Monomer-Micelle Equilibrium in the Diffusion of Surfactants in Binary Systems Through Collagen Films

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Three different binary systems (two anionic/nonionic and one anionic/amphoteric) were selected to study the behavior of these mixtures in their diffusion through a collagen film and the formation of micelle aggregates in such systems. The inhibition observed in the surfactant diffusion of anionic/nonionic and anionic/amphoteric binary mixtures through a collagen film, in comparison with that of single surfactants, has been related to the behavior of these binary systems in the micellization process. The surfactant flux in these systems is mainly determined by the monomeric species. The modification of the equilibrium monomers-micelle aggregates shown by these surfactant binary systems could be also associated with the reduction of the irritancy power for such binary systems.

KEY WORDS: CMC, collagen, diffusion, monomer, surfactant mixtures.

Binary mixtures of anionic/nonionic or anionic/amphoteric surfactants are widely used because they show different physico-chemical properties than individual components and they can achieve great synergism in various physical processes (1-3). On the other hand, the diffusion process is one of the factors involved in the skin irritation phenomenon caused by a surfactant's action (4). Several types of membranes (5,6) have been used to simulate skin penetration by chemicals in diverse *in vitro* tests. In previous works (7-9) the authors used a collagen film for the study of surfactant diffusion. For single surfactants it was verified that when the concentration of surfactant is above its critical micelle concentration, the flux of surfactant through the collagen film remains constant.

In the present study, the formation of micelle aggregates in three binary systems is considered in order to relate the results obtained in the diffusion process with the equilibrium of monomers-micelle aggregates in solution.

MATERIALS AND METHODS

Materials. Sodium dodecyl sulphate (SDS) was a reagent-grade product from Merck (Darnstadt, Germany). Its active matter was 99%. Dodecyl dimethyl amine oxide (C12-AO) was specially prepared by Tenneco España S.A. (Barcelona, Spain). The active matter was 30% in aqueous solution. Free amine content was 0.16%. Dodecyl betaine (C12-BET) was specially prepared by Albright & Wilson Ltd. (Oldbury, U.K.). The active matter was 30% in aqueous solution. Free amine content was 0.20%. Nonylphenol with 10 ethylene oxide units (NP-10 EO) was supplied by Tenneco España S.A. as a 100% active matter product. The collagen film used was a thin edible protein film (with a thickness of 15 microns), purchased from Naturin-Werck Becker & Co., Weinhein, Germany. Diffusion test apparatus: Diffusion of surfactants through the collagen film was measured in a bichamber cell already described elsewhere (7-9). The surfactant solution was introduced into one of the chambers and an equal quantity of distilled water was placed into the other. The diffusion process was allowed to proceed for 24 hr at 25°C; an aliquot was drawn off in order to analyze the amount of surfactant diffused through the collagen film. Automatic titrator: An automatic Radiometer-Copenhagen titrator equipped for turbidimetric measurements was used for analyzing the surfactants and their mixtures. Tensiometer: Surface tension values used to calculate the critical micelle concentration (CMC) were determined by the ring method with a Lauda automatic tensiometer (Königshofen, Germany). Apparent surface tension values were corrected according to the Harkins-Jordan factors (10).

Scanning electron microscopy: Samples were prepared by instantaneously freezing collagen films by inmersion in liquid nitrogen, slicing it with a microtome, and finally coating it with a thin film of gold. The photographs were made with a 840 JEOL scanning electron microscope, Tokyo, Japan.

Surfactant analysis: The analysis of surfactant mixtures of SDS/C12-AO and SDS/C12-BET was carried out turbidimetrically by either direct or back titration, with a cationic surfactant (Hyamine 1622); the end point was detected by the maximum optical density, *i.e.,* at maximum turbidity (7,9). The analysis of surfactants in the mixture SDS/NP-10 EO was carried out by spectrophotometric methods (11,12).

