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Krystyna B. Mdrzycka<sup>a</sup>; Włodzimierz Zwierzykowski<sup>a</sup>

<sup>a</sup> DEPARTMENT OF FAT CHEMISTRY AND TECHNOLOGY, INSTITUTE OF ORGANIC AND FOOD CHEMISTRY AND TECHNOLOGY GDAŃSK TECHNICAL UNIVERSITY, GDAŃSK, POLAND

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# The Effect of Surfactant Concentration on the Flotation of Hydrocarbons from Their Emulsions.

## I. Removal of Mesitylene

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KRYSTYNA B. MĘDRZYCKA and  
WŁODZIMIERZ ZWIERZYKOWSKI

DEPARTMENT OF FAT CHEMISTRY AND TECHNOLOGY  
INSTITUTE OF ORGANIC AND FOOD CHEMISTRY AND TECHNOLOGY  
GDAŃSK TECHNICAL UNIVERSITY  
GDAŃSK, POLAND

### Abstract

The removal of mesitylene from its aqueous emulsions by the foaming method was investigated. As frothing agents, sodium dodecylbenzenesulfonate (NaDBS) and cetyltrimethylammonium bromide (CTMABr) were used. The influence of the concentration of those compounds on the removal effect of mesitylene is presented. It was found that the effective index of the surfactants is best when their concentration in the foamed mixture is the lowest possible one. Taking into account the foam stability, these concentrations equal  $1.0 \times 10^{-4}$  mol/dm<sup>3</sup> for CTMABr and  $1.7 \times 10^{-4}$  mol/dm<sup>3</sup> for NaDBS. The effect of the initial mesitylene concentration in the emulsion on its removal was also determined.

### INTRODUCTION

It is known that oils which pollute water may appear as a thin film on the water surface, or in the bulk as a partly soluble but mainly emulsified form. Oil removal from the water surface is easier than the removal of emulsified oil. Thus, the methods generally used are mainly based on the destruction of the water-oil emulsion, removal of the oil from the water surface, or its deposition on the bottom. The most often used methods for this purpose are coagulation, adsorption, filtration, centrifuging, and biodegradation. Flotation, including foam separation, is another widely used method. The presence of detergents in the solution during foaming assures that gas bubbles with attached oil droplets form a stable foam after floating out of the liquid phase.

Thus the oil separated from the water emulsion does not form a film on the water surface but is removed with the foam.

The purpose of our investigations was to find parameters of the foaming process which will make possible the best removal of hydrocarbons from their aqueous emulsions. We also tried to find out if it is possible to predict the foaming effect on the basis of physicochemical investigations of three-phase systems (1, 2).

Naturally, the kind of surface-active agent used during the foaming process will play an important role. Therefore this question was also taken into consideration in our investigations.

The results presented here concern the relationship between the removal of hydrocarbon from its emulsions by foaming and the surfactant concentration used for this purpose.

In our experiments we used emulsions of different hydrocarbons found in petroleum. As one of the aromatic hydrocarbons, mesitylene (1,3,5-trimethylbenzene) was used in our experiments.

## EXPERIMENTAL

The foaming processes were carried out in a continuously working glass column like that described in our previous papers (3). The height of the column,  $h_c$ , was 120 cm, the height of the liquid phase,  $h_l$ , was 95 cm, the feeding solution flow rate,  $V_0$ , was  $1.9 \text{ dm}^3/\text{h}$ , and the gas flow rate,  $V_g$ , was  $5 \text{ dm}^3/\text{h}$ .

In the foaming processes we used two different surface active compounds: cationic cetyltrimethylammonium bromide (CTMABr) and anionic sodium dodecylbenzenesulfonate (NaDBS). Their concentrations in the feeding solution are given in Table 1. The lowest concentration producing a stable foam was  $1.0 \times 10^{-4} \text{ mol}/\text{dm}^3$  for CTMABr and  $1.7 \times 10^{-4} \text{ mol}/\text{dm}^3$  for NaDBS.

The foaming processes were carried out in the presence of sodium chloride, and its concentration in the column was  $1 \times 10^{-2} \text{ mol}/\text{dm}^3$ .

The water-mesitylene emulsion, the surfactant solution, and the sodium chloride solution were introduced into the column independently. Those solutions were mixed only in the column.

