Micelle Formation in Mixtures of Nonionic and Anionic Detergents

M. J. SCHICK and D. J. MANNING, Lever Brothers Company Research Center, Edgewater, New Jersey

Abstract

This paper describes the effect of a homologous series of polyoxyethylene n-dodecanols on the critical micelle concentration (CMC) of sodium n-dodecyl alcohol sulfate as a function of composition of the mixtures and temperature. The CMC of the nonionic component of the mixed micelles is about one-hundredth of that of the anionic. Only a gradual increase in the CMC values of the mixed micelles above the values of the nonionic components was observed in the composition range of 0–90 mole % anionic detergent. This is followed by an abrupt transition to the high CMC values of the anionic component. The gradual increase of the CMC values in the range below 90 mole % anionic detergent of n-dodecanol + 4 EO exceeds that of the higher homologs containing 7, 23 and 30 ethylene oxide units. It is postulated that the degree of ionic repulsion of the ionic component in mixed micelles is markedly decreased as the proportion of nonionic component reaches a threshold range of 10 mole %. This effect is more pronounced with large ethylene oxide coils operating at the periphery of the micelle core than with short ethylene oxide coils. Thermodynamic data have been included.

Introduction

WHEREAS MUCH IS KNOWN about micelle formation in systems of a single nonionic or anionic component, there has been relatively little work reported on micelle formation in mixtures of nonionic and anionic detergents (1–9). A study of micelle formation of mixtures of nonionic and anionic detergents with comparable hydrophobic groups holds, however, promise of shedding light upon the structure of mixed micelles. Nakagawa and Inoue (3,4) were the first to confirm definitely the existence of mixed micelles in an electrophoretic and diffusion study of mixtures of ionic and nonionic detergents in aqueous solutions. At all mixing ratios single peaks were observed in the electrophoresis diagrams. The trend in the change in mobility from a high value to almost zero as a function of the mole fraction of the mixture agrees with our expectations. In further work Kuriyama, Inoue and Nakagawa (7) have investigated the temperature dependence of the micellar weights of mixtures of a nonionic and an anionic detergent as a function of mixing ratio. These authors have demonstrated that the micellar weight of the nonionic detergent increases with rising temperature, whereas that of the ionic detergent decreases. In mixtures the increase in micellar weight of the nonionic detergent due to the temperature increase is progressively suppressed by increased addition of ionic detergent, and at a definite mixing ratio 20:80 (wt %) the temperature dependence reverses. Corkill, Goodman and Tate (8) describe a detailed investigation of the effect of a nonionic detergent, n-dodecanol + 6 EO, on the micelle formation of sodium dodecyl sulfonate, particular attention having been paid to changes in the degree of dissociation of the anionic detergent brought about by its incorporation in micelles. Below a critical concentration the surface-active anions are adsorbed by the nonionic micelles, while above this critical concentration mixed micelles of constant composition are found as evidenced by electrophoresis, conductivity, emf and other type of measurements. A relevant point has been raised by Mysels and Otter (10) in their development of an empirical method for the determination of the composition of mixed anionic micelles. Namely, in the pure system the composition of micelles and monomers is the same and must remain constant since only one component is present, whereas in the mixed system the compositions of micelles and monomers are different and change with overall concentration.

Whereas these investigations (3–9) dealt with micelle formation of mixtures consisting of a single nonionic and a single anionic detergent, Yoda, Meguro, Kondo and Ino (1) investigated mixtures of a single anionic detergent with a homologous series of polyoxyethylene n-dodecanols. These authors determined the CMC from electrical conductivity vs. concentration curves. For each homolog the break points in the specific or equivalent conductivity curves become progressively more ambiguous with increasing mole ratio of nonionic detergent.

The object of this investigation was an experimental study of micelle formation in mixtures of a homologous series of a polyoxyethylene type nonionic detergent with a single anionic detergent by means of experimental procedures, which are amenable to accurate measurement of the CMC over the entire range of mole ratios.

