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The Effect of Emulsified Compounds Properties on Flotation Efficiency

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Abstract

A mathematical model for the removal of partly soluble and slightly volatile hydrocarbons from their emulsions was applied. The removal of aliphatic and aromatic hydrocarbons due to interception and evaporation was computed. The effect of the hydrocarbon volatility and its solubility in water on the evaporation efficiency was discussed. If the hydrocarbon volatility is greater than 0.1 mmHg and its solubility exceeds 10 ppm, then the evaporation process should be included in the computation of the efficiency of flotation from emulsions having concentrations lower than 100 ppm.

INTRODUCTION

Flotation of mineral oils emulsified in water has been widely investigated. There are some papers concerning the flotation of single hydrocarbons (*1–5*) but usually the crude oils have been investigated. There is very little information on the effect of the oil type on its removal from the emulsion (*6, 7*).

Strickland (*6*) stated that there are different flotation efficiencies for different types of oil: oils which contain greater amounts of aromatics and nonhydrocarbons are floated to about 83–85%, and other oils (with lower aromatics content and greater amounts of saturated hydrocarbons) are floated 39 to 59%.

Our investigations (*3–5*) show that the removal of aliphatic hydrocarbons by flotation from their emulsions is much poorer than the removal of aromatic hydrocarbons. As was shown earlier (*8*), these observations are connected with the different mechanisms by which these hydrocarbons are removed during aeration of the emulsion. For hydrocarbons which are nonvolatile and insoluble in water (for example, aliphatic hexadecane), removal proceeds according to the hydrodynamic model of the flotation of fine particles (*9–13*) and depends on the interception of emulsified droplets by rising bubbles. If the hydrocarbon is slightly soluble in water, and even has a very low volatility, then its removal proceeds according to a mixed mechaninism (*8*) which consists of three simultanous processes:

Interception of emulsified droplets by a rising bubble resulting from hydrodynamics forces

Dissolution of hydrophobic droplets in water

Mass transport of the dissolved molecules from water into the bubble as a result of evaporation

The contribution of the evaporation process to the cumulative hydrocarbon removal efficiency depends on hydrocarbon volatility and its solubility in water. Hydrocarbons, as a class, are normally regarded to be insoluble in water, but aromatics are more soluble than aliphatics. As was shown earlier for mesitylene emulsions of 100 ppm concentration (*8*), 63% of this hydrocarbon is removed by evaporation and 37% by the interception process. Thus the evaporation process should be included in consideration of the flotation model.

The question arises: What are the boundary values of solubility and volatility below which the evaporation process need not be taken into account when flotation is being analyzed.

THEORY

To solve the above question, the mathematical model previously developed for the removal of partly soluble and slightly volatile hydrocarbons from their emulsions was applied (*8*).

This model allows one to calculate the amount of hydrocarbon removed due to the interception of emulsified particles by a rising bubble:

$$M_i = V_s C_0 \left[1 - \exp\left(- \frac{3 E_c V_g \tau}{r_b D} \right] \right) \qquad (1)$$

and due to the evaporation of dissolved hydrocarbon into the bubble:

$$M_e = V_s C_{aq} \left\{ 1 - \exp\left[- \frac{V_g K_H \tau}{V_s} \left(1 - \exp\left(- \frac{3kh}{r_b u} \right) \right) \right] \right\} \tag{2}$$

Equation (2) is valid when the rate of solution of hydrocarbon droplets during flotation is very slow, and when only evaporation influences the changes of C values. However, if the rate of hydrocarbon molecules transfer from the emulsified droplets into the aqueous solution is so fast that the mass transfer coefficient for oil–water transfer of hydrocarbon is much greater than the diffusion coefficient of hydrocarbon in water, then the concentration of hydrocarbon in the aqueous solution may be treated as a constant during the aeration process. In such a case the total mass of hydrocarbon carried out of solution on the basis of evaporation may be calculated from

$$M_e = V_g C_{aq} K_H \tau \left[1 - \exp\left(- \frac{3kh}{r_b u} \right) \right] \tag{3}$$

Equation (3) may be used only until all droplets disappear (dissolved or captured by a bubble due to hydrodynamic forces). From that moment, Eq. (2) is valid.

THEORETICAL RESULTS

The above equations were used for the calculation of the flotation efficiency of several aliphatic and aromatic hydrocarbons. The physical constants of the hydrocarbons used to simulate the flotation runs are presented in Table 1. Compounds denoted as “X” and “Y” in this table are imaginary compounds with chosen values of molecular weights, solubilities, and vapor pressures. The analysis of their removal has only theoretical meaning. Henry’s law constant (Table 1), which is the ratio of hydrocarbon concentration in the gaseous phase to the concentration in the aqueous phase, was calculated from

$$K_H = \frac{pM}{sT \times 760 \times 82.05} \tag{4}$$

TABLE 1
Physical Constants of Hydrocarbons Used to Simulate Flotation Runns (*14, 15*)

	Compound	Molecular weight, M	Water solubility, s (ppm)	Vapor pressure, p (mmHg)	Henry's law constant, K_H
I	Mesitylene	120	57	1.95	0.2244
II	Naphthalene	128	30	0.16	0.0386
III	X	130	10	0.10	0.0711
IV	Y	150	7	0.05	0.0587
V	Phenanthrene	178	2.7	0.02	0.0722
VI	Pentane	72	39	420	43.0
VII	Hexane	86	9.8	120	60.8
VIII	Heptane	100	2.9	35	67.1

Table 2 gives the parameters used in computing the simulated experimental evaporation and interception processes. These values were chosen on the basis of a series of experimental results.

Figure 1 presents the effect of Henry's law constant of the dissolved compounds on their evaporation into the bubbles during aeration of the solution. The evaporation efficiency was calculated relative to the maximum solubility of the compound and is $(M_e/C_{aq}V_s) \times 100\%$. As we expected, the greater the K_H value, the faster the evaporation of the dissolved compound.

