Micelle Formation in Mixtures of Nonionic and Cationic Detergents

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Abstract

The effect of a homologous series of polyoxyethylene n-dodecanols on the critical micelle concentration (cmc) of mixtures with n-dodecyl trimethyl ammonium bromide (DTAB) and of polyoxyethylene n-hexadecanols on the cmc of mixtures with n-hexadecyl trimethyl ammonium bromide (CTAB) has been studied in terms of the composition of the mixtures. The cmc of the nonionic component of the mixed micelles is approximately one hundredth of that of the cationic component. 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 0–75 mole % or 0–90 mole %, respectively, of cationic detergent. This is followed by an abrupt transition to the high cmc values of the cationic component. This abrupt transition is considerably reduced by addition of NaBr. It is postulated that in the absence of added electrolyte the degree of ionic repulsion of the cationic component in mixed micelles is markedly decreased as the proportion of nonionic component reaches a threshold range of 25 or 10 mole %, respectively. Swamping of charges reduces ionic repulsion in NaBr solutions and, consequently, the abrupt transition in the cmc vs. composition curves is reduced.

Introduction

Micelle formation in mixtures of nonionic and anionic detergents has been the subject of a previous paper (1). A related investigation on micelle formation in mixtures on nonionic and cationic detergents is reported here. Mixtures of two homologous series of polyoxyethylene alkanols with quaternary detergents containing a comparable hydrophobic group to that of the nonionic detergents, have been investigated by means of an experimental procedure which allows accurate assessment of the cmc over the entire range of mole ratios.

Experimental

Molecularly distilled ethylene oxide (EO) adducts of two alkanols were 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. CTAB was obtained from Eastman Organic Chemicals and DTAB was prepared in the Organic Section of this laboratory. The purity of these materials was established from the shape of the surface tension vs. logarithm of concentration plots near the cmc. The water was redistilled from alkaline permanganate. The NaBr was of cp grade.

The procedure of the surface tension measurements using a Wilhelmy plate has been described previously (2).

Results

The cmc data are amenable to interpretation in terms of the structure of mixed micelles. Therefore, cmc values of single detergents and of mixtures thereof were determined over the entire composition range. The data were taken from the sharp breaks in the surface tension vs. logarithm of detergent concentration plots (2); equally sharp breaks were observed for mixtures as for single components. All measurements throughout this investigation were carried out at 25.0C.

The cmc data of mixtures of CETAB and n-hexadecanol + n EO in aqueous solutions are given in Figure 1, and those of DTAB and n-dodecanol + n EO in aqueous solutions in Figure 2. Whereas variations in the number of oxyethylene units in the homologous series of polyoxyethylene n-dodecanols caused marked differences in these plots, no difference was observed between the two polyoxyethylene n-hexadecanols with 18 and 30 oxyethylene units, respectively. In general the cmc of the nonionic component of the mixed micelles is about one-hundredth of that of the cationic component. With the poly-

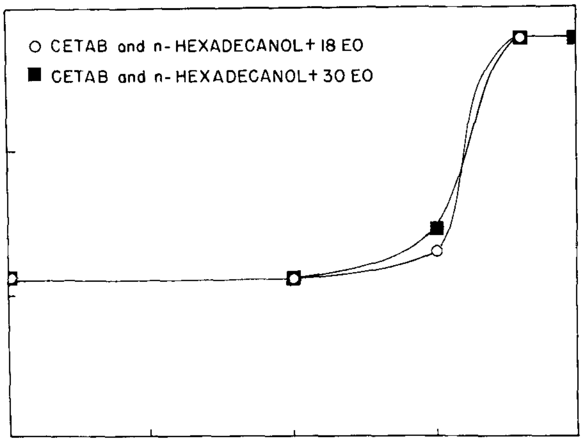

Fig. 1. Cmc of mixtures of CETAB and n-hexadecanol + n EO in aqueous solutions.

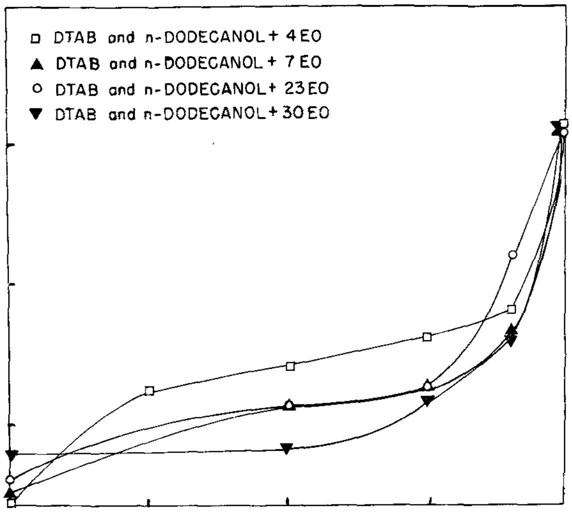

Fig. 2. Cmc of mixtures of DTAB and n-dodecanol + n EO in aqueous solutions.

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oxyethylene n-hexadecanols only a slight increase in the cmc values of the mixed micelles above the values of the nonionic components was observed in the composition range of 0–75 mole % cationic detergent. This is followed by an abrupt transition to the high cmc value of the cationic component. Similar results were obtained with the homologous series of n-dodecanols. However, the abrupt transition was shifted to 90 mole % of cationic detergent. It is worth noting that the gradual increase in the range below 90 mole % cationic detergent with n-dodecanol + 4 EO exceeds that of the higher homologs containing 7, 23 and 30 oxyethylene units.

