

Surfactants with Natural Hydrophobic Tails HLB-CMC Relationship of Polyoxyethylenated Cholesterol

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Abstract: The critical micelle concentration (CMC) values were obtained from the discontinuities in surface tension (λ)-concentration (c) relationship, through the least-squares regression analysis. The determined CMC values of eleven polyoxyethylenated cholesterol nonionic surfactants, were plotted against the respective Hydrophile-Lipophile Balance (HLB) values of these compounds. The developed HLB-CMC relationship for the investigated compounds could be represented satisfactorily by the linearized equation in $CMC = a-b (HLB)$. Values of the two constants (a) and (b) representing the intercept and slope for the investigated compounds, were determined at 28, 38, 48 and 58°C. The study revealed that both a and b values decrease with increasing the number of oxyethylene units (n) condensed per cholesterol molecule. The most striking feature of the obtained equation is that the CMC is seen to decrease with increasing HLB. This observation is contrary to what is generally expected for both ionic and nonionic surfactants.

Key words: Cholesterol ethoxylates – Nonionic surfactants-Nonionics having natural hydrophobic tail-Sterol surfactants–HLB-CMC relationship.

INTRODUCTION

Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but because it affects other interfacial phenomena, such as surface or interfacial reduction, that do not directly involve micelles (Rosen, 1989). Micelles have become a subject of great interest to the organic chemist and the biochemist – to the former because of their unusual catalysis of organic reactions (Fendler and Fendler 1975), and to the latter because of their similarity to biological membranes and globular proteins (Jonsson *et al.*, 1998).

Micelle formation in aqueous solutions of polyoxyethylenated cholesterol has been reported in literature with some occasional controversy (Soderlund *et al.*, 1989, Beugin *et al.*, 1998, Folmer *et al.*, 1999). The controversy in critical micelle concentration (CMC) values determined from surface tension (g)-concentration (c) isotherms of some nonionics, may be due to the way in which a number of data points involved in each of the two linear portions below and above the CMC are dealt with (Barakat *et al.*, 1989, Gendy *et al.*, 1994). Another reason for such controversy may be the long time taken to reach equilibrium surface tension which is a common phenomenon for many steroid and high molecular weight surfactants (Meissner *et al.*, 2000; Folmer, 2003; Meissner *et al.*, 2000). However, there have been no published systematic studies concerning the behaviour of this nonionic class of surfactants at interfaces.

In the Egyptian Petroleum Research institute (EPRI), systematic investigations, employing both polymeric and monomeric nonionics, have been carried out (Barakat *et al.*, 1989, Youssef *et al.*, 1990, Gendy *et al.*, 1994; Ibrahim, 2006). The ultimate target of these studies was the performance of these surfactants at aqueous solution – air and aqueous solution-hydrocarbon interfaces. Such performance has been largely recognized to be of great importance from the practical and theoretical points of view.

CMC values of eleven polyoxyethylenated cholesterol were determined (Barakat *et al.*, 2008). In this investigation, the HLB-CMC relationship was studied at 28, 38, 48 and 58°C and subsequently four equations were developed.

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MATERIALS AND METHODS

Experimental:

Surfactants:

Polyoxyethylenated cholesterol nonionics, having an average number (n) of oxyethylene units (EO) from 7.37 to 37.53, were prepared by reacting ethylene oxide with cholesterol in two-stage reaction (Fig. 1) using an apparatus similar to that reported in previous work with little modifications (El-Kholy, 1988; Ezzat, 1988; Ibrahim, 1998). Ethylene oxide was fed from cylinder (s) with recommended valve (Fluka). Boron trifluoride etherate (Lewis acid catalyst, purified, Aldrich) was employed in the first-stage which is not suitable for oxyethylenating cholesterol with more than five oxyethylene units, i.e. n is less than 5 EO (Holmberg, 2001; Folmer, 2003). Pulverized sodium hydroxide, as a base catalyst, was employed in the second-stage to get polyoxyethylenated cholesterol adducts having longer polyoxyethylene chains.