TABLE 2
Input Parameters for Program Simulating Theoretical Flotation

Parameter	Value
Droplet diameter, d_p	4 μm
Bubble diameter, d_b	0.1 cm
Volumetric gas flow rate, V_g	1.1 cm^3/s
Bubble rise velocity, u	12.8 cm/s
Mass transfer rate coefficient, k	0.01

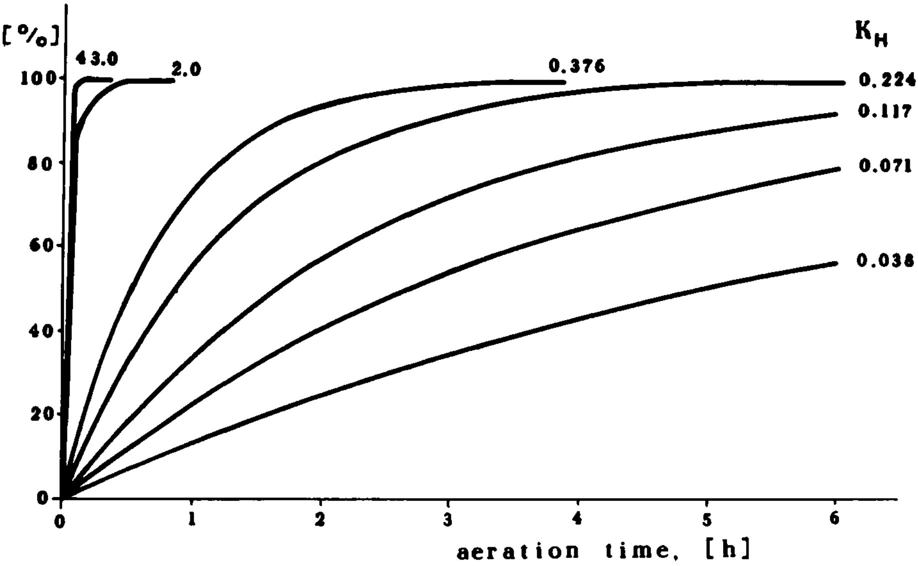

FIG. 1. The effect of Henry's law constant (K_H) on dissolved compound evaporation into the bubbles. $(M_e/C_{aq}V_s) \times 100\% = f(\tau)$.

Figure 2 presents the evaporation efficiency of the dissolved hydrocarbons calculated relative to their total content in the emulsion as follows: $(M_e/C_0V_s) \times 100\%$. The mass of the evaporated hydrocarbon (M_e) was calculated according to Eq. (2), so that droplet dissolution was not taken into account.

It has been stated that the evaporation efficiency is greater if the hydrocarbon content in the emulsion is lower. For example, from an emulsion containing 40 ppm of naphthalene, 43% of this hydrocarbon is removed by evaporation (after 6 h aeration), but from an emulsion of 70 ppm only 24% (Fig. 2).

The evaporation of aromatic hydrocarbons proceeds in a way different from that for the evaporation of aliphatic hydrocarbons. The amount of aromatics removed increases slowly during aeration, and the maximum removal is reached in a few hours (Fig. 2). On the other hand, complete evaporation of aliphatics is achieved in a few minutes because of their high vapor pressures (and also K_H values) in comparison with those of aromatics (Table 1).

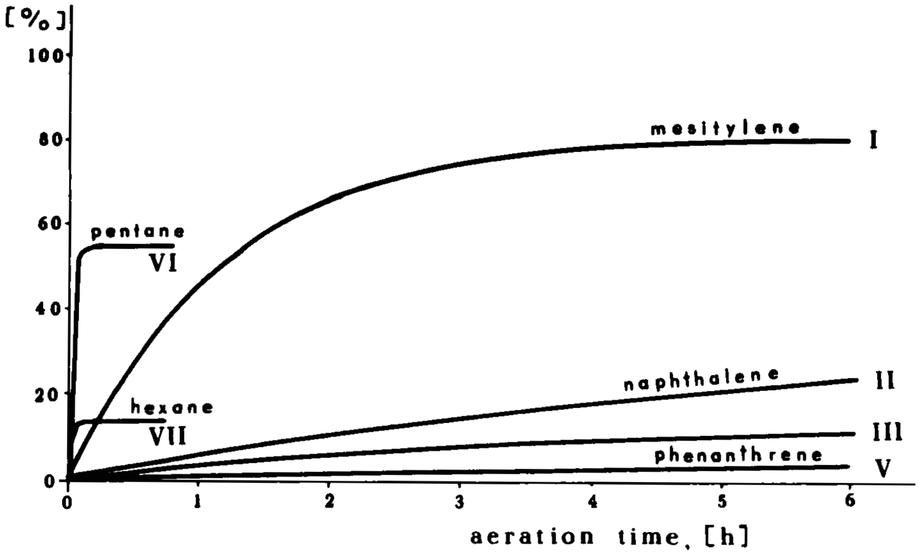

FIG. 2. The efficiency of dissolved hydrocarbon evaporation calculated in relation to total hydrocarbon content in the emulsion. $(M_e/C_0V_s) \times 100\% = f(\tau)$. $C_0 = 70$ ppm.

