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The Removal of Emulsified Oil Particles: Verification of the Flotation Model Based on Interception

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ABSTRACT

The removal of several liquid alkanes from their O/W type emulsions was carried out by bubble column aeration. For the calculation of the removal efficiency, hydrodynamic models based on the theory of fine particle flotation were applied. Equations derived by Sato for the interception of oil particles can be used for the mathematical description of flotation of alkanes whose vapor pressure is lower than 1 mmHg and whose water solubility is lower than 0.1 ppm. If the solubility and volatility of hydrocarbons are greater, then they are also removed by evaporation. In such a case the rate of dissolution of alkanes in water is a very important parameter, and knowledge of its value is necessary in order to calculate the removal rate properly.

INTRODUCTION

From the very beginning, investigations on flotation mechanisms were related to the application of this process to the flotation of ores (1–3). Sutherland (4) made a significant contribution in this field by developing the theory of collisions of particles with gas bubbles, based on the equation of Ramsey (5) which describes flow around a spherical body. Subsequent researchers (6–11) of the flotation process based their investigations on Sutherland's work. The forces acting on a particle and the interaction between a particle and a bubble govern the mutual approach of a particle and a bubble (12). The relation between the magnitudes of the particular forces determines the flotation mechanism. Sufficiently large particles, moving almost rectilinearly due to inertial forces, collide with bubbles, since in this case the inertial forces definitely exceed the hydrodynamic forces. In the case of fine particles, the inertial forces are small. Hence, under the influence of the hydrodynamic forces, the particle deflects from the rectilinear path in such a way that the trajectory coincides with the liquid streamline. The inertial parameter Stk (Stokes number) is the criterion allowing one to distinguish whether the transport is accomplished with or without the effect of inertial forces, hence whether the particles can be treated as fine (13–15). It is usually assumed that when Stk < 0.1, then the inertial forces do not affect the deposition of the particles on the bubble surface. Flotation can proceed in such cases by the interception of particles. The theory of flotation of fine and medium-sized particles has been further developed by Derjaguin and Dukhin (6, 8). According to them, contactless flotation is possible, in addition to contact flotation, in the case of fine particles. This phenomenon takes place when small detaching forces are overcome by the attractive van der Waals–London forces. According to Sylvester (16), the fine particles, e.g., oil droplets, can also be trapped by the vacuum in the wake behind the moving bubble.

In the light of the theory of flotation of fine particles, it has been assumed that flotation of oils from O/W type emulsions should proceed according to the model of inertialess interception. This is due to the fact that the Stk values calculated for droplets of 1–10 μm diameter and bubbles of 0.2–4 mm diameter, most often encountered in the flotation systems, are equal to 10^{-5}–10^{-3}, hence are much smaller than the critical Stk value of 0.1.

When calculating the flotation rate, the majority of researchers utilize the collection efficiency E term, which may be defined as the fraction of particles in the bubble's path which are actually picked up by the bubble. Reay (17) defined the collection efficiency E by

$$E = E_c E' \tag{1}$$

where E_c is the collision efficiency, i.e., the fraction of particles in the bubble's path which collide with the bubble, and E' is the attachment efficiency, i.e., the fraction of particles colliding with the bubble which actually stick to it.

E_c depends mainly on the particle and bubble sizes. E' depends mainly on the chemical nature of the particle and the bubble surfaces as well as on the properties of the liquid film separating them. E_c may be regarded as an upper limit of the collection efficiency E, corresponding to an attachment efficiency E' of 1.0. Hence, a number of researchers tried to find expressions for the calculation of the collision efficiency E_c. The theoretical equations are based on the trajectory of a particle moving around a bubble.

For the laminar regime of bubble flow, Reay (17) took only gravity and the hydrodynamic forces into account to yield the equation

$$E_c = \frac{K^2}{1 + G}\left[1 + G - \frac{3}{2K} + \frac{1}{2K^3}\right] \tag{2}$$

where $K = 1 + (r/R)$, $G = 2r^2g(\rho_p - \rho)/9u\eta$ (G is the dimensionless settling velocity of the particle), r is the radius of the particle, R is the radius of the bubble, g is the gravitational constant, ρ is the aqueous layer density, ρ_p is the particle density, u is the bubble rise velocity, and η is the aqueous layer viscosity.

