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The Effect of Surfactant Adsorption on the Evaporation of Volatile Hydrocarbons from Their Aqueous Solutions

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Abstract

The mass transport of dissolved hydrocarbon molecules from water to the interior of air bubbles was analyzed. The effect of ionic surfactant adsorption at the bubble surface on the evaporation of mesitylene from aqueous solutions into the bubble was investigated. It has been stated that the presence of surfactants does not affect the evaporation efficiency until the surface coverage θ exceeds ca. 0.7. A certain decrease of the mass transport coefficient has been observed only in cases when interaction occurred between the hydrocarbon and surfactant molecules.

INTRODUCTION

It was stated earlier (*1*, *2*) that the removal of hydrocarbons from their emulsions proceeds according to two different mechanisms:

1. Interception of emulsified droplets by a rising bubble resulting from hydrodynamic forces.
2. Mass transport of the dissolved molecules from water into the bubble as a result of evaporation.

The evaporation has proved to be of great importance because its contribution to the cumulative hydrocarbon removal may predominate over the contribution of the interception process.

Transport of a substance dissolved in water to the interior of a bubble rising through a layer of this solution consists of the following stages: 1) mass transfer from the bulk solution to the water/gas interface, 2) evaporation from the interface, 3) mass transfer from the interface to the interior of the bubble. The rates of processes 1 and 3 depend on the diffusion coefficients of the solute in the liquid and in the gas. The evaporation rate from the interface is dependent on the equilibrium vapor pressure of the solute above the surface and is given by

$$v = S\alpha\sqrt{\frac{RT}{2\pi M}}(C_{eq} - C_b) \qquad (1)$$

usually referred to as the Hertz–Knudsen equation (*3*). The evaporation coefficient α is equal to unity for all the liquids provided that certain experimental conditions are met. One of the necessary conditions is that the liquid surface should be free from any impurities. It follows from the experiments that even a small surface contamination changes the evaporation rate. An additional resistance changing the evaporation rate appears when the liquid surface is covered with a monomolecular film. Hence the total resistance of transport of a molecule from one phase to another through an adsorption film consists of resistance of the molecule diffusion in one phase, resistance of transfer through the film, evaporation resistance, and diffusion resistance in the second phase. Barnes calculated that the diffusion resistance in the liquid is the greatest (of the order of 10^3–10^5 s/cm), and thus controls the rate of the evaporation process (*3*). For a comparison, Barnes reported that monomolecular film resistances vary between 0 and 10 s/cm, hence it can be greater than the evaporation resistances (10^{-5}–10^{-1} s/cm), yet much smaller than the diffusion resistance in the liquid. Princen and coworkers (*4, 5*) investigated the transfer of gases through soap monolayers. They concluded that the transfer occurs through aqueous pores in the film between the surfactant molecules. Bulgarian scientists (*6, 7*) claim that the transfer of molecules through mono- and bilayers takes place through vacancies in the adsorption film.

Fowkes (*8*) examined the penetration of hydrocarbons into adsorption films of quaternary ammonium salts adsorbed at the oil/water interface. He found that both hydrocarbon and water molecules penetrate the films. Pluciński (*9, 10*) analyzed the effect of the kind of surfactant on the diffusion resistance of an adsorption film, and found that aliphatic hydrocarbons diffuse through the adsorption layer faster than aromatic hydrocarbons. However, at properly thick membranes the transfer rate of hydrocarbons depends on their diffusivity and solubility in the aqueous core of the membrane; in such cases the transfer rate of aromatic hydrocarbons is greater than that of alkanes.

Condensed monomolecular films are encountered at suitably high surfactant concentrations (close to and above the critical micelle concentration). However, even when interfacial coverage is complete, the resistance of diffusion through the layer of adsorbed surfactant molecules can be neglected because, according to Barnes' calculations, this resistance is smaller than diffusion resistance in the liquid.

This work is aimed at examining the effect of the presence of various surfactants on the evaporation rate of volatile hydrocarbons dissolved in water. Mesitylene has been selected for the investigations due to its considerable water solubility and vapor pressure (*1*, *2*).

THEORY

Surfactant concentrations lower than the cmc are used in flotation of hydrocarbons, hence the interfacial coverage is not complete. Due to this, the molecules of volatile substances dissolved in water can evaporate to the interiors of flotation gas bubbles through the noncovered surfaces, equal to $S(1 - \theta)$. As a result, the rate of mass transfer into a single bubble is described by

$$dm/dt = kS(1 - \theta)(C_{eq} - C_b) \tag{2}$$

After rearrangement, an equation in the following form is obtained:

$$m = \frac{4}{3}\pi R^3 K_H C_{aq}\left\{1 - \exp\left[-\frac{3kh(1 - \theta)}{Ru}\right]\right\} \tag{3}$$

This equation allows calculation of the solute mass m evaporated into one bubble, and is similar to the equation described earlier (*1*).