All the prepared nonionics are more than 90% active, containing less than 10% of free polyoxyethylene glycols. The method of separation and determination of these secondary reaction products, were carried out using the modified Weibull technique (Schonfeldt, 1969; Weibull, 1960; Longman, 1977). After the removal of these glycols, the average number (n) of oxyethylene (EO) units condensed per cholesterol molecule was determined through $^1\text{H-NMR}$ measurements. The hydrophile-lipophile balance, HLB, was calculated using the well-known Griffin's equation, $\text{HLB} = (\% \text{EO}) / 5$, (Griffin, 1954).

The critical micelle concentration (CMC) values of the prepared nonionics were determined from the surface tension (σ)-concentration (c) isotherms through the least-squares regression analysis. Fig. (2) illustrates the determination of CMC values at, 28, 38, 48 and 58°C of polyoxyethylenated cholesterol having 23.19 EO as a representative figure.

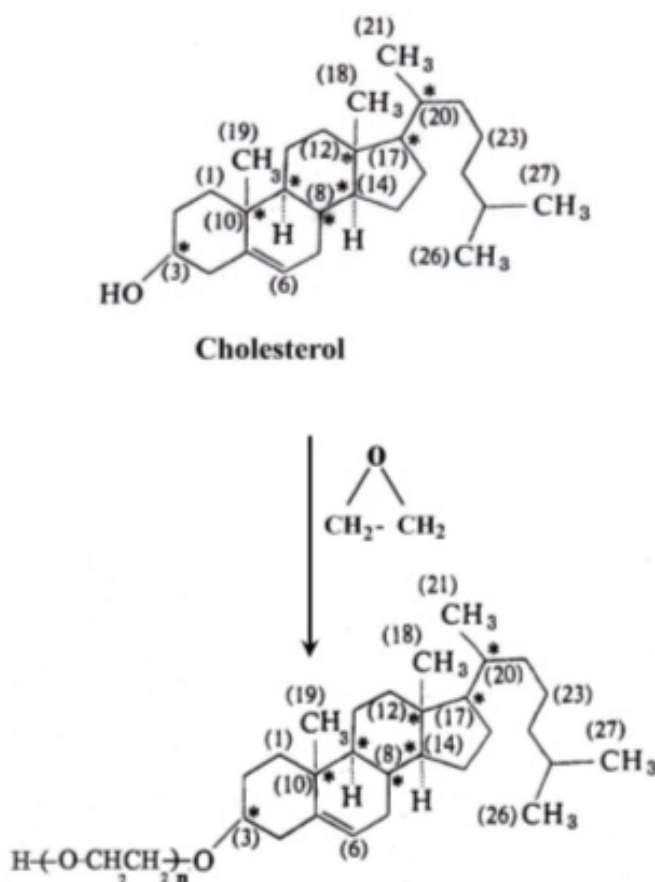


Fig. 1: Polyoxyethylenated Cholesterol (n is the average number of oxyethylene units, EO)

RESULTS AND DISCUSSION

Polyoxyethylenated Cholesterol Nonionics:

In brief, cholesterol represents the natural hydrophobic tail of this group of nonionic surfactants. Cholesterol is a solid alcohol which possesses a hydroxyl group at position 3, a double bond between carbons 5 and 6, a side chain on carbon 17, and methyl groups joined to ring carbons numbered 10 and 13. Cholesterol, $C_{27}H_{46}O$, one of the most widely distributed sterols, is found in almost all animal tissue but is particularly abundant in the brain, the spinal cord, and in gallstones. The structure of this natural hydrophobic tail plays an important role in the effectiveness and efficiency of adsorption at L/G and L/L interfaces. The structure of cholesterol and polyoxyethylenated products are shown in Fig. (1).

