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## Effect of Some Volatile Organic Compounds on the Foaming of Detergents from Their Aqueous Solutions

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### Abstract

The influence of gaseous phase composition on the surface properties of surface-active substances was investigated. The surface tensions of sodium dodecylbenzenesulfonate and oxyethylated nonylphenol solutions were determined. Also the removal of both detergents from their water solutions by the foaming method was investigated. Air or air-containing vapors of methanol, butanol, ethyl ether, and pentane were used as the gaseous phase in the surface tension measurements and as the foaming gas. The presence of organic vapors in air under a water surface causes a greater decrease of surface tension than in pure air. The greatest effect was observed in the presence of pentane vapors. The foaming of both detergents from the water also depends on the gaseous phase composition and is best when pentane vapors are present in the foaming gas. When methanol vapors are in the foaming gas the removal effect is worse compared with the processes in which pure air was used.

### INTRODUCTION

The adsorption of surface-active substances at the phase boundary depends on the polarity of those phases. The change of the hydrophilicity of one of the phases changes the surface adsorption of the surfactant.

In the foaming process the gas-liquid boundary plays an important role. The influence of solution properties on the foaming effect has been investigated many times. It is known that surface adsorption of surface-active substances or the effect of their foaming increases in the presence of inorganic salts in the solution.

It would be interesting to find out how the composition of the gaseous phase influences the surface adsorption of surface-active agents. As has

been stated by Maas (1), the introduction of certain organic vapors into the gaseous phase during bubble fractionation of low-foaming solutions accelerated and improved fractionation. Maas conducted investigations with water solutions of certain dyes (Patent Blue, Neucocccin, Säuregrün, Titangelb). He wanted to solve the problem of concentration growth of the solution as well as the problem of fractionation of a few dissolved components. He pointed out that the vapors of ethyl ether and ethyl acetate had no effect on foaming and fractionation while chloroform and pentane vapors considerably improved the fractionation of solution components. He called these processes "booster bubble fractionation." He assigned the enriching action to the formation of water/organic solvent layers which are stabilized by surface-active substances.

The purpose of our studies was to find out how the presence of certain organic vapors in the foaming gas influences the detergent's foaming out effect.

## EXPERIMENTAL

In the course of our studies we have conducted foaming processes of two detergents solutions: nonionic oxyethylated nonylphenol and anionic sodium dodecylbenzenesulfonate. The solutions of the nonionic compound contained no inorganic salts, while the anionic compound solutions contained sodium chloride ( $0.01 \text{ mol/dm}^3$ ).

Foaming processes were carried out in the column described in our previous papers (2, 3). The height of the column  $h_c = 82 \text{ cm}$ , the height of the liquid phase  $h_l = 32 \text{ cm}$ , and the feeding solution flow rate  $V_0 = 2.3 \text{ L/h}$  (Fig. 4) or  $4.6 \text{ L/h}$  (Fig. 5).

Before being introduced into the column, the foaming gas was passed through a saturator with organic liquid. Air or air-containing vapors of methanol, butanol, pentane, or ethyl ether were used in the foaming process.

It would be of advantage to keep the same content of all organic vapors in the experiments, but because the solvents used differ in their heats of vaporization and in their water solubility, this was not realized. Table I contains the mean content of the individual compounds in the gaseous phases used in physicochemical and foaming experiments.

The gas flow rates chosen were such that the volume of the gaseous phase in the foam was constant.

The surface tension of the detergent-water solutions at the interface with the gaseous phase which was air containing organic vapors was measured. The results are shown in Figs. 1 and 2. It can be seen from these figures that the surface tension of both detergent solutions depends

TABLE 1

Characteristics of Organic Solvents Used for Saturation of Gaseous Phases

Organic solvent	Molecular weight	Heat of vaporization (kJ/mol)	Content in gaseous phases (wt-%)
Pentane	72	25.77	37
Ethyl ether	74	26.60	35
Methanol	32	35.30	11
Butanol	74	43.97	8

