Hydrocarbon Separation Through a Liquid Water Membrane: Modeling of Permeation in an Emulsion Drop

The mass transfer of hydrocarbons within an emulsion drop has been modeled. The selective behavior of the process is attributed to the controlling effect of the aqueous phase; calculations show that the presence of a very thin membrane of water separating the inner core of the hydrocarbon droplets from the surrounding solvent is sufficient to explain observed selectivities.

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SCOPE

The work of N. N. Li (1971) on selective extraction from emulsified hydrocarbon mixtures constitutes a valuable contribution to one of the challenges of modern chemical engineering, the development of low cost separation techniques. The idea is to interpose a water membrane, stabilized by emulsification, between a mixture of the hydrocarbons to be separated and a standard organic solvent. The permeation of the various hydrocarbon species through the emulsion water membrane, under rate controlled conditions, then proceeds in a selective manner due to the different solubilities of the hydrocarbon in water.

Casamatta and co-workers (1974, 1975) have recently analyzed the separation of various emulsified binary organic solutions by kerosene extraction. Their study showed that under gentle mixing, the emulsion moves through the extracting solvent in an aggregative manner (Figures 2 and 3); drops of emulsion consisting of an inner core of emulsified hydrocarbon droplets and an outer layer of water become the locus of the transfer operation. Under these conditions, the overall mass transfer coefficient for a given species is shown to be time independent and proportional to the hydrocarbon solubility. A simplifying physical interpretation of the process suggests that the quasi steady state controlling influence of the outer water layer may explain the behavior of the system.

The objective of this work is to model the mass transfer within an emulsion drop by solving the transport equation of each species through each of the particular transfer zones as observed physically by previous workers. A simple practical expression for the mass transfer coefficient was found and compared to existing quantitative transfer results. The model underlines the various factors required for the efficient operation of a given system and predicts reasonable estimates of its performance from first principles of mass transfer and operating conditions.

CONCLUSIONS AND SIGNIFICANCE

The model developed in this work clearly identifies the outer water membrane of an emulsion drop as the controlling mass transfer resistance for the conditions usually employed in the selective extraction of an hydrocarbon species from a given emulsified organic solution. The overall mass transfer coefficient for an emulsion drop is given by

$$K_i = \frac{D_{im}\, m_i}{\delta}$$

Calculation of the transfer rate relies on the evaluation of the thickness of the outer water layer of an emulsion drop. A reasonable estimate of the performance is obtained if δ is taken to be the maximum thickness predicted from the minimal close packing of emulsion droplets in the inner core of the emulsion drop. The model further predicts that for negligible differences of molecular diffusivity, selectivity will indeed be proportional to the relative solubility of the hydrocarbon species considered.

The approach used in this work is particularly relevant to the design of extraction processes involving the above technique. The design emphasis should not be aimed at minimizing the mass transfer resistance around an emulsion drop but rather at producing a suitable emulsion and at dispersing it in the smallest possible stable state.

In previous work (Casamatta et al., 1974, 1975), a simple permeation model was established and tested using batch separation of emulsified heptane-toluene mixtures dispersed as drops in kerosene. This model, based on the concentration profile shown in Figure 1, led to the following transport equation:

$$W_{i_e} = \Gamma_i(\overline{C}_{iR} - \overline{C}_{iE}) = \frac{d}{dt}(V_E \cdot \overline{C}_{iE}) \tag{1}$$

where

$$\frac{\Gamma A}{\Gamma B} = \frac{m_A}{m_B} \tag{2}$$

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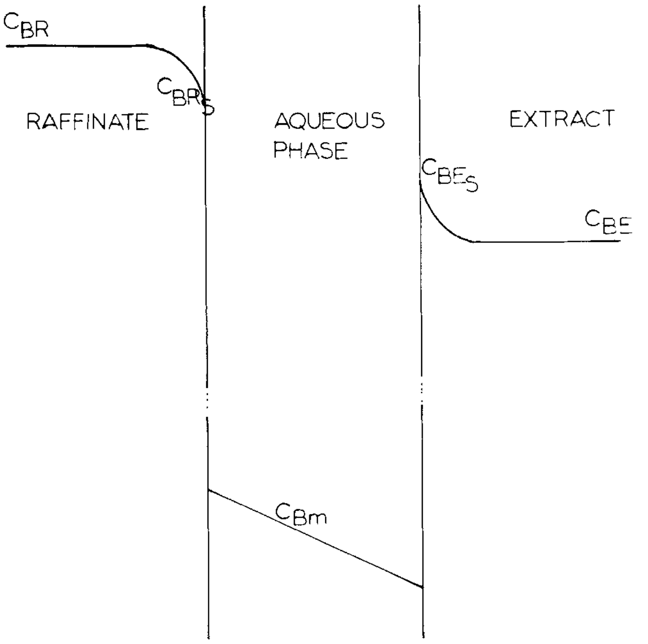

Fig. 1. Linear transfer model.

In agreement with Li (1971, 1972), these equations readily explain the direct relationship between selectivity and the relative solubilities of the various hydrocarbons in water.

This model has been established rather crudely by assuming the liquid membrane to be planar and of constant thickness (Figure 1); this assumption is quite remote from the actual geometrical configuration.