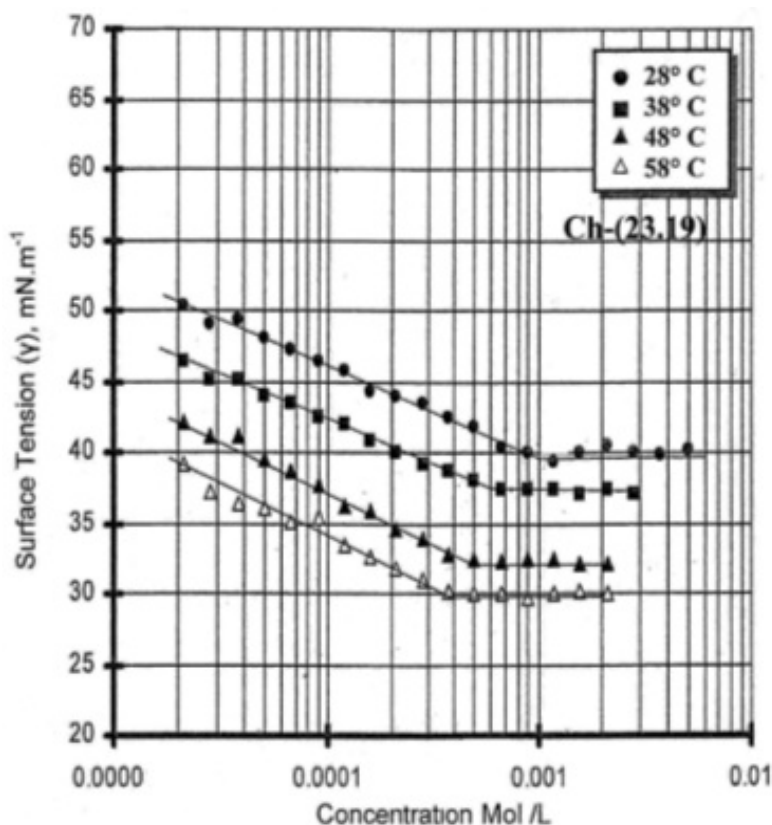


Fig. 2: Surface Tention - Concentration Relationship for Polyoxyethylenated Cholesterol Different Temperatures (A Representative Figure).

Designations and some characteristics of the prepared polyoxyethylenated cholesterol nonionics are listed in Table (1). Data in Table (1) show that the first four members, Ch-(7.37), Ch-(10.16), Ch-(13.87) and Ch-(14.75), are pale to amber yellow soft waxy-like materials. The next three members, Ch-(15.23), Ch-(16.89) and Ch-(19.52) are light brown viscous material. The last four members, Ch-(23.19), Ch-(32.56), Ch-(33.90), and Ch-(37.53), are highly viscous masses. The average number (n) of oxyethylene units, condensed per cholesterol molecule are given in paranthesis in all designations.

It is obvious from data in Table (1) that the prepared polyoxyethylenated cholesterol nonionics have not sharp melting points, the melting range decrease with increasing n i.e., the length of polyoxyethylene chain. The temperature at which clouding of aqueous solutions occurs for nonionics having a particular hydrophobic group, the larger the percentage of oxyethylene (%EO) in the surfactant molecule, the higher the cloud point (Kuwamura, 1984), although the relation between oxyethylene percentage and cloud point is not linear. In Table (2), the percentage of oxyethylene and the calculated hydrophile-Lipophile balance (HLB) values are listed. The determined CMC values at 28, 38, 48 and 58°C are given in Table (3).

Table 1: Designations and some Characteristics of the Prepared Polyoxyethylenated Cholesterol.

Surfactant Designation	^a n	appearance	Cloud Point °C	Melting Range °C
Ch-(7.37)	7.37	Soft waxy like	71	67-84
Ch-(10.16)	10.16	Soft waxy-like	75	65-80
Ch-(13.87)	13.87	Soft waxy-like	78	60-73
Ch-(14.75)	14.75	Soft waxy-like	84	58-71
Ch-(15.23)	15.23	Viscous waxy	86	55-68
Ch-(16.89)	16.89	Viscous waxy	89	51-65
Ch-(19.52)	19.52	Viscous waxy	92	45-58
Ch-(23.19)	23.19	Highly viscous	>100	40-55
Ch-(32.56)	32.56	Highly viscous	>100	40-48
Ch-(33.90)	33.90	Highly viscous	>100	40-48
Ch-(37.53)	37.53	Highly viscous	>100	40-48

^a n = average number of oxyethylene units (E0) condensed per cholesterol molecule, n is determined through NMR analysis.

