Studies on Surface Activity of Linear Alkylbenzene Sulfonates II: Effect of Water Hardness[1]

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Adsorption behavior of a mixture of homologs and isomers of sodium linear alkylbenzene sulfonates from their aqueous solutions in hard water at the solution/air interface has been investigated. Increasing the concentration of surfactant in hard water results in the precipitation of the surfactant, which starts redissolving in the solution with further increases in surfactant concentration beyond a certain value characteristic of the surfactant, and finally results in a clear solution. Surface tension versus the logarithm of concentration curves shows an unusual behavior of multiple breaks. Attempts have been made to explain the results in terms of the equilibrium existing among the different forms of the surfactant, namely monomer, precipitate and the micelle.

The improved biodegradability of the surfactants derived from linear alkylbenzenes (LAB) over alkylbenzene sulfonates has given rise to a spectacular rise in their production and consumption all over the world (1). At present, linear alkylbenzene sulfonate is the single largest volume of surfactant used in the detergent industry (2,3). However, the presence of linear alkyl chain decreases its solubility in water and increases its sensitivity toward polyvalent cations frequently encountered during usage, particularly in detergency and oil recovery by surfactant flooding (4-6). The precipitation of these surfactants by polyvalent cations is detrimental to their performance, as it not only results in the loss of surfactant but also modifies their adsorption characteristics at the solid/liquid, liquid/liquid, and liquid/air interfaces, thereby changing their soil release, soil redeposition, oil recovery and foaming behavior.

Although the precipitation of anionic surfactants in aqueous solutions by polyvalent cations has long been known, the mechanics of the phenomenon attracted attention only recently (7-10). It has been shown that the precipitated salts of the surfactants with polyvalent cations are redissolved in the solution by increasing the surfactant concentration beyond a certain value, characteristic of the surfactant used (8-10). Most of these studies are based on pure surfactants and deal with the solubility product of the precipitated surfactant. In actual applications, a mixture of surfactants generally is used, and their adsorption characteristics at the solid/liquid and liquid/air interface determine their end-use performance. It was therefore thought worthwhile to study the effect of water hardness on the adsorption characteristics of a mixture of LAB homologs and isomers commonly used in the detergent industry.

EXPERIMENTAL

Linear alkylbenzene sulfonate mixtures were derived from linear alkylbenzenes having different levels of alkyl chain length and phenyl isomer distribution prepared by alkylation of benzene with a mixture of linear internal monoolefins using hydrofluoric acid (HF) as catalyst. Homolog distribution in the LAB samples, used in the present investigation, is shown in Figure 1; typical distribution of phenyl isomer in the chain is shown in Figure 2 (11). A sample of dodecylbenzene, a propylene tetramer, also was studied for comparison and is noted as C. Samples having higher and lower levels of C_{14} are noted as A and B, respectively.

All the alkylbenzene samples were sulfonated using 20% oleum following the standard sulfonation procedure. Acid slurry was neutralized with aqueous sodium hydroxide. The unsulfonated matter was removed by repeated extraction with petroleum ether. Surfactant was then separated from the inorganic salt by repeated extraction with 95% (v/v) aqueous alcohol. It was then dried to constant oven dry weight. Calcium chloride ($CaCl_2 \cdot 2H_2O$) used for the preparation of hard water was of guaranteed reagent (GR) grade. The calcium salt

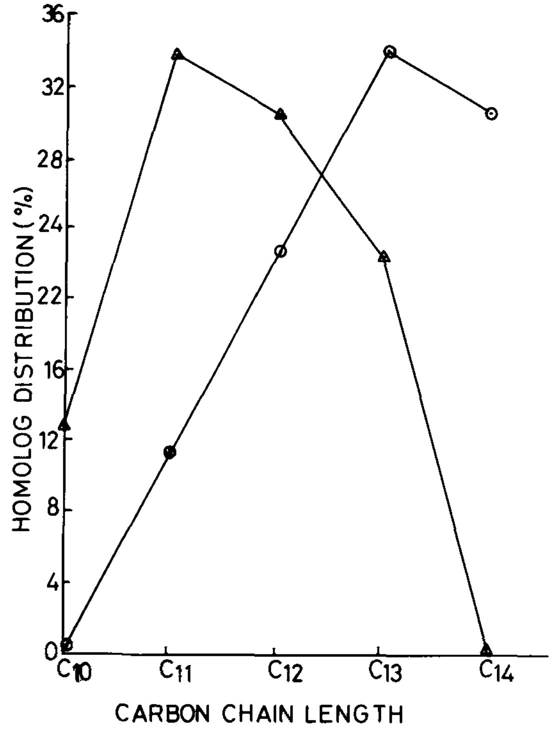

FIG. 1. Distribution of homologs in linear alkylbenzene. ⊙, LAB A; △, LAB B.

