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The Effect of Surfactant Concentration on the Flotation of Hydrocarbons from Their Emulsions. II. Removal of Hexadecane

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NOTE

The Effect of Surfactant Concentration on the Flotation of Hydrocarbons from Their Emulsions.
II. Removal of Hexadecane

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INTRODUCTION

Flotation of hydrocarbons from their aqueous emulsions depends to a considerable extent on the efficiency of the collision of air bubbles with the emulsified globules.

The collision efficiency greatly depends on the surface energy of the boundaries: air–water, hydrocarbon–water, and hydrocarbon–air. Two of the parameters which influence those energies are type and concentration of the surface-active compound present in the flotation system.

It was stated in a previous paper (*1*) that the lower the surfactant concentration, the more effective is the flotation of mesitylene from its emulsion. We suppose that in the case of the flotation of hexadecane the dependence will be similar. We also expect that flotation without any surfactant will be the most effective.

EXPERIMENTAL

The flotation of hexadecane from its emulsions was carried out in a manner similar to that of mesitylene (*1*). The process parameters were as follows: 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 dm^3/h; and the gas flow rate, V_g, was 5 dm^3/h.

Two ionic surface active compounds, cetyltrimethylammonium bromide (CTMABr) and sodium dodecylbenzenesulfonate (NaDBS), were used. The water–hexadecane emulsion, the surfactant solution, and the sodium chloride solution were introduced into the column independently. Those solutions were mixed only in the column.

The concentrations of hexadecane in the emulsion and in the raffinate were determined by the GLC method (*2*). A column filled with Chromosorb W 30/60 mesh covered with polypropylene glycol UCON LB 550 X (Carlo Erba, Italy) as the liquid phase (20%) was used. Samples of water–hexadecane emulsions were injected at the top of the column without extraction of hydrocarbon. *n*-Octanol was used as the internal standard. The analysis temperature was 458 K.

The efficiency of the flotation process was expressed as a percentage of hexadecane removal from the emulsion.

Figure 1 presents the removal of hexadecane versus its concentration in the initial solution in cases where CTMABr was present during the flotation processes. Sodium chloride concentration was 0.01 mol/dm^3. It is observed that hexadecane flotation depends on the concentration of

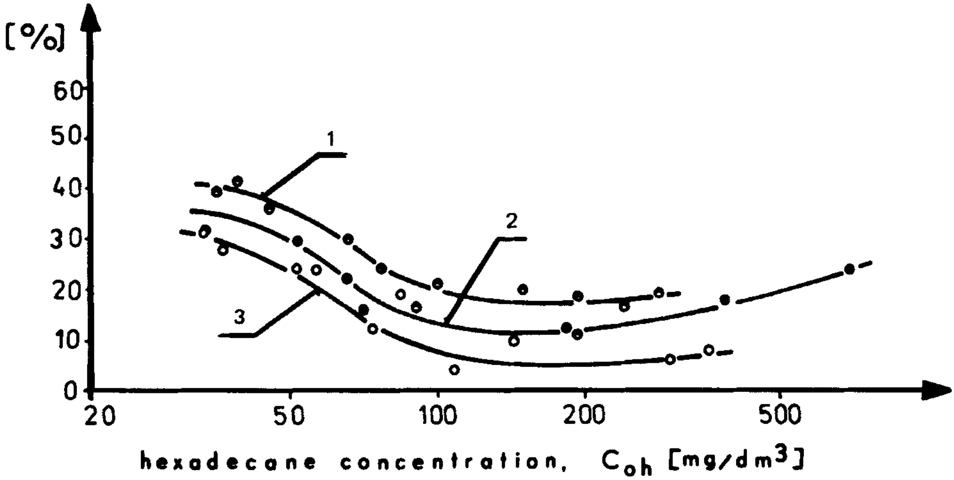

FIG. 1. Removal of hexadecane during flotation processes with cetyltrimethylammonium bromide; dependence on hydrocarbon concentration in the initial emulsion. CTMABr concentration: (1) 1.0×10^{-4} mol/dm^3, (2) 1.5×10^{-4} mol/dm^3, (3) 2.0 mol/dm^3. NaCl concentration: 0.01 mol/dm^3.