On the other hand, the equations obtained by Flint and Howarth (18) are identical for both laminar and potential flow regions:

$$E_c = \frac{G}{1 + G} \tag{3}$$

Weber (14) derived equations interrelating the E_c value with the Reynolds number (Re) of the collector bubble. He expressed the collision efficiency as the sum of collisions by gravitation (E_g) and by interception (E_i):

$$E_c = E_g + E_i \tag{4}$$

For the calculation of the E_g value, he utilized the equation given by Reay:

$$E_g = \frac{G}{1 + G}\left[1 + \frac{r}{R}\right]^2 \sin^2 \phi_g \tag{5}$$

where ϕ_g is the value of the angle, measured from the front stagnation point of the bubble, over which gravity deposition occurs. He calculated the efficiency of interception collisions for the intermediate region from Eq. (6):

$$\frac{E_i}{E_{is}} = 1 + \frac{(3/16)\mathrm{Re}}{1 + 0.249\mathrm{Re}^{0.56}} \tag{6}$$

where E_{is} corresponds to the collision efficiency by interception for laminar conditions (Stokes' region):

$$E_{is} = \frac{3(r/R)^2}{2(1 + \mathrm{Stk})} \tag{7}$$

where $\mathrm{Stk} = 2\rho_p r^2 u/9R\eta$.

Oil flotation has been examined by Sato et al. (19). Basing their work on the theory of particle trajectory, they derived equations for the efficiency of collisions of a droplet with a bubble in the interception process for the laminar region:

$$E_c = \frac{3}{2}\left(\frac{r}{R}\right)^2\left(1 + \frac{2r}{3R}\right)\Big/\left(1 + \frac{r}{R}\right) \tag{8}$$

and for the transient region:

$$E_c = 0.995\left(\frac{r}{R}\right)^2\sqrt{\mathrm{Re}} \tag{9}$$

From a simple material balance, the authors derived the equation describing the dependence of residual oil concentration in the emulsion C on the collection efficiency E:

$$C = C_0 \exp\left[-\frac{3EV_g}{\pi RD^2}\right] \tag{10}$$

where C_0 is the initial oil concentration in the emulsion, V_g is the volumetric gas flow rate, and D is the diameter of the flotation column.

Good agreements have been found by the authors (19) between the experimentally determined values of collection efficiency (from the results of flotation) and the theoretically calculated values of collision efficiency (from Eq. 8 or 9). It should be emphasized that the repulsive electrostatic forces have been minimized in their experiments by reducing the pH to ~4, which, according to Spielman and Fitzpatrick (20), is sufficient to permit neglect of these forces.

It was demonstrated in our previous investigations (21–23) that the efficiencies of flotation of aromatic and aliphatic hydrocarbons from their emulsions differ significantly, and the differences cannot be elucidated on the basis of the interceptive model of flotation of fine particles. It became evident that to reach agreement between the theoretical and experimental results, it is necessary to take into account the evaporation of hydrocarbon molecules dissolved in water to the interior of bubbles (24). It was demonstrated in a recent paper (25) that the contribution of the evaporation process in the removal of hydrocarbons can be much greater than that of the interception process, but this depends on vapor pressure and the solubility of the hydrocarbon in water. Alkanes are usually less soluble than aromatics, but they are more volatile. The present paper aims at determining the extent to which the interceptive model is satisfied by the flotation of various aliphatic hydrocarbons.

EXPERIMENTAL

Flotation of hexane, heptane, octane, decane, dodecane, and tetradecane from their O/W type emulsions was investigated. Hydrocarbons were purified by passage through an alumina column. The emulsions were prepared mechanically and used after about 12 hours of storage. The mean droplet sizes in the treated emulsions ranged from 2 to ~6 μm in diameter.

TABLE 1
Selected Properties of Hydrocarbons in the Flotation Experiments (at 20°C) (26, 27) and the Parameters of the GLC Analysis

Hydrocarbon	Molecular weight	Water solubility s (ppm)	Vapor pressure p (mmHg)	Henry's law constant K_H	GLC analysis parameters: Temperature (°C)	GLC analysis parameters: Internal standard
Hexane	86	9.8	120	57.6	36	*n*-Butanol
Heptane	100	2.9	35.5	67.1	40	*n*-Butanol
Octane	114	0.66	10.4	98.3	55	*n*-Butanol
Decane	142	0.043[a]	0.9[b]	162.7	68	*n*-Butanol
Dodecane	170	0.0027[a]	0.08[b]	275.8	130	*n*-Hexanol
Tetradecane	198	0.00017[a]	0.007[b]	446.5	158	*n*-Hexanol

[a] Values estimated on the basis of the solubility vs molar volume dependence.