Table 2: Number (n) and percentage (%E0) of Oxyethylene Units Along With HLB Values of Polyoxyethylenated Cholesterol.

n (No. of E0)	F.W of n E0 @	Average Mol. Wt. of Surfactant *	%E0 **	HLB (%E0/5)
7.37	324.28	710.94	45.61	9.12
10.16	447.04	833.70	53.62	10.72
13.87	610.28	996.94	61.22	12.24
14.75	649.00	1035.66	62.66	12.53
15.23	670.12	1056.78	63.41	12.68
16.89	743.16	1129.82	65.78	13.16
19.52	858.88	1245.54	68.96	13.79
23.19	1020.36	1407.02	72.52	14.50
32.56	1432.64	1819.30	78.75	15.75
33.90	1491.16	1878.26	79.39	15.87
37.53	1651.32	2037.98	81.03	16.21

@ Formula weight of polyoxyethylene chain = n x 44

* Calculated (386.66+ n x 44)

$$**\%E0 \left(\frac{n \times 44}{3.86.66 + n \times 44} \right) \times 100$$

Table 3: CMC Values of Polyoxyethylenated Cholesterol at Different Temperatures.

Surfactant	HLB	CMC, M/L			
		28 °C	38 °C	48 °C	58 °C
Ch-(7.37)	9.12	3.6 x 10 ⁻³	2.0 x 10 ⁻³	1.4 x 10 ⁻³	4.7 x 10 ⁻⁴
Ch-(10.16)	10.72	2.5 x 10 ⁻³	1.5 x 10 ⁻³	1.1 x 10 ⁻³	4.3 x 10 ⁻⁴
Ch-(13.87)	12.24	1.7 x 10 ⁻³	1.1 x 10 ⁻³	7.2 x 10 ⁻⁴	3.9 x 10 ⁻⁴
Ch-(14.75)	12.53	1.6 x 10 ⁻³	1.0 x 10 ⁻³	7.0 x 10 ⁻⁴	3.8 x 10 ⁻⁴
Ch-(15.23)	12.68	1.5 x 10 ⁻³	1.0 x 10 ⁻³	6.8 x 10 ⁻⁴	3.8 x 10 ⁻⁴
Ch-(16.89)	13.16	1.4 x 10 ⁻³	9.3 x 10 ⁻⁴	6.6 x 10 ⁻⁴	3.7 x 10 ⁻⁴
Ch-(19.52)	13.79	1.1 x 10 ⁻³	8.3 x 10 ⁻⁴	6.1 x 10 ⁻⁴	3.5 x 10 ⁻⁴
Ch-(23.19)	14.50	9.8 x 10 ⁻⁴	7.3 x 10 ⁻⁴	5.5 x 10 ⁻⁴	3.3 x 10 ⁻⁴
Ch-(32.56)	15.75	7.2 x 10 ⁻⁴	5.7 x 10 ⁻⁴	4.5 x 10 ⁻⁴	3.1 x 10 ⁻⁴
Ch-(33.90)	15.87	7.0 x 10 ⁻⁴	5.6 x 10 ⁻⁴	4.3 x 10 ⁻⁴	3.1 x 10 ⁻⁴
Ch-(37.53)	16.21	6.5 x 10 ⁻⁴	5.3 x 10 ⁻⁴	4.1 x 10 ⁻⁴	2.8 x 10 ⁻⁴

Table 4: HLB-CMC Relationship of Polyoxyethylenated Cholesterol at 28 and 38oc.

Surfactant	Temp., °C	HLB	Ln CMC	HLB – CMC Relationship	R ² - value
Ch-(7.37)		9.12	-5.6268		
Ch-(10.16)		10.72	-5.9915		
Ch-(13.87)		12.24	-6.3771		
Ch-(14.75)		12.53	-6.4378		
Ch-(15.23)		12.68	-6.5023		
Ch-(16.89)	28	13.16	-6.5713	Ln(CMC)=-3.5117-0.2332(HLB)	0.9963
Ch-(19.52)		13.79	-6.8124		
Ch-(23.19)		14.50	-6.9280		
Ch-(32.56)		15.75	-7.2363		
Ch-(33.90)		15.87	-7.2644		
Ch-(37.53)		16.21	-7.3385		