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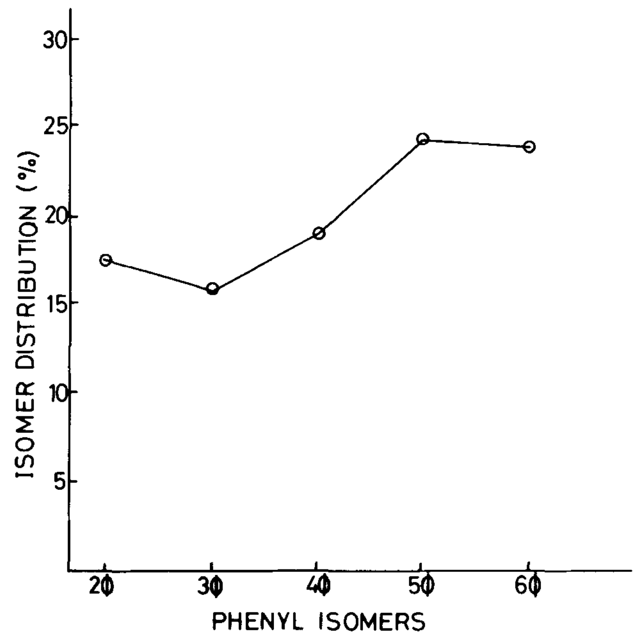

FIG. 2. A typical isomer distribution in linear alkylbenzene.

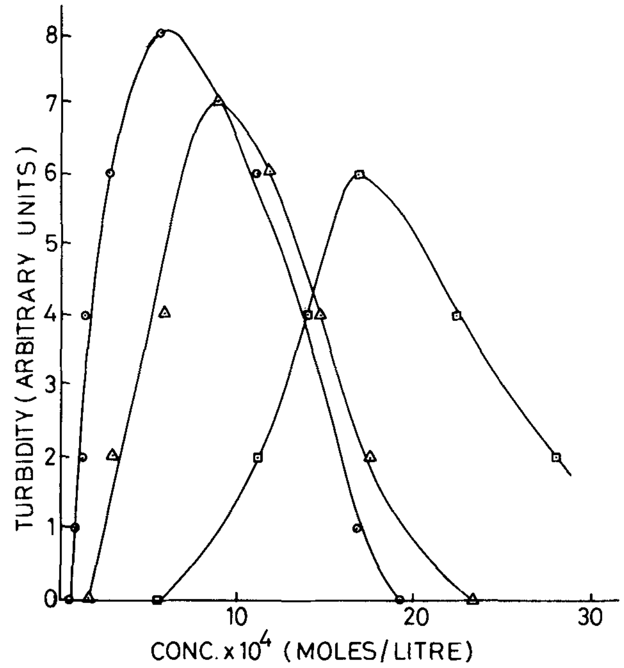

FIG. 3. Calcium sensitivity of the aqueous surfactant solutions. ⊙, Surfactant A; △, surfactant B; ⊡, surfactant C.

of the surfactant was prepared by precipitation from aqueous solution of sodium salt of the surfactant using aqueous calcium chloride solution. The crystalline precipitate was washed repeatedly with distilled water until it was free of chloride and was then recrystallized from water. Distilled water was redistilled over alkaline potassium permanganate before use. It had a specific conductance of the order of 1-2 × 10^{-6} Ohm^{-1} Cm^{-1}.

