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Foaming of Ionic and Nonionic Detergents from Their Aqueous Solution Mixtures

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Abstract

During the foaming of aqueous solutions of surface-active substances, the fractionation of components on the basis of their surface activity has been observed. This fact was stated for crude oxyethylated nonylphenol which is a mixture of compounds with different oxyethylene chain length as well as for a mixture of solutions of anionic with nonionic and cationic with nonionic detergents. From solutions of nonionic and cationic or nonionic and anionic detergents, the nonionic compounds are removed more favorably. For solutions of equimolar concentration of both components, the decontamination factor was the best for nonionic and the worst for anionic or cationic detergents. With an increase or decrease of ionic detergent concentration in the mixture, their decontamination factor increases while the decontamination factor of the nonionic decreases. This is connected with the c.m.c. value of the mixed micelles. It was found that the introduction of inorganic salts into the foamed solution mixtures increases the degree of ionic detergents removal but decreases the nonionic detergent removal.

INTRODUCTION

The possibility of the removal of surface-active substances from their aqueous solutions by foaming depends on the surface activity of these substances. Also, the observed physicochemical phenomena of various surfactant solution mixtures are dependent on the surface activity of the mixture components.

Numerous authors have devoted studies to the micelle formation in solutions containing anionic and nonionic surface-active substances.

Schick (*1*) proved that the critical micelle concentration (c.m.c.) for mixtures of polyethoxylated *n*-dodecanol (with 7 oxyethylene groups) and sodium lauryl sulfate containing below 90 mol-% of sulfate is almost constant and equal to the concentration of the corresponding nonionic compound. A further increase of sodium lauryl sulfate concentration in the mixture causes an abrupt rise of c.m.c. up to the corresponding c.m.c. of pure sodium lauryl sulfate.

Akasu (*2*) reported that nonionic penta-ethylene glycol-*n*-dodecyl ether forms micelles in aqueous solutions with concentration above 5.6×10^{-5} mol/L, while for its solutions containing anionic sodium lauryl sulfate (NaLS) with a concentration near its c.m.c., the formation of mixed micelles takes place at a concentration of the nonionic compound 10 times lower. For a NaLS concentration 5 to 10 times lower than its c.m.c., the micelles are formed at a concentration of nonionic compound twice as low as its c.m.c.

Muto (*3*) observed that even the nonionic copolymer of ethylene oxide and propylene oxide considerably lowers the critical micelle concentration of NaLS solutions. Therefore, though the nonionic copolymer does not form micelles itself, a micelle formation takes place in the presence of the anionic surfactant.

In the processes of separation by foaming, surfactants with different surface activities may be separated due to the differences in their adsorption at the air–solution interface.

Studies on the foam separation of two anionic compounds from a mixture of their solutions have been carried out by Rubin (*4*). He reported that in the mixture of sodium dodecylbenzenesulfonate and sodium lauryl sulfate, the former is more surface active and its adsorption at the gas–solution interface as well as its solubility in the mixed micelles is higher than the corresponding properties of a pure NaLS solution.

The relative distribution coefficient α is

$$\alpha_{\mathrm{NaDBS,NaLS}} = \frac{\Gamma_{\mathrm{NaDBS}}/C_{\mathrm{NaDBS}}}{\Gamma_{\mathrm{NaLS}}/C_{\mathrm{NaLS}}}$$

where Γ is the surface excess and C is the detergent concentration in the bulk liquid. Below the critical concentration of mixed micelles, α is high (from 2 to 4) and over this concentration the value of α decreases abruptly due to the preferential solubility of NaDBS in the mixed micelles (NaDBS + NaLS). Thus fractionation takes place during the foaming of solutions containing surface-active solutes of different surface activities.

We have previously reported (*5*) that the technical oxyethylated nonylphenol (Rokaphenol NX-8) contains over 20 components with varying oxyethylene chain lengths. It was proved that the removal of these components by foaming is better the shorter the oxyethylene chain (*5*). In this case we observe a higher value of the decontamination factor C_0/C_r, where C_0 is the detergent concentration in the feeding solution and C_r is the detergent concentration in the raffinate.

According to Schönfeld (*6*), the surface tension for solutions of ethylene oxide adducts is lower, the lower the content of ethoxy groups in the molecule. We have stated that the removal by foaming of adducts with longer polyether chains is more difficult because of their higher affinity to water. Compounds with a mean number of oxyethylene groups equal to 6.7 were removed least, but this fact was due to the poorer water solubility of compounds having less than 7 oxyethylene groups (*7*).