The value of Henry's law constant does not influence the evaportion efficiency when it is calculated in relation to the total content of aliphatic hydrocarbons in an emulsion. For example, in the case of an emulsion having a total hydrocarbon concentration of 70 ppm, pentane is removed by evaporation to the extent of 56% and hexane to the extent of 14% (Fig. 2), while Henry's law constant for pentane is lower ($K_H = 43$) than that of hexane ($K_H = 60.8$). The solubility of pentane is greater ($s = 39$ ppm) than the solubility of hexane (9.8 ppm, Table 1), so we may state that the differences in the evaporation efficiency of aliphatic hydrocarbons result from the differences of their solubility in water. If the dissolution of aliphatic hydrocarbon droplets does not occur during the flotation process, then in a very short time the evaporation efficiency reaches its maximal value and is as large as the solubility of the hydrocarbon. For example, hexane is removed by evaportion from a 70-ppm emulsion to the extent of 14% (Fig. 2), which relates to the contribution of the dissolved part in the total content of hexane in an emulsion: (9.8 ppm/70 ppm) × 100% ≅ 14%.

Figures 3-7 present different hydrocarbon removal efficiencies calculated for the interception and evaporation models. The efficiency for each model was calculated in relation to the total initial content of hydrocarbon in an emulsion (C_0), i.e., in relation to 70 ppm (Figs. 3, 4, 6, 7) or to 40 ppm (Fig. 5). The mass of hydrocarbon removed by the interception process was computed according to Eq. (1), and the mass removed by the evaporation process was computed from Eq. (2) (evaporation only) or from Eq. (3) (dissolution + evaporation).

Analysis of Figs. 3-7 allows one to state that mesitylene removal due to evaporation is the largest and after 6 h aeration equals 81% (Fig. 3), while the removal of phenanthrene is the smallest and equals only 3% (Fig. 6). However, the interception process gives the largest phenanthrene removal (75.3%) and the smallest mesitylene removal (14.5%). These values relate to the emulsion of hydrocarbon concentrations of 70 ppm. If the hydrocar-

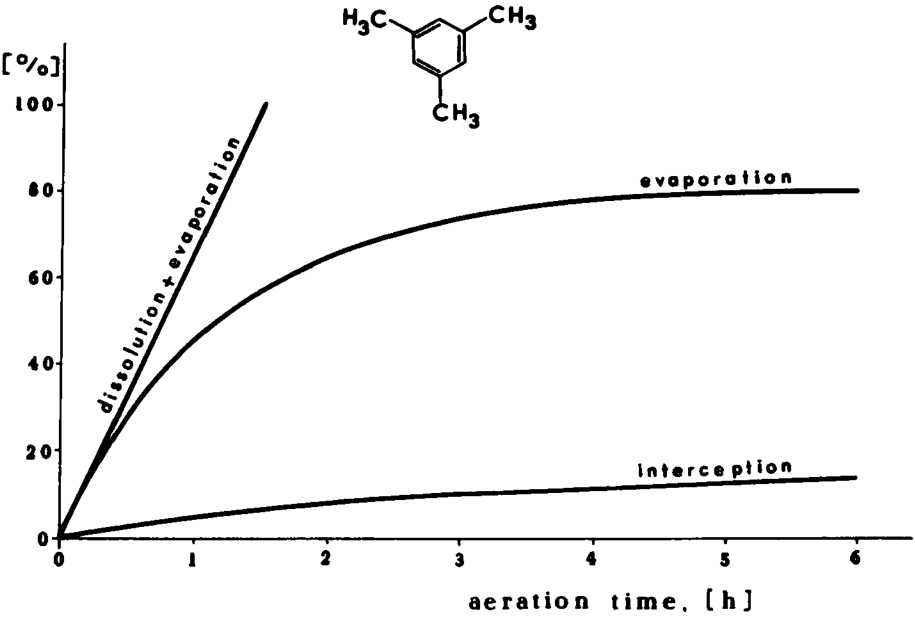

FIG. 3. Mesitylene removal efficiency calculated for interception and evaporation. $(M_i/C_0V_s) \times 100\% = f(\tau)$ and $(M_e/C_0V_s) \times 100\% = f(\tau)$. $C_0 = 70$ ppm.

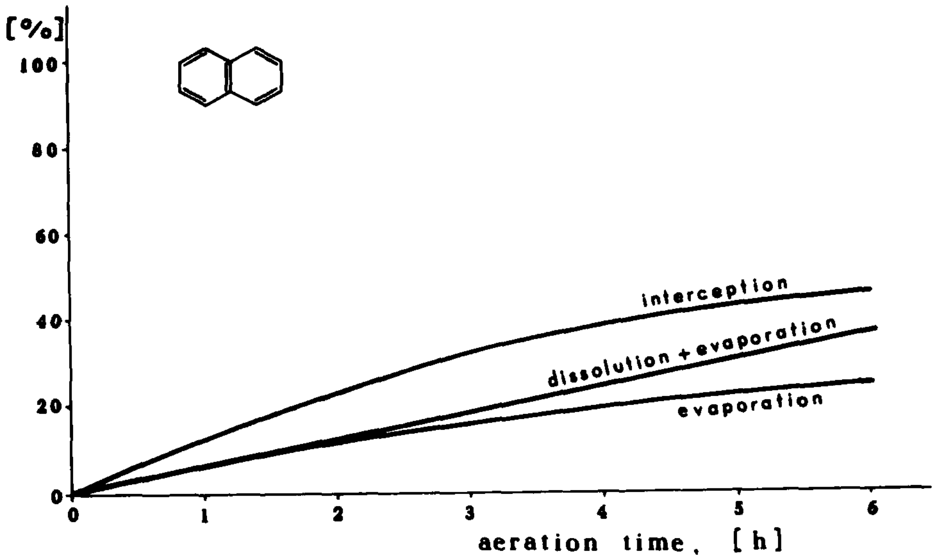

FIG. 4. Naphthalene removal efficiency calculated for interception and evaporation. $(M_i/C_0V_s) \times 100\% = f(\tau)$ and $(M_e/C_0V_s) \times 100\% = f(\tau)$. C_0 = 70 ppm.