CTMABr in the flotation system and increases as that concentration decreases. But even at the lowest CTMABr concentration, flotation efficiency does not exceed 40%.

An increase of NaCl concentration in the flotation systems improves the hexadecane removal. As can be seen from Fig. 2 which presents the results for runs in which CTMABr was used, the flotation efficiency was about 10–30% at 0.01 *M* NaCl concentration, about 30–35% at 0.1 *M* NaCl concentration, and about 70–90% at 0.5 *M* NaCl concentration. For processes in which NaDBS was used, the flotation efficiency was about zero if the NaCl concentration equaled 0.01 or 0.1 mol/dm^3. At 0.5 *M* NaCl concentration, the flotation was about 50–80%.

It can be seen from Fig. 3 that in cases when surfactant is absent, the flotation of hexadecane also depends on the salt concentration. The lowest value of hexadecane removal is observed when the NaCl concentration is zero. The higher the NaCl content, the better the flotation. At 0.1 *M* NaCl solution, about 60% removal of hexadecane in the continuous process was reached. Batch flotation runs, the results of

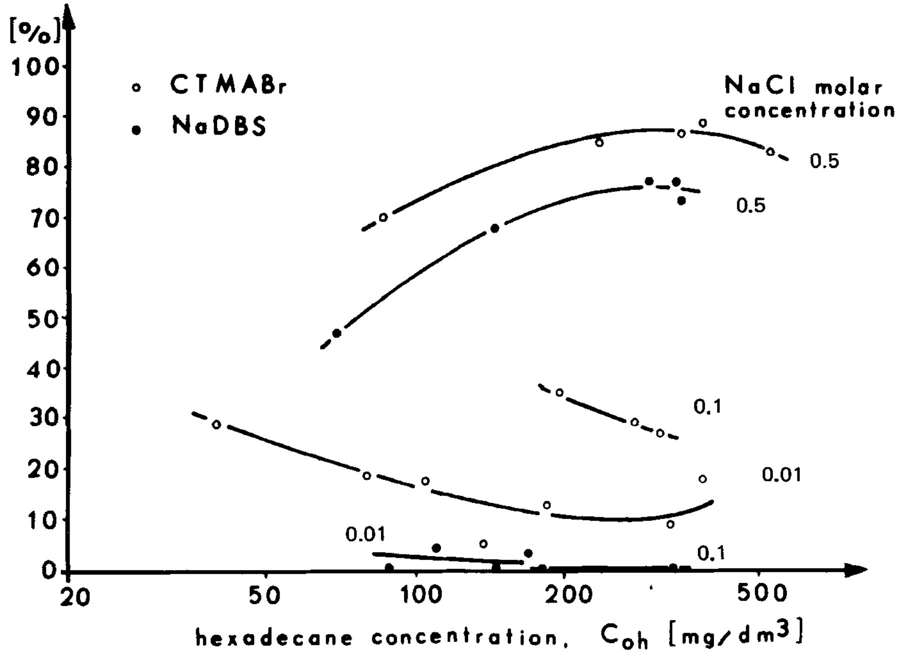

FIG. 2. Removal of hexadecane during flotation processes with sodium chloride and ionic surfactants; dependence on hexadecane concentration in the initial emulsion.