Experimental

Molecularly distilled ethylene oxide (EO) condensates of n-dodecanol have been obtained from General Aniline and Film Corporation. The average chain length of the ethylene oxide adducts has been determined from their hydroxyl values. The homogeneity of the nonionic detergents has been assessed from the observed sharp breaks in the surface tension vs. logarithm of concentration plots; only samples exhibiting sharp breaks have been used. Sodium n-dodecyl sulfate was prepared by the method of Dreger et al. (11), recrystallized several times from ethanol, and extracted with petroleum ether. The purity of this material was readily checked from the shape of the surface tension vs. logarithm of concentration plots near the CMC. The water was redistilled from alkaline permanganate. For the procedure of the surface tension measurements see our previous communication (12).

Results

A convenient way of assessing the balance of forces, i.e., van der Waals and opposing electrostatic or hydration forces to which micelle formation is ascribed, is the determination of the concentration of maximum molecular dispersion or, in other words, the CMC.

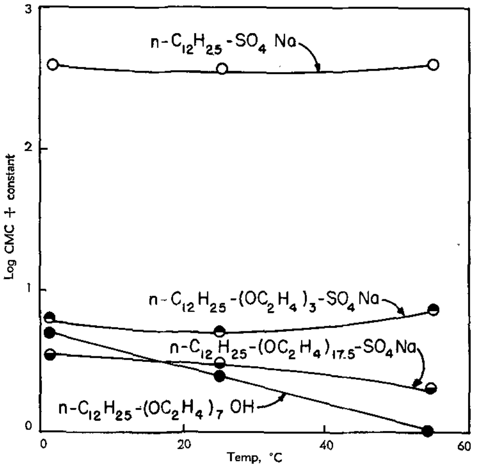

FIG. 1. CMC of sodium n-dodecyl alcohol sulfate, sodium n-dodecyl ether alcohol sulfates and polyoxyethylene n-dodecanol in aqueous solutions as a function of temperature. Data taken from reference (12).

Since at this particular concentration the interaction between micelles is negligible, CMC data permit interpretation of experimentally measured behavior of micelles in terms of their structures. Therefore, CMC values of single detergents or mixtures thereof have been determined throughout this investigation, which were taken from the sharp breaks in the surface tension vs. logarithm of detergent concentration plots (12–14). It is worth noting that these plots exhibited equally sharp breaks for mixtures and for single components. All measurements have been carried out in aqueous solutions at 5,25 or 45C (±0.1).

Figure 1 shows that the temperature dependence of the CMC of sodium n-dodecyl ether alcohol sulfate with a short polyether group follows the pattern of sodium n-dodecyl alcohol sulfate (SDS); in contrast, the corresponding data of the homolog with a long polyether group follow that of polyoxyethylene n-dodecanol (12). These findings have now been amplified by this investigation of the CMC's of mixtures of nonionic and anionic detergents with comparable hydrophobic groups as a function of composition of the mixtures and temperature.

Let us first examine the temperature dependence of the CMC of the single components of the mixtures of nonionic and anionic detergents. The familiar plot of log CMC vs. 1/T for a homologous series of polyoxyethylene n-dodecanol is given in Figure 2. These plots are linear and show a marked increase in CMC values on lowering the temperature. The latter is in line with the inverse temperature solubility relation of nonionic detergents. At a specific temperature, the CMC increases with increasing length of the ethylene oxide chain. This is attributed to the increased hydration of the hydrophilic group resisting aggregation. In contrast to the nonionic detergent, the CMC of SDS passes through a minimum at 25C and increases with increasing temperature in the range from 25 to 45C, as shown in Figure 1. The latter is attributed to decreased hydrocarbon chain attraction resulting from increased Brownian motion.

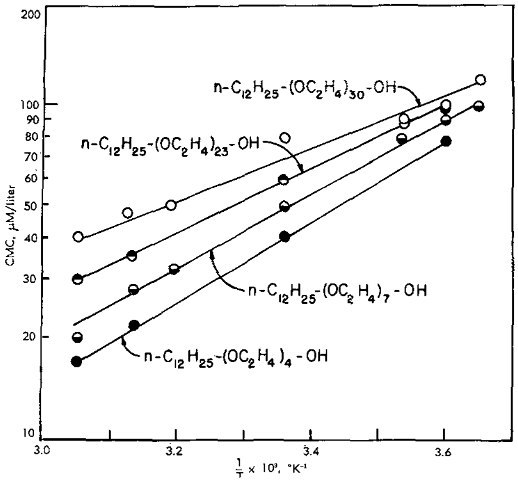

FIG. 2. Plot of log CMC vs. 1/T of polyoxyethylene n-dodecanols in aqueous solutions. Data also taken from references (12) and (14).