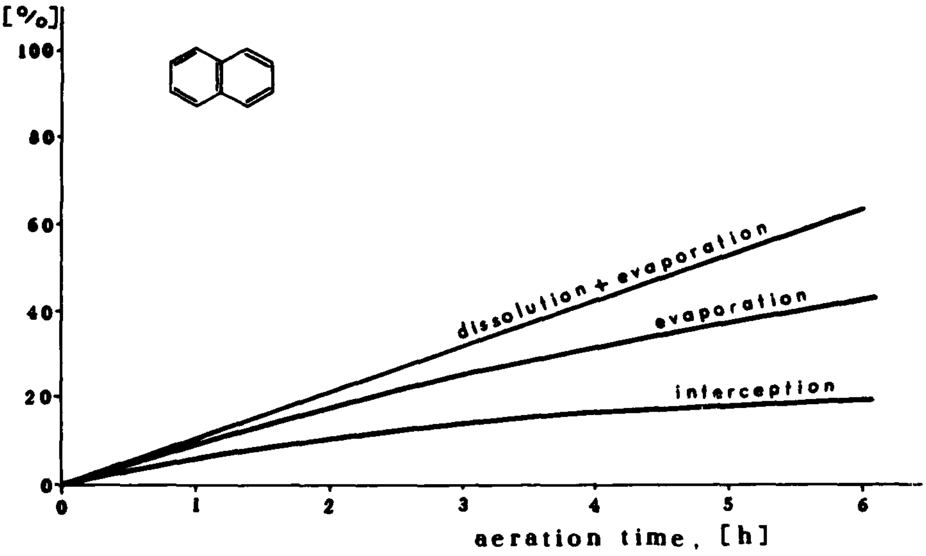

FIG. 5. Naphthalene removal efficiency calculated for interception and evaporation. $(M_i/C_0V_s) \times 100\% = f(\tau)$ and $(M_e/C_0V_s) \times 100\% = f(\tau)$. C_0 = 40 ppm.

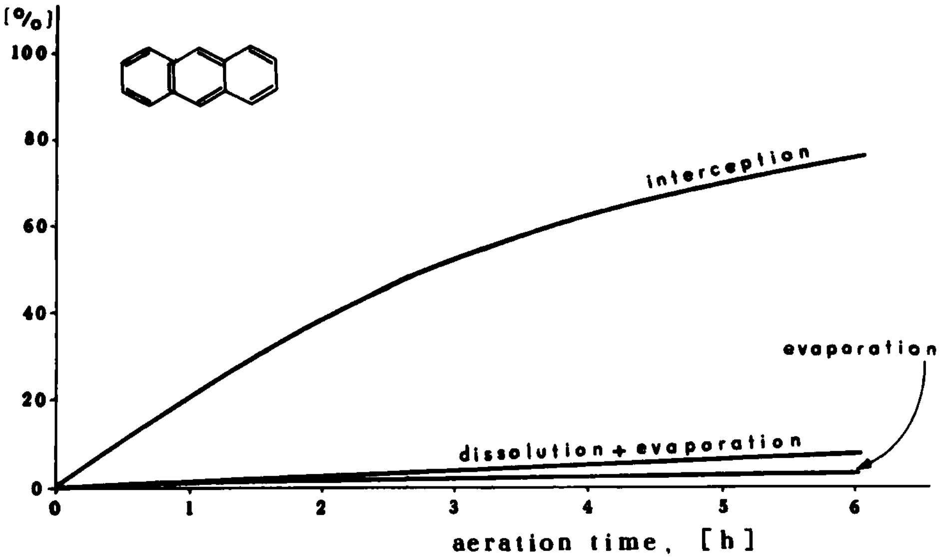

FIG. 6. Phenanthrene removal efficiency calculated for interception and evaportion. $(M_i/C_0V_s) \times 100\% = f(\tau)$ and $(M_e/C_0V_s) \times 100\% = f(\tau)$. $C_0 = 70$ ppm.

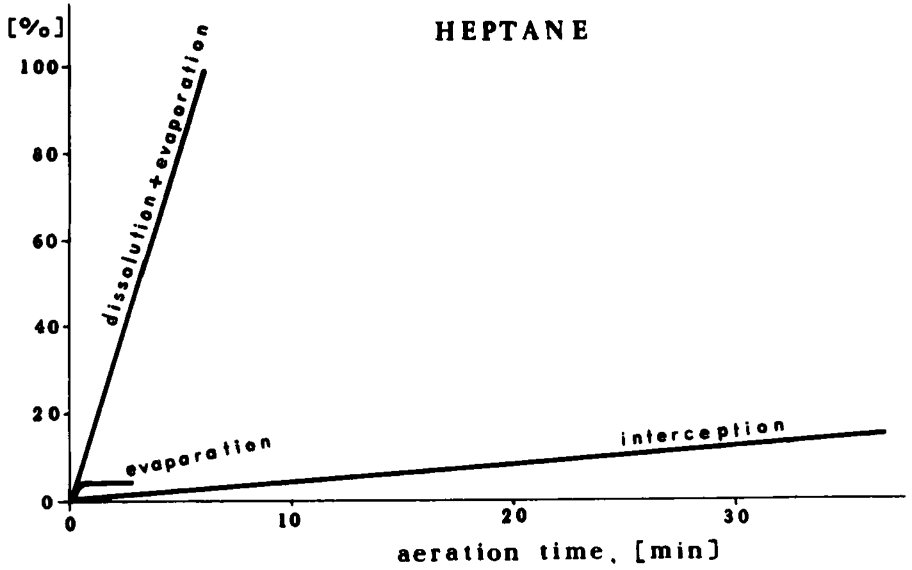

FIG. 7. Heptane removal efficiency calculated for interception and evaportion. $(M_i/C_0V_s) \times 100\% = f(\tau)$ and $(M_e/C_0V_s) \times 100\% = f(\tau)$. $C_0 = 70$ ppm.

bon content in the emulsion is smaller (40 ppm), then the efficiency of evaporation calculated in relation to the total concentration becomes larger, and the efficiency of interception becomes smaller. This is seen if we compare the results presented in Figs. 4 and 5 for naphthalene.

