactants, viz., Tween 20, Tween 40 and Tween 80 are reported. The cmc values obtained from the polarographic and electrocapillary curve methods have been compared with the values obtained by surface tension, iodine solubilization and radiometric methods.

EXPERIMENTAL PROCEDURES

Reagents and Materials

Nonionic surfactants, viz., Tween 20 (polyoxyethylene sorbitan monolaurate), Tween 40 (polyoxyethylene sorbitan monopalmitate) and Tween 80 (polyoxyethylene sorbitan monooleate) were commercial products of Atlas Chemical Co. and were used as such without further

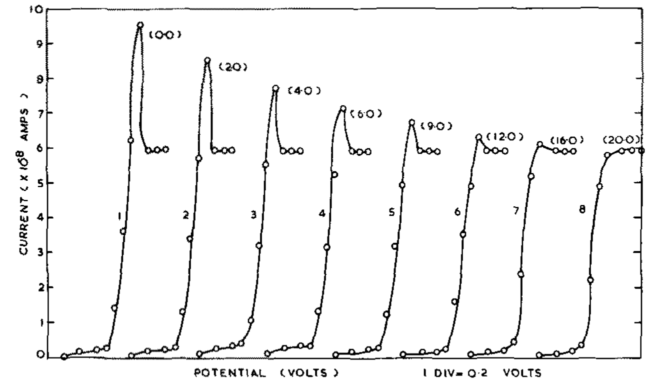

FIG. 1. Suppression of cadmium ion maximum by Tween 20. Values in parentheses represent amount of Tween 20 (x 10^{-3} g/l). Each curve starts at -0.3 v.

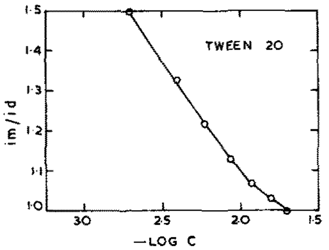

FIG. 2. Plot between $i_{\text{maximum}}/i_{\text{diffusion}}$ and logarithm of surfactant concentration.

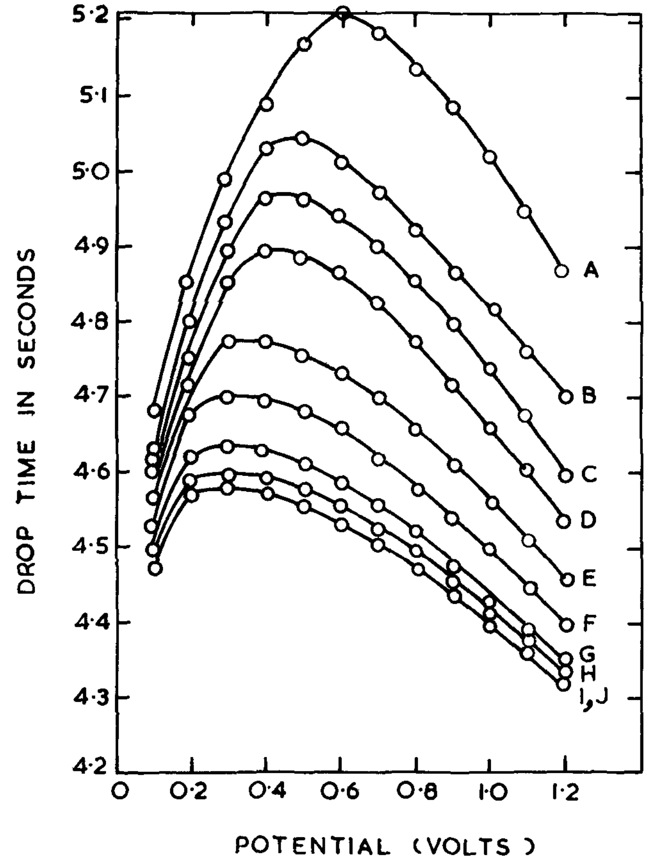

FIG. 3. Effect of Tween 20 on electro capillary curves in 0.1 M KCl. Plot between drop time and potential applied in presence of 0.1 M KCl. Curve: A=0.0, B=1.0, C=2.0, D=3.0, E=4.0, F=5.0, G=6.0, H=7.0, I=8.0, J=10.0 (x 10^{-2} g/l).

purification. Their solutions were prepared in doubly distilled water (all glass). All reagents used were analytical grade.