All processes were continuously carried out for 5 h. The concentration of both surfactants in the raffinate was determined by the titration method (anionic-cationic titration) (4). A mixture of methylene blue and eosine was used as the indicator. The concentrations of mesitylene in the emulsion and in the raffinate were determined by the GLC method (5). We used a column filled with Chromosorb W 30/60 mesh covered with polypropylene glycol D-

TABLE I

Surfactants Concentrations During the Foaming Processes, and the Values of Slopes of the Lines  $E = A \times C_{OH}$ .

Surfactant	Surfactant concentration in feed		Slope $A$	
	mol/dm <sup>3</sup> $\times 10^4$	mg/dm <sup>3</sup>	mg <sup>-1</sup>	mol <sup>-1</sup>
NaDBS	1.7	59.2	0.0137 $\pm$ 0.00043	4.77 $\pm$ 0.150
	2.5	67.0	0.0101 $\pm$ 0.00049	3.52 $\pm$ 0.170
	4.2	146.3	0.0057 $\pm$ 0.00033	1.99 $\pm$ 0.115
CTMABr	1.0	36.4	0.0215 $\pm$ 0.00111	7.83 $\pm$ 0.403
	1.5	54.6	0.0146 $\pm$ 0.00092	5.31 $\pm$ 0.335
	2.0	72.8	0.0118 $\pm$ 0.00056	4.29 $\pm$ 0.204
	2.5	91.0	0.0087 $\pm$ 0.00050	3.18 $\pm$ 0.182

425 (Fluka AG Buchs SG, Switzerland) as the liquid phase (20%). The samples of water-hydrocarbon emulsions were injected at the top of the column without extraction of hydrocarbon. *n*-Butanol was used as the internal standard. The analysis temperature was 358 K.

The effect of the foaming process was expressed as a percentage of mesitylene removal from the emulsion. Also, the quantity of water removed with the foam and the surfactant amounts remaining in the raffinate were determined.

The experiments were carried out for emulsions containing mesitylene over a wide range of concentration (from 10 to 500 mg/dm<sup>3</sup>).

Figures 1 and 2 present the removal of mesitylene (expressed in %) versus the hydrocarbon concentration in the initial emulsion. The results are plotted for analytical data obtained after the process reached the equilibrium state.

It can be seen from Figs. 1 and 2 that removal of mesitylene depends on its initial concentration in the emulsion and is best when the concentration is about 100 mg/dm<sup>3</sup>. If the mesitylene concentration rises above 100 mg/dm<sup>3</sup>, the foaming effect diminishes, especially if NaDBS is used (Fig. 1).

The surfactant concentration also influences the removal effect. We observe that the highest removal of mesitylene takes place if the NaDBS concentration is  $2.5 \times 10^{-4}$  mol/dm<sup>3</sup> and the CTMABr concentration is  $2.0 \times 10^{-4}$  mol/dm<sup>3</sup>. Lower or higher than optimum surfactant concentrations give a reduced removal of mesitylene.

It can be seen from Figs. 1 and 2 that the highest removal of mesitylene was about 95% if NaDBS was used and about 90% if CTMABr was used.

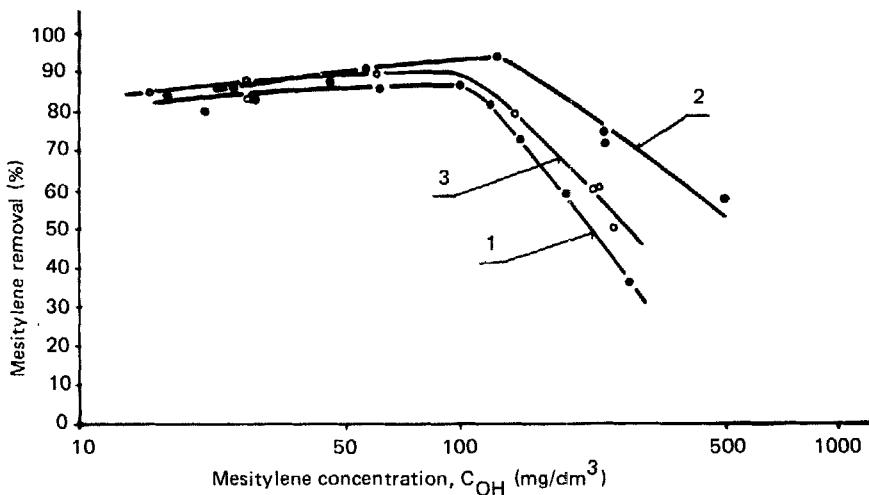


FIG. 1. Removal of mesitylene during the foaming processes with sodium dodecylbenzenesulfonate; dependence on mesitylene concentration in the initial emulsion. NaDBS concentration: (1)  $1.7 \times 10^{-4}$  mol/dm $^3$ , (2)  $2.5 \times 10^{-4}$  mol/dm $^3$ , (3)  $4.2 \times 10^{-4}$  mol/dm $^3$ .