THEORETICAL RESULTS

The theoretical efficiency of mesitylene evaporation from water to air bubbles at various coverages of the interfacial surface with surfactant molecules has been calculated by using Eq. (3). Then the retardation coefficient f, the ratio of the amount of hydrocarbon removed without the presence of surfactant to the amount removed at surface coverage equal to θ, was calculated:

$$f = \frac{[m]_{\theta=0}}{[m]_{\theta}} \tag{4}$$

Figure 1 presents the dependence of the retardation coefficient on surface coverage θ for bubbles of various sizes. It follows from the figure that the effect of θ on the evaporation efficiency increases with an increase in the size of the bubbles in the flotation gas. At the same time it can be seen that this effect becomes significant only at higher θ values, e.g., for bubbles

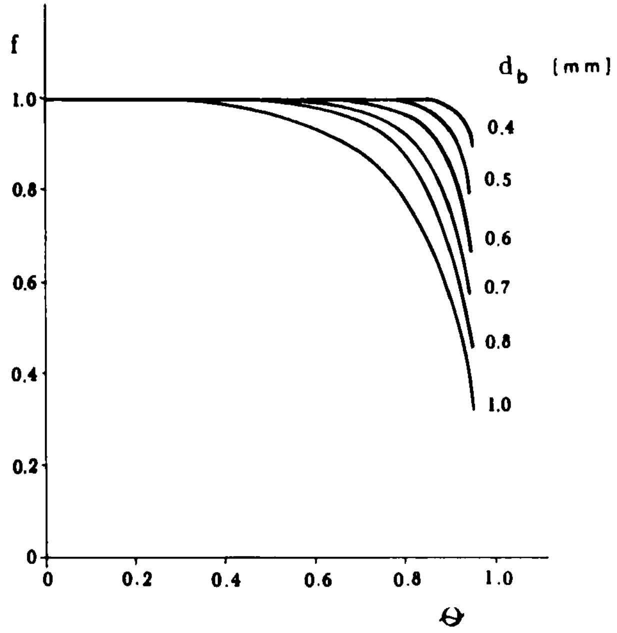

FIG. 1. The dependence of the retardation coefficient f on bubble surface coverage θ. The effect of bubble size. Mass transport coefficient k = 0.01 cm/s.

with a diameter lower than 0.6 mm, evaporation is retarded only when θ exceeds 0.7. Free evaporation through the interface stops at complete coverage. This does not mean that there is no mass transport through this interface; however, it takes place at an additional resistance to transfer through the adsorption film.

EXPERIMENTAL

The evaporation of mesitylene (1,3,5-trimethylbenzene) from its aqueous solution to the interiors of rising bubbles was investigated. The batch aeration processes were carried out in a glass column previously used for flotation experiments (*11*). The gas flow rate was 1.7 cm^3/s. The concentration of mesitylene in the solution was determined by the GLC method described earlier (*11*).

The effect of the following surfactants on mesitylene evaporation was investigated: cetyltrimethylammonium bromide (CTAB), sodium lauryl sulfate (NaLS), and sodium dodecylbenzenesulfonate (NaDBS). Surfactant concentrations in the solutions were determined by the two-phase titration method (*12*).

Surface Coverage Determination

The values of θ occurring in Eq. (3) were determined from measurements of the surfactant adsorption at a free surface. It is known that adsorption depends on time. The rate of surfactant adsorption at an air/water interface under static conditions has been the subject of numerous investigations (*13*, *14*). On the other hand, papers concerning the adsorption rate under dynamic conditions, e.g., during foam separation, are scarce (*15*, *16*). Kato (*15*) found that the adsorption rate of NaDBS at the surface of bubbles flowing through a solution becomes established after a dozen or so seconds. It is known, however, that the adsorption rate is different for different compounds. Figure 2 presents examples of surface tension isotherms for CTAB determined by the drop weight method. It can be seen that lowering of the water surface tension depends on adsorption time; however, the differences between θ values for 30 and 60 s are small. In the flotation experiments performed, the résidence time of gas bubbles in the column did not exceed a dozen or so seconds. Adsorption measurements at such short times are cumbersome; hence, the results of adsorption measurements after 30 s have been applied in the following considerations, assuming that the differences are negligible. The values of $\theta = \Gamma/\Gamma_\infty$ have been calculated from the values of surface concentrations calculated according to Gibbs equation, substituting Γ_{cmc} for Γ_∞. The dependence $\theta = f(C)$