Analysis of Figs. 3–7 allows us to state that the dissolution of aromatic hydrocarbon droplets during aeration of the emulsion causes the evaporation efficiency to increase in comparison with the evaporation process without dissolution.

In the case of aliphatic hydrocarbon (Fig. 7), there is a great difference between the evaporation efficiency calculated from Eq. (2) (only evaportion) and from Eq. (3) (dissolution + evaporation). This difference results from the fact that the volatilities of aliphatics are larger than the volatilities of aromatics, but the solubilities in water are greater for aromatics than for aliphatics. For example, the large volatility of heptane (Table 1) causes the evaporation of the soluble part of heptane to be very fast during aeration (~1 min), but its low solubility causes the evaporation effect to be low (~4%) because only the soluble part of heptane may evaporate into the bubbles. If fast dissolution takes place, then the evaporation efficiency is much larger (Fig. 7, curve marked "dissolution + evaporation"). The experiments which were carried out answered the question: Which model is appropriate?

Figure 8 presents diagrams in which the participation of the interception and evaporation mechanisms in the total removal of hydrocarbons is shown. The evaporation and interception efficiencies were calculated as follow: $[M_e/(M_e + M_i)] \times 100\%$ and $[M_i/(M_e + M_i)] \times 100\%$, respectively.

It may be seen in these diagrams that the participation of evaportion in cumulative removal efficiency is higher when the compound content in the emulsion is lower. For example, if the emulsion contains 40 ppm of naphthalene (30 ppm dissolved and 10 ppm as droplets), and the total removal after 6 h equals 21 ppm, then we found that evaporation gives 81% (17 ppm) and interception gives 19% (4 ppm) of the total removal (Fig. 8, II). If the emulsion contains 100 ppm of naphthane (30 ppm dissolved and 70 ppm as droplets), then evaporation gives only 23.5% and interception gives 76.5% of the total removal (Fig. 8, II).

If we compare the results for different compounds (Fig. 8, I–V), we can say that the lower the vapor pressure and the lower the hydrocarbon solubility in water, the higher the participation of interception and the lower the participation of evaportion in the cumulative hydrocarbon removal during aertion of the emulsion.

Similar conclusions may be drawn for cases where the dissolution of the droplets during aeration is taken into account. In such cases the par-

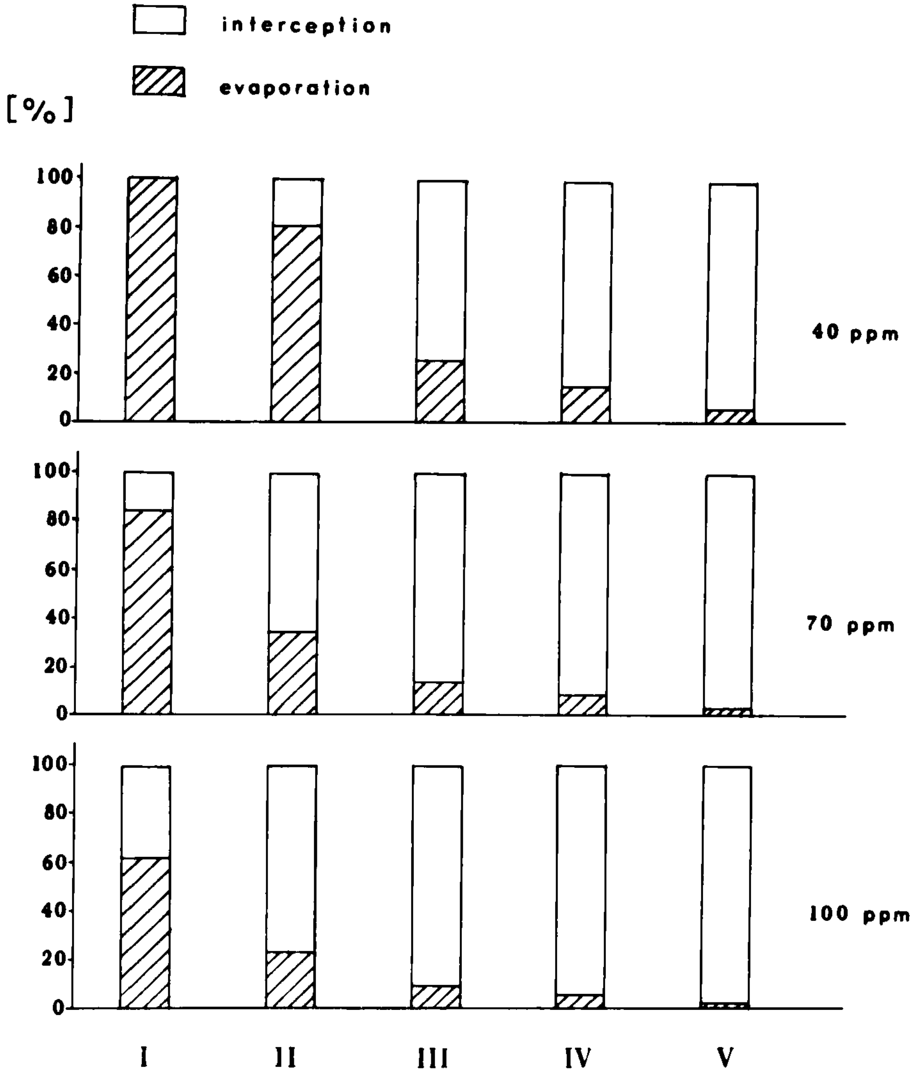

FIG. 8. Participation of interception and evaporation in the total hydrocarbons removal efficiency after 6 h aeration. $[M_i/(M_i + M_e)] \times 100\%$ and $[M_e/(M_i + M_e)] \times 100\%$. Evaporation calculated from the model based on Eq. (2). Hydrocarbons I-V as in Table 1. C_0 = 40, 70, and 100 ppm.

ticipation of evaporation is greater than in cases where dissolution is omitted, but generally the dependences are similar.