Studies on surface tension of surfactant solutions in distilled water and hard water were carried out by the drop weight method. The experimental set-up and procedure used were the same as that described earlier (12). As the mass of drop under flowing conditions depends not only on the surface tension but also on the drop formation rate due to hydrodynamic effect, the observed drop mass was corrected for the latter. The corrected drop mass of the surfactant solution was calculated from the observed time dependent drop mass using the "master equation" suggested by Jho and Carreras (13,14).

$$M_e(t) = \frac{9.44\ M(t) + 5.37\ t^{-3/4}}{9.44 + t^{-3/4}} \qquad [1]$$

where $M_e(t)$ and M(t) are the corrected and observed masses of the drop, respectively, at drop time t, defined experimentally as the time between the release of two successive drops. The dynamic surface tension γ(t) at different intervals of time was then calculated from the corresponding corrected mass of drops using the equation (15):

$$\gamma(t) = \frac{M_e(t)g}{R}\ F \qquad [2]$$

where g is the acceleration due to gravity, R is the radius of the capillary tip and F is a correction factor, the values of which were taken from (15).

Precipitation of sodium alkylbenzene sulfonates with aqueous calcium chloride solutions was observed visually. Surfactant solutions of increasing concentration were prepared in hard water containing the same concentration of calcium chloride corresponding to 10 ppm calcium. Turbidity of the solution was assessed visually and rated on an arbitrary turbidity scale of eight units.

All the measurements were carried out at a constant temperature of 30 ± 0.1 C.

RESULTS AND DISCUSSION

Presence of Ca^{++} ions was found to precipitate the anionic surfactants from aqueous solution. Under fixed concentration of Ca^{+++} ions, precipitation increased with increasing concentration of the surfactant, reached a maximum and then started redissolving in the solution with further increase in concentration and finally resulted in a clear solution. Results of the precipitation and redissolution of different surfactants in the presence of 10 ppm Ca^{++} ions are compared in Figure 3. it can be seen from the figure that:

- Concentration of the surfactant corresponding to (i) the occurrence of precipitation; (ii) maximum in the turbidity versus concentration of surfactant curve, and (iii) complete disappearance of precipitate decrease with increasing percentage of higher homologs in the mixture.
- Maximum turbidity of the surfactant solution was higher for the surfactants having a higher percentage of higher homologs in the mixture.
- Surfactant C, which is a branched surfactant derived from propylene tetramer, exhibits the least sensitivity toward hard water.

Results of the precipitation of these surfactants are in accordance with the expectations on the basis of the length and branching of their hydrophobic chain. It may be noted that results similar to the above have been observed by other investigators (8,10).

Equilibrium surface tension of aqueous surfactant solutions in the presence of 10 ppm Ca^{++} ions, obtained from the surface tension versus drop time plots, are given in Figures 4, 5 and 6 for surfactants A, B and C, respectively, wherein surface tension, γ values have been plotted against the surfactant concentration on a logarithmic scale. Corresponding results in the case of surfactant solutions in distilled water also are included for comparison. It can be seen from the figures that in all cases:

- Surface tension versus logarithm of concentration (γ vs log C) curves exhibit two breaks in the presence of Ca^{++} ions as compared to only one corresponding to the CMC of the surfactant in distilled water. Both the breaks are sharp enough to enable precise determination of the point of inflections.
- Surface tension decreases steeply with increasing concentration of the surfactant up to the concentration corresponding to the first break, and then relatively slowly to the second break. Increase in concentration of the surfactant beyond the second break results in an increase in surface tension of the solution which tends to approach the value obtained with the surfactant solution in the absence of calcium ions.
- The initial rate of decrease of surface tension with increasing concentration in the presence of Ca^{++} ions is steeper than the value obtained in their absence. Surfactant solution in hard water exhibited surface tension much lower than the value obtained with the surfactant solution in distilled water with the extent of lowering decreasing with increasing concentration of the surfactant.
- Concentrations corresponding to the breaks are lower for the surfactant having a higher percentage of higher homologs in the mixture. Further, second break in the γ vs log C curves is in the region of the critical micelle concentration of the surfactant in the absence of Ca^{++}.