RESULTS AND DISCUSSION

Diffusion of mixed surfactant systems. The binary systems selected were two anionic/nonionic mixtures (SDS/C12-AO and SDS/NP-10 EO) and one anionic/amphoteric mixture (SDS/C12-BET). Prior to the study of binary mixtures, diffusion experiments as a function of concentration were carried out for the individual surfactants. The results obtained are plotted in Figure 1. A clear change in the slope of each surfactant diffusion curve can be observed in a concentration range that corresponds to its experimental CMC value. This fact could be explained by a monomeric-type mechanism already proposed by the authors (13). The experimental behavior observed suggested the convenience of performing diffusion tests of binary systems at total surfactant concentration of 25 mM, which is higher than any of the CMC values of the surfactants used. The total surfactant concentration was maintained constant and the surfactants' molar ratio in the mixture was varied. The results for the different systems studied are shown in Figures 2, 3 and 4. In all cases (in comparison with the results plotted in Fig. 1), each surfactant inhibited the diffusion of the other in the mixture. Figures 2 and 3 also show a minimum in the total surfactant diffusion of the mixture. In Figure 4 this

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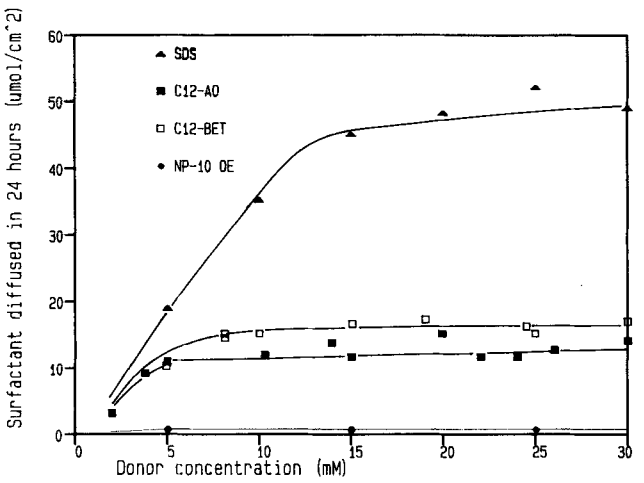

FIG. 1. Surfactant amount diffused after 24 hr *vs* donor surfactant concentration.

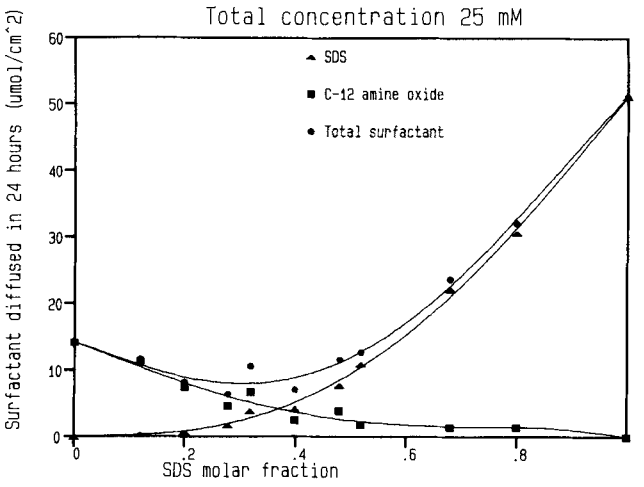

FIG. 2. Surfactant diffusion from the SDS/ C12-AO system *vs* SDS mole fraction.

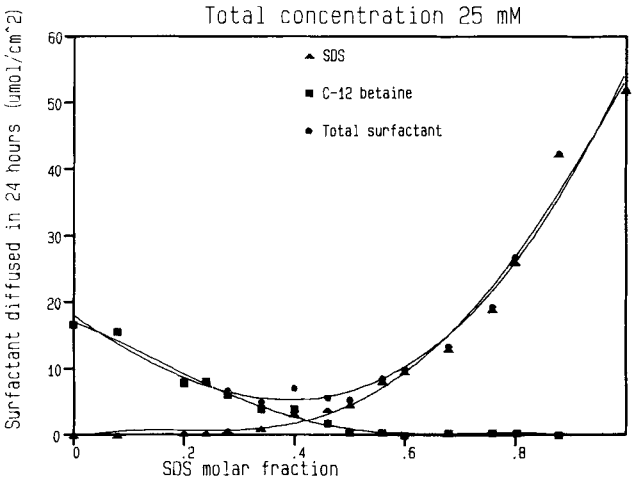

FIG. 3. Surfactant diffusion from the SDS/ C12-BET system *vs* SDS mole fraction.