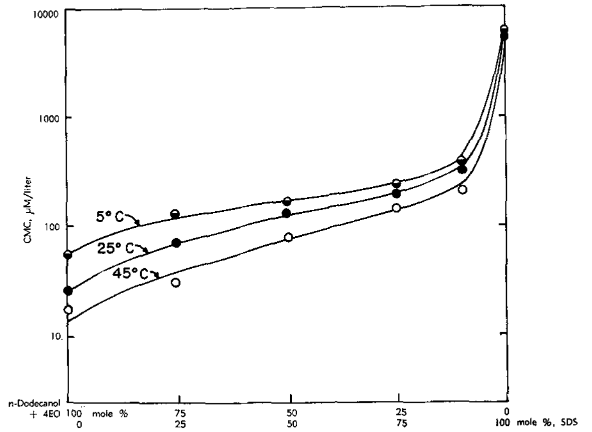

FIG. 3. CMC of SDS and n-dodecanol + 4 EO mixtures in aqueous solutions as a function of mixing ratio and temperature.

The effect of a homologous series of polyoxyethylene n-dodecanols on the CMC of SDS is illustrated in Figures 3 to 6 as a function of composition and temperature. Variations in the number of ethylene oxide units (i.e., 4,7,23, and 30) and in temperature (i.e., 4, 25 and 45C) have been studied. The CMC of the nonionic component of the mixed micelles is about one-hundredth of that of the anionic. Whereas the CMC of the nonionic component decreases markedly on increasing the temperature from 5 to 45C, the CMC of the anionic changes only slightly in the reverse direction. With the four homologous polyoxyethylene n-dodecanols, only a gradual increase in the CMC values of the mixed micelles above the values of the nonionic components was observed in the composition range of 0–90 mole % anionic detergent. This is followed by an abrupt transition to the high CMC values of the

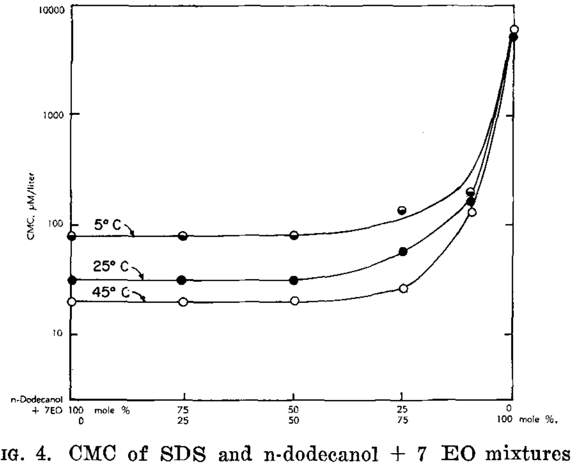

FIG. 4. CMC of SDS and n-dodecanol + 7 EO mixtures in aqueous solutions as a function of mixing ratio and temperature.

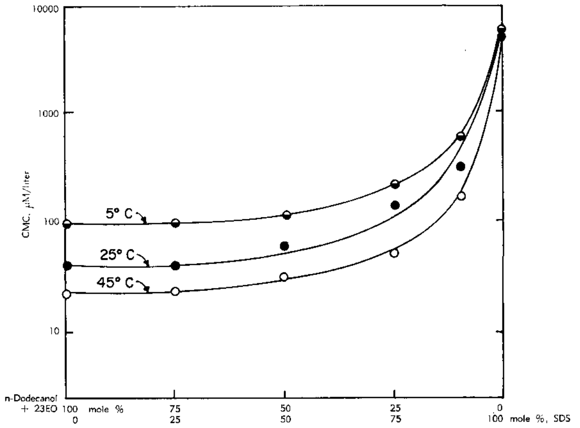

FIG. 5. CMC of SDS and n-dodecanol + 23 EO mixtures in aqueous solutions as a function of mixing ratio and temperature.

anionic component. The gradual increase in the range below 90 mole % anionic detergent of n-dodecanol + 4 EO exceeds that of the higher homologs containing 7, 23 and 30 ethylene oxide units. A clearer picture of the temperature dependence of the CMC of these mixtures is presented in Figures 7 and 8. From these figures, the transition from a plot characteristic of SDS with a minimum of 25C and negligible temperature dependence to the linear plot of n-dodecanol + n EO with a marked temperature dependence is apparent. This transition is more pronounced for mixtures containing n-dodecanol + 4 EO than for those with n-dodecanol + 30 EO.