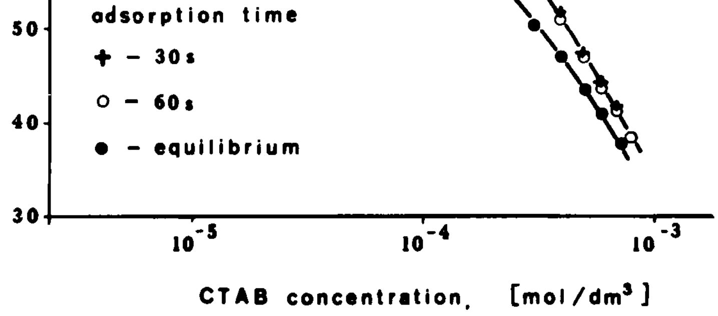

FIG. 2. Surface tension isotherms for cetyltrimethylammonium bromide at different adsorption times.

obtained in this manner was applied for the determination of the bubble surface coverage with surfactant molecules during flotation processes. However, it is known that the surface coverage of a moving bubble with surfactant molecules is not uniform. This is due to viscous drag of the medium at the interface. Thus, in the upper part of a rising bubble, the surface concentration is lower than the equilibrium concentration, ap-

TABLE 1
Selected Parameters of the Mesitylene Evaporation Processes

	Concentration of		Surface coverage		Parameters of rank differences test		Agreement of the experiments with theory[a]
Run	Mesitylene, mg/dm^3	Surfactant, mol/dm^3 × 10^4	Initial θ	Final θ	T	T_α	
			Without Surfactant				
1	28.0	—	—	—	8.5	0	+
2	30.0	—	—	—	12.5	2	+
3	38.5	—	—	—	15.0	4	+
4	48.5	—	—	—	19.0	8	+
			CTAB				
5	35.0	0.50	0.11	0.01	9.0	4	+
6	43.0	0.73	0.24	0.005	14.0	4	+
7	36.3	0.96	0.33	0.01	12.0	4	+
8	31.4	1.56	0.50	0.05	17.5	6	+
			NaLS				
9	42.5	0.64	0.09	0.06	7.0	6	+
10	35.5	0.95	0.14	0.08	7.0	2	+
11	40.8	1.22	0.20	0.10	7.0	4	+
12	29.5	1.74	0.30	0.12	0.0	2	−
			NaDBS				
13	36.2	0.56	0.09	0.04	4.0	4	−
14	49.7	0.65	0.10	0.08	4.0	6	−
15	34.7	1.19	0.20	0.08	0.0	6	−
16	22.0	1.63	0.26	0.08	0.0	4	−

[a] Good agreement of the experimental and theoretical results (when $T > T_\alpha$) is marked as "+," disagreement is marked as "−."

proaching zero at the bubble top (*17*, *18*). On the other hand, on the downstream part of a bubble, the surface concentration is higher than equilibrium due to crowding of surfactant molecules. As a result, the exact extent of the surface free for evaporation is impossible to determine. After accepting the necessity of the simplifications, the above described manner of determination of θ has been adopted in this work.

Aeration of Mesitylene Solutions

Aeration removal of mesitylene from its aqueous solutions was carried out in the presence of various amounts of selected surfactants. Table 1 presents the θ values determined. It can be seen that they are different in the beginning and at the end of the process. This is due to the fact that during aeration of the solutions, the surfactants undergo foaming and their concentration decreases, fastest for NaLS and slowest for CTAB. However, the degree of foaming of CTAB was the largest, as evidenced by the greatest changes of θ. Fortunately, partial foaming of surfactants caused a change of θ that was insignificant with respect to its effect on mesitylene evaporation.

The course of the mesitylene removal process is presented in Figs. 3–10. The points correspond to experimental results, while the lines present