EXPERIMENTAL

It may be assumed that, due to concurrent adsorption at the phase boundary for solutions containing a mixture of ionic and nonionic surfactants, the foaming effect of each component will be different from the foaming of a solution containing only a single component. In our studies, solutions containing nonionic ethoxylated nonylphenol (Rokaphenol NX-8) and sodium dodecylbenzenosulfonate (Nansa HS-55) were subjected to foaming. The initial concentrations of both compounds in the solution were changed to keep the total concentration equal to 40×10^{-5} mol/L.

Detergent concentrations in the initial solution and the raffinate were obtained from UV absorption measurements (*8*), and the content of an anionic compound was determined by the Longwell-Maniece method. The concentration of the nonionic detergent is the difference of the above estimated concentrations.

Figure 1 presents the relation between the decontamination factor (C_0/C_r) and the initial concentration of sodium dodecylbenzenesulfonate. The Rokaphenol concentrations were such that total detergents concentrations in all initial solutions equaled 40×10^{-5} mol/L.

As seen in Fig. 1, the values of the decontamination factor for NaDBS solutions containing Rokaphenol (dotted line) are lower than those for solutions without Rokaphenol (solid line). In addition, it has been observed that sodium chloride very markedly improves the decontamination factor of the anionic detergent in solutions without Rokaphenol while the effect of NaCl is slight in the presence of Rokaphenol.

Figure 2 shows that the foaming of an equimolar solution of Rokaphenol and NaDBS leads to a higher decontamination factor of Rokaphenol (dotted line) than the decontamination factor obtained for a solution

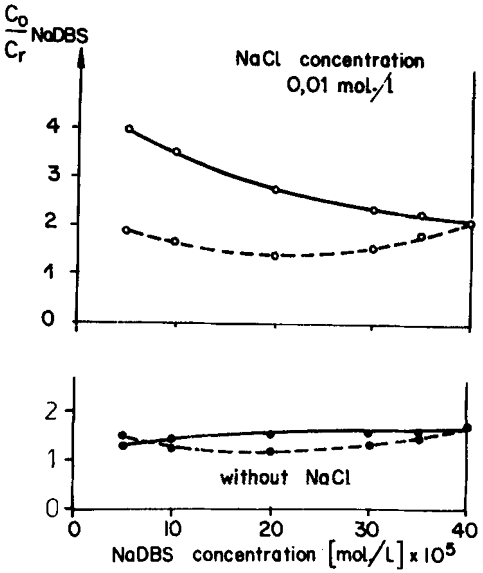

FIG. 1. Decontamination factor dependence on sodium dodecylbenzenesulfonate concentration in solution: (——) foaming of pure NaDBS solutions, (- -) foaming of NaDBS and Rokaphenol mixture.

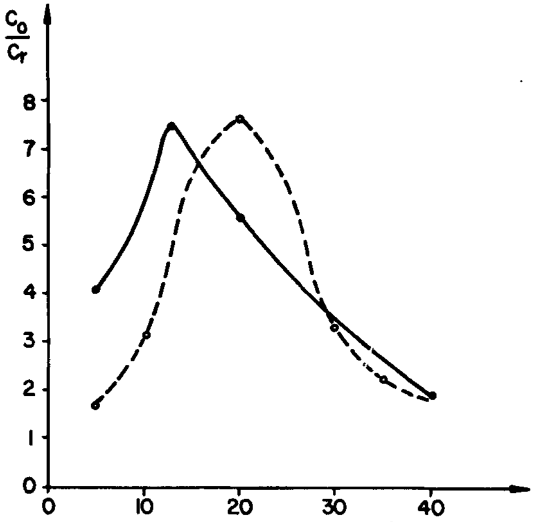

FIG. 2. Decontamination factor dependence on Rokaphenol concentration in solution: (——) foaming of pure Rokaphenol solution, (- -) foaming of NaDBS and Rokaphenol mixture.

containing only Rokaphenol in the same concentration as in the mixture with NaDBS. For all other Rokaphenol concentrations in the mixture, the foaming has a poorer effect on detergent removal than does its foaming in one component solutions.

Figure 3 presents the relationship between the decontamination factors of both detergents and the composition of the mixture subjected to foaming. The graph shows that decontamination factors for ethoxylated nonylphenol (Rokaphenol NX-8) are considerably higher (Curves 1) than for sodium dodecylbenzenesulfonate (Curves 2) in the entire range of concentrations.