Table 4: Continued

Ch-(7.37)		9.12	-6.2146		
Ch-(10.16)		10.72	-6.5023		
Ch-(13.87)		12.24	-6.8124		
Ch-(14.75)		12.53	-6.9078		
Ch-(15.23)		12.68	-6.9078		
Ch-(16.89)		13.16	-6.9803		
Ch-(19.52)	38	13.79	-7.0941	$\text{Ln (CMC)} = -4.4817 - 0.1924(\text{HLB})$	0.9953
Ch-(23.19)		14.50	-7.2225		
Ch-(32.56)		15.75	-7.4698		
Ch-(33.90)		15.87	-7.4875		
Ch-(37.53)		16.21	-7.5426		

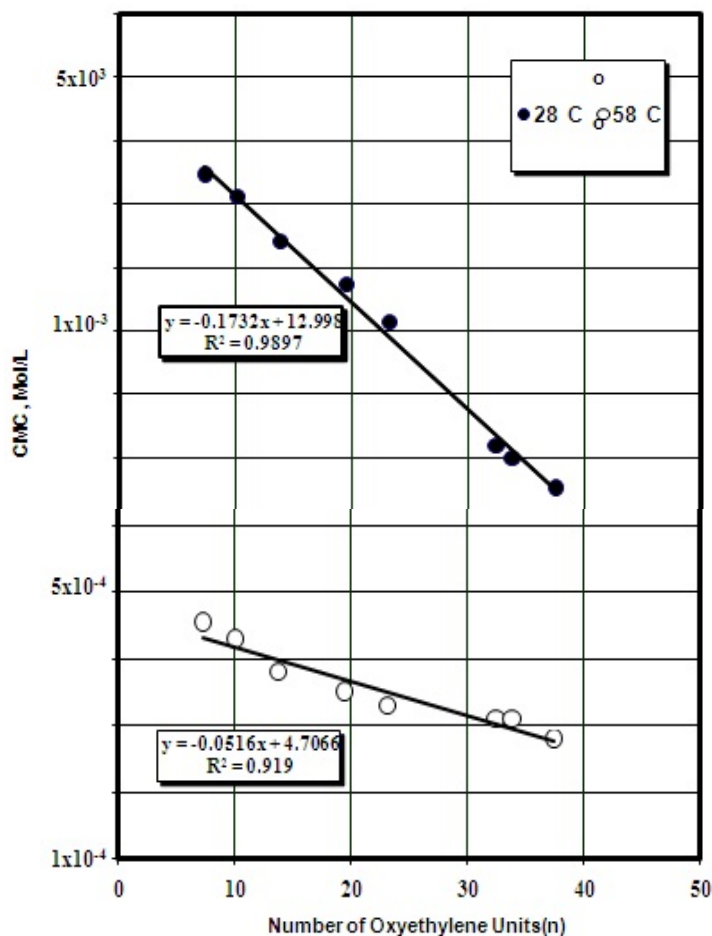


Fig. 3: Relation Between CMC and The Number of Oxyethylene Units (n) at 28 and 58 °C

Equations Relating HLB, CMC, EO of Some Nonionics:

Feasibility of equations relating HLB and some polarity terms has been extensively studied for six different polyoxyethylenated hydrophobes (Barakat *et al.*, 1997 and Mostafa, 1996). Polarity terms, in these investigations, have been measured through reverse phase GC. Important conclusions have been reached by these investigators: More accurate HLB values could be achieved by applying equations relating HLB and polarity index. These equations diminish the influence of hydrophobic portion and hence reduce the molecular structure gap between the six different hydrophobes. Also, less deviation could be achieved between the determined HLB values, using the developed equations and that deduced from NMR analysis.

HLB was first introduced by Griffin (1954) as a numerical rating system for the polarity of polyoxyethylenated alkylphenols. The HLB values of this class of nonionics are linearly related to the percent of ethylene oxide (%EO) in the molecule by the well-known equation [1].

$$\text{HLB} = (\% \text{EO}) / 5 \quad [1].$$

It has been generally observed that as the hydrophilicity and hence the HLB, of polyoxyethylenated alkylphenols, increases with increasing the critical micelle concentration (CMC) i.e., increasing the number of oxyethylene units causes a subsequent increase in CMC. Becher (1966) pointed out that a relationship of the form