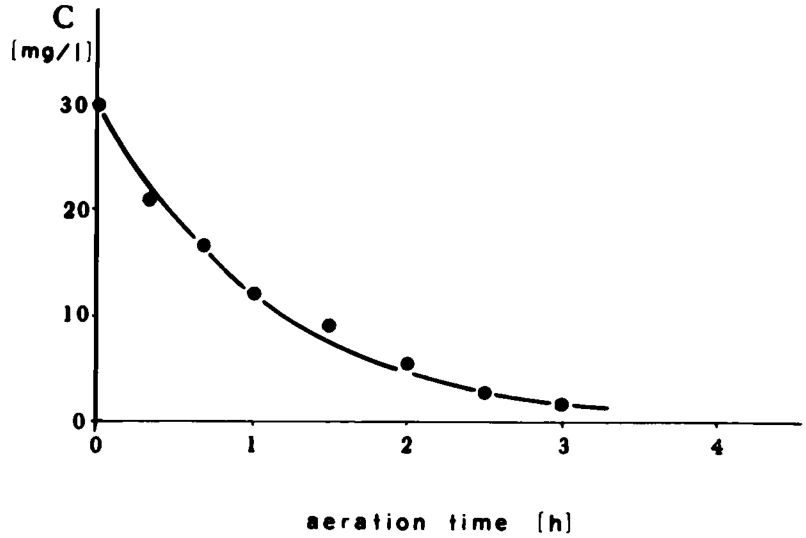

FIG. 3. The change of mesitylene concentration in aqueous solution as a result of evaporation; dependence on aeration time. Mass transport coefficient k = 0.01 cm/s, bubble diameter d_b = 0.58 mm.

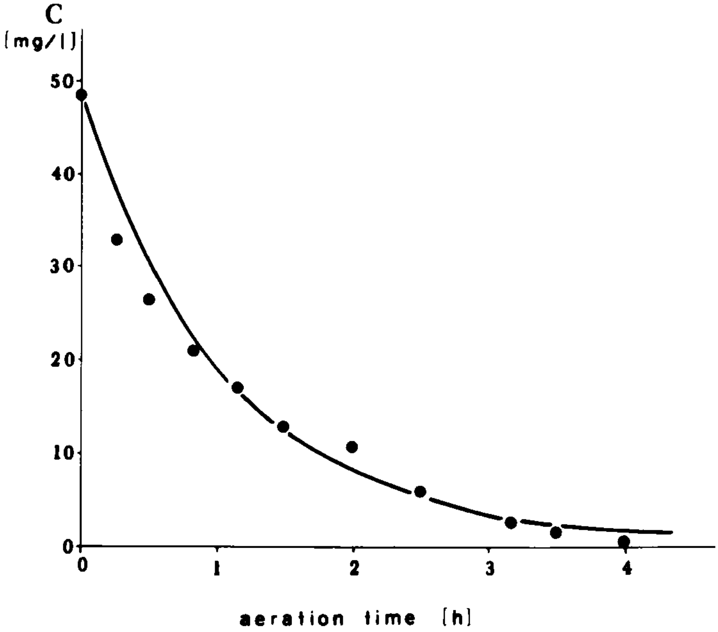

FIG. 4. See the Fig. 3 legend.

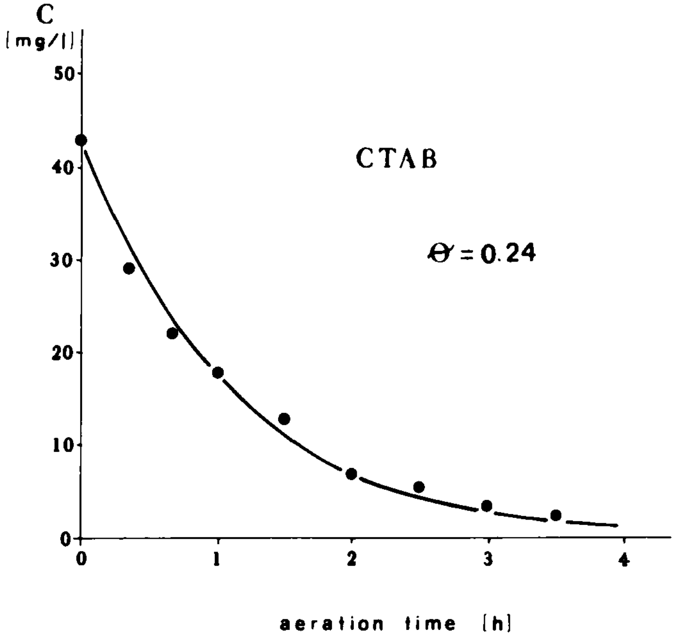

FIG. 5. The change of mesitylene concentration in aqueous solution containing CTAB; dependence on aeration time. Mass transport coefficient $k = 0.01$ cm/s.