[b] Values estimated on the basis of the vapor pressure vs molecular weight dependence.

Batch flotation runs were carried out at room temperature in a column described previously (21). The hydrocarbon concentration in the emulsions was determined by the GLC method described earlier (22); however, the internal standards used in the analysis were different (Table 1). The temperature of GLC analysis was different for different hydrocarbons, and ranged from 36 to 158°C.

The transformed form of Eq. (10) was applied for the calculation of the mass of hydrocarbon M_i removed due to interception after time τ:

$$M_i = V_s C_0 \left[1 - \exp\left(- \frac{3 E V_g \tau}{\pi R D^2} \right) \right] \tag{11}$$

where V_s is the volume of the solution. In Eq. (11) the values of collision efficiency E_c, calculated according to the formulas of different authors, were applied instead of the collection efficiency E.

RESULTS

Figures 1–8 present examples of the results of the flotation of different alkanes from their emulsions in distilled water. The points correspond to experimental results, and the lines are theoretical results computed according to Eq. (11). Collision efficiencies were calculated from Eqs. (2), (3), (6), (7), (8), and (9).

It is known that hydrocarbon droplets as well as air bubbles are negatively charged in water as a consequence of the adsorption of hydroxyl ions from

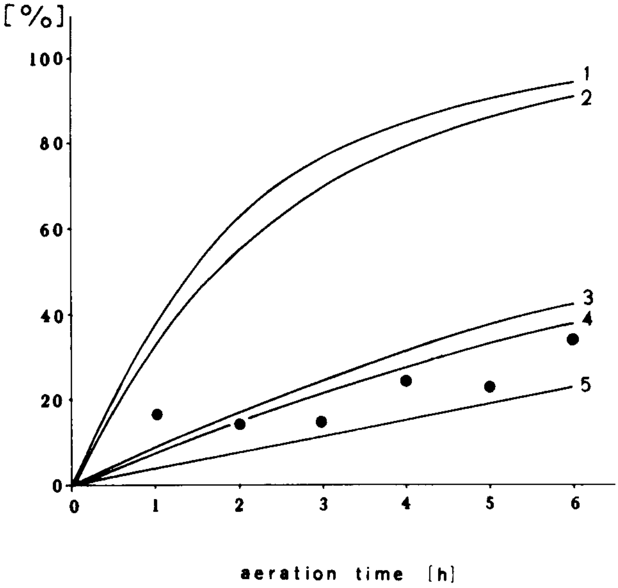

FIG. 1 Removal of tetradecane by flotation; dependence on aeration time. The points present the experimental results; the lines relate to the theoretical results computed from Eq. (11). Collision efficiencies E_c calculated from different equations: Curve 1, Eq. (9); Curve 2, Eq. (6); Curve 3, Eq. (2); Curve 4, Eqs. (7) and (8); Curve 5, Eq. (3). C_0 = 375 ppm, particle diameter d_p = 2.7 μm.

the dissociation of water. Thus, in pure water, electrostatic repulsion between hydrocarbon droplets and air bubbles occurs, therefore the discussed models are not valid for the flotation of hydrocarbons from pure water. These models involve gravity and hydrodynamic forces only, and if they are to be valid, the electrostatic repulsion must be diminished. This can be done by the adsorption of cations (e.g., H^+ ions or surface-active cations) on negatively charged surfaces (28). Reduction of the pH to ~4 allows the electrostatic repulsion to be minimized (20), and this was done in the next series of experiments (Figs. 9–11).

In the range of bubbles sizes tested, Eqs. (2), (3), (7), and (8) (which refer to laminar flow) should not be applied. Thus, Curves 3, 4, and 5 do not describe the examined systems because they concern models pertaining to the Stokes' region.

