Effect of Additives on the Critical Micelle Concentration of Some Polyethoxylated Nonionic Detergents

W. U. MALIK and S. M. SALEEM, Chemical Laboratories, University of Roorkee, Roorkee, India

Abstract

The effect of electrolytes and other additives influencing water structure, viz., urea and formamide, has been studied on the micelle formation of polyethoxylated nonionic detergents in their aqueous solutions. The decrease in critical micelle concentration (c.m.c.) by electrolytes has been interpreted in terms of salting out mechanism and evidence has been obtained in support of the contention that micelles of polyethoxylated nonionic detergents are weakly positively charged. Effect of urea and formamide on the c.m.c. values of these nonionic detergents indicate that hydrophobic bonding is loosened in their presence with a consequent increase in the c.m.c. of these detergents.

Introduction

THE EFFECT OF ELECTROLYTES on the critical micelle concentration (c.m.c.) of ionic surfactants has been extensively studied by several workers (1,2). Recently, Becher (3) and Schick (4–6) have reported the effect of several additives on nonionic surfactants. The results have been interpreted mostly in terms of ion hydration and water structure. The problem, however, has not received an extensive and systematic treatment as it deserves. A detailed study incorporating the influence of variegated additives—e.g., electrolytes belonging to the lyotropic series, substances well known as breakers of water structure—acids, and bases on a few polyethoxylated nonionic detergents was planned. The results of these studies are reported in this paper.

Experimental Procedures

The nonionic detergents Nonex 501 (methoxy polyethylated glycol laurate), Nonidet P40 (100% polyethyleneoxide condensate), and Nonidet P42 (condensation product of dioctylphenol and ethylene oxide) were BDH products used without any further purification. Other chemicals used were analytical reagent grade.

The surface tension values of aqueous solutions of the nonionic detergents were determined by the du Nouy's ring method at 30C ± 1C. Identical glass containers and volumes were used, and the container wall was kept at a minimum to reduce the effects due to adsorption on the container. The c.m.c values were taken from the sharp breaks in the surface tension vs. logarithms of detergent concentration plots. The c.m.c. values are expressed in gm/dl.

Results and Discussion

Effect of electrolytes

The addition of salts brings about a decrease in the c.m.c. of the detergents. The behavior is similar to that observed for the variation in properties like flocculation, swelling, viscosity, heat of hydration, adsorption, etc., of lyophilic colloids in presence of various anions and cations of the lyotropic series. The relative effectiveness of ions is in accordance with their position in the lyotropic series (Table I), i.e., to the size of the hydrated ions. The order of effectiveness of ions in lowering the c.m.c. of these soaps is depicted in Fig. 1. The c.m.c. also decreases with the increase in concentration of a particular electrolyte as evident from Fig. 2.

The above observations find support in the work of Schick et al. (4,5) who explained variation in c.m.c. of nonionic surfactants in terms of salting out mechanism. In general the salting out of the neutral molecules depends on the concentration and the ionic radii of the added electrolyte, and the dielectric constant of the neutral molecules. Small hydrated ions (low lyotropic numbers) are more effective in salting out neutral molecules, than large hydrated ions (high lyotropic numbers).

From these results it may be concluded that the hydration factor plays an important role in bringing about changes in the c.m.c. values. The hydration of the polyoxyethylene chains is brought about through the formation of hydrogen bonds between the ether oxygens and water molecules. The addition of the electrolyte shifts the equilibrium towards the dehydration side, with the result that the solubility of the detergent and consequently its c.m.c. is lowered.

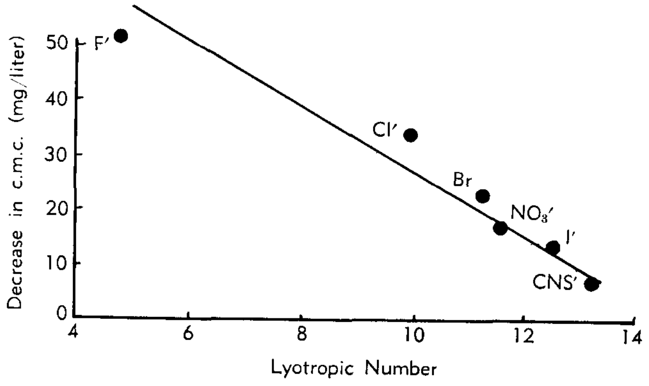

FIG. 1. Relation between the lyotropic number of anions and decrease in c.m.c. of nonidet P40.

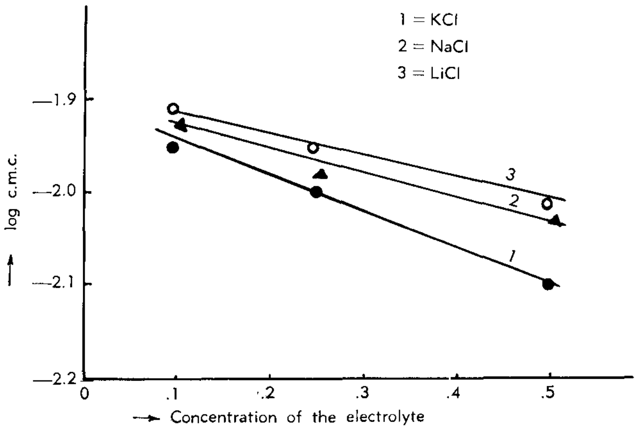

FIG. 2. Effect of the concentration of the electrolytes on the c.m.c. of nonidet P40.