On the basis of the results presented, it can be stated that for less volatile and less soluble hydrocarbons, participation of the evaporation process in cumulative removal efficiency becomes insignificant. If we neglect the evaporation process in the calculation of removal efficiency, then we make an error which depends on the emulsified compound properties and on its concentration in the emulsion. In the case of a hydrocarbon for which s = 10 mg/dm^3 and p = 0.1 mmHg, and for an emulsion concentration of 40 ppm, the error equals 26%. If the emulsion concentration is 70 ppm, the error equals ~15%. So we can state that the error is inversely related to the concentration of the emulsion. In the case of an emulsion with a concentration larger than 100 ppm, the error does not exceed 10%. The error will be smaller if the solubility and volatility of the compound are lower than 10 mg/dm^3 and 0.1 mmHg, respectively. For example, in the case of phenanthrene, for which s = 2.7 mg/dm^3 and p = 0.02 mmHg (Table 1), we can completely omit the evaporation process because the error will be 7% for an emulsion of 40 ppm concentration and only 2.8% for an emulsion of 100 ppm concentration.

EXPERIMENTAL

Batch runs of the flotation were carried out in the glass column described previously (*8*). The emulsions of hexane and heptane were prepared mechanically, and the dispersions of naphthalene were prepared ultrasonically. The concentratins of hydrocarbons in the emulsion, in the dispersion, and in the raffinates were determined by the GLC method (*4, 8*). The droplet sizes were determined by microscopic measurements. The bubble sizes were measured photographically. The mean volume-number diameter (so-called Sauter diameter) (*8, 16*) was calculated for bubbles and droplets. The parameters characterizing flotation runs are summarized in Table 2.

Figures 9–13 present the results of experimental flotation runs (circles) and the theoretical results computed for related parameters (lines).

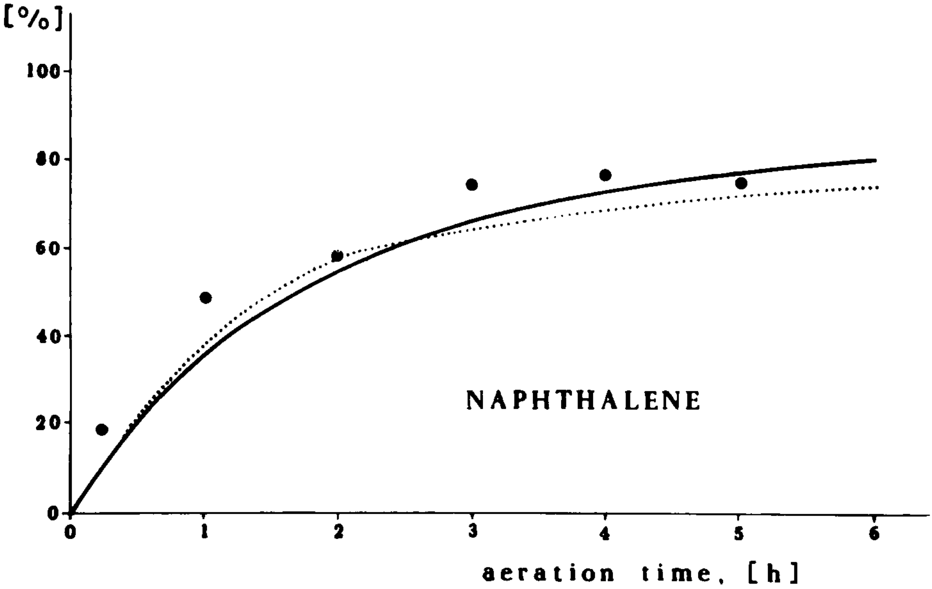

FIG. 9. Removal of naphthalene by flotation. Comparison of experimental data (circles) and computed results (lines) for Run 1. Solid line computed according to the interception (Eq. 1) and evaporation (Eq. 2) models. Dotted line computed according to interception, dissolution, and evaporation models (Eqs. 1-3). Parameters: k = 0.01 cm/s, other parameters as in Table 3.

DISCUSSION

The flotation of mesitylene has been carried out previously (*8*), and good agreement was found between experimental and theoretical results. In the case of naphthalene, fairly good agreement was found for a less concentrated dispersion (Fig. 9) but not for a more concentrated dispersion (Fig. 10), especially at the beginning of the run. The solid lines correspond to the results computed according to the model correspond to the results computed according to the model including the interception and evaporation processes (without the dissolution of droplets). The dissolu-