It can also be seen that in the case of equimolar concentrations of both detergents, the decontamination factor of Rokaphenol reaches its maximum $[(C_0/C_r)_{\mathrm{Rok.}} = 7.5]$ while the decontamination factor for NaDBS is at its lowest $[(C_0/C_r)_{\mathrm{NaDBS}} = 1.1]$.

The presence of sodium chloride in the mixture subjcted to foaming increases the surface adsorption of the anionic compound, thus increasing its decontamination factor. Simultaneously, the decrease of the Rokaphenol decontamination factor can be observed when compared with solutions without sodium chloride (Fig. 3, open circles).

The quantity of water removed with the foam is an important parameter of the foaming process. The lower it is, the higher is the efficiency of the

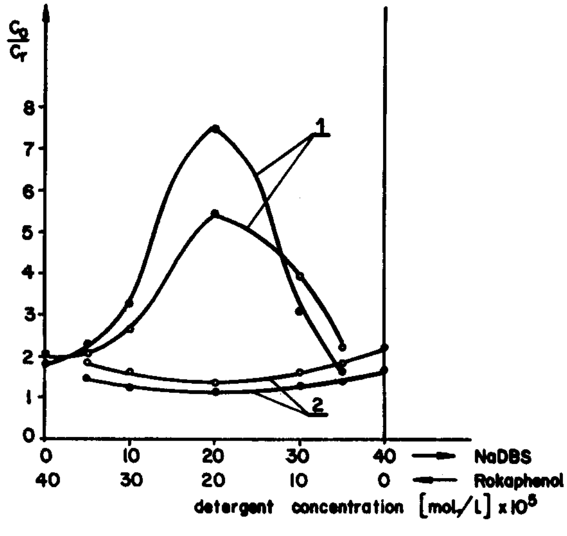

FIG. 3. Decontamination factors of Rokaphenol (1) and sodium dodecylbenzenesulfonate (2) dependence on the mixture composition: (●) without NaCl, (○) solutions containing NaCl.

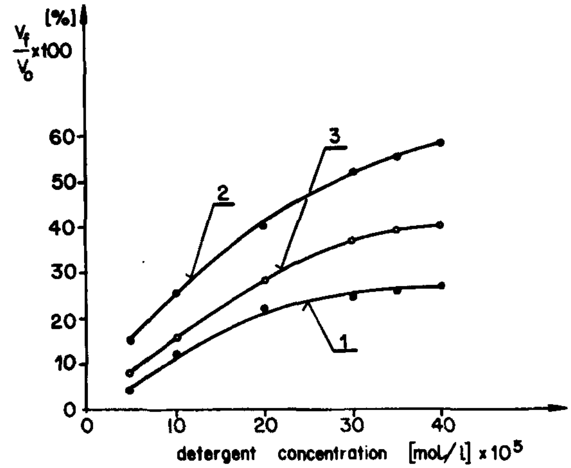

FIG. 4. The dependence of water removal with the foam on the detergent concentration in the solution: (1) Rokaphenol, (2, 3) NaDBS, (3) with NaCl.

process. During the foaming of one-component detergent solutions, the quantity of water removed rises with an increase of the detegent initial concentration (Fig. 4). The foaming of Rokaphenol causes the removal of less water with foam (Curve 1) than the foaming of NaDBS (Curve 2). The presence of sodium chloride in the solution of an anionic detergent leads to a less wet foam (Curve 3).

Figure 5 presents the relationship between the quantity of water removed with foam and the composition of the solution subjected to foaming. It is seen that the higher the content of the nonionic detergent in the mixture of NaDBS and Rokaphenol, the less wet is the foam (contrary to the foaming of a solution of Rokaphenol alone). The addition of sodium chloride to the foamed mixture leads to less wet foam, similar to the case of NaDBS foaming from solutions containing sodium chloride.

The foaming of solutions containing nonionic and cationic surfactants was carried out for ethoxylated nonylphenol (Rokaphenol NX-8) and cetyltrimethylammonium bromide (CTMABr). Figure 6 shows the relationship between the decontamination factors of both compounds and the composition of the mixture subjected to foaming. Analysis of Fig. 6 leads to the conclusion that the shapes of the curves are similar to the shapes of the curves obtained for mixtures of anionic and nonionic detergents. The decontamination factors of a nonionic compound (Curves 2) are much higher than those of a cationic compound (Curves 1). A maximum of the decontamination factor for a nonionic detergent and a minimum of the decontamination factor for a cationic detergent can be