$$\ln(\text{CMC}) = A+B(W) \quad [2].$$

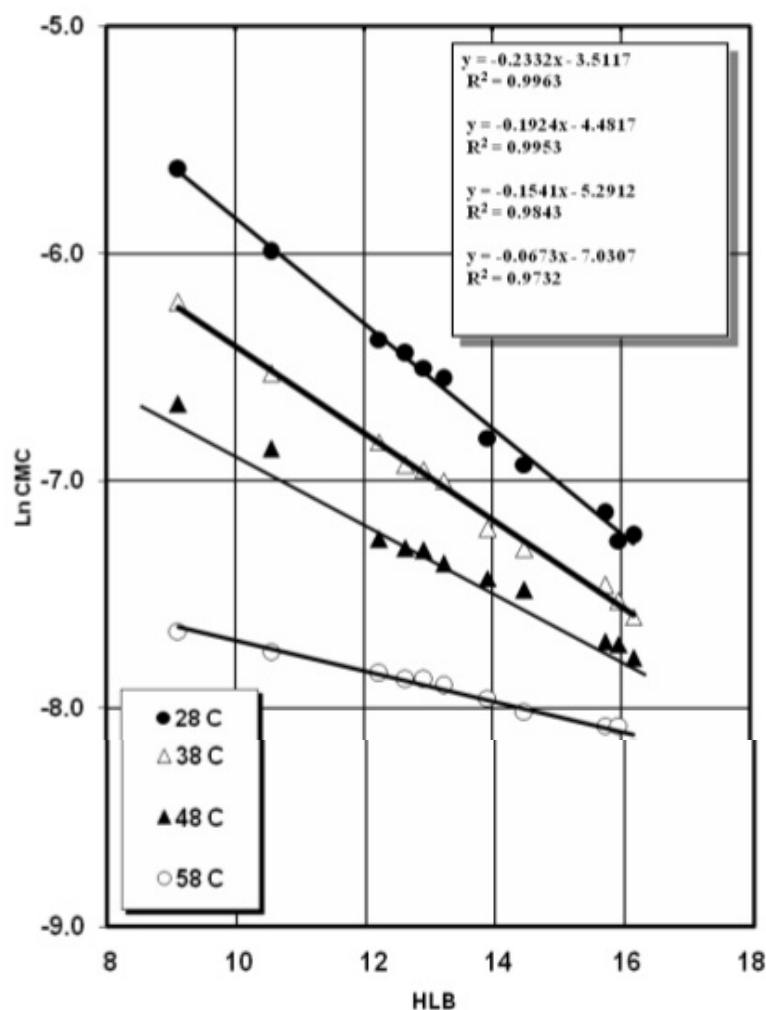


Fig. 4: CMC-HLB Relationship of Polyoxyethylenated Cholesterol at Different Temperatures.

represents much of the reported CMC data over a wide range of polyoxethylene chain lengths and to a great degree of accuracy. In equation [2] A and B are constants for a given nonionic surfactant and W is the weight fraction of ethylene oxide (EO). The linear relationship between W (or % EO) and HLB in equation [2] suggests that this equation can be written in the form:

$$\ln(\text{CMC}) = a+b(\% \text{EO}) \quad [3]$$

or

$$\ln(\text{CMC}) = c+d(\text{EON}) \quad [4]$$

where a and b in equation [3] are related to A and B in equation [2] and EON in equation [4] represents the number of ethylene oxide units.

It must be noted here that the original HLB concept has no provision for branching in the hydrophobic part of the surfactant. Thus the influence of structural variations, such as branching or unsaturation in the alkyl

chain, or changes in the point of attachment of the alkyl chain is not reflected in the HLB value. In equation [3], the influence of such variations will be reflected in the values of the constants a and b. (El-Kholy, 1993 and Mostafa, 1996). Also, when the cmc values, of ethoxylated alkylphenol formaldehyde polymeric nonionics, are plotted against the respective HLB values, equation [3] can be written as:

$$\text{Ln (CMC)} = a-b (\text{HLB}) \quad [5]$$

The most striking feature of equation [5] is that the CMC is seen to decrease with increasing HLB (negative slope). This observation is contrary to what is generally expected for the usual type of polyoxyethylenated nonionic, in which the hydrophobic group is a hydrocarbon residue, i.e., monomeric not bulky polymeric hydrophobic group (Barakat *et al.*, 1989 and Gendy *et al.*, 1994). However, such negative slope have been reported by other investigators (Rosen, 1989 and Becher, 1966). Becher (1966) has reported a negative slope for polyoxyethylenated oleyl alcohol, whereas, polyoxyethylenated steary alcohol (a hydrophobe having the same number of carbon atoms as oleyl alcohol, but with no double bond) show a positive slope. Becher (1966) suggested that the slope was apparently dependent on the hydrophobe. Several authors have reported a negative slope for polyoxyethylenated fatty alcohols and suggested that the result may be attributed to low solubility (Rosen, 1989).