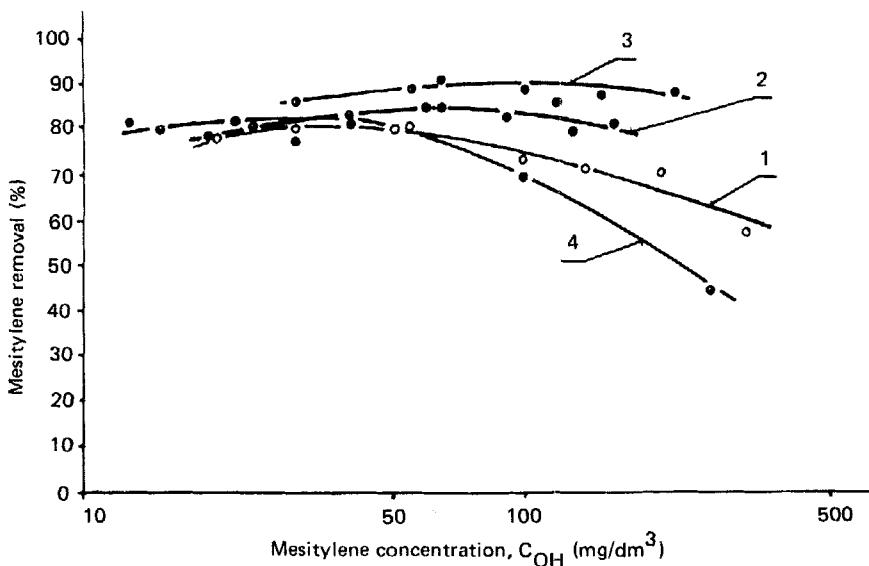


FIG. 2. Removal of mesitylene during the foaming processes with cetyltrimethylammonium bromide; dependence on mesitylene concentration in the initial emulsion. CTMABr concentration: (1)  $1.0 \times 10^{-4}$  mol/dm $^3$ , (2)  $1.5 \times 10^{-4}$  mol/dm $^3$ , (3)  $2.0 \times 10^{-4}$  mol/dm $^3$ , (4)  $2.5 \times 10^{-4}$  mol/dm $^3$ .

## DISCUSSION

In comparing the removal of mesitylene by the two different surfactants used, the problem arises as to which of them is more effective. Such information could also be of economic value. It seems that this question could be answered by the introduction of an effective index ( $E$ ):

$$E = \frac{C_{OH} - C_{RH}}{C_{OS}} = \frac{\Delta C_H}{C_{OS}} \quad (1)$$

where  $C_{OH}$  = hydrocarbon concentration in the emulsion

$C_{RH}$  = hydrocarbon concentration in the raffinate

$C_{OS}$  = initial surfactant concentration in foamed mixture

As can be seen, this index defines the quantity of hydrocarbon removed by a mole or gram of surfactant added.

Figures 3 and 4 show the dependences of  $E$  in relation to the initial mesitylene concentration ( $C_{OH}$ ).

As can be seen, these dependences are given by straight lines and can be described by

$$E = AC_{OH} \quad (2)$$

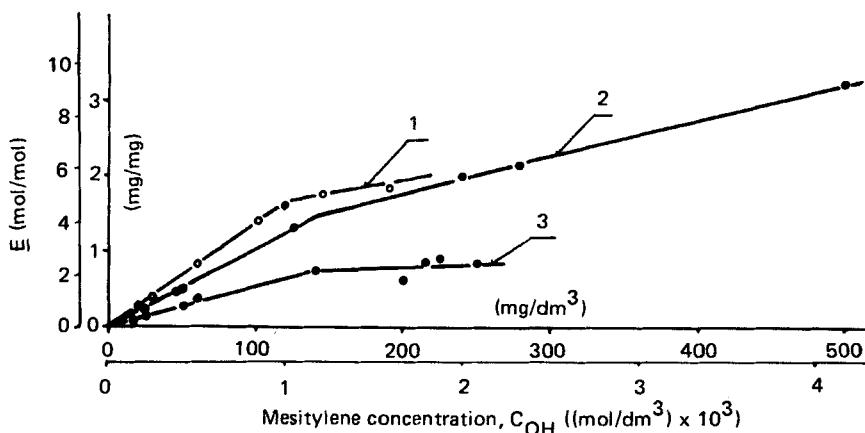


FIG. 3. The dependence of effective index of mesitylene concentration in the initial emulsion. NaDBS concentration: (1)  $1.7 \times 10^{-4} \text{ mol}/\text{dm}^3$ , (2)  $2.5 \times 10^{-4} \text{ mol}/\text{dm}^3$ , (3)  $4.2 \times 10^{-4} \text{ mol}/\text{dm}^3$ .