Finally, the effect of electrolyte addition has been investigated. A comparison of the cmc of mixtures of DTAB and n-dodecanol + 23 EO in water and in NaBr solutions is illustrated in Figure 3. As anticipated the cmc values of the cationic component were markedly depressed by addition of electrolyte (3), whereas no significant change occurred with the pure nonionic component (4). In other words the large difference between the cmc values of the nonionic component of the mixed micelles and the cationic component observed in aqueous solution decreases progressively with increasing amount of added NaBr. The cmc values of DTAB in NaBr solutions follow the general relation that the logarithm of the cmc of a colloidal electrolyte is a linear function of the logarithm of the total concentration of the counterion. These results may be expressed by the equation

$$\log\ (\text{cmc of DTAB, moles/l}) = -0.77\ \log\ \text{Br}^-\ (\text{moles/l}) - 3.27$$

The data of Figure 3 on nonionic/cationic detergent mixtures show that a progressive reduction in the abrupt transition to the high cmc values of the cationic component occurs with increasing amounts of added NaBr.

Discussion

The results of this investigation on mixtures of nonionic and cationic detergents follow the same pattern as those of the previous investigation on mixtures of nonionic and anionic detergents (1). Consequently, the same general hypothesis may be applied to interpret the current results. The continuous decrease from the high cmc values of the quaternaries to the low values of the polyoxyethylene alkanols is attributed to the increased suppression of the repulsive forces between the ionic head groups by incorporation of the nonionic head groups into the micellar/solution interface. Or in other words the reduction in ionic repulsion is caused by the shielding of the polar head groups by the oxyethylene chain.

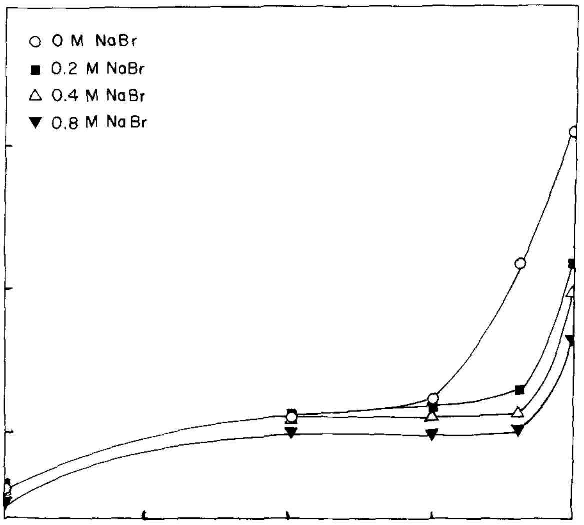

FIG. 3. Cmc of mixtures of DTAB and n-dodecanol + 23 EO in aqueous and NaBr solutions.

It is evident from the abrupt transition in the cmc plots of mixtures in aqueous solutions that the degree of ionic repulsion of the cationic component in mixed micelles is markedly decreased as the proportion of nonionic component reaches a threshold range of 25 mole % for mixtures of CETAB and n-hexadecanol + n EO or 10 mole % for mixtures of DTAB and n-dodecanol + n EO. Thus, one oxyethylene chain seems to shield several polar head groups. The absence of variations in the cmc vs. c plots as a result of changes in the number of oxyethylene units of the polyoxyethylene n-hexadecanols is ascribed to the high contribution of the cohesive forces in the balance between cohesive and opposing electrostatic or hydration forces (1). It is well known that the molar cohesion expressed in terms of calories per mole of interacting groups amounts to 990 cal/mole for the $-CH_2-$ group and that this quantity is additive (6). The marked differences observed with the polyoxyethylene n-dodecanols, i.e., larger increases of the cmc values of n-dodecanol + 4 EO in the range of added cationic detergent up to 90 mole % as compared to those of the higher homologs containing 7, 23 and 30 oxyethylene units, are attributed to differences in the coil size of the oxyethylene chain. Smaller coil sizes (4 EO) are less effective in suppressing ionic repulsion when operating at the periphery of the micellar core than larger coils (7, 23 or 30 EO units). Or in other words the shielding capacity of the oxyethylene chain for the polar head groups, and consequent reduction in ionic repulsion, becomes more pronounced with increasing length of the oxyethylene chain.

The proposed model for mixed micelles is reinforced by the results in electrolyte solutions. It is a well-known fact that addition of electrolyte to ionic detergents results in swamping of charges (2,5). From this it follows that the electrostatic repulsion between polar head groups of mixed micelles in NaBr solutions must be significantly decreased and, consequently, the cmc vs. c plots show a progressive reduction in the abrupt transition to the high cmc values of the cationic component with increasing amounts of added NaBr. A recent article by Mukerjee (7) is worthy of note in the light of this simultaneous effect of electrolyte on ionic and nonionic detergents in mixed micelles.[1] Although the major effects of added electrolytes on the cmc of ionic detergents are due to interionic interactions, this author suggests that salting out effects, generally neglected, can be quite substantial. Similarly, the salting out of the hydrophobic chains is according to Mukerjee the most important factor to be considered for polyoxyethylene systems also. The data of this investigation, however, are not such as to give support to this hypothesis for ionic detergents.[1]

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[1] For polyoxyethylene compounds log cmc = constant — $k_s c_s$ where k_s is the salt effect constant and c_s the molar concentration of the salt; e.g., k_s for dodecanol + 30 EO is about 0.8.

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