Further, an examination of Figures 3-6 indicates that the concentrations where precipitation appears and completely redissolves correspond to the first and second breaks, respectively, and that corresponding to the maximum in the turbidity versus

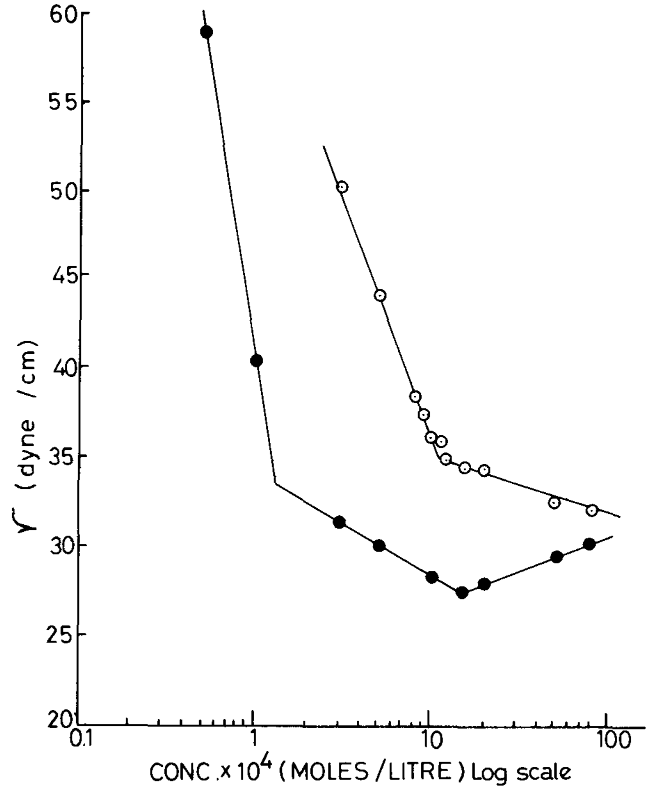

FIG. 4. Surface tension of the aqueous solution of surfactant A in ⊙, water, and ●, hard water (10 ppm Ca^{++}).

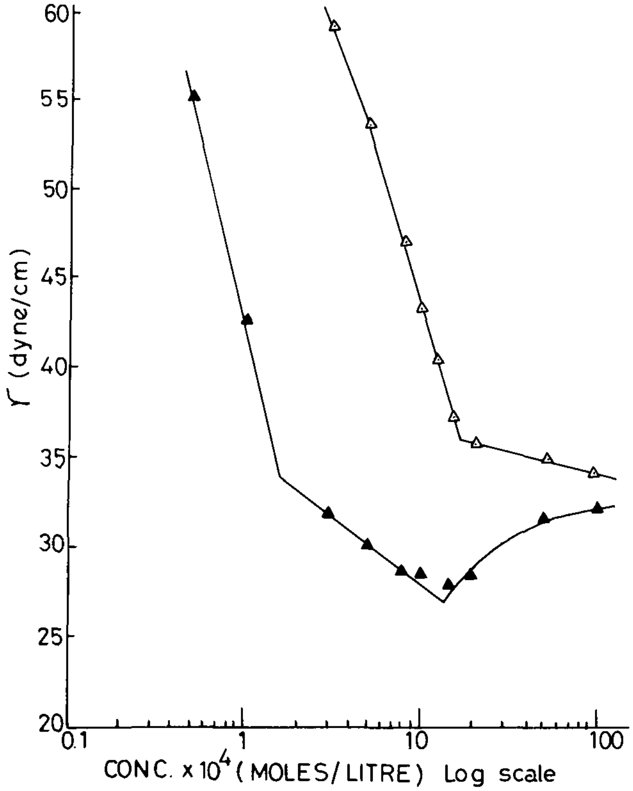

FIG. 5. Surface tension of the aqueous solution of surfactant B in △, water, and ▲, hard water (10 ppm Ca $^{++}$).