On the other hand, it is anticipated that the Weber or Sato model for the intermediate region (Eqs. 6 and 9, Curves 1 and 2) is best suited to the hydrodynamic conditions encountered in the experiments, but only when electrostatic forces are absent. However, as can be seen from Figs. 1–3, the results for tetradecane, dodecane, and decane are worse than

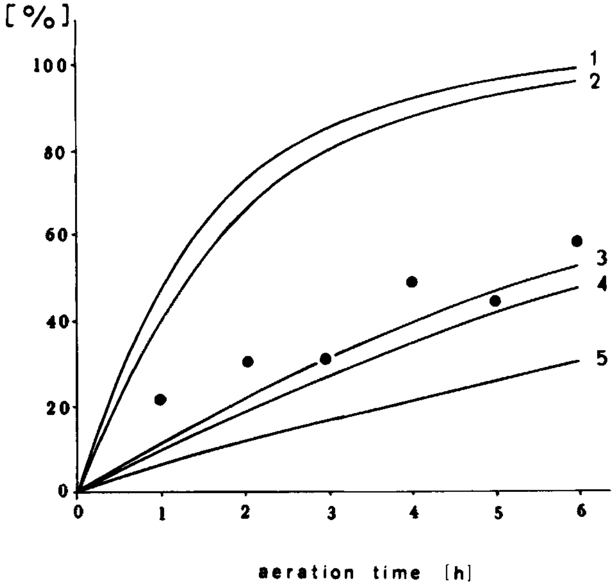

FIG. 2 Dodecane removal efficiency; dependence on aeration time. Remarks as in Fig. 1. C_0 = 180 ppm, d_p = 3.48 μm.

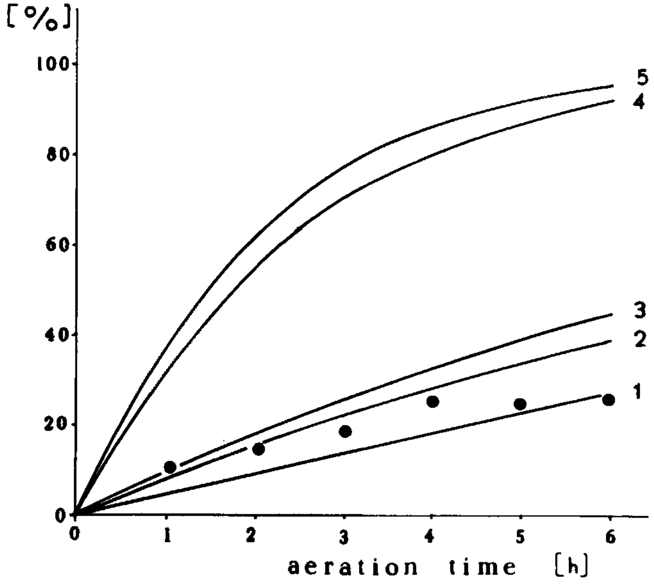

FIG. 3 Decane removal efficiency; dependence on aeration time. Remarks as in Fig. 1. C_0 = 125 ppm, d_p = 2.0 μm.

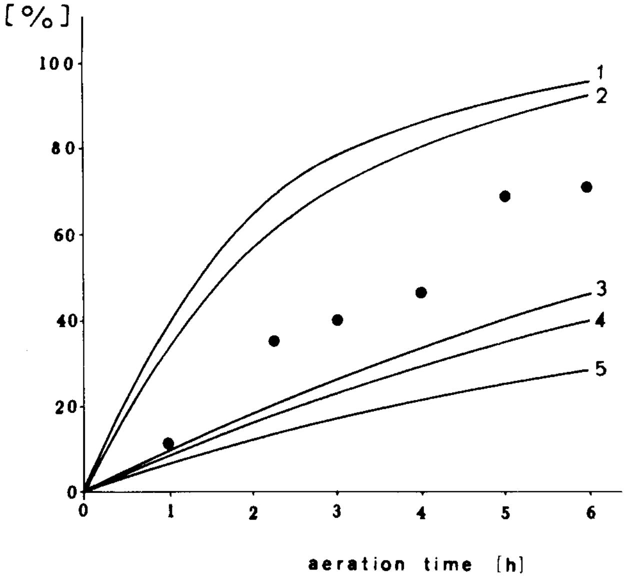

FIG. 4 Octane removal efficiency; dependence on aeration time. Remarks as in Fig. 1. C_0 = 298 ppm, d_p = 2.55 μm.