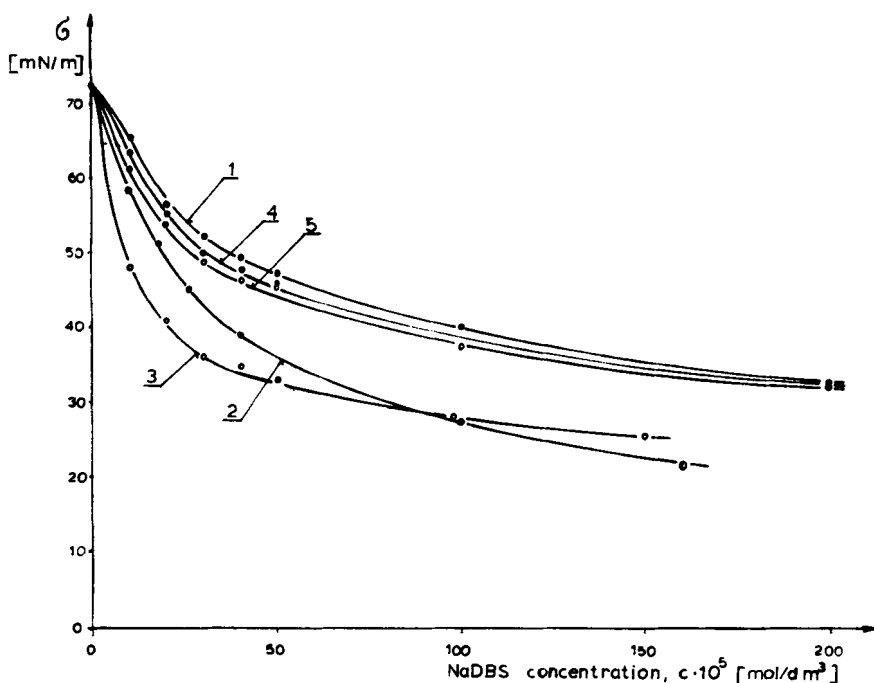


FIG. 1. The dependence of the surface tension on the NaDBS concentration in the solution. The compositions of the gaseous phases: (1) air, (2) air + pentane, (3) air + ethyl ether, (4) air + methanol, and (5) air + butanol. Concentration of NaCl in the solution: 0.01 mol/L.

on the composition of the gaseous phase. It is always highest with pure air, a little lower when the air contains methanol and butanol vapors, much lower when pentane is present, and lowest when ethyl ether vapors are present in the air. The contents of ethyl ether and pentane vapors were similar and reached about 36%; the contents of alcohols, because of their lower volatility, were about 8–13%.

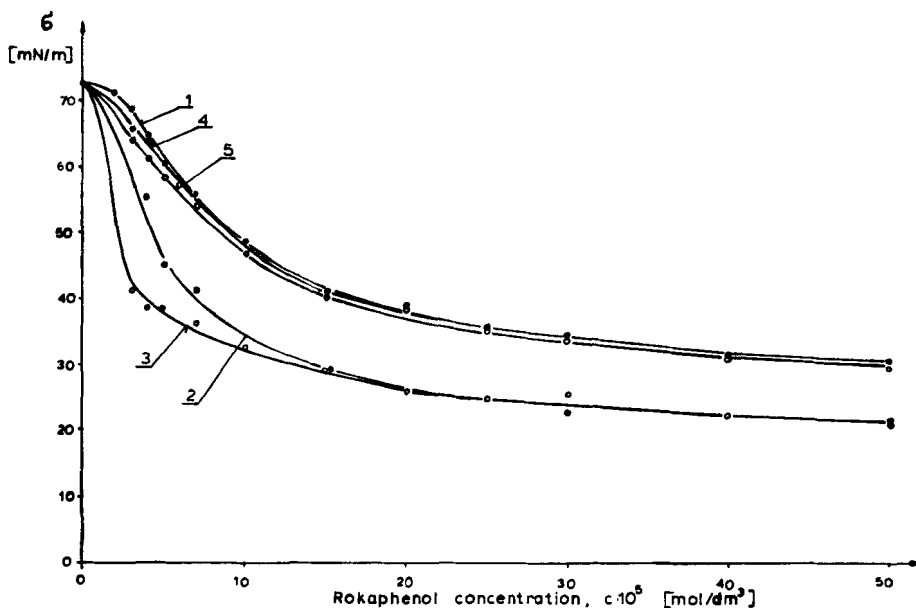


FIG. 2. The dependence of the surface tension of the Rokaphenol solution on its concentration. The compositions of the gaseous phases: (1) air, (2) air + pentane, (3) air + ethyl ether, (4) air + methanol, and (5) air + butanol.