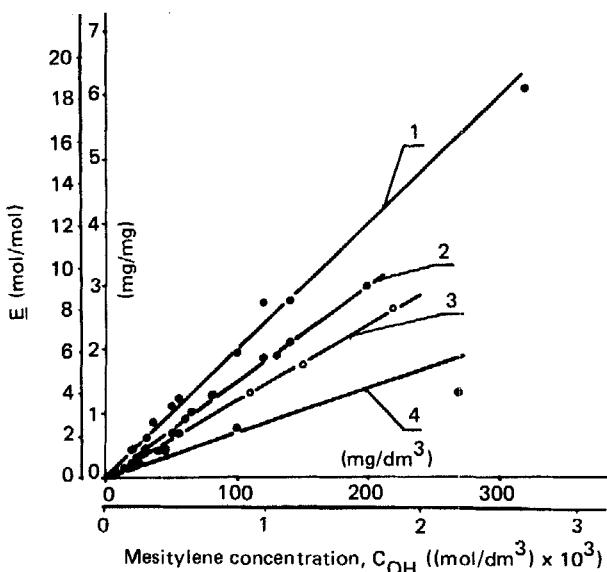


FIG. 4. The dependence of effective index on mesitylene concentration in the initial emulsion. CTMABr concentration: (1)  $1.0 \times 10^{-4}$  mol/dm $^3$ , (2)  $1.5 \times 10^{-4}$  mol/dm $^3$ , (3)  $2.0 \times 10^{-4}$  mol/dm $^3$ , (4)  $2.5 \times 10^{-4}$  mol/dm $^3$ .

For processes with CTMABr, Eq. (2) is obeyed in the whole range of  $C_{OH}$  concentrations used (Fig. 4). For processes with NaDBS (Fig. 3), Eq. (2) is fulfilled only in the range  $C_{OH} = 0$ –120 mg/dm $^3$ . Above this concentration range the following equation is valid:

$$E = A' C_{OH} + B \quad (3)$$

Analyzing Figs. 3 and 4, it may be stated that the lower the surfactant concentration, the higher is the effective index. Although the highest removal effect of mesitylene was observed at concentrations of  $2.0 \times 10^{-4}$  mol/dm $^3$  CTMABr and  $2.5 \times 10^{-4}$  mol/dm $^3$  NaDBS (Figs. 1 and 2), the best effectiveness in terms of the calculated effective index of added surfactants is observed when those concentrations were the smallest, i.e.,  $1.0 \times 10^{-4}$  mol/dm $^3$  of CTMABr and  $1.7 \times 10^{-4}$  mol/dm $^3$  of NaDBS (Figs. 3 and 4, Curves 1). For example, during foaming the mesitylene emulsion of concentration 100 mg/dm $^3$ , we remove 2 mg of mesitylene per 1 mg of added CTMABr.

For our discussion of the usefulness of both surfactants used, the slopes of the dependences shown in Figs. 3 and 4 have been drawn in Fig. 5 versus the

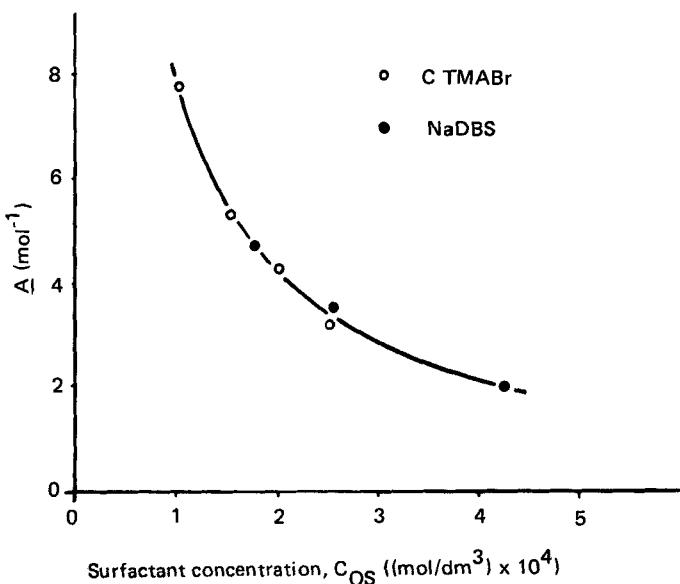


FIG. 5. The dependence of slope  $A$  on the surfactants concentration.