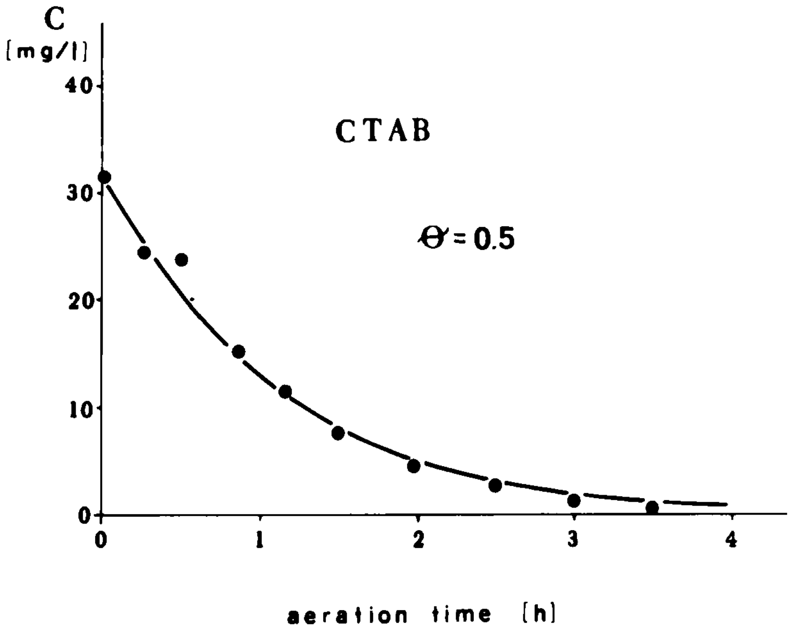

FIG. 6. See the Fig. 5 legend.

theoretical results calculated according to Eq. (3). In the cases of a lack of surfactant (Figs. 3 and 4) and of the presence of CTAB in the solution (Figs. 5 and 6), the experimental results agree well with the theoretical results. In the presence of NaLS, good agreement is observed only for θ lower than 0.3, since at this value the results of mesitylene evaporation are already worse than those determined theoretically (Figs. 7 and 8). Finally, in the presence of NaDBS the experimental results are worse than the theoretical predictions even at low concentrations ($\theta < 0.09$) (Figs. 9 and 10).

DISCUSSION

Figures 11–14 present mesitylene evaporation efficiency for four series of experiments. Solid lines correspond to theoretical yield, not dependent on the initial hydrocarbon concentration in the solution. The theoretical yield also does not depend on the θ value within the surfactant concentration range examined. It can be seen that deviations from the theoretical results are the greatest at the beginning of the processes, decreasing to almost zero after ca. 2 h. Statistical analysis of the results carried out using the rank differences test (*19*) showed good fitting of the theoretical equations to the experimental results in most series (Table 1). Measurements

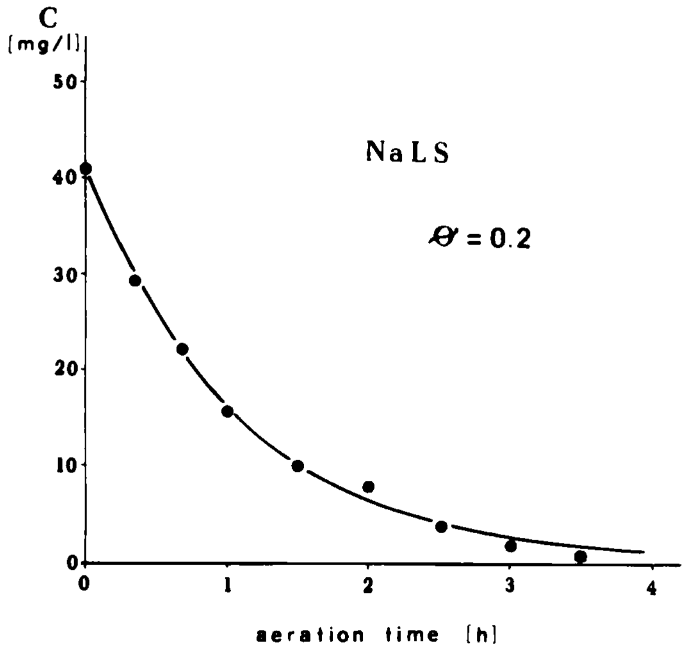

FIG. 7. The change of mesitylene concentration in aqueous solution containing NaLS; dependence on aeration time. Mass transport coefficient k = 0.01 cm/s (——) and 0.001 cm/s (- - -).