From Fig. 3 it follows that the increase of the organic vapors content (e.g., pentane vapors in the gaseous phases) causes a decrease in the surface tension of the detergent solution.

The foaming effect was determined as in our previous papers (2, 3). This means using the decontamination factor  $C_0/C_r$ , where  $C_0$  is the detergent concentration in the initial solution and  $C_r$  is the detergent concentration in a raffinate after foaming.

In order to compare the effect in the processes in which different gaseous phases were used, it was important to keep the same gas flow rates before the gaseous phase was introduced into the column and after saturation with the organic vapors. Because of the possibility of vapor condensation in a rotameter, we did not measure this flow directly. In addition, it must be remembered that because of the solubility of organic vapors in water, their content in the gaseous phases before the column differs from that in the gas going out with the foam. The gas flow rate ( $V_g$ ) was adjusted in two ways. First,  $V_g$  was adjusted before coming into the saturator by taking into account the quantity of evaporated solvent which depends on the volatility of the solvent. Second, we adjusted the

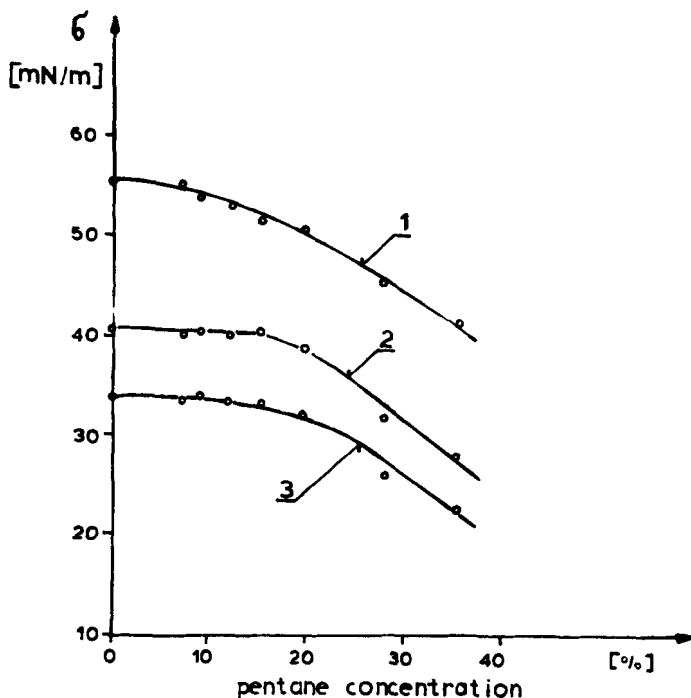


FIG. 3. The dependence of the surface tension of Rokaphenol solutions on the pentane concentration in the gaseous phase. Rokaphenol concentrations: (1)  $7 \times 10^{-5}$  mol/L, (2)  $15 \times 10^{-5}$  mol/L, and (3)  $25 \times 10^{-5}$  mol/L.

gas flow rate before the saturator by assuming that the quantity of the gaseous phase in the foam had a constant value.

Thus, in the first method of gas flow rate adjustment we have taken into consideration only the volatilities of solvents, and in the second method we have used their solubility in water which takes place during the passage of foaming gas through the solution in the column.

Figure 4 shows the dependence of the decontamination factor on the initial concentration of Rokaphenol in the solution. Before saturation we have used gas flow rates such that the same quantity of the gaseous phase for different organic solvents was removed with the foam.