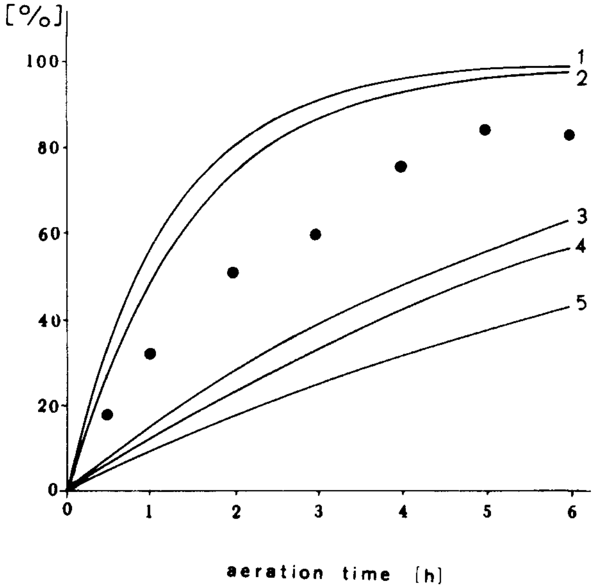

FIG. 5 Heptane removal efficiency; dependence on aeration time. Remarks as in Fig. 1. C_0 = 340 ppm, d_p = 3.24 μm.

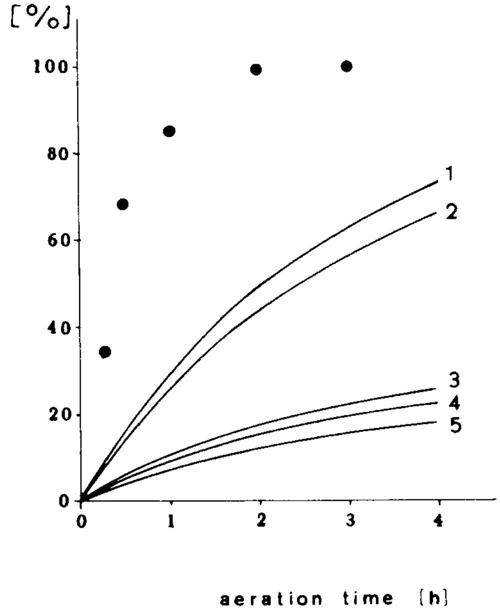

FIG. 6 Heptane removal efficiency; dependence on aeration time. Remarks as in Fig. 1. C_0 = 63 ppm, d_p = 2.0 μm.

theoretically predicted for the intermediate region and lie close to the curves for the laminar region. On the other hand, some results for heptane (Fig. 6) and hexane (Figs. 7 and 8) are better than predicted from any of the equations. This seems incomprehensible, since it can be assumed that the magnitude of the gravity, inertial, and electric forces acting on droplets suspended in water during flotation should be similar for all the hydrocarbons examined. It can therefore be concluded that the observed differences are not due to these forces. Removal of heptane and hexane to an extent greater than predicted by Eqs. (6) and (9) results from additional removal due to evaporation to the floating gas bubbles. On the other hand, the worse than predicted results for tetradecane, dodecane, decane, and octane are due to the fact that repulsive electrostatic interactions have not been eliminated in the experiment, although this is one of the assumptions of the model. However, owing to the fact that the flotation conditions have not been modified, it was possible to demonstrate how great the differences in the flotation rates of various alkanes can be. This can occur during the flotation of oils of different compositions—the phenomenon noticed by Strickland (among others) in his investigations (29). Barrierless flotation (no electric barrier) would cause faster hydrocarbon removal, and differ-

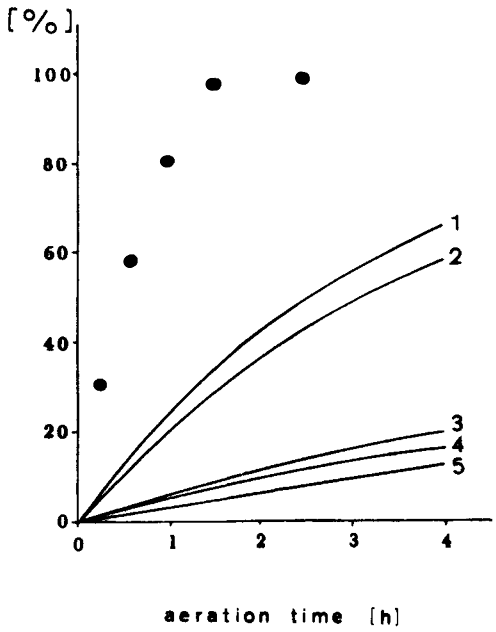

FIG. 7 Hexane removal efficiency; dependence on aeration time. Remarks as in Fig. 1. C_0 = 200 ppm, d_p = 1.96 μm.