Apparatus and Methods

Polarographic measurements were made using Heyrovsky polarograph (model LP55A) operated manually in conjunction with Pye scalamp galvanometer (model 7903/5).

Polarographic measurements were carried out after putting a known volume of the metal salt or the complex metal ion in the polarographic cell, making up the total volume to 15.0 ml after adding the supporting electrolyte. The solutions were deaerated by passing purified nitrogen gas through them for about 10 min. The polarogram was taken and the same procedure was then repeated in the presence of various surfactants under investigation. Increasing amounts of the surfactant solutions were added by microburette until the maximum was completely eliminated. A typical polarogram is shown in Figure 1.

For drop time measurements an appropriate amount of the electrolyte (0.1M KCl) was taken into the cell and the total volume was made up to 10 ml by adding water. After passing nitrogen through the cell for 10 min, drop time measurements were made in the potential range 0.0 to -1.2 volts, with reference to a standard calomel electrode (SCE). At least 20 drops were counted and the time was measured with a precision stop watch of least count 0.1 sec. Each set of measurements at a constant applied potential was repeated three times. The electrocapillary data were repeated in the presence of different concentrations of the surfactant.

Drop time was plotted against logarithm of surfactant concentration (Figs. 4,5). The cmc values were obtained by finding the surfactant concentration at the intersection of the extrapolations of the steep part of the curve and of the final horizontal portion.

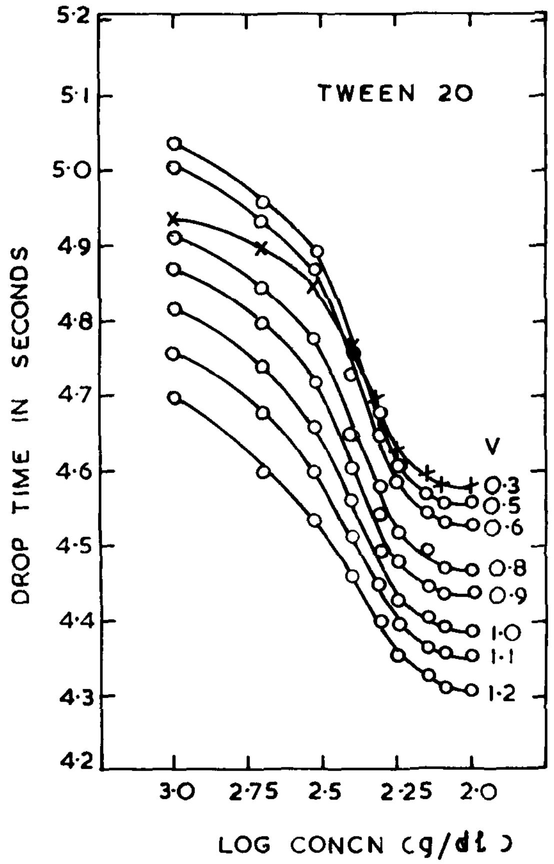

FIG. 4. Effect of Tween 20 on electro capillary curves in 0.1 M KCl. Plot between log concentration of Tween 20 and drop time in presence of 0.1 M KCl at different potentials.

RESULTS AND DISCUSSION

The plot between $i_{\text{maximum}}/i_{\text{diffusion}}$($i_m/i_d$) and logarithm of the surfactant concentration (Fig. 2) can be used to determine the two polarographic characteristics of the surfactants, viz., polarographic micelle point (pmp) and maximum suppression point (msp) (2). The former is obtained from the point where the first discontinuity appears in the curve. The pmp is shown here to be identical with the classical cmc of the surfactants. Furthermore, this concentration seems to be equal to the concentration of colloidal agent just sufficient to suppress the maxima. The msp is defined as the minimum concentration of the surfactant which is necessary to make i_m/i_d equal to 1. It was determined by extrapolating the curve to i_m/i_d = 1. The data on the msp and pmp values obtained from the respective curves, together with earlier (1) data on other nonionic surfactants, are given in Table I.

The pmp and smp values can both be related to the cmc of the surfactants, although it is usual to relate it with the former. In either case, however, the values are much lower than those obtained by other methods, viz., iodine solubilization, radiotracer, spectral dye and surface tension, which incidentally compare favorably with each other and give cmc values in the same range. The low cmc values obtained by the polarographic maximum suppression method are due to the lowering of the cmc value in the presence of supporting electrolyte. The polarographic method therefore gives the cmc data only in the presence of electrolyte and not with pure surfactants as other methods do.