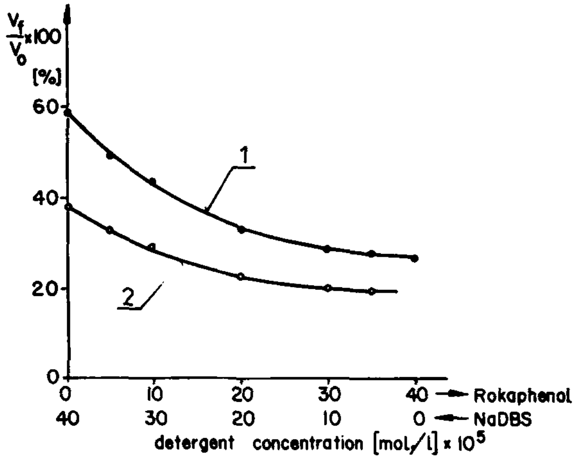

FIG. 5. The dependence of water removal with the foam on the mixture of Rokaphenol and NaDBS composition: (1) without NaCl, (2) with NaCl.

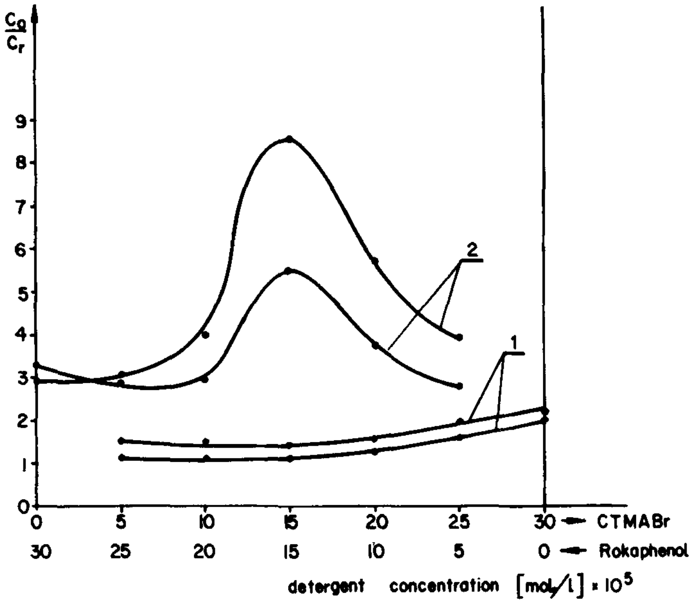

FIG. 6. Decontamination factor of Rokaphenol (2) and cethyltrimethylammonium bromide (1) dependence on the mixture composition: (●) without NaCl, (○) with NaCl.

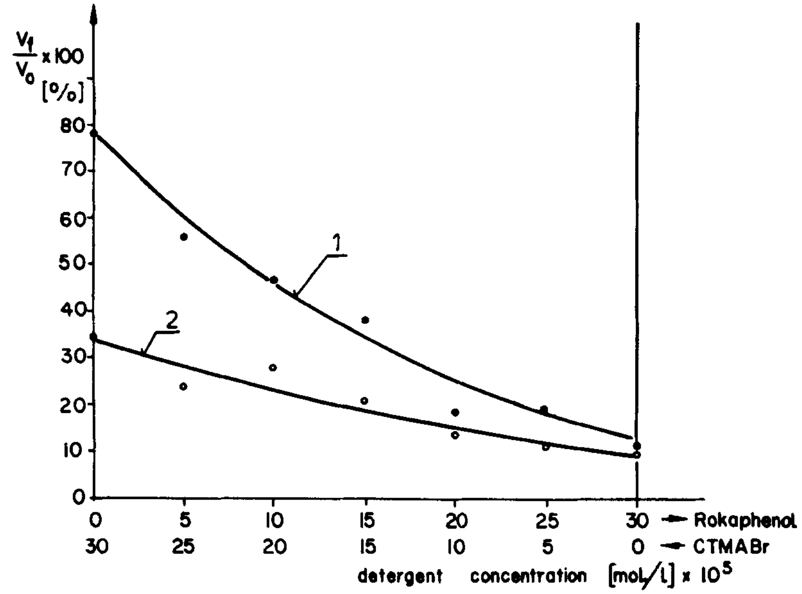

FIG. 7. The dependence of water removal with the foam on the mixture of Rokaphenol and CTMABr composition: (1) without NaCl, (2) with NaCl.

observed when an equimolar mixture is used. The addition of sodium chloride improves CTMABr foaming and hinders the removal of Rokaphenol from the mixture (Fig. 6).