HLB-CMC of Polyoxyethylenated Cholesterol:

It is obvious from data in Table (3) that in aqueous medium, the CMC values of polyoxyethylenated cholesterol nonionics, decrease with increase in the number of oxyethylene units (n) in the polyoxyethylene chain and subsequently with increase in HLB number. Also, it is noteworthy that over the investigated number of oxyethylene range, the rate of decrease in CMC is more pronounced at 28°C than at 58°C as shown in Fig. (3).

Table 5: HLB-CMC Relationship of Polyoxyethylenated Cholesterol at 48 and 58°C.

Surfactant	Temp. , °C	HLB	Ln CMC	HLB – CMC Relationship	R ² value
Ch-(7.37)	48	9.12	-6.5713	Ln (CMC)=- 5.2912 -0.1541 (HLB)	0.9843
Ch-(10.16)		10.72	-6.8124		
Ch-(13.87)		12.24	-7.2363		
Ch-(14.75)		12.53	-7.2644		
Ch-(15.23)		12.68	-7.2934		
Ch-(16.89)		13.16	-7.3233		
Ch-(19.52)		13.79	-7.4021		
Ch-(23.19)		14.50	-7.5056		
Ch-(32.56)		15.75	-7.7062		
Ch-(33.90)		15.87	-7.7517		
Ch-(37.53)		16.21	-7.7994		

Ch-(7.37)	58	9.12	-7.6628	Ln CMC= - 7.0307-0.0673 (HLB)	0.9732
Ch-(10.16)		10.72	-7.7517		
Ch-(13.87)		12.24	-7.8494		
Ch-(14.75)		12.53	-7.8753		
Ch-(15.23)		12.68	-7.8753		
Ch-(16.89)		13.16	-7.9020		
Ch-(19.52)		13.79	-7.9576		
Ch-(23.19)		14.50	-8.0164		
Ch-(32.56)		15.75	-8.0789		
Ch-(33.90)		15.87	-8.0789		
Ch-(37.53)		16.21	-8.1807		

Table 6: Deduced and Predicted CMC Values Polyoxyethylenated Cholesterol at 28 and 38°C.

Surfactant Designation	HLB	CMC, Mol/L			
		at 28 °C		at 38 Oc	
		Deduced	Predicted	Deduced	predicted
Ch-(7.37)	9.12	3.6x10 ⁻³	3.6 x10 ⁻³	2.0 x 10 ⁻³	2.0x10 ⁻³
Ch-(10.16)	10.72	2.5 x 10 ⁻³	2.5 x10 ⁻³	1.5 x 10 ⁻³	1.4 x10 ⁻³
Ch-(13.87)	12.24	1.7 x 10 ⁻³	1.7 x10 ⁻³	1.1 x 10 ⁻³	1.1 x10 ⁻³
Ch-(14.75)	12.53	1.6 x 10 ⁻³	1.6 x10 ⁻³	1.0 x 10 ⁻³	1.0 x10 ⁻³
Ch-(15.23)	12.68	1.5 x 10 ⁻³	1.5 x10 ⁻³	1.0 x 10 ⁻³	9.9 x10 ⁻⁴
Ch-(16.89)	13.16	1.4 x 10 ⁻³	1.4 x10 ⁻³	9.3 x 10 ⁻⁴	9.0x10 ⁻⁴
Ch-(19.52)	13.79	1.1 x 10 ⁻³	1.2 x10 ⁻³	8.3 x 10 ⁻⁴	8.0x10 ⁻⁴
Ch-(23.19)	14.50	9.8 x 10 ⁻⁴	1.0 x10 ⁻³	7.3 x 10 ⁻⁴	7.0 x10 ⁻⁴
Ch-(32.56)	15.75	7.2x 10 ⁻⁴	7.6 x10 ⁻⁴	5.7 x 10 ⁻⁴	5.5 x10 ⁻⁴
Ch-(33.90)	15.87	7.0 x 10 ⁻⁴	7.4 x10 ⁻⁴	5.6 x 10 ⁻⁴	5.3 x10 ⁻⁴
Ch-(37.53)	16.21	6.5 x 10 ⁻⁴	6.8 x10 ⁻⁴	5.3 x 10 ⁻⁴	5.0 x10 ⁻⁴

Table 7: Deduced and Predicted CMC Values of Polyoxyethylenated Cholesterol at 48 and 58°C.