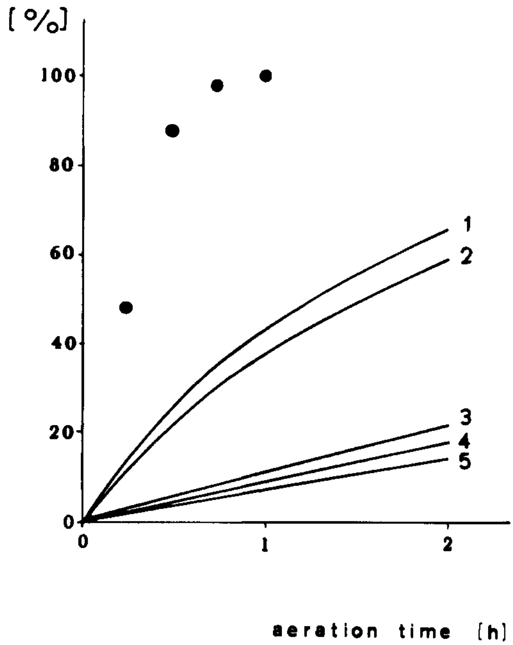

FIG. 8 Hexane removal efficiency; dependence on aeration time. Remarks as in Fig. 1. C_0 = 89 ppm, d_p = 2.9 μm.

ences between the flotation rates of the hydrocarbons investigated would be much smaller and even not visible.

However, in order to verify the hydrodynamic interception model, an experiment has been performed in which flotation was carried out under barrierless conditions, i.e., in an emulsion having a pH of ~4. Decane emulsions were chosen for the experiments since it was concluded on the basis of Ref. 30 and of data from Table 1 that evaporation does not occur during flotation of aliphatic hydrocarbons with a molecular weight higher than that of octane.

Figures 9–11 present the results of decane flotation and the theoretical curves corresponding to the Sato and Weber models for the transition region. The few percent differences between the results from the two models are due to the fact that the gravity forces have not been taken into account in the Weber model calculations because it was impossible to determine the value of the angle ϕ occurring in Eq. (5). After an approximate estimation of the E_g value and after using this value in the calculations, the flotation yields calculated from the Weber model were very close to those from the Sato model (Curves 1). A comparison of the experimental

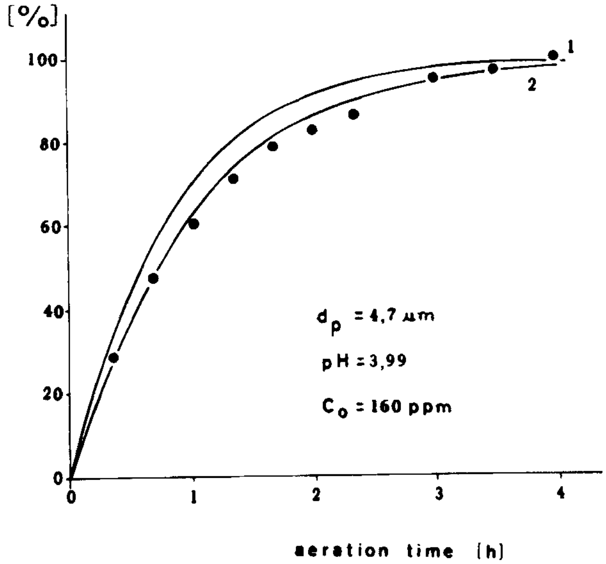

FIG. 9 The efficiency of decane removal during barrierless flotation; dependence on aeration time. Remarks as in Fig. 1.