Discussion

It is generally accepted that with ionic detergents micelle formation is ascribed to a balance between hydrocarbon-chain attractions and electrostatic repulsions, whereas with nonionic detergents the hydrocarbon-chain attractions are opposed by the hydration and space requirement of the ethylene oxide chains (13). Consequently, it is expected that this balance between cohesive and opposing electrostatic or hydration forces, respectively, varies in mixed ionic-nonionic micelles as a function of the mixing ratio. This is borne out by our results on CMC values of mixtures of anionic and nonionic detergents. The continuous decrease from the high CMC value of SDS to the low values of polyoxyethylene n-dodecanols may be attributed to the increased suppression of the repulsive forces between the ionic head groups by the incorporation of the nonionic head groups into the micellar/solution interface.

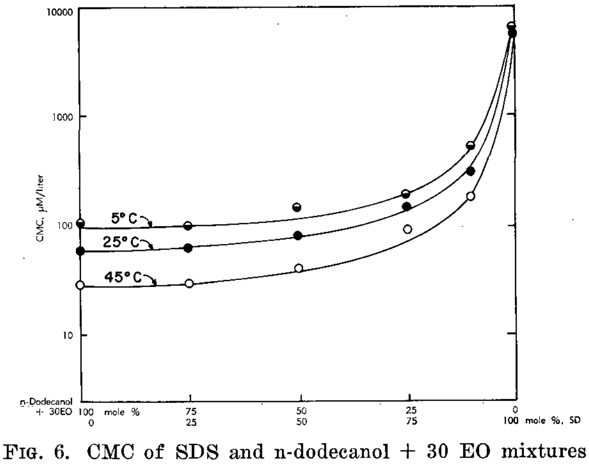

FIG. 6. CMC of SDS and n-dodecanol + 30 EO mixtures in aqueous solutions as a function of mixing ratio and temperature.

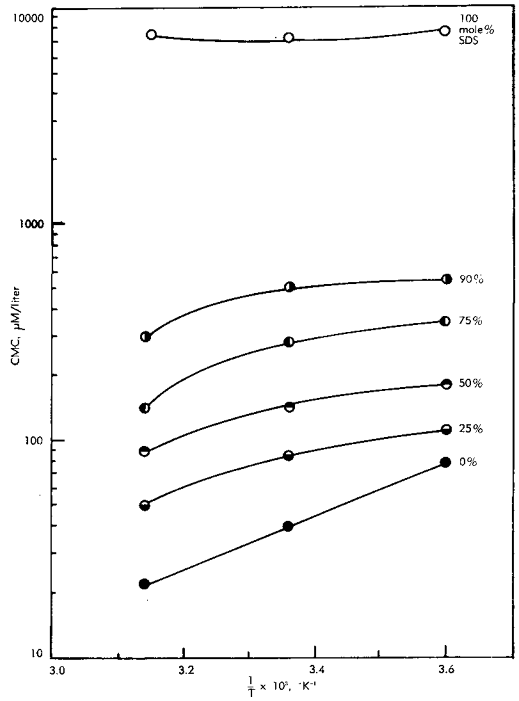

FIG. 7. Plot of log CMC vs. 1/T of SDS and n-dodecanol + 4 EO mixtures as a function of mixing ratio.