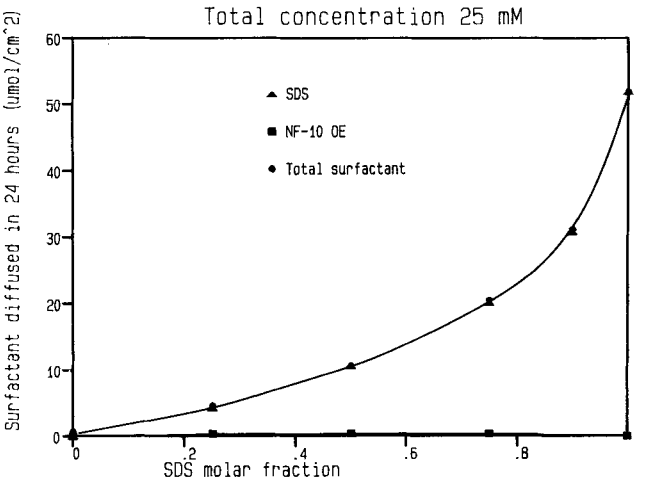

FIG. 4. Surfactant diffusion from the SDS/ NP-10 EO system *vs* SDS mole fraction.

minimum is not observed, due to the low diffusion level of NP-10 EO that can be attributed to its low CMC value. It is somehow surprising that in spite of its low flux level through the collagen film, NP-10 EO produced a marked inhibition of SDS diffusion.

Formation of mixed micelles in the binary systems. In order to elucidate the causes that produce the observed inhibition in the diffusion of surfactant mixtures, a study was carried out on the formation of mixed micelles in the three binary systems tested. If the variation of the surface tension is plotted against the surfactant concentration for the different SDS/amphoteric or SDS/nonionic surfactant molar ratios, CMC values for the different molar ratios can be determined from the corresponding graphs. In Tables 1, 2 and 3 the results are given for the different binary systems.

Assuming that the thermodynamics of the micellization process for these systems obey the ideal solution theory, when monomer and micelles are in equilibrium in the system Equation 1:

$$1/C = (X/C_1) + (1-X)/C_2 \qquad [1]$$

where C is the CMC value of the mixture, C_1 is the CMC value of surfactant 1, C_2 is the CMC of surfactant 2 and X is the mole fraction of the surfactant 1 in the mixture.

TABLE 1

CMC Values of SDS/C12-AO System for Different SDS Mole Fractions

SDS mole fraction	CMC (mM)
0.0	1.80
0.10	0.30
0.20	0.19
0.35	0.21
0.50	0.25
0.80	0.32
0.90	0.40
1.00	7.50

TABLE 2

CMC Values of SDS/C12-BET System for Different SDS Mole Fractions

SDS mole fraction	CMC (mM)
0.0	2.00
0.1	1.25
0.2	0.60
0.35	0.60
0.50	0.60
0.80	0.95
0.90	1.40
1.00	7.50

TABLE 3

CMC Values of SDS/NP-10 EO System for Different SDS Mole Fractions

SDS mole fraction	CMC (mM)
0.00	0.20
0.25	0.19
0.50	0.25
0.80	0.44
0.90	0.75
1.00	7.50

This expression relates the CMC value of the binary mixture to the SDS molar fraction.

In Figures 5, 6 and 7, the theoretical CMC values of the binary systems from the ideal solution theory are plotted together with the experimental values as a function of the SDS molar fraction. For all mixtures studied, the CMC values of the mixed surfactant systems are substantially lower than those predicted by Equation 1. That means that mixed micelle formation shows negative deviation from ideality. The values of the interaction parameter, β, for each molar fraction of SDS in the different mixtures were calculated from the experimental CMC values by applying the regular solution theory proposed by Rubingh (14). These values are given in Tables 4, 5 and 6. Figures 5, 6 and 7 show also that the curves obtained by using the mean value of the interaction parameter fit the experimental data in an acceptable way.

Comparing the mean value of the interaction parameters, the most negative value is obtained for the SDS/C12-AO system. That means that the greatest degree of nonideality is verified for this system, whereas the lowest degree of nonideality is obtained for the SDS/NP-10 EO.