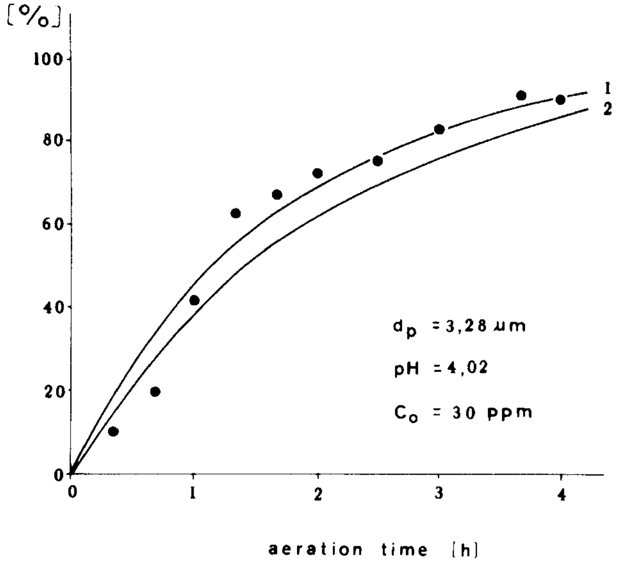

FIG. 10 The efficiency of decane removal during barrierless flotation; dependence on aeration time. Remarks as in Fig. 1.

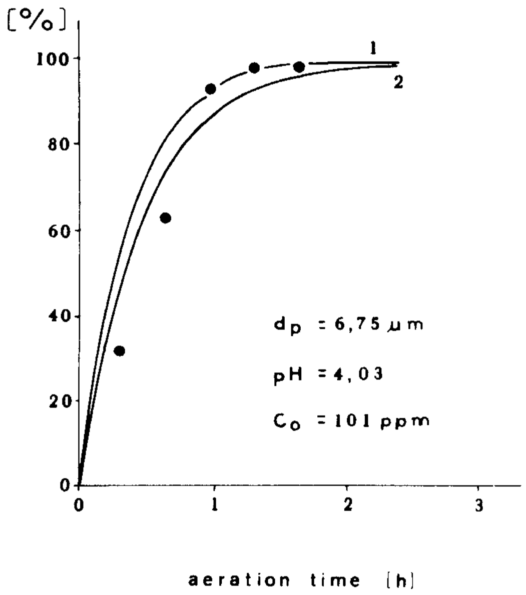

FIG. 11 The efficiency of decane removal during barrierless flotation; dependence on aeration time. Remarks as in Fig. 1.

results with the theoretical curves leads to the conclusion that the hydrodynamic interception model developed by Sato is well suited for the description of flotation of nonvolatile and water-insoluble hydrocarbons under barrierless condition.

Removal of heptane from emulsions has also been examined under the conditions of barrierless flotation. Two parallel processes contribute in the removal of this hydrocarbon: interception and evaporation. Hence, Eq. (11), as well as Eq. (12) or (13), were used for the theoretical calculations. Derivation of these equations has been described in Ref. 24.

$$M_e = V_s C_{aq}\left\{1 - \exp\left[-\frac{V_g K_{\mathrm{H}} T}{V_s}\left(1 - \exp\left(-\frac{3kh}{Ru}\right)\right)\right]\right\} \tag{12}$$

$$M_e = V_g C_{aq} K_{\mathrm{H}} T\left[1 - \exp\left(-\frac{3kh}{Ru}\right)\right] \tag{13}$$

where M_e is the hydrocarbon mass removed by evaporation, C_{aq} is the concentration of the hydrocarbon dissolved in water, K_{H} is Henry's law

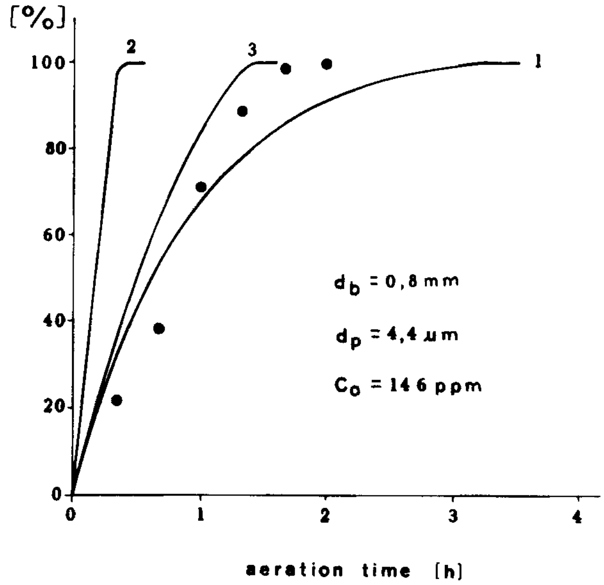

FIG. 12 The efficiency of heptane removal during barrierless flotation; dependence on aeration time. The points present the experimental results. Theoretical results are computed according to interception (Eq. 11) and evaporation (Eq. 12) models (Curve 1), or according to interception (Eq. 11), evaporation, and dissolution (Eqs. 12 and 13) models (Curves 2 and 3). Mass transfer rate coefficient: k = 0.01 cm/s (Curves 1 and 2) and k = 0.001 cm/s (Curve 3). Diameter of bubble d_b as on figure.