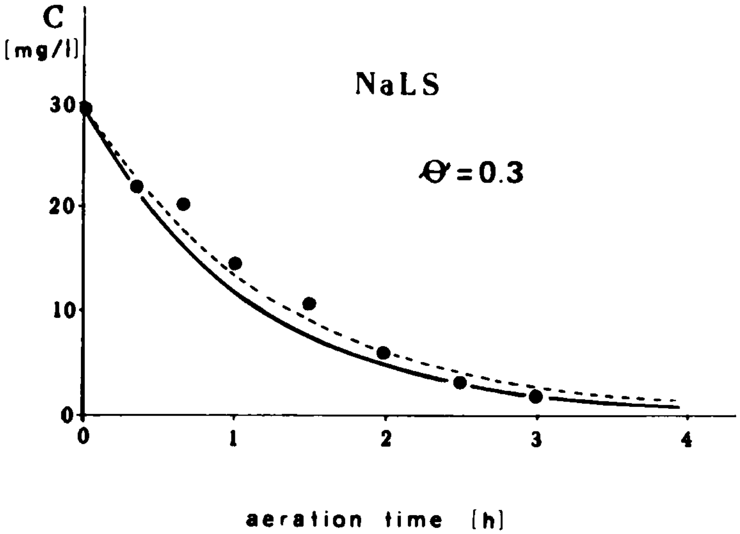

FIG. 8. See the Fig. 7 legend.

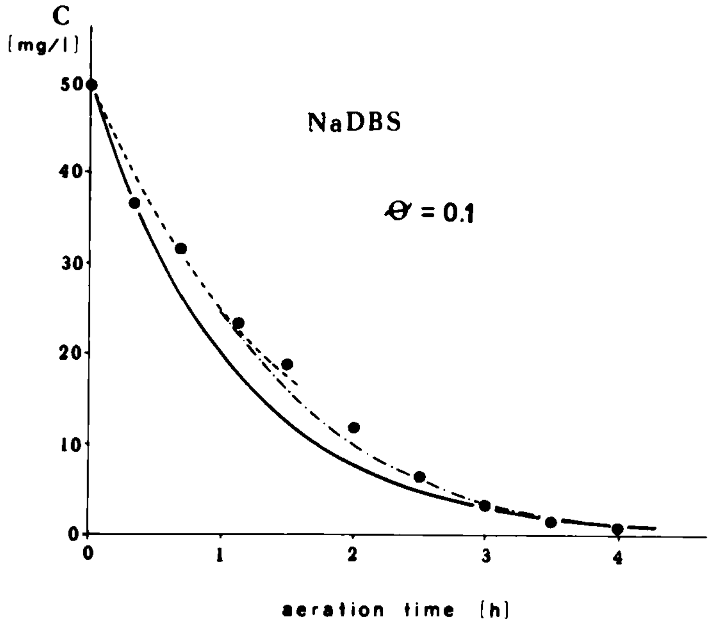

FIG. 9. The change of mesitylene concentration in aqueous solutions containing NaDBS; dependence on aeration time. Mass transport coefficient k = 0.01 cm/s (——, - · -) and 0.001 cm/s (- - -).

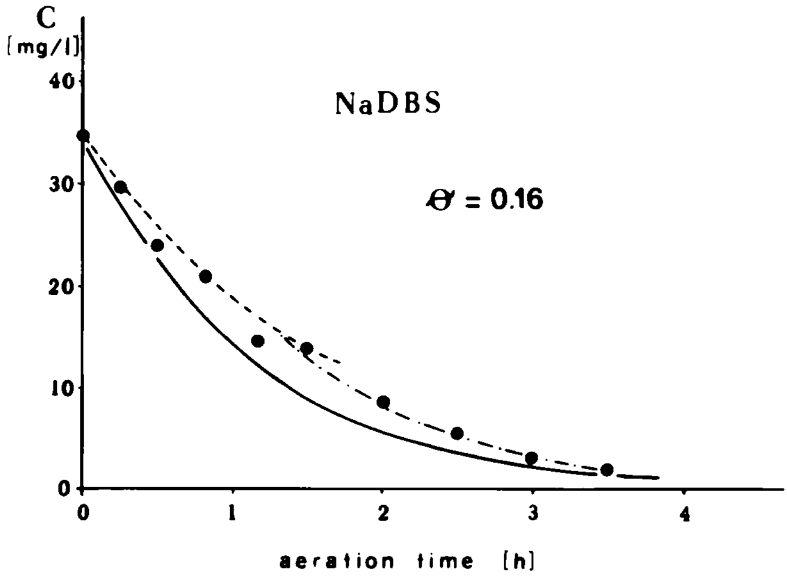

FIG. 10. See the Fig. 9 legend.