The quantity of water removed with foam decreases with an increase of the nonionic detergent content when a mixture of cationic and nonionic surfactants is used. The presence of sodium chloride lowers the foam wetness (Fig. 7).

CONCLUSIONS

The c.m.c. values for the solutions of individual detergents have been determined (Table 1). The highest concentrations of anionic and cationic detergents used in the solutions subjected to foaming were 5–10 times lower than the c.m.c. values of sodium dodecylbenzenesulfonate and about 1.3–3 times lower than c.m.c. values of cetyltrimethylammonium bromide. Rokaphenol concentrations in the solutions subjected to foaming were of the order of the c.m.c. and sometimes higher. Therefore the formation of nonionic compound micelles was possible. As the result of the presence of ionic surfactants, the formation of mixed micelles could also take place.

TABLE 1

Critical Micelle Concentrations of Detergent Used in Experiments

Detergent	Critical micelle concentration (c.m.c.) ((mol/L) × 10^{-5}) Without NaCl	With 0.01 mol/L NaCl	Detergent concentrations during foaming processes ((mol/L) × 10^5)
Sodium dodecylbenzenesulfonate	426	209	5–40
Oxyethylated nonylphenol	33	28	5–40
Cetyltrimethylammonium bromide	85.2	38.1	5–30

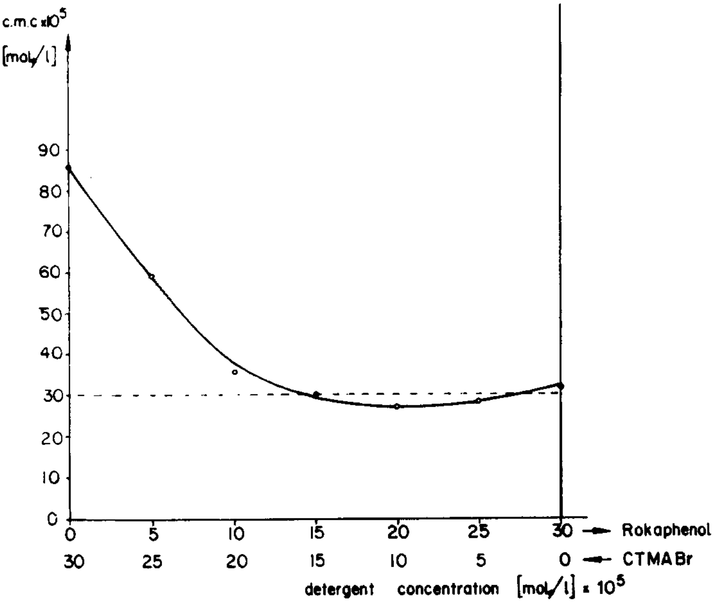

FIG. 8. Critical micelle concentration of Rokaphenol and CTMABr mixed micelles dependence on the mixture composition.

We determined the c.m.c. values in solutions containing Rokaphenol and cetyltrimethylammonium bromide. As can be seen from Fig. 8, the c.m.c. of mixed micelles depends on the solution's composition. It appears from this figure that the c.m.c. of equimolar solutions equals 30.3 × 10^{-5} mol/L, which corresponds to the total concentration of detergent solution mixtures used in foaming experiments. When the contribution of CTMABr in the mixture increases above 15 × 10^{-5} mol/L, the c.m.c. increases too. Thus, in foaming detergent mixture solutions of 30 × 10^{-5} mol/L total concentration, we have no micelles. If the contribution of Rokaphenol in the mixture increases above 15 × 10^{-5} mol/L, the c.m.c. of mixed micelles decreases below 30 × 10^{-5} mol/L. In this case there are mixed micelles of Rokaphenol and CTMABr in the solution. Zwierzykowski (*9*) has stated that the thermodynamic potential of adsorption on the micelle surface is proportional to the same potential at the free surface of the solution. Thus, when micelles start to be formed, the more surface-active compound decreases its concentration at the free surface and tends to be incorporated into the micelles. Therefore, when the contribution of Rokaphenol in the mixture increases above the equimolar concentration, a sudden drop of its decontamination factor can be observed because only the surface excess influences the decontamination factor value. The decontamination factor falls below the value corresponding to the solution of Rokaphenol alone (Fig. 2).

The surface excess reaches its maximum before the c.m.c. (that is, before the micelles start to be formed), and then the decontamination factor is at its highest, as we observed for equimolar composition.

In solutions of different surface-active compound mixtures, a preferential surface adsorption of one of them can take place which results in its better removal from the solution during foaming. In the case of ionic and nonionic compound mixtures, the latter are foamed better.

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