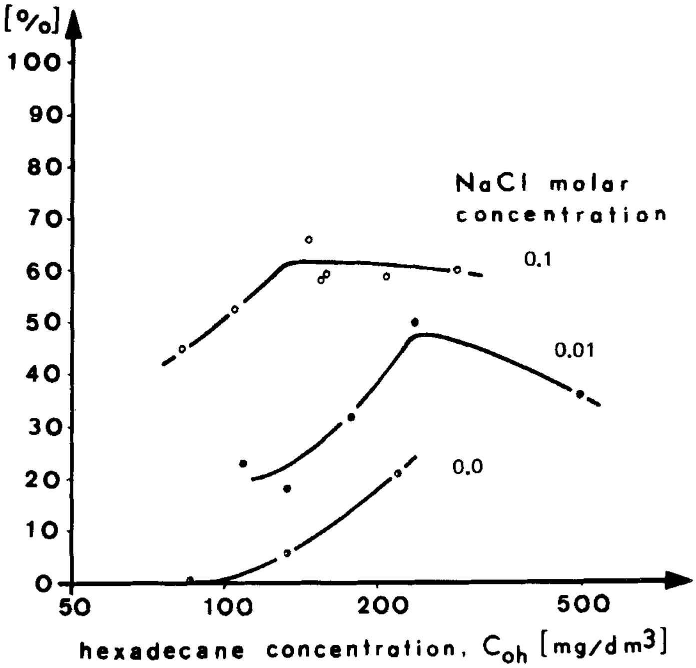

FIG. 3. Removal of hexadecane during flotation processes with sodium chloride; dependence on hydrocarbon concentration in the initial emulsion.

which are shown in Fig. 4, give higher values of removal efficiency; e.g., at 0.1 *M* NaCl solution, 100% removal is reached after about 3 h of the process, and a 0.01 *M* NaCl concentration gives 70–80% of the flotation efficiency after the same time.

A high NaCl concentration produces very good hexadecane removal (95–100%) in batch flotation processes even in the presence of both surfactants.

DISCUSSION

The above observations can be explained on the basis of the flotation model of small particles (*3*). The attachment of the oil globule to the air bubble as well as the coalescence of two oil globules depends on the electric potential of surfaces which must be in contact. If surface-active ions are present in the flotation system, the above-mentioned surfaces became charged. The electric charge causes repulsion of globules and

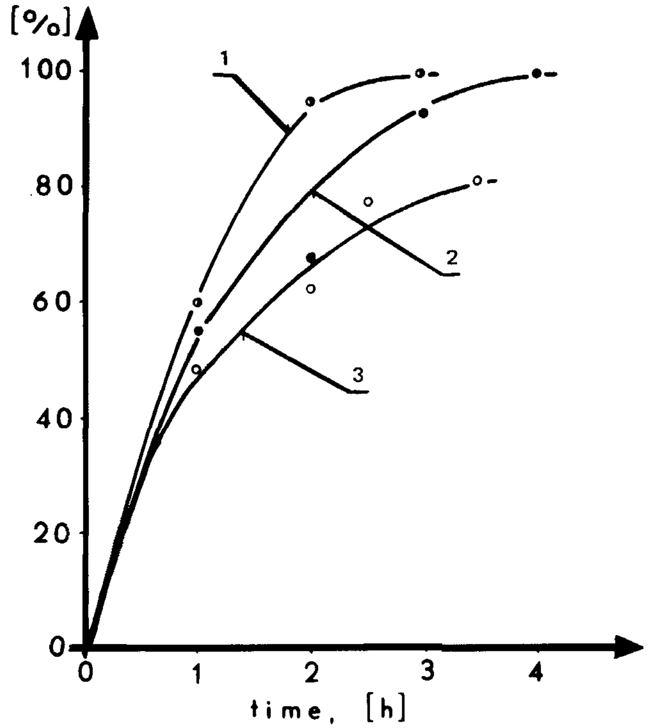

FIG. 4. Removal of hexadecane during the periodic flotation process with sodium chloride; dependence on process duration time. Hexadecane concentration in the initial emulsion: (1) 80 mg/dm^3, (2) and (3) 240 mg/dm^3. NaCl concentration: (1) and (2) 0.1 mol/dm^3, (3) 0.01 mol/dm^3.

bubbles, thus the coalescence as well as flotation efficiency will be lowered. Although the addition of inorganic salts improves the adsorption of surface-active ions and causes the surface electric potential to increase, it simultaneously reduces the thickness of the diffuse layer. At the proper salt concentration a thickness of the diffuse layer is reached at which the probability of the near approach of two emulsion globules or the globule and an air bubble increases; then the van der Waals attractive forces overcome electrostatic repulsion (*4, 5*). This is the reason why at a certain concentration of sodium chloride we observe a sharp increase in flotation efficiency.