surfactant concentration  $C_{OS}$ . Values of coefficient  $A$  from Eq. (2) (Table 1) are taken for this purpose from Figs. 3 and 4 in the concentration range up to 120 mg/dm<sup>3</sup> of mesitylene, because over this concentration the dependence of  $E$  on  $C_{OH}$  for systems containing NaDBS is not described any longer by the same equation but is governed by Eq. (3). Therefore, above 120 mg/dm<sup>3</sup> mesitylene concentration, for our discussion of the usefulness of both surfactants,  $E$  was used. In Fig. 6 the results are plotted for mesitylene concentrations of 150 and 200 mg/dm<sup>3</sup>.

As can be seen from Fig. 5, the slopes for NaDBS and CTMABr are nearly the same. This means that by using NaDBS and CTMABr solutions of the same concentrations we will obtain similar effective index values. This means that every added milligram of both surfactants removes approximately the same amount of mesitylene if the concentration of the surfactant solutions used are the same.

If the emulsions of mesitylene are more concentrated ( $C_{OH} > 120$  mg/dm<sup>3</sup>), then using CTMABr is more profitable than using NaDBS because the effective index is higher for CTMABr than for NaDBS (Fig. 6). Thus every milligram of CTMABr removes more mesitylene than every milligram of NaDBS. For example, the use of detergents solutions of 70 mg/dm<sup>3</sup> concentration in emulsion foaming processes with a mesitylene

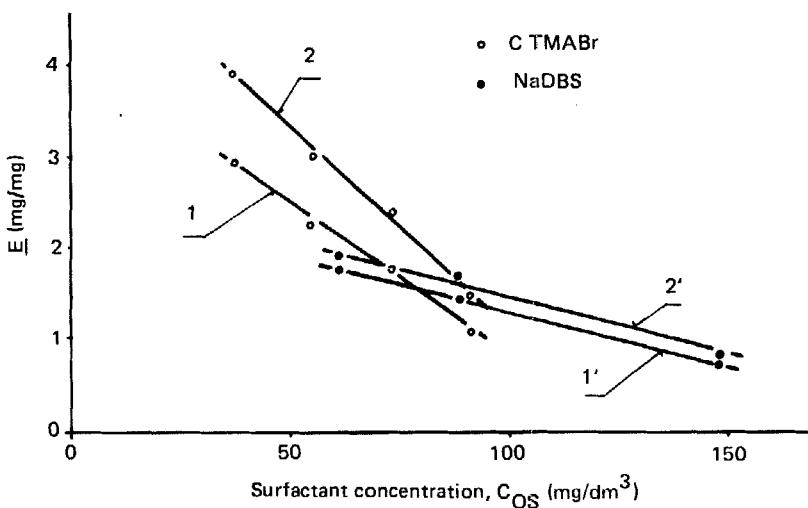


FIG. 6. The dependence of effective index on surfactants concentration. Mesitylene concentration in emulsion: (1, 1') 150 mg/dm<sup>3</sup>, (2, 2') 200 mg/dm<sup>3</sup>.

concentration of 200 mg/dm<sup>3</sup> gives an  $E$  equal to 2.45 for CTMABr but only 1.83 for NaDBS (Curves 2 and 2', Fig. 6).

## CONCLUSIONS

Foam stability is a necessary condition in order to realize a flotation process, and therefore a minimum surfactant concentration is needed. Simultaneously, as may be seen from this paper, the lower the surfactant concentration, the higher the effective index. Regarding the foam stability, concentrations of  $1.7 \times 10^{-4}$  mol/dm<sup>3</sup> NaDBS and  $1.0 \times 10^{-4}$  mol/dm<sup>3</sup> CTMABr are sufficient.

Taking into account that the effective indexes versus concentrations for both surfactants are practically the same, CTMABr is the preferred surfactant for mesitylene concentrations up to 120 mg/dm<sup>3</sup>.

For a concentration of mesitylene over 120 mg/dm<sup>3</sup>, CTMABr has a higher effective index than NaDBS at the same surfactant concentration.

Generally, it may be stated that for the removal of mesitylene from its aqueous emulsion, cetyltrimethylammonium bromide is more effective than sodium dodecylbenzenesulfonate.

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