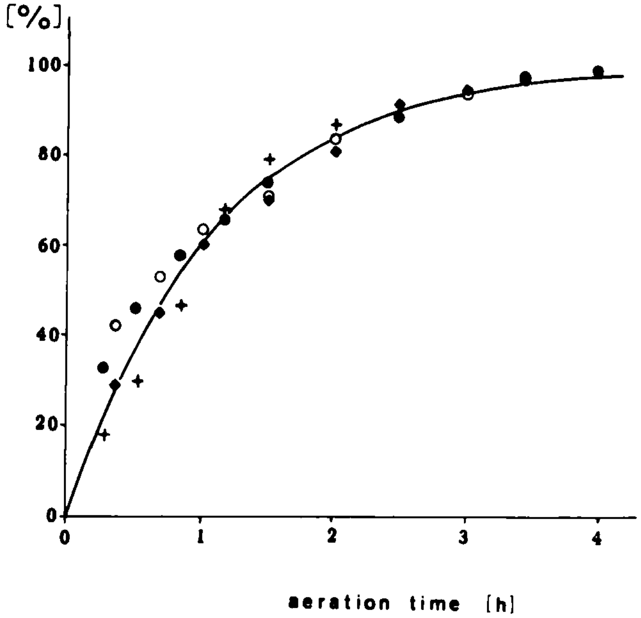

FIG. 11. The efficiencies of mesitylene evaporation from water (Fig. 11) and from aqueous solutions of surfactants (Figs. 12–14); dependence on aeration time.

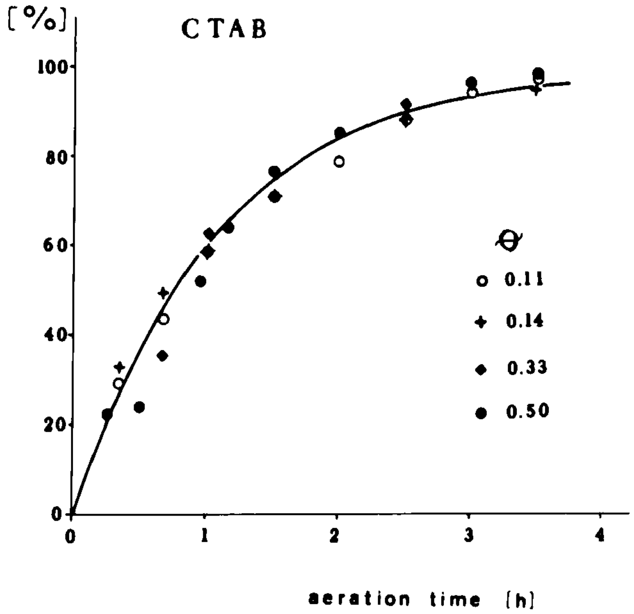

FIG. 12. See the Fig. 11 legend.

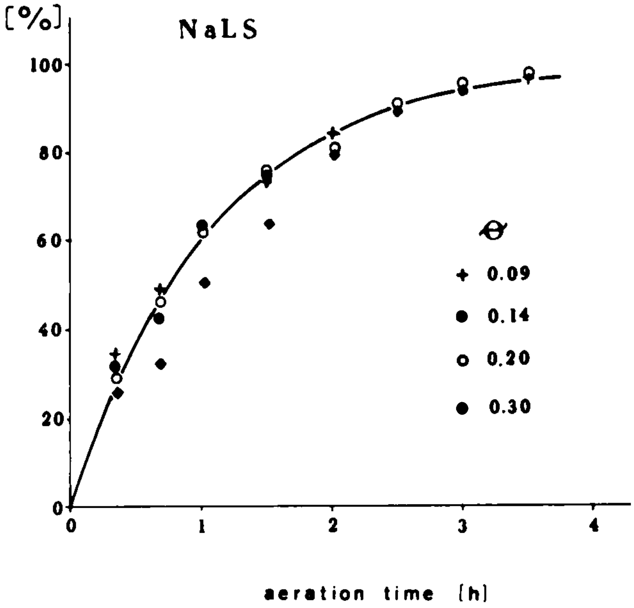

FIG. 13. See the Fig. 11 legend.

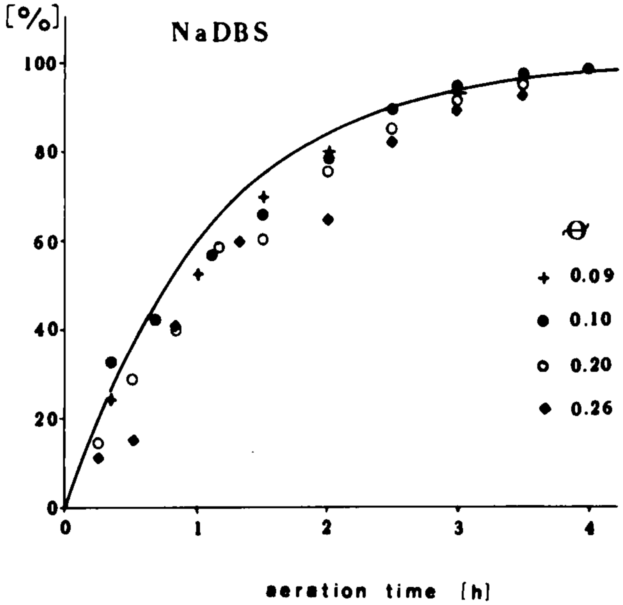

FIG. 14. See the Fig. 11 legend.