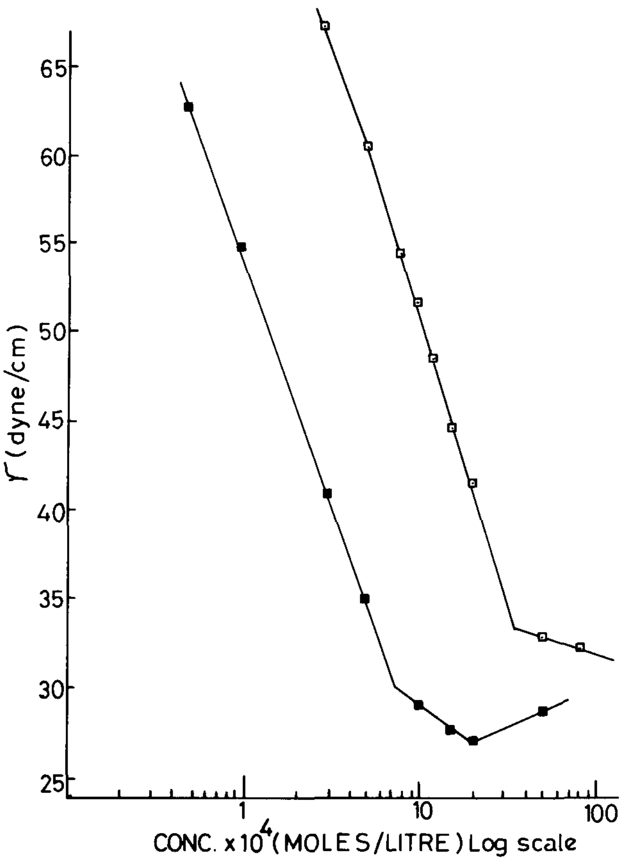

FIG. 6. Surface tension of the aqueous solution of the surfactant C in ☐, water, and ■, hard water (10 ppm Ca^{++}).

concentration curves lies in the region between the two breaks in γ versus log C curves in the presence of Ca^{++} ions.

The observed results on the precipitation and redissolution of the surfactant can be explained in terms of the calcium-LAS precipitation boundaries (8-10,16).

An increase in surfactant concentration results in the precipitation of the calcium salt of the surfactant when its solubility limit in the presence of Ca^{++} ions is reached. This results in an increase in turbidity of the solution with increasing concentration of the surfactant. The decrease in turbidity with increase in concentration beyond a certain value is due to resolubilization of the precipitated calcium surfactant by the surfactant micelles, or in other words due to adsorption/association of Ca^{++} ions onto the micelle. It appears, therefore, that the critical micelle concentration of the surfactant in the presence of added CaCl$_2$ lies in the region of the maximum in turbidity versus concentration curves. Because addition of surfactant increases the precipitation of Ca salt due to 'common ion effect' and the number of micelles in the neighborhood of CMC is relatively small, the decreasing trend in turbidity versus concentration curves may be observed at a concentration slightly higher than the CMC of the surfactant in the presence of added CaCl$_2$. It may be noted that a similar observation was made earlier by Baviere et al. (9). The steep decrease in surface tension of the solution up to the first break and increase in surface tension beyond the second break with increasing concentration of the surfactant are, however, difficult to explain satisfactorily with the help of the above model based on Ca-LAS precipitation boundary.

We have proposed a model for the arrangement of surfactant molecules for the explanation of the observed unusual behavior of surface tension of surfactant solutions in hard water. The γ versus log C curves, shown in Figures 4-6, in the absence of Ca^{++} ions can be divided into two parts denoted I and II and representing the portions of the curves before and after break, respectively, whereas those in the presence of Ca^{++} ions consist of three segments denoted III, IV and V and representing portions of the curves up to the first break, between the breaks and after the second break,