TABLE I

Effect of electrolytes on the c.m.c. of the non-ionic detergents

Detergent	c.m.c in gm/dl	Decrease in the c.m.c. in 0.5M electrolyte expressed in mg/liter										
		NH_4Cl	KCl	NaCl	LiCl	$1/2MgCl_2$	NaF	NaBr	$NaNO_3$	NaI	NaCNS	$1/2Na_2SO_4$
Nonex 501	6.23×10^{-3}	40.6	32.5	28.8	23.1	12.3	42.3	17.7	17.7	9.2	7.2	38.7
Nonidet P40	12.58×10^{-3}	46.1	46.4	34.0	29.4	16.7	50.8	22.8	16.7	13.6	6.9	41.6
Nonidet P42	39.80×10^{-3}	239.6	230.2	160.9	81.1	39.2	186.8	132.04	81.8	19.7	11.7	174.2

Lyotropic numbers of various anions and cations: K = 75, Na = 100, Li = 115, F = 4.8, Cl = 10.0, Br = 11.3, NO_3 = 11.6, I = 12.6, CNS = 13.3.

Relative position of various anion and cations in the Hofmeister series: $F > SO_4 > Cl > Br > NO_3 > I > CNS$
$NH_4 > K > Na > Li > Mg$.

The large effectiveness of the anions of the lyotropic series in bringing about change in the c.m.c. of nonionic soaps also lends support to the view of Becher (3) who considered the micelles of the polyoxyethylated nonionic detergents to be weakly positively charged. His view is further confirmed by studying the effect of proton donors and acceptors on the c.m.c. of these detergents as discussed below.

Effect of acids and bases

The c.m.c. of these nonionic detergents is greatly influenced by the addition of acids and bases. A decrease in c.m.c. is observed at lower concentrations (up to 0.1M) of HCl and HNO_3, but at higher concentrations (2.0–3.0M) a marked increase is observed (Table II). On the other hand the presence of the base lowers the c.m.c. over the entire concentration range. Reliable data could not be obtained with Nonex 501 where turbidity sets in presence of sodium hydroxide.

The decrease in c.m.c. at lower concentration of the acids and with alkali can be attributed to the usual electrolyte effect. At higher concentrations of the proton donor, oxonium ions are formed with the ethyleneoxide, thereby imparting ionic character to the nonionic soaps. The c.m.c. of the detergent is therefore increased.

Effect of urea and formamide

The effect of substances known for their so called water structure breaking properties on the c.m.c. of nonionic detergents was studied as a function of their concentration (Table III). The ratio of the c.m.c. in presence of the additives to the c.m.c. in their absence was adopted as a convenient means to represent the data. At low concentration (0.2M) these additives have little influence, on the micelle formation, but at higher concentration (2–6M) the c.m.c. values are markedly increased. Furthermore, at higher concentration of these additives, a linear relationship exists between $(c.m.c.)/(c.m.c.)_0$ and concentration of the additive (Fig. 3,4).

Recently considerable interest has been focused on the relation between hydrophobic bonding and water structure by several workers (6–8). The general consensus of opinion is that structural consideration of the medium is of ample importance in explaining the role of hydrophobic bonding, i.e., the phenomenon in which the nonpolar residues or moieties (usually hydrocarbon) in presence of water associate together to form intermolecular aggregates as in native protein solutions, or such as micelles in surfactant solu-

TABLE II

Effect of Proton Donor and Acceptors on the c.m.c. of the Nonionic Detergents

Detergent	c.m.c. $\times 10^{-3}$ (in gm/di) in presence of sodium hydroxide		c.m.c. $\times 10^{-3}$ (in gm/dl) in presence of acids			
			HCl		HNO_3	
	0.1 M	0.5 M	0.1 M	3.0 M	0.1 M	1.0 M
Nonex 501	......	......	......	......	......	......
Nonidet P40	10.5	6.3	12.5	22.3	11.8	23.0
Nonidet P42	31.6	25.8	31.6	47.3	33.4	59.5

TABLE III

Effect of Urea and Formamide on the c.m.c. of the Nonionic Detergents

Conc. of the additive M	c.m.c. gm/dl $\times 10^{-3}$		
	Nonex 501	Nonidet P40	Nonidet P42
Urea			
0.0	6.23	12.58	39.81
1.0	6.59	14.12	50.11
2.0	8.91	19.95	....
3.0	11.88	26.60	66.83
4.0	14.96	31.62	....
5.0	17.78	37.58	119.43
6.0	22.38	66.98	158.40
Formamide			
1.0	6.97	14.35	43.45
2.0	7.94	21.13	84.10
3.0	10.91	29.00	....
4.0	13.33	37.15	141.20