Monomer concentrations in equilibrium with mixed micelles were calculated from the set of relations between mixed-system critical micelle concentration, micelle composition, monomer concentration and the interaction parameter β provided by regular solution theory (14). Predicted monomer concentrations are given in Figures 8, 9 and 10. The observed inhibition in the diffusion process can be correlated with the decrease in the monomer concentration. It means that the inhibition in diffusion can be explained by a surfactant flux mainly of monomeric character. So, the decrease in the monomer concentration

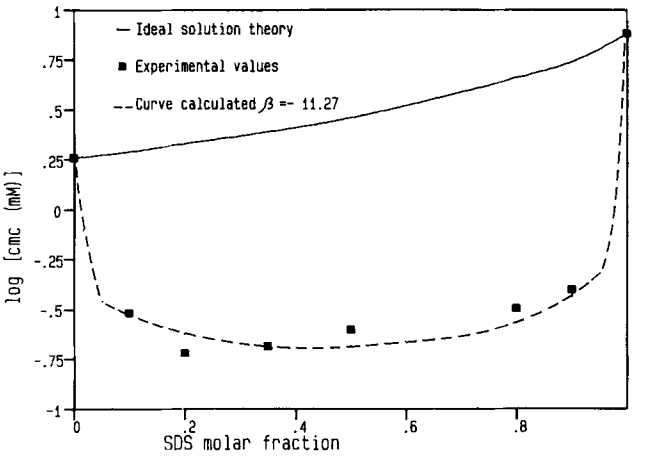

FIG. 5. CMC values of the SDS/C12-AO system *vs* SDS mole fraction.

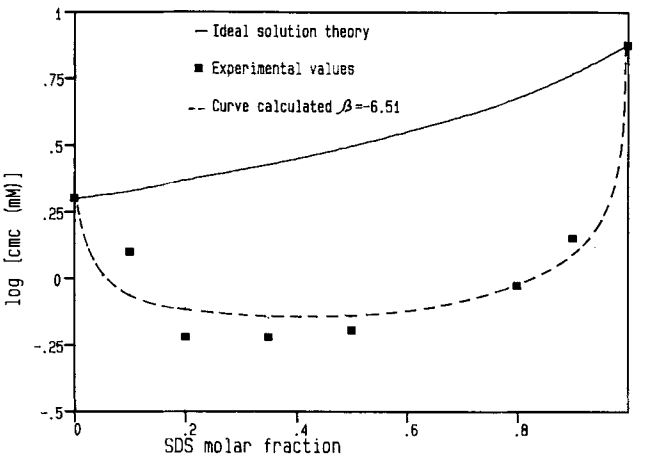

FIG. 6. CMC values of the SDS/C12-BET system *vs* SDS mole fraction.

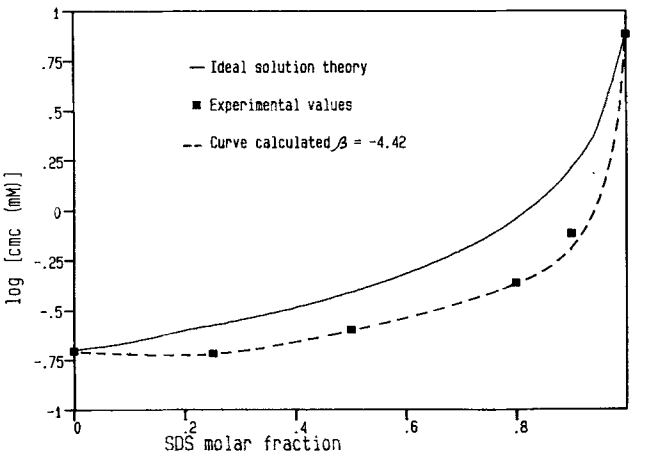

FIG. 7. CMC values of the SDS/NP-10 EO system *vs* SDS mole fraction.

TABLE 4

Interaction Parameters for the SDS/C12-AO System

SDS mole fraction	β parameter
0.00	—
0.10	−12.02
0.20	−12.18
0.35	−11.32
0.50	−10.59
0.80	−10.66
0.90	−10.87
1.00	—
	mean values = −11.27

TABLE 5

Interaction Parameters for the SDS/C12-BET System

SDS mole fraction	β parameter
0.00	—
0.10	−4.76
0.20	−7.59
0.35	−7.24
0.50	−6.94
0.80	−6.51
0.90	−6.02
1.00	—
	mean value = −6.51

TABLE 6

Interaction Parameters for the SDS/NP-10 EO System

SDS mole fraction	β parameter
0.00	—
0.25	−4.86
0.50	−4.31
0.80	−4.86
0.90	−3.65
1.00	—
	mean value = −4.42