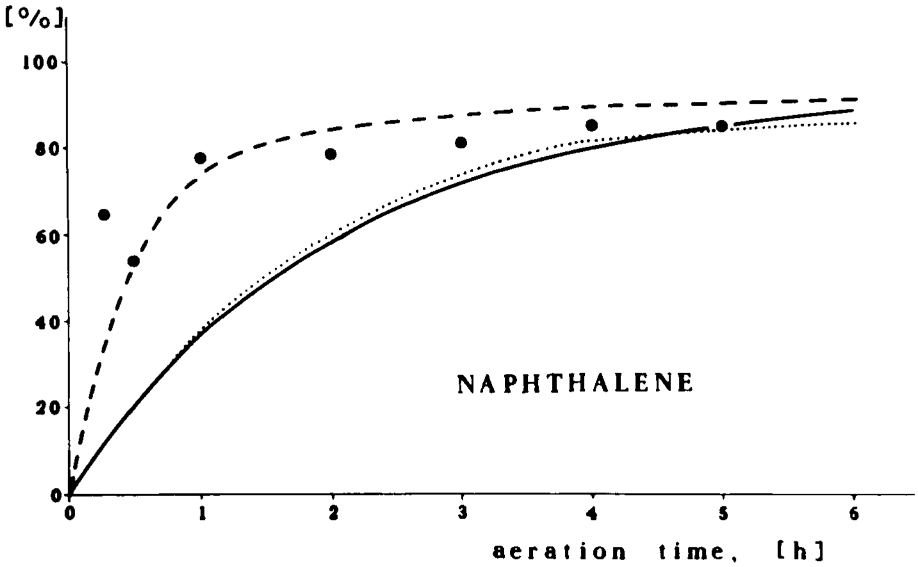

FIG. 10. Removal of naphthalene by flotation for Run 2. Remarks and parameters as in Fig. 9 except that the dashed line relates to particles of 10 μm diameter.

tion of naphthalene in water is rather fast and, as shown by Baumgardt (*17*), the maximum concentration (equal to its solubility) is achieved in about 50 min. So the dissolution of naphthalene particles during the flotation process should be considered. However, the theoretical results, including the process of droplets dissolution (dotted lines, Figs. 9 and 10), do not fit the experimental results better than the solid line does. It is difficult to state whether the dissolution of particles should be considered in the flotation of naphthalene [as should be done in the case of mesitylene (*8*)]. The differences between the experimental points and the theoretical lines result from the fact that the particles of naphthalene have a tendency to flocculate and to form aggregates. And, as shown earlier (*8*), the larger the particles, the greater the efficiency of their removal by the interception process. It may be seen in Fig. 10 that the dashed line, calculated for particles of 10 μm diameter, fits the experimental results better than does the solid line which was calculated for particles of 5 μm diameter (5 μm corresponds to the mean diameter in the initial dispersion,

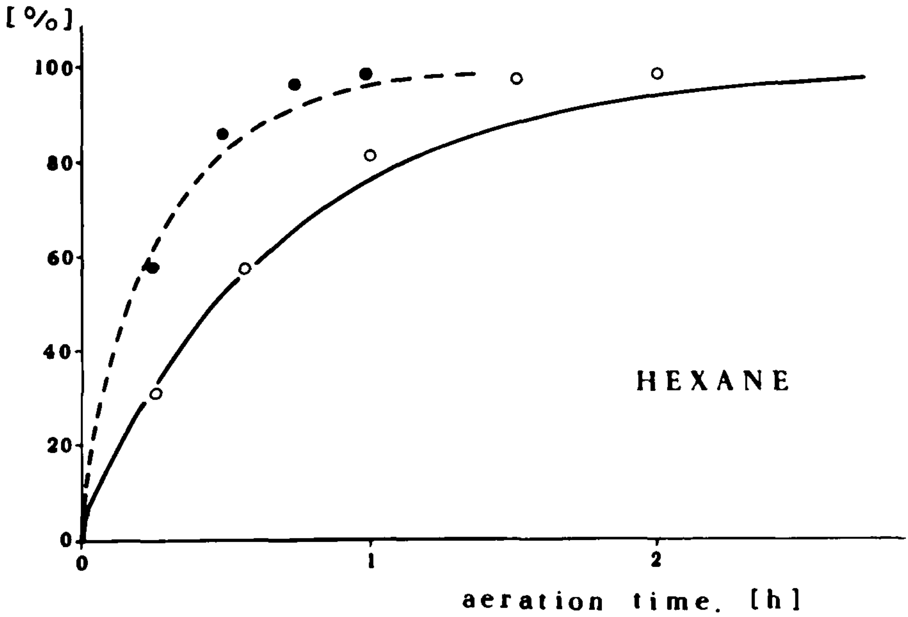

FIG. 11. Removal of hexane by flotation. Dashed line and full circles relate to Run 3; solid line and open circles relate to Run 4. Remarks and parameters as in Fig. 9.

Table 3). The flocculation process influences the flotation efficiency, especially in more concentrated dispersions, where the participation of the particles in the whole mass of naphthalene is greater (Table 3). For testing the model, it would be better if the emulsified compounds were liquid hydrocarbons that formed droplets rather than particles.

The results obtained for hexane and heptane are shown in Figs. 11-13. It is seen that there is fairly good agreement between the experimental points and the results computed according to the interception-evaporation model (Eqs. 1 and 2). If dissolution of the droplets is taken into account (Eq. 3), then complete removal of these hydrocarbons is observed in a few minutes. The very slow solution of aliphatic hydrocarbon droplets during flotation means that the efficiency of interception predominates in the total removal efficiency. Participation of the evaporation process depends on the solubility of an aliphatic hydrocarbon and its content in the emulsion. In the case of hexane, this participation was about 11 and 5% for Runs 3 and 4, respectively; in the case of heptane, the participation of evaporation was 5.6 and 1.4% for Runs 5 and 6, respectively (Table 3).