The flow rate of air without organic vapors equals  $10 \text{ dm}^3/\text{h}$ . The flow rate of air before its saturation with pentane was  $7.5 \text{ dm}^3/\text{h}$ , before saturation with ethyl ether  $8.6 \text{ dm}^3/\text{h}$ , before saturation with butanol  $9.5 \text{ dm}^3/\text{h}$ , and before saturation with methanol  $9.8 \text{ dm}^3/\text{h}$ . The volatilities of pentane and ethyl ether are similar (Table 1), so to keep the same gaseous phase volumes, it is necessary to use the same air flow rates.

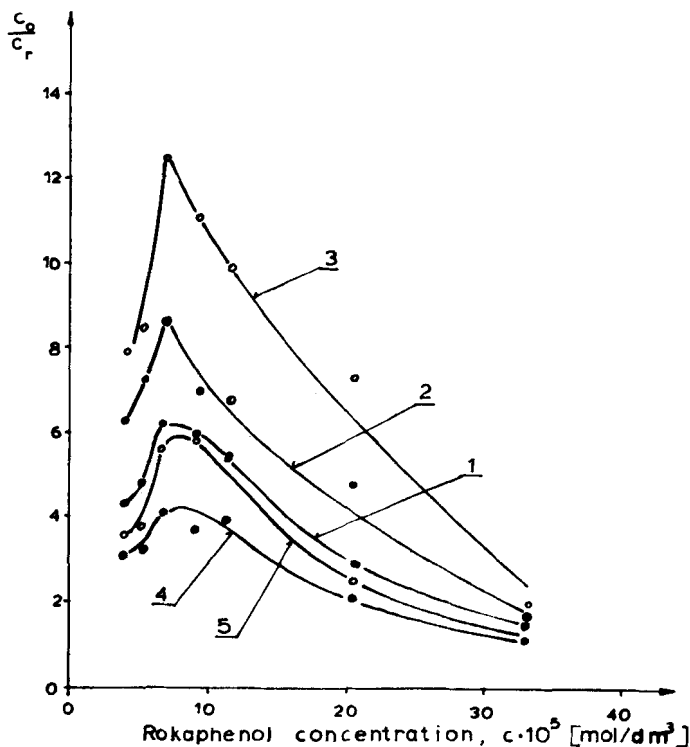


FIG. 4. Decontamination factor dependence on the Rokaphenol concentration in the solution. Foaming gases: (1) air, (2) air + pentane, (3) air + ethyl ether, (4) air + methanol, and (5) air + butanol.

However, the much higher solubility of ethyl ether in water causes much higher losses of the gaseous phase, so higher air flow rates are needed when ethyl ether is used.

Figure 5 presents the results obtained in the processes in which the same air flow rates before saturation with pentane, ethyl ether, and methanol as in processes with pure air (e.g., 10 dm<sup>3</sup>/h) were used.

It follows from Figs. 4 and 5 that the presence of pentane and ethyl ether vapors in the foaming gas increases the removal of oxyethylated nonylphenol, and the observed effect depends on the organic vapors contents in the gas. In the case when their contents in the gas introduced are the same (Fig. 5, Curves 2 and 3), this effect is higher than when pentane is used (Curve 2). This is due to the decrease of the gas flow rate at the outlet being the result of the ethyl ether solubility in the water.