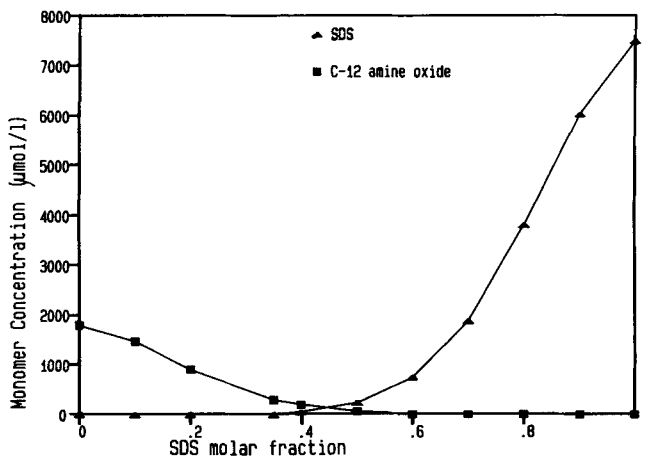

FIG. 8. Monomer concentrations in the SDS/C12-AO system calculated from regular solution theory.

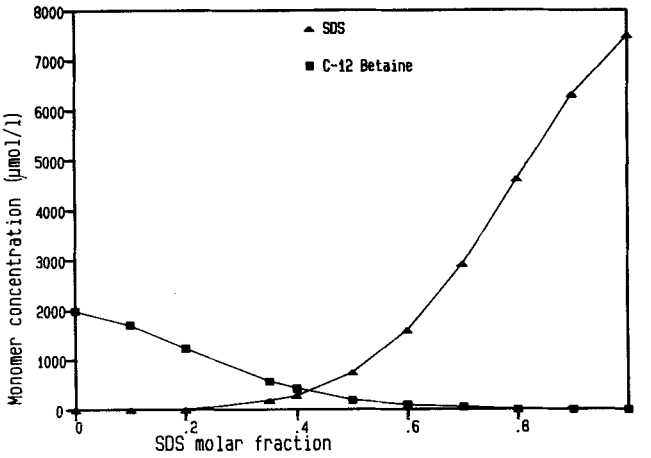

FIG. 9. Monomer concentrations in the SDS/C12-BET system calculated from regular solution theory.

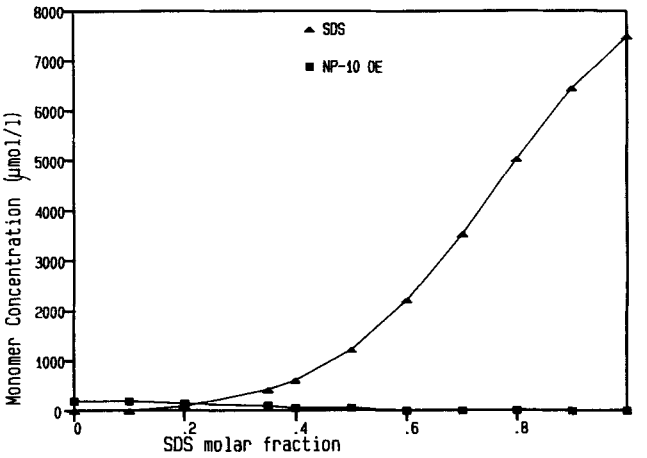

FIG. 10. Monomer concentrations in the SDS/NP-10 EO system calculated from regular solution theory.

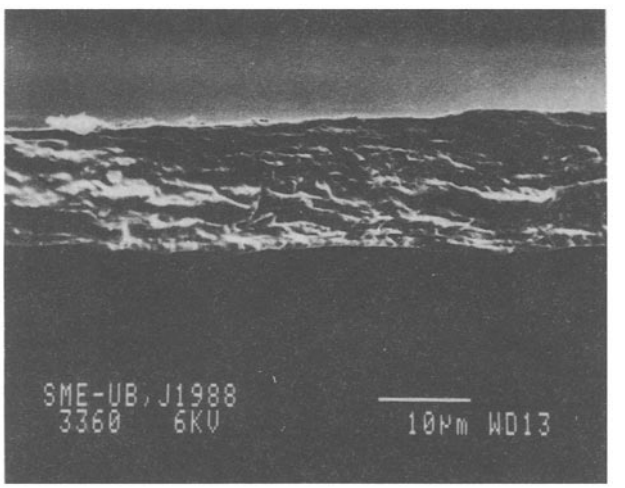

FIG. 11. Collagen film soaked in water for 24 hr.