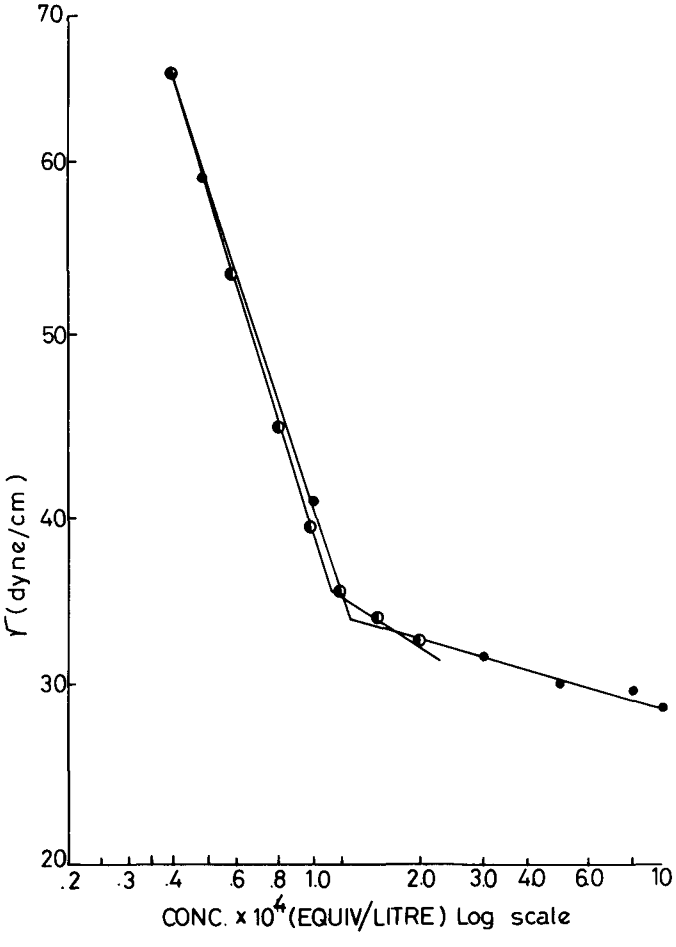

FIG. 7. Comparison of surface tension of surfactant A in hard water (10 ppm Ca^{++}) with its calcium salt in water. ●, NaLAS in hard water (10 ppm Ca^{++}), and ◐, Ca(LAS)$_2$ in water.