performed in the presence of NaDBS constitute the sole exception. Deviations of the experimental results from the theoretical expectations do not result from a decrease of the interfacial surface attainable by evaporation, but from a change in the mass transport coefficient of mesitylene molecules. This coefficient is a parameter that was fitted to model calculations. According to earlier considerations (*1*), the results of evaporation to gas bubbles of 0.4–0.8 mm diameter should not change for *k* values from 0.005 to 0.05 cm/s. Therefore, a *k* value of 0.01 cm/s was adopted for the calculations. However, it follows from Fig. 15 that the dependence of mesitylene evaporation efficiency on bubble surface coverage is stronger the smaller the value of the mass transport coefficient. Hence, in the case of NaDBS, we tried to adjust the theoretical curves to the experimental results by changing the values of this coefficient (Figs. 9 and 10). The results presented confirm the conclusion that the higher the NaDBS concentration, the greater the total resistance in the transferring process of the mesitylene molecules from the aqueous solution to the bubble interior.

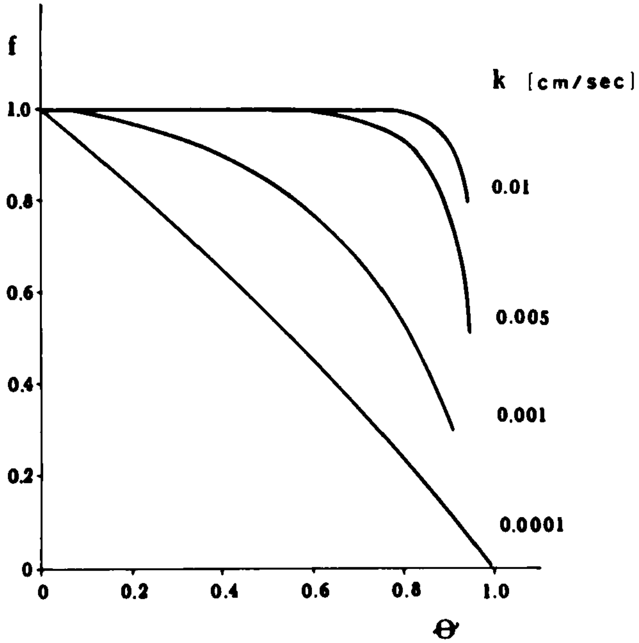

FIG. 15. The dependence of the retardation coefficient f on bubble surface coverage θ. The effect of mass transport coefficient. The bubble diameter d_b = 0.6 mm.

CONCLUSIONS

It has been established that the presence of surfactants does not negatively influence the efficiency of evaporation to the bubble interior until the coverage of the bubble surface with surfactant molecules exceeds ca. 0.7. However, in cases where interaction occurred between the hydrocarbon and surfactant molecules, the mass transport coefficient was found to be lower than that theoretically calculated.

It can be assumed that the increase of transport resistance, observed mainly in the case where NaDBS was present in the solution, results from the interaction of benzene rings in mesitylene and NaDBS molecules; it is hardly possible that such a large reduction of the mass transport coefficient results from a decrease of the diffusion coefficient in the liquid. It should rather be anticipated that the strong interaction between the mesitylene and NaDBS molecules in the adsorption layer causes an increase in the resistance to mesitylene-molecule evaporation from the surface. Thus, evaporation from the surface rather than diffusion is the slowest process for determining the solute transport rate in this case.

SYMBOLS

C_{aq}	hydrocarbon concentration in water
C_b	hydrocarbon concentration in the gaseous phase
C_{eq}	equilibrium hydrocarbon concentration in the gaseous phase
d_b	diameter of bubble
h	height of the liquid head
k	mass transport rate coefficient
K_H	Henry's law constant for hydrocarbon in water
M	molecular weight of hydrocarbon
R	radius of bubble
S	interfacial area
t	aeration time
u	bubble rise velocity
v	evaporation rate
α	evaporation coefficient
θ	bubble surface coverage by surfactant molecules

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