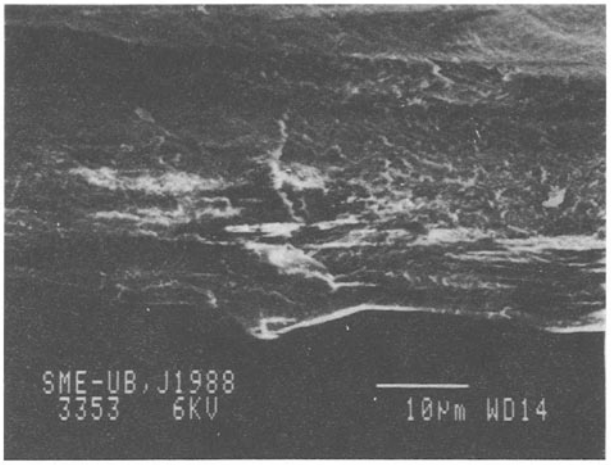

FIG. 12. Collagen film soaked in SDS 25 mM for 24 hr.

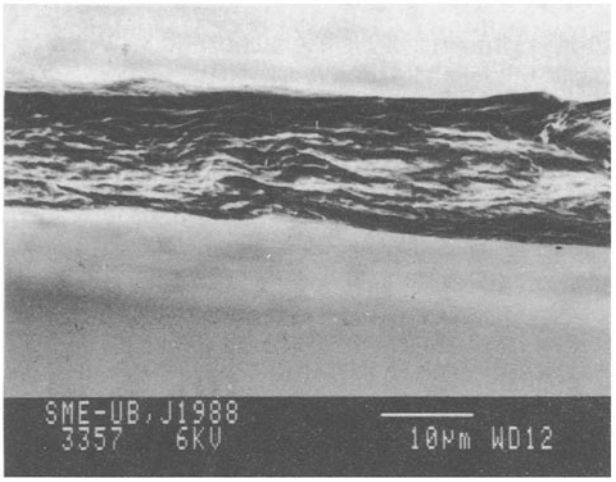

FIG. 14. Collagen film soaked in a mixture of SDS/C12-BET (1:1) 25 mM for 24 hr.

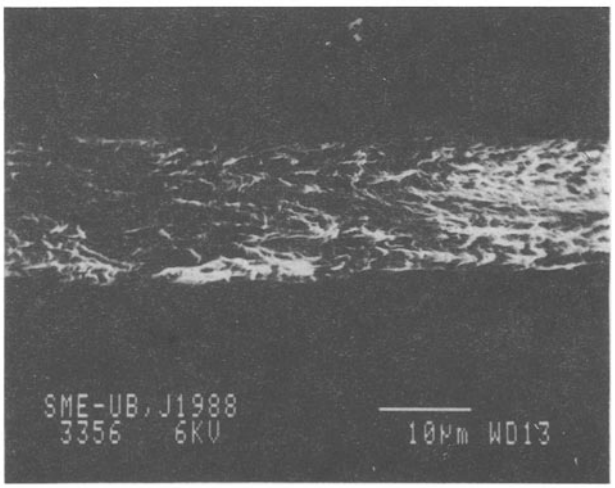

FIG. 13. Collagen film soaked in C12-BET 25 mM for 24 hr.

produces the decrease in the total surfactant flux. Except for the diffusion curve for SDS in SDS/C12-AO and in SDS/NP-10 EO mixtures that shows certain positive and negative deviations from the monomer concentration curve, respectively, all the diffusion curves obtained fit well with the monomer concentration values calculated from the regular solution theory. The comparison of both diffusion values and monomer concentrations allow one to state that the surfactant flux through collagen film is mainly due to monomeric species.

Electron microscopy of the collagen samples. In order to analyze the effect caused by surfactant solutions on the collagen film during the diffusion process, a study by scanning electron microscopy was carried out. The SDS/C12-BET binary system was selected to be compared with either single surfactant or distilled water. A series of collagen samples that had been soaked in the different solutions for 24 hr at 25°C was examined by freeze fraction electron microscopy. The microphotographs obtained are shown in Figures 11, 12, 13 and 14. A fibrous structure can be seen in Figures 11, 13 and 14, whereas this structure is not shown in Figure 12. A significant swelling of the collagen film can also be observed in this Figure. It is important to remark that the inhibition in the surfactant diffusion for the anionic/amphoteric binary system seems to be associated with a decrease in the structural modifications of the collagen film.

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