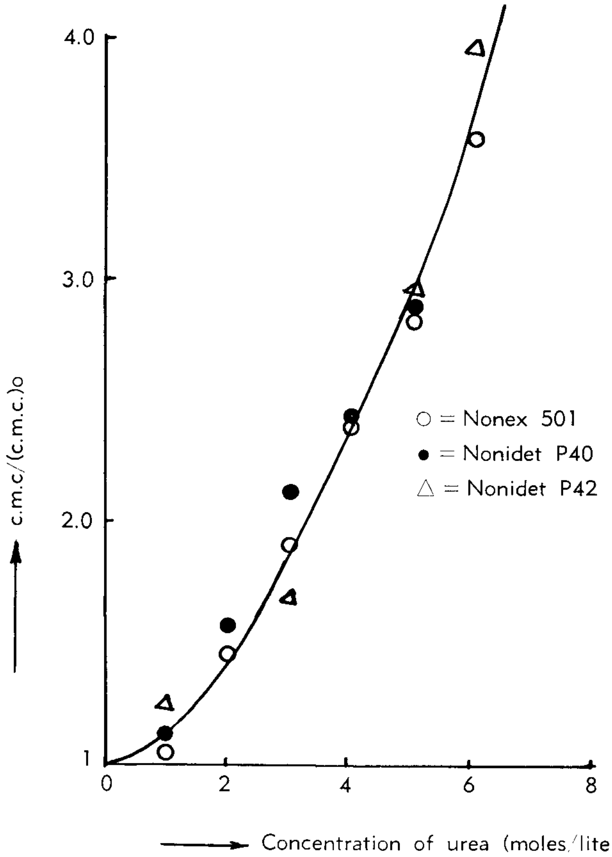

FIG. 3. Effect of urea on the c.m.c. of the detergents.

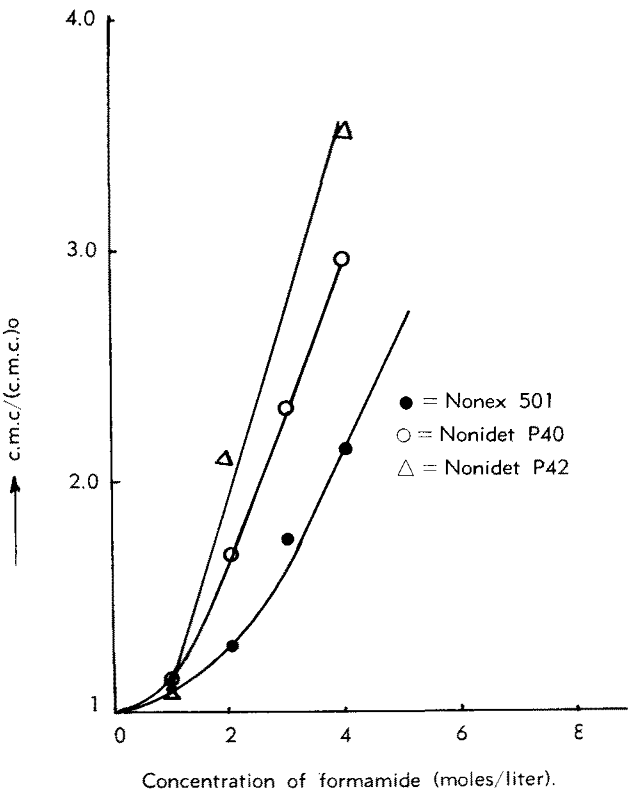

FIG. 4. Effect of formamide on the c.m.c. of the detergents.

tions. According to recent studies (9–10) the effect of urea is to reduce the strength of hydrophobic bonding. Urea solutions shift the equilibrium of the hydrophobic forces by providing an environment for nonpolar groups, which is less unfavorable than the environment provided by pure water.

Water molecules become more ordered around a nonpolar solute, with an increasing extent of hydrogen bonding in this region, urea behaves in a way to reduce the ordered regions provided by another solute and, being itself a good hydrogen bonding agent, participates in the formation of mixed clusters and thus can be regarded as water structure breaker.

The overall solubility of polyethoxylated nonionic detergents is determined by the extent of hydration of the hydrophilic groups through the formation of hydrogen bonds between ether oxygens and water molecules. The c.m.c. of these detergents depends on the balance of forces between the Vander Waal's interaction in the hydrophobic groups and opposing hydration of ethyleneoxide chains. The marked increase in the c.m.c. of these detergents in presence of urea can therefore be attributed to the increased hydration of ethylene–oxide chains and loosening of the hydrophobic bonding.

The results on the effect of formamide on c.m.c. can also be explained in the light of the above reasoning. The water structure breaking property of formamide has been fully demonstrated by Rupley (11) on the basis of the viscosity of its aqueous solutions.

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