In the light of these general considerations and two specific phenomena, i.e. (1) the abrupt transition at a composition of 90 mole % anionic detergent from the low CMC values corresponding to the nonionic component to the high CMC values of the anionic component, and (2) the larger increase of the CMC values of n-dodecanol + 4 EO in the range below 90 mole % anionic detergent as compared to the higher homologs containing 7, 23 and 30 ethylene oxide units, it is postulated that the degree of ionic repulsion of the

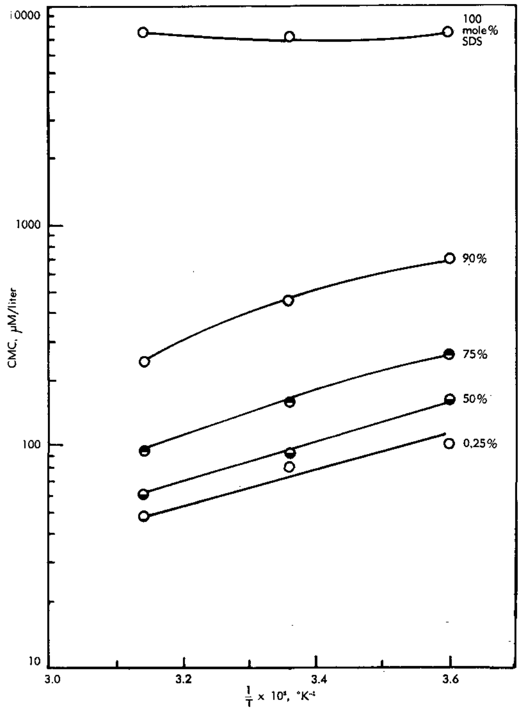

FIG. 8. Plot of log CMC vs. 1/T of SDS and n-dodecanol + 30 EO mixtures as a function of mixing ratio.

TABLE I

Partial Molal Heats of Micelle Formation of Mixtures of SDS and n-Dodecanol + nEO

Detergent	SDS, mole %	n-Dodecanol + nEO, mole %	$\overline{\Delta H}$m, kcal/mole		
			Temp		
			5–25C	OC	25–45C
SDS	100	0	0.4	0	—0.6
	90	10	1.0		4.9
	75	25	1.9		6.4
	50	50	2.0		4.1
	25	75	2.2		5.1
n-Dodecanol + 4EO	0	100		←5.5→	
SDS	100	0	0.4	0	—0.6
	90	10	3.3		4.2
	75	25	5.6		5.5
	50	50	4.8		4.9
	25	75	5.0		5.5
n-Dodecanol + 7EO	0	100		←5.0→	
SDS	100	0	0.4	0	—0.6
	90	10	4.1		7.4
	75	25	5.8		7.6
	50	50	4.1		4.0
	25	75	4.1		5.7
n-Dodecanol + 23EO	0	100		←4.5→	
SDS	100	0	0.4	0	—0.6
	90	10	3.5		6.2
	75	25	3.8		4.7
	50	50	4.6		3.8
	25	75		←3.7→	
n-Dodecanol + 30EO	0	100		←3.7→	

ionic component in mixed micelles is markedly decreased as the proportion of nonionic component reaches a threshold range of 10 mole %. This effect is more prounounced with large ethylene oxide coils operating at the periphery of the micellar core than with short ethylene oxide coils.

This contention is supported by considerations of the dimensions reported for micellar models of nonionic and ionic detergents, respectively. First, let us examine the mode of packing of the ethylene oxide chains in the outer shell of nonionic micelles as shown by Schick, Atlas and Eirich (13). A comparison of the experimental area available to one ethylene oxide chain at the periphery of the spherical oil droplet; i.e., 25 Å^2 (calculated on the assumption of extended hydrocarbon chains in the core) or 44 Å^2 (calculated on the assumption of an oil droplet of density one) for n-dodecanol + 14 EO, with that at the micellar periphery, i.e., 117 Å^2 for n-dodecanol + 14 EO, indicates that the volume encompassed between is that of a truncated cone. The cross-sectional area of the corresponding undistorted ethylene oxide coil amounts to 142 Å^2, which exceeds by far the mean area of this truncated cone (half height). It is concluded that the ethylene oxide chains in the outer spherical shell of the nonionic micelle are appreciably compressed to a volume much smaller than required for the undistorted polymer coil. The increased space requirement on increasing the length of the ethylene oxide chain from 14 to 30 ethylene oxide units is demonstrated by the concomitant increase of the cross-sectional area of the undistorted ethylene oxide coils of the corresponding n-dodecanol condensates from 142 Å^2 to 303 Å^2. These conclusions are supported by the volumes of the ethylene oxide unit in the outer shell, which increase with increasing ethylene oxide chain length of the nonionic detergents, as anticipated from the increased hydration.