TABLE 3
Parameters Characterizing Flotation Runs

		Emulsion (dispersion) characteristic					
		Hydrocarbon content					
Run	Hydrocarbon	Total (mg/dm^3)	As droplets (%)	Dissolved (%)	Mean droplet (particle) diameter (μm)	Volume gas flow rate (cm^3/s)	Mean bubble diameter (cm)
1	Naphthalene	64	53.1	46.9	5.0	1.1	0.12
2	Naphthalene	152	80.3	19.7	5.0	1.1	0.13
3	Hexane	89	88.9	11.1	4.6	1.1	0.08
4	Hexane	200	95.1	4.9	3.4	1.1	0.09
5	Heptane	52	94.4	5.6	3.0	1.1	0.09
6	Heptane	202	98.6	1.4	5.1	1.1	0.12

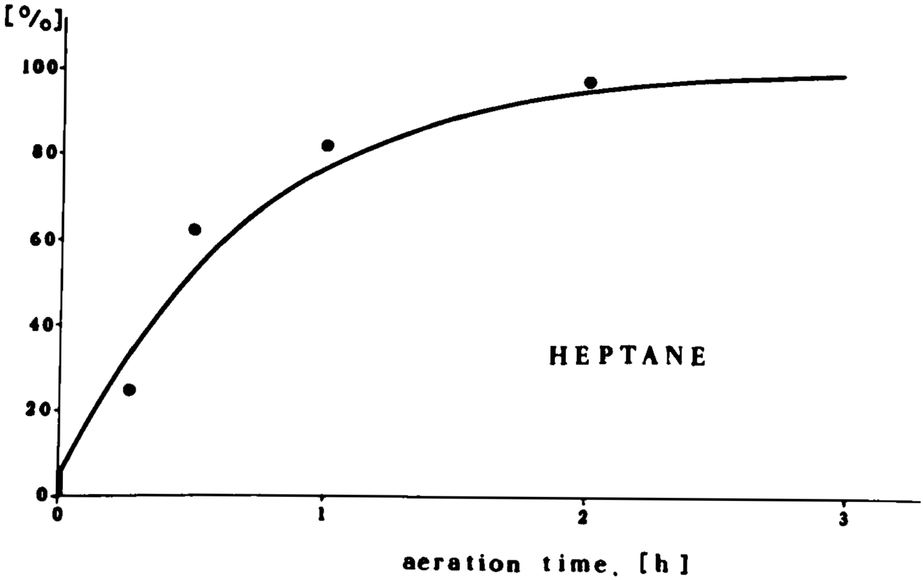

FIG. 12. Flotation efficiency of heptane for Run 5. Remarks and parameters as in Fig. 9.

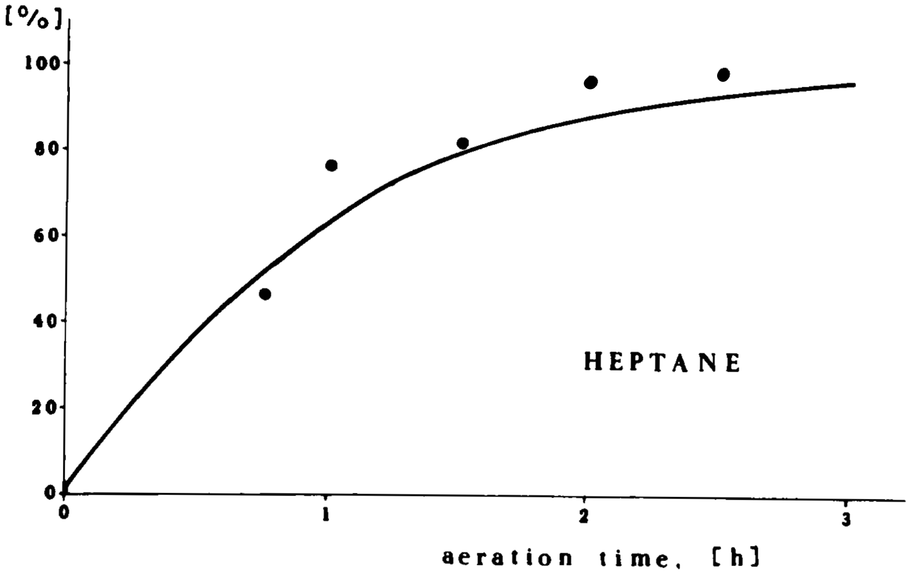

FIG. 13. Flotation efficiency of heptane for Run 6. Remarks and parameters as in Fig. 9.

CONCLUSIONS

On the basis of the above the results we draw the following conclusions:

The rate of solute evaporation as a result of bubble aeration depends on the Henry's law constant; the higher the K_H value, the faster the evaporation into the rising bubbles.

The participation of the evaporation process in total hydrocarbon removal during aertion of the emulsion depends mainly on the hydrocarbon solubility in water, not on the K_H value.

The participation of the evaporation process in the total removal efficiency is lower when the emulsion concentration is higher.

If the emulsion concentration is higher than 100 ppm and the hydrocarbon solubility in water does not exceed 10 ppm and its volatility is not greater than 0.1 mmHg, then the evaporation process may be neglected in the computation of the flotation efficiency if an error of about 10% is accepted. If better accuracy is needed, then the lower boundary values of the hydrocarbon solubility and volatility and the higher emulsion concentration should be used.

On the basis of the experimental results, one can state that the model based on the interception and evaporation mechanisms (without droplets dissolution) can be applied for the analysis of the flotation of aliphatic hydrocarbons, while for aromatics the droplets dissolution process has to be included.

SYMBOLS

r_b, r_p	radius of bubble and particle, respectively
u	bubble rise velocity
η	aqueous layer viscosity
ρ	aqueous layer density
h	height of the liquid head
V_g	volumetric gas flow rate
V_s	volume of the solution
D	flotation column diameter
τ	time from the beginning of the run

C, C_0	residual and initial hydrocarbon concentration in emulsion, respectively
C_{aq}	concentration of dissolved hydrocarbon
k	mass transfer rate coefficient
K_H	Henry's law constant for solute in water
Re	Reynolds number $= 2ur_b\rho/\eta$
M_i	hydrocarbon mass removed by interception
M_e	hydrocarbon mass removed by evaporation
E_c	collision efficiency $= 0.995(r_p/r_b)^2\sqrt{\mathrm{Re}}$ (Ref. *13*)
s	hydrocarbons solubility in water
p	vapor pressure of pure hydrocarbon
M	molecular weight of hydrocarbon

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