Surfactant Designation	HLB	CMC, Mol/L			
		at 48 °C		at 58 °C	
		Deduced	Predicted	Deduced	predicted
Ch-(7.37)	9.12	1.4x10 ⁻³	1.2 x10 ⁻³	4.7 x10 ⁻⁴	4.8 x10 ⁻⁴
Ch-(10.16)	10.72	1.1 x10 ⁻³	9.7 x10 ⁻⁴	4.3 x10 ⁻⁴	4.3 x10 ⁻⁴
Ch-(13.87)	12.24	7.2 x10 ⁻⁴	7.6 x10 ⁻⁴	3.9 x10 ⁻⁴	3.9 x10 ⁻⁴
Ch-(14.75)	12.53	7.0 x10 ⁻⁴	7.3 x10 ⁻⁴	3.8 x10 ⁻⁴	3.8 x10 ⁻⁴
Ch-(15.23)	12.68	6.8 x10 ⁻⁴	7.1 x10 ⁻⁴	3.8 x10 ⁻⁴	3.8 x10 ⁻⁴
Ch-(16.89)	13.16	6.6 x10 ⁻⁴	6.6 x10 ⁻⁴	3.7 x10 ⁻⁴	3.6 x10 ⁻⁴
Ch-(19.52)	13.79	6.1 x10 ⁻⁴	6.0 x10 ⁻⁴	3.5 x10 ⁻⁴	3.5 x10 ⁻⁴
Ch-(23.19)	14.50	5.5 x10 ⁻⁴	5.4 x10 ⁻⁴	3.3 x10 ⁻⁴	3.3 x10 ⁻⁴
Ch-(32.56)	15.75	4.5 x10 ⁻⁴	4.4 x10 ⁻⁴	3.1 x10 ⁻⁴	3.1 x10 ⁻⁴
Ch-(33.90)	15.87	4.3 x10 ⁻⁴	4.4 x10 ⁻⁴	3.1 x10 ⁻⁴	3.0 x10 ⁻⁴
Ch-(37.53)	16.21	4.1 x10 ⁻⁴	4.1 x10 ⁻⁴	2.8 x10 ⁻⁴	3.0 x10 ⁻⁴

In polyoxyethylenated cholesterol, the hydrophobic tail is bulky which produces an almost parallel arrangement of the surfactant molecules in the micelle, similar to that at the planar liquid-air interface. At the interface, the introduction of an EO group causes a slight increase in the hydrophobic nature of the molecule, as evidenced by an increase in the value of $-DG_{ad}$ (Rosen, 1989^b). Such an increase in the hydrophobic character of the molecule when the surfactant molecules are arranged in the micelle in a similar, more or less parallel fashion should produce a decrease in the CMC.

HLB-CMC relationship of polyoxyethylenated cholesterol can be represented by applying Equation [5]. When the CMC values are plotted against the respective HLB numbers in semilogarithmic coordinates, the plots are remarkably linear (Fig. 4). From the least-squares regression analysis of data, the values of the two constants a (intercept) and b (slope) are obtained and presented in Tables (4 and 5).

Data for the deduced and predicted CMC values of these nonionic surfactants are presented in Tables (6 and 7) at the four investigated temperatures. R² values show the reliability of the four developed equations. From the data in Tables (6 and 7), it is apparent that a strong relationship exists between the HLB and CMC of the investigated polyoxyethylenated cholesterol at any of the investigated temperatures.

Conclusion:

The CMC-HLB relationship for polyoxyethylenated cholesterol nonionics is represented by the equation:

$$\ln(\text{CMC}) = a - b(\text{HLB})$$

which is contrary to the usual type of POE nonionic surfactants.

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