Secondly, let us consider the mode of packing in ionic micelles. In the absence of electrostatic repulsions the minimum space requirement for the polar head groups at the periphery of the oil droplet amounts to 20 Å^2. Tartar (15) estimated the area of the dissociated polar head groups to be 66 Å^2. Intermediate values are expected in mixed micelles. The ethylene oxide coils in the outer shell of mixed micelles may have the shape of either undistorted coils or truncated cones depending on the mixing ratio. It follows from these considerations that one ethylene oxide chain in either of these two forms will solubilize several polar head groups, and consequently suppress ionic repulsion. This effect becomes more pronounced with increasing length of the ethylene oxide chain.

Thirdly, hydrogen bonding forces between ionic and nonionic head groups may also play a vital role in suppressing ionic repulsion (2,5). This may result in uncoiling of the ethylene oxide chain at the micellar periphery. For example, a coil containing 30 ethylene oxide units may be extended to 75 Å. In the light of these arguments the predominantly nonionic character of the mixed micelles is easily understood.

Finally, the thermodynamics of mixed micelle formation is briefly covered (12,16,17). Molyneux, Rhodes and Swarbrick have recently critically reviewed the general problem of the thermodynamics of micelle formation (18). The temperature variation of the CMC for mixtures of anionic and nonionic dedetergents has been converted into partial molal heats of micelle formation $\overline{\Delta H}_m$, and these have been compared with the corresponding values obtained for the components (12). The pertinent data are given in Table I. SDS exhibits a reversal in sign of $\overline{\Delta H}_m$ at 25C, which has been explained by Goddard and Benson in terms of the "iceberg" picture of water (19). In contrast, the $\overline{\Delta H}_m$ values of nonionic detergents and mixtures of anionic and nonionic detergents containing at least 10 mole % of the nonionic component are always positive. These results signify the importance of desolvation of the ethylene oxide chains on aggregation in all the mixtures (12), which is in line with the model postulated for the mixed micelles.

REFERENCES

1. Yoda, O., K. Meguro, T. Kondo and K. Ino, Nippon Kagaku Zasshi, *77*, 905 (1956); Chem. Abstr., *51*, 7805 g (1957).
2. Schick, M. J., and F. M. Fowkes, J. Phys. Chem., *61*, 1062 (1957).
3. Nakagawa, T., and H. Inoue, Nippon Kagaku Zasshi, *78*, 636 (1957); Chem. Abstr. *52*, 2429 h (1958).
4. Shinoda, K., T. Nakagawa, B. Tamamuchi and T. Isemura, "Colloidal Surfactants," Academic Press, New York (1963), p 135 and 138.
5. Biswas, A. K., and B. K. Mukherji, J. Phys. Chem. *64*, 1 (1960).
6. Corkill, J. M., J. F. Goodman and R. H. Ottewill, Trans. Far. Soc. *57*, 1627 (1961).
7. Kuriyama, K., H. Inoue and T. Nakagawa, Kolloid-Z. u. Z. für Polymere, *183*, 68 (1962).
8. Corkill, J. M., J. F. Goodman and J. R. Tate, Trans. Far. Soc. *60*, 986 (1964).
9. Mankowich, A. M., JAOCS *41*, 449 (1964).
10. Mysels, K. J., and R. J. Otter, J. Colloid Sci. *16*, 462 (1961), (Fig. 6).
11. Dreger, E. E., I. Keim, G. D. Miles, L. Shedlovsky and J. Ross, Ind. Eng. Chem. *36*, 610 (1944).
12. Schick, M. J., J. Phys. Chem. *67*, 1796 (1963).
13. Schick, M. J., S. M. Atlas and F. R. Eirich, Ibid. *66*, 1326 (1962).
14. Schick, M. J., J. Colloid Sci. *17*, 810 (1962).
15. Tartar, H. V., Ibid. *14*, 115 (1959).
16. Matijevic, E., and B. A. Pethica, Trans. Faraday Soc. *54*, 587 (1958).
17. Corkill, J. M., J. F. Goodman and S. P. Harrold, Ibid. *60*, 202 (1964).
18. Molyneux, P., C. T. Rhodes and J. Swarbrick, Ibid. *61*, 1043 (1965).
19. Goddard, E. D., and G. C. Benson, Can. J. Chem. *35*, 986 (1957).

[Received October 5, 1965]