If, however, different gas flow rates are used in order to get the same

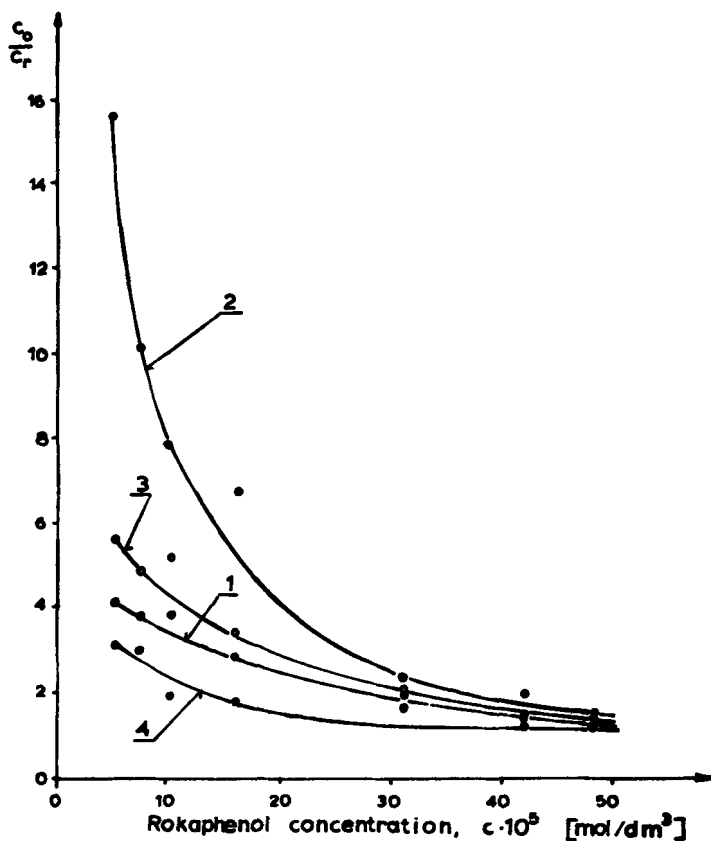


FIG. 5. Decontamination factor dependence on the Rokaphenol concentration in the solution. Foaming gases: (1) air, (2) air + pentane, (3) air + ethyl ether, and (4) air + methanol.

volume of gaseous phases in the foam (Fig. 4, Curves 2 and 3), the use of ethyl ether gives better results. This is related to the higher content of ethyl ether vapor in the gaseous phase being introduced than of pentane vapors.

Figure 6 relates to the foaming processes of sodium dodecylbenzene-sulfonate carried out in parameters analogous to those shown in Fig. 5 for Rokaphenol. In the case of the anionic detergent foaming process, the pentane vapors present in the gas increase the removal of this detergent but are lower than for nonionic Rokaphenol (Figs. 5 and 6, Curves 2). The presence of ethyl ether vapors have little influence on the foaming effect of dodecylbenzenesulfonate.



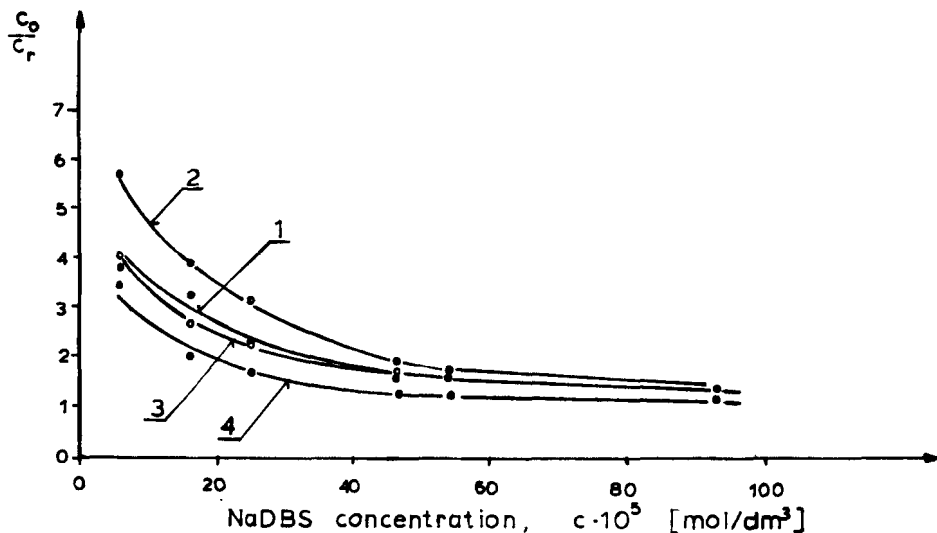


FIG. 6. Decontamination factor dependence on the NaDBS concentration in the solution. Foaming gases: (1) air, (2) air + pentane, (3) air + ethyl ether, and (4) air + methanol.