constant for the solute in water, h is the height of the liquid head in the column, and k is the mass transfer rate coefficient. The values of k used in the model calculations were fitted on the basis of the earlier analysis of the evaporation of hydrocarbons from water (31).

In the case when the emulsified droplets dissolve (i.e., the hydrocarbon molecules transfer from droplets to the aqueous solution) very slowly and only the evaporation influences changes of the C values, the total mass of the hydrocarbon carried out of the water by evaporation M_e was calculated from Eq. (12). On the other hand, Eq. (13) corresponds to the case where droplet dissolution is faster than evaporation of the dissolved molecules and the concentration of hydrocarbon in the aqueous solution C_{aq} is considered to be a constant during the aeration process until all the droplets disappear (dissolved or captured by bubbles) (24).

The experimental results do not coincide with any of the theoretical curves, as can be seen from Figs. 12 and 13. Heptane removal is better than what is calculated from the model involving interception and evaporation, but worse than what is predicted from the model that also takes

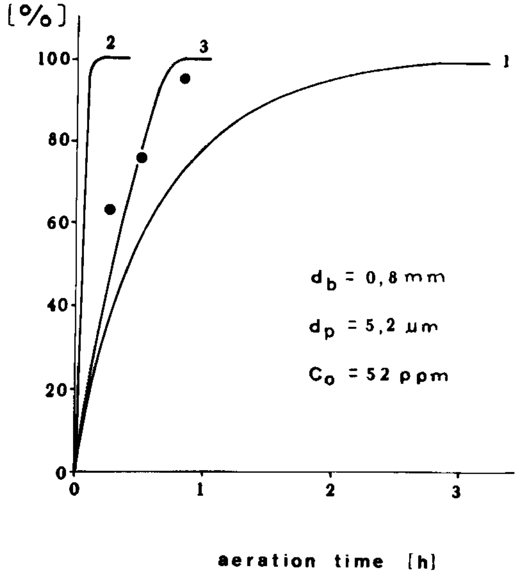

FIG. 13 The efficiency of heptane removal during barrierless flotation; dependence on aeration time. The points present the experimental results. Theoretical results are computed according to interception (Eq. 11) and evaporation (Eq. 12) models (Curve 1), or according to interception (Eq. 11), evaporation, and dissolution (Eqs. 12 and 13) models (Curves 2 and 3). Mass transfer rate coefficient: k = 0.01 cm/s (Curves 1 and 2) and k = 0.001 cm/s (Curve 3). Diameter of bubble d_b as on figure.

the dissolution of a droplet into account. It can be seen in Figs. 12 and 13 that Curves 3, calculated by using the lower values of the mass transport coefficient, are the closest to the experimental results. This does not mean, however, that this value of k is more correct. Only knowledge of the rate of dissolution of the hydrocarbon in water would allow calculation of the theoretical values corresponding to the real system.

CONCLUSIONS

On the basis of the above results, it can be stated that the equations derived by Sato and Weber for the interceptive model can be used to a good level of approximation for the mathematical description of flotation of hydrocarbons with a vapor pressure lower than 1 mmHg and a water solubility lower than 0.1 ppm. Good agreement between the theoretical and the experimental results has been obtained for decane flotation under barrierless conditions. In the case of hydrocarbons with Henry's law constants $\gg 1$, the removal of which proceeds according to the mixed mechanism, it is necessary to know the rate of dissolution of these hydrocarbons in order to describe the removal process properly. It is particularly important for alkanes since the results calculated for the boundary conditions differ very significantly (Figs. 12 and 13, Curves 1 and 2). In the case of aromatic hydrocarbons (with Henry's law constants < 1), knowledge of the dissolution rate is not as significant because the differences for the boundary conditions are small, as has been demonstrated in previous papers (24, 25).

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