From Table II it is evident that the cmc values of nonionic surfactants are smaller as compared to the ionic ones given in Table III found previously (3). The difference

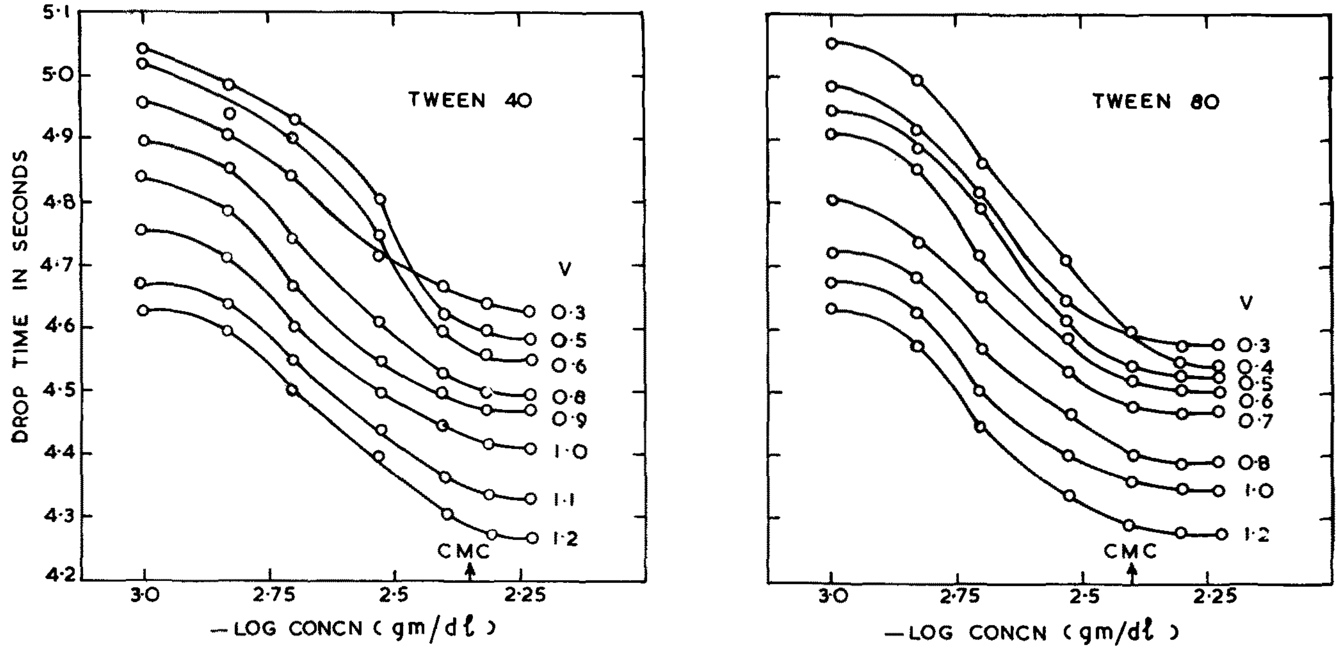

FIG. 5. Effect of surfactants on electro capillary curves in 0.1 M KCl. Plots between log concentration of surfactants and drop time in presence of 0.1 M KCl at different potentials.

may be attributed to several factors, viz., (a) greater hydration of the nonionized polar groups, (b) absence of gegen ions in nonionic surfactants, (c) greater tendency of nonionic groups to associate because of lack of electrical charge.

From the above experimental results it can be concluded that these surfactants are generally very effective in suppressing the polarographic maximum and are preferable to gelatin in the following respects: (a) these surfactants seem to lack any tendency of complex formation with metallic ions under ordinary conditions and (b) they are completely free of deterioration.

It is interesting to note that the suppression of polarographic maximum not only concerns the adsorption or the change in interfacial tension due to the presence of surfactants but also the slight change in structure of the electrical double layer. It is thus possible in the polarographic method with dropping mercury electrode (DME) to study both the electrode process and the electrocapillary phenomenon at the same interface, which seems to be a great advantage in the study of the effect of surface active substances on the electrode process. The height of the mercury reservoir gives the magnitude of the surface tension according to the equation:

$$2\pi\gamma\delta = \pi\gamma^2 h\, s\, g$$

or

$$\delta = 1/2\ \gamma ghs = K^1 h$$

Where γ is the internal diameter of the capillary at the level of the meniscus, δ the surface tension, h the height of the reservoir, s the specific density and g the gravitational constant. The height of the mercury column and hence the drop time will give a measure of the interfacial tension at the surfactant mercury interface.