Because flotation also depends on the dispersion of the emulsion, we determined the dependence of suspended drop size distribution on hydrocarbon concentration in the emulsion. The determinations were made with a microscope. It was found that the smallest globules exist in the hexadecane emulsion in the amount of 5-25%. The weight fraction of the largest hexadecane globules in the emulsion changes from 5% to about 20%.

By comparing the flotation of hexadecane emulsions (Fig. 1) and their drop size distribution, it can be stated that the amount of hexadecane removed approximately equals the amount of largest globules in the emulsion. This confirms our supposition and the conclusions of other scientists (*6, 7*) that mainly big globules ($d \geqslant 5$ μm) are floated during the flotation process.

By analyzing the size distributions of the emulsions and of the raffinate from the continuous process with NaCl present (Fig. 5), it was observed that the fraction of material present in big globules in the raffinate was markedly higher. This explains the very good removal of hexadecane in the batch flotation process (see Fig. 4). As mentioned earlier (*8*), the coalescence of hydrocarbon droplets in the emulsion in the presence of CTMABr and 0.01 *M* NaCl is rather slight. That is the reason why globules larger than 5 μm in diameter were not found (Fig. 5C) in the raffinate from the process with the surfactant present.

These observations correspond with the better removal of hexadecane when only NaCl is added (Fig. 3) compared with the poorer removals when CTMABr or NaDBS was present (Fig. 2).

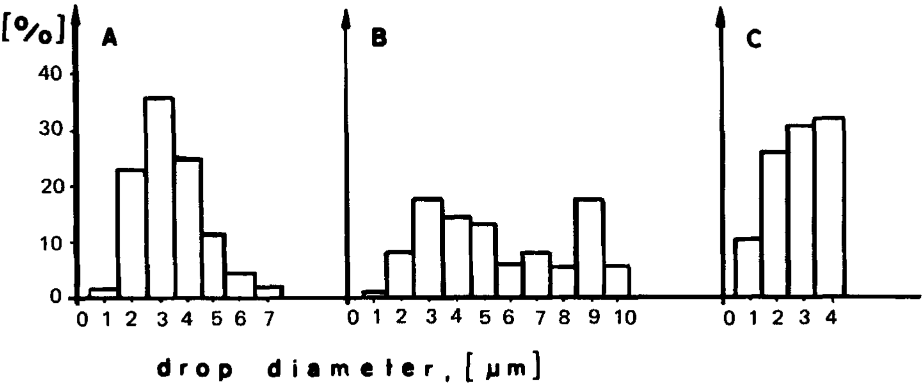

FIG. 5. Drop size distribution of hexadecane emulsion. (A) Fresh emulsion. (B) Raffinate from continuous process with 0.1 *M* NaCl. (C) Raffinate from continuous process with 0.01 *M* NaCl and CTMABr.

CONCLUSIONS

On the basis of the flotation results, it is stated that the removal of hexadecane from its aqueous emulsions is much poorer than the removal of mesitylene as described earlier (*1*).

The improvement of flotation efficiency by lowering the surfactant concentration is insignificant, but the lower this concentration, the higher the flotation efficiency of hexadecane. The best effect was observed in the absence of surfactants.

The flotation efficiency of hexadecane is improved when agents increasing the coalescence are used. Therefore, the proper sodium chloride concentration is needed to reduce the thickness of the diffuse electric layer, which positively influences the coalescence of oil droplets and their attachment to gas bubbles. This NaCl concentration was about 0.5 mol/dm^3, and the use of such a concentration in the flotation mixture results in good flotation efficiency, especially in batch process for which 100% removal was found.

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