In this paper, a tentative model of mass transfer within an emulsion drop is proposed to predict values for the Γ_i transfer parameters.

ACTUAL MEMBRANE CONFIGURATION

From a practical point of view, transfer takes place between the emulsion drops and the solvent phase.

The interstitial membrane separates emulsified hydrocarbon droplets from each other and these droplets from the bulk hydrocarbon phase (Figure 2).

The peripheral water layer may have an infinitesimal thickness around the droplets, but it has been noticed when observing stagnant emulsions that the aqueous phase settles out under gravity. On the other hand, when these emulsion drops move through the solvent phase, the aqueous phase which normally settles out spreads around the drops in a more or less uniform manner (Figure 3). Therefore, the transfer of a given hydrocarbon from the emulsion towards the solvent phase includes two steps: diffusion through the bulk emulsion, that is, for $0 < r < R^-$, and diffusion through the peripheral water layer of thickness δ. It will be shown later in this paper that the order of magnitude of δ is a few micrometers.

TRANSFER THROUGH THE BULK EMULSION

Hypotheses

1. The organic phase is distributed into rigid globules of about 1 μm in diameter, and transport may be considered as merely diffusional. Moreover, the interstitial aqueous phase is made motionless by these closely packed globules, and mass transfer very likely occurs by molecular diffusion.

2. The mass transfer occurs through two interfaces of very different surface areas: A, the emulsion drop area, and $A\mu$, the area of all the emulsified droplets within that drop. Hence, if

$$A\mu = n\mu \, 4\pi R^2 \tag{3}$$

with

$$n\mu = \phi \left(\frac{R}{R\mu}\right)^3 \tag{4}$$

then

$$\frac{A\mu}{A} = \phi \frac{R}{R\mu} \tag{5}$$

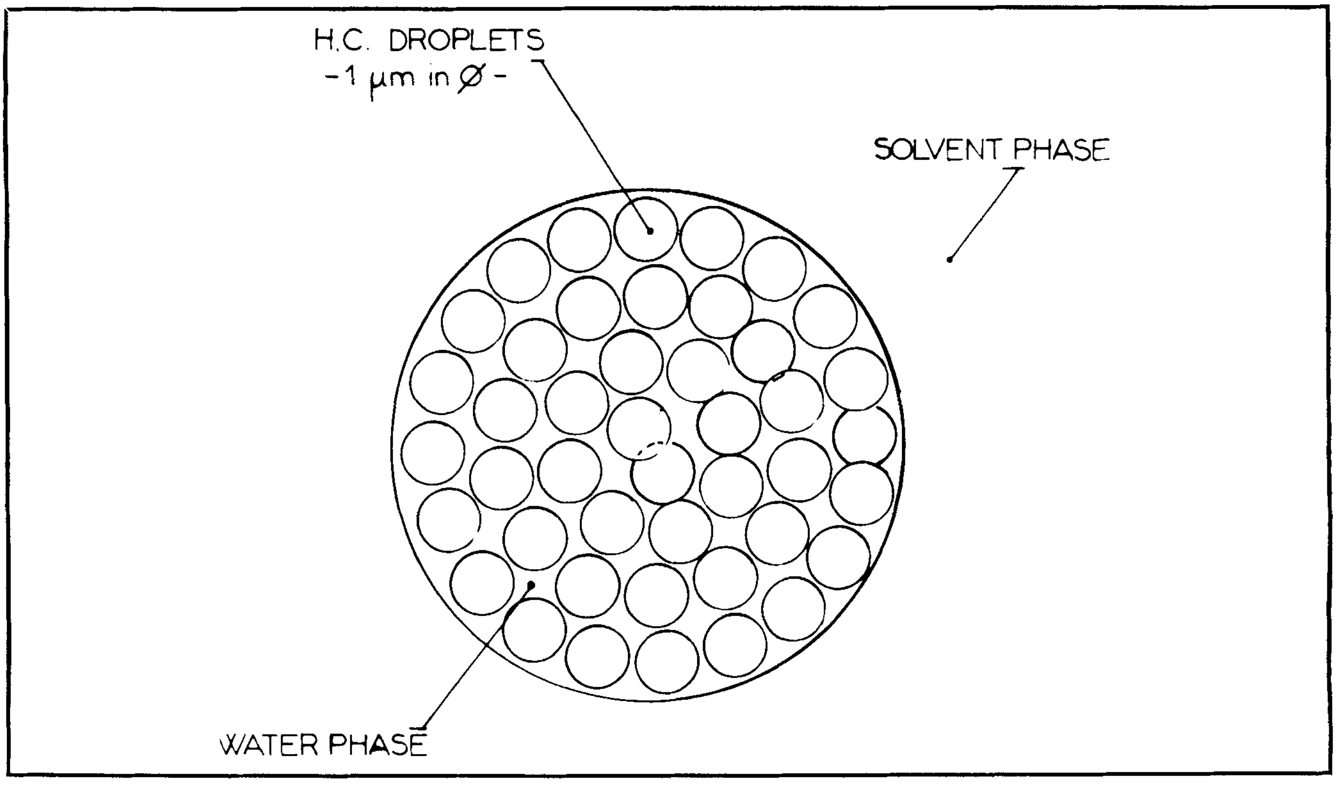

Fig. 2. Emulsion drop: homogeneous structure.