Therefore on plotting drop time against applied potential, the so-called electrocapillary parabola (5) are obtained. Figure 3 is the plot between drop time and the potential applied. It is evident from Figure 3 that the presence of a certain amount of surfactant changes both the position of electrocapillary maximum (E-C max) and the shape of the E-C curve. The curve is shifted downward and toward the more positive side on the potential axis with increasing concentration of the surfactant. This behavior indicates that the adsorption of the surfactant at the interface takes place even at the beginning when the applied potential on DME is zero. With increasing cathodic potential relative lowering of the drop time increases, indicating that the increasing cathodic polarization of DME augments the adsorption of the surfactant at the mercury-solution interface. Moreover, the cathodic branch of the curve seems to merge with that of the base electrolyte, indicating that the adsorption of the surfactant is not accomplished even at sufficiently high negative potentials (-1.2 volts).

Figures 4 and 5 are the plots between drop time vs. logarithm of the surfactant concentration in the potential range 0.0 to -1.2 volts. These curves show an initial slow change followed by a sharp decrease in drop time and finally signs of flattening out.

The shift in the electrocapillary maximum and the shapes of the electrocapillary curves can be explained on the basis of adsorption of surfactants on the DME as proposed by Barradas and Kimmerle (4) for multilayer adsorption in the case of Triton X-100, Triton X-35 and similar compounds.

The first adsorbed layer on the mercury surface is formed with its hydrocarbon part towards mercury and extending its zigzag hydrophilic portions through the solution so that the positive end of the dipole remains close to the mercury surface, thereby attributing a positive shift in the electrocapillary maximum. The second adsorbed layer is then assumed to form by intermolecular hydrogen bonding between the perpendicular array of the surfactant molecules. Besides, each compact array of molecules may hydrogen bond some water molecules, since the micellar structure of the polyoxyethylated nonionic surfactants is known to be highly hydrated (5).

When the adsorbed molecules reach a certain critical concentration at the interface they begin to associate in the same way as they associate to form micelles in the bulk of the solution. The forces responsible for the association of the molecules at the surface are the same as those operating in the bulk leading to micelle formation (except the coulombic attraction for the adsorption sites which add to the association tendency). The surface associates have often been referred to as hemi-micelles (6). Further increase in concentration of the surfactant results only in increasing the compactness of the adsorbed layer and hence after this concentration range the curves (Figs. 4-5) show signs of flattening. Since flattening sets in at the same concentration, irrespective of the potential applied, this concentration can safely be regarded as the point of incipient micelle formation. The cmc values determined by this method, unlike those of the polarographic method, compare favorably with those obtained by iodine solubilization, radiotracer, spectral dye and surface tension methods. The comparative cmc values are given in Table II.

The slightly lower values obtained by electrocapillary curves are due to the fact that these cmc values refer more adequately to the concentration at which the association of the surfactant molecules onsets at the surface. Here (at the surface) the coulombic attractions of the adsorption sites also contribute towards association, in addition tothe forces responsible for micelle formation in the bulk of the solution. The second factor may be the presence of electrolytes which are known to augment the micelle formation tendency with a consequent decrease in cmc values.

The polarographic maximum suppressor method suffers from many limitations. For example it has been found that even traces of capillary active substances exert a remarkable suppressing effect, e.g., an oxygen maximum is greatly suppressed by filtration of the solution through quantitative filter paper or by contact with a stopcock (7). Moreover, polarographic maximum current depends on the nature of the electro-reducible substance, concentration of the supporting electrolyte, drop time and temperature. Malik and Haque (8-10) have shown that the pH of the system affects the height of the maximum even more seriously. Thus the polarographic method fails to give reliable results in the case of nonionic surfactants but may be quite useful in determining the cmc of ionic surfactants. Moreover, the cmc values of ionic surfactants are quite high with the result that the small deviations observed in the polarographic maximum suppressor method do not affect the cmc values very much. This is, however, not so with the nonionic surfactants and large deviations are observed when this method is applied to these surfactants. For these surfactants the electrocapillary method would prove to be most suitable.

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