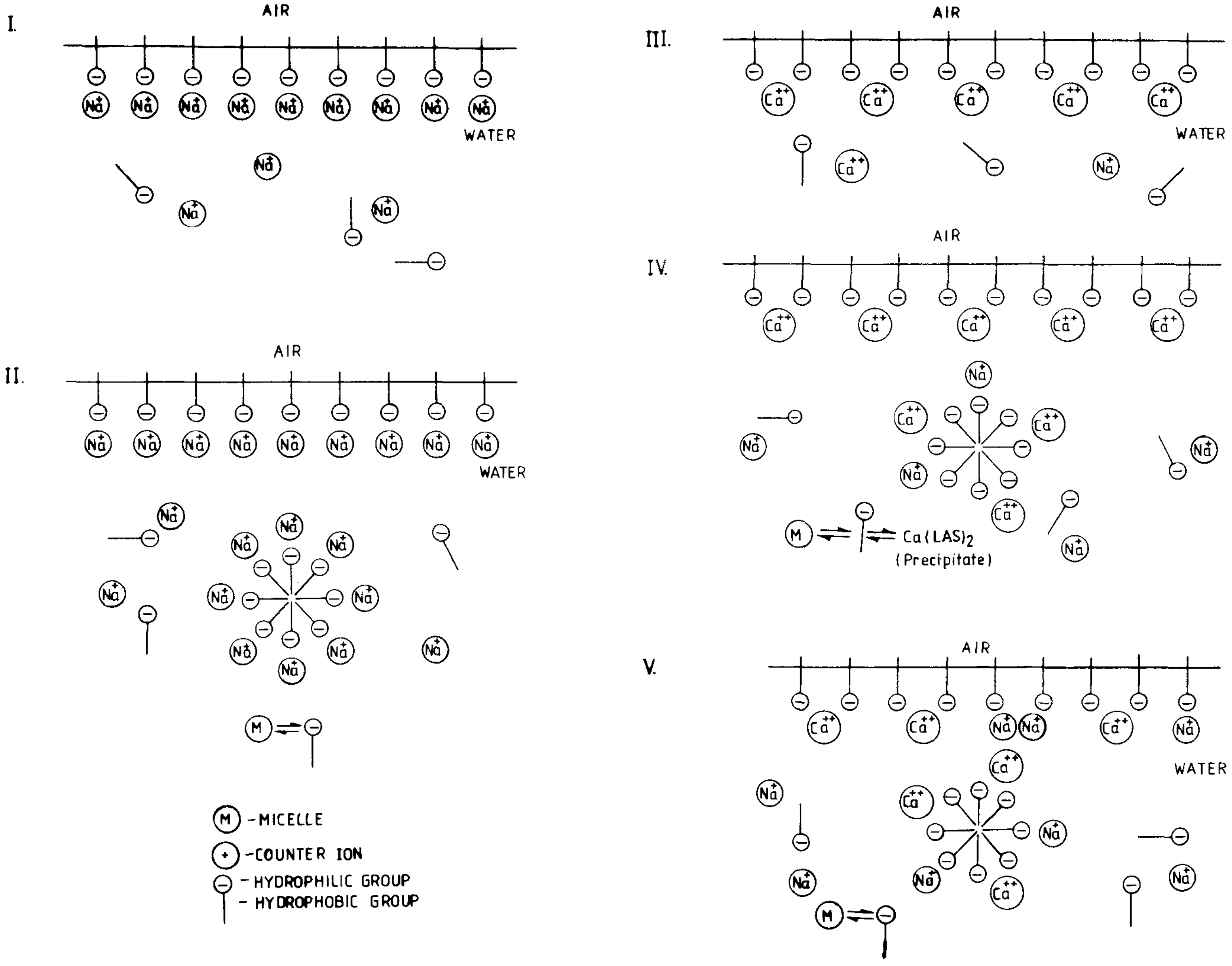

FIG. 8. A schematic representation of the arrangement of surfactant molecules for adsorption from aqueous solutions in the presence and absence of Ca^{++} ions.

respectively. Arrangement of surfactant molecules, postulated for the explanation of different segments of curves given in Figures 4-6, is shown schematically in Figure 8. In the absence of Ca^{++}, the nature of γ vs. log C curves is well known (6). Addition of surfactant up to a concentration corresponding to the break determined as critical micelle concentration results in a preferential adsorption of surfactant at solution/air interface (Fig. 8-I) beyond which further addition results in the formation of surfactant clusters or micelles which rest in equilibrium with the monomeric form of the surfactant (Fig. 8-II). In the presence of Ca^{++} ions, the initial sharp decrease of surface tension of the surfactant solution seems to be due to the formation of the calcium salt of the surfactant and its preferential adsorption at the solution/air interface (Fig. 8-III). The presence of Ca^{++} as counter ions probably forms a more coherent structure at the solution/air interface, thereby resulting in a higher decrease in surface tension of the solution than in the absence of Ca^{++} ions. The first break in the γ versus log C curves in the presence of Ca^{++} ions may, therefore, be due to the formation of micelles or precipitation of the calcium salt of the surfactant or a combination of both factors.

To ascertain the validity of the above mechanism, the adsorption behavior of calcium salt of the surfactant from aqueous solution at the solution/air interface was studied. Data on surface tension obtained with calcium salt of the surfactant in distilled water are compared with those obtained with the sodium salt of surfactant in the presence of 10 ppm Ca^{++} for surfactant A in Figure 7. The similarity in the nature of the two curves clearly indicates that the sharp decrease in surface tension with concentration up to the first break is due mainly to the preferential adsorption of the calcium salt of the surfactant at the solution/air interface.

With the increase in the concentration of the surfactant beyond the first break it appears that additional surfactant goes into the precipitate or the surfactant micelle. In the region between the breaks, both micelle and precipitate coexist and rest in equilibrium with each other through the monomeric form of the surfactant. As adsorption capacity of Ca^{++} ions onto the micelle is higher than that of the Na^{+} ion, the equilibrium between the precipitate of $Ca(LAS)_2$ and monomeric surfactant is shifted toward the latter, resulting in the gradual dissolution of the precipitate (Fig. 8-IV). Hence, the precipitate acts as a reservoir for the supply of the Ca^{++} ions to the micelle. In the region of the second break complete redissolution of the precipitate occurs, resulting in a clear solution. The continued decrease in surface tension between the breaks may be due partly to the preferential adsorption of the more surface active homolog/isomer at the solution/air interface and partly to modification in activities of the monomers with increasing concentration of the surfactant beyond first break under the influence of micellization, precipitation and redissolution of the precipitate.

With the increase in concentration of the surfactant beyond the second break we believe the demand for Ca^{++} ion association with the micelle is met by their replacement from the surface by Na^{+} ions from the solution, with the extent of the replacement increasing with increasing concentration of the surfactant (Fig. 8-V). As a result, the surface tension of aqueous surfactant solution in the presence of Ca^{++} ions beyond the second break shows an increasing trend and finally tends to approach the value obtained in the absence of Ca^{++} ions in the solution.

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