It was shown, however, that for both detergents the saturation of foaming gas with methanol vapors considerably decreases their decontamination factors (Figs. 4-6, Curves 4). As can be seen from Figs. 1 and 2, the presence of methanol vapors in the gaseous phase influences the surface tension of water solutions of detergents in the same way as the other organic vapors; i.e., it decreases this tension insignificantly. Thus the decontamination factor should not be lower from that when pure air was used. However, due to the excellent solubility of methanol in water, it is probable that its vapors pass from the foaming gas to the water. It was shown that the surface tension of water and water solutions of detergent depends on the presence of methanol in the water.

Figure 7 shows the dependence of the surface tension decrease  $\Delta\sigma$  is caused by the addition of methanol to the Rokaphenol concentration in the solution.  $\Delta\sigma$  expresses the difference between the surface tension of a solution containing methanol and that of a solution without methanol:

$$\Delta\sigma = \sigma_2 - \sigma_1$$

where  $\sigma_1$  is the surface tension of the water-detergent solution and  $\sigma_2$  is the surface tension of the water-methanol-detergent solution.

As can be seen from Fig. 7, lowering of surface tension is increased with an increase of the content of methanol in the solution. The decrease of

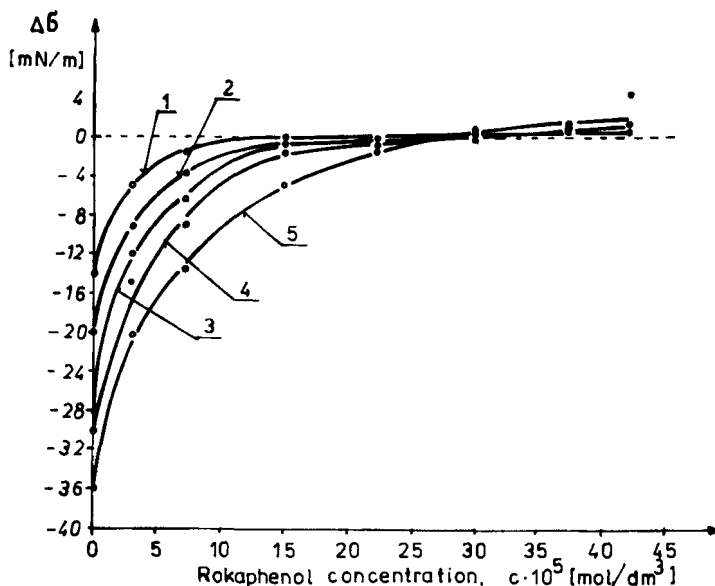


FIG. 7. The changes of surface tension dependence on the Rokaphenol concentration in the solution after the addition of methanol. Methanol concentrations in the solution: (1) 5%, (2) 10%, (3) 15%, (4) 20%, and (5) 30%.

the surface tension caused by methanol addition to the water solution increases as the detergent concentration decreases.

## CONCLUSIONS

The presence of pentane and ethyl ether causes a significant decrease of surface tension when their vapors are in the gaseous phase under the free surface of water solutions. The presence of these vapors in the foaming gas increases the removal of detergents from their aqueous solutions. At the same concentration in the foaming gas (at the outlet of the column), the vapors of ethyl ether increase the decontamination factor more than do pentane vapors (Fig. 4). If the concentrations of ethyl ether and pentane vapors are the same in the foaming gas at the inlet into the column, then, because of the considerable solubility of ethyl ether in water, its concentration in the gas decreases and we observe that the foaming effect is better when pentane is used (Figs. 5 and 6).

In spite of the fact that methanol and butanol in the gaseous phase decrease the surface tension of water solutions of anionic and nonionic detergents to some extent, they do not increase the foaming effect.

The passing of methanol vapors to the liquid phase probably causes the decrease of detergent removal with the foam. But even with the complete absorption of methanol from the gaseous phase into the solution, its content in the foamed solution only equals 0.2%. However, the observed influence on surface tension occurred at methanol concentrations above 3%.

For a complete explanation of the observed phenomenon, it will be necessary to carry out a wide range of investigations of surface adsorption processes to find correlations between the contents of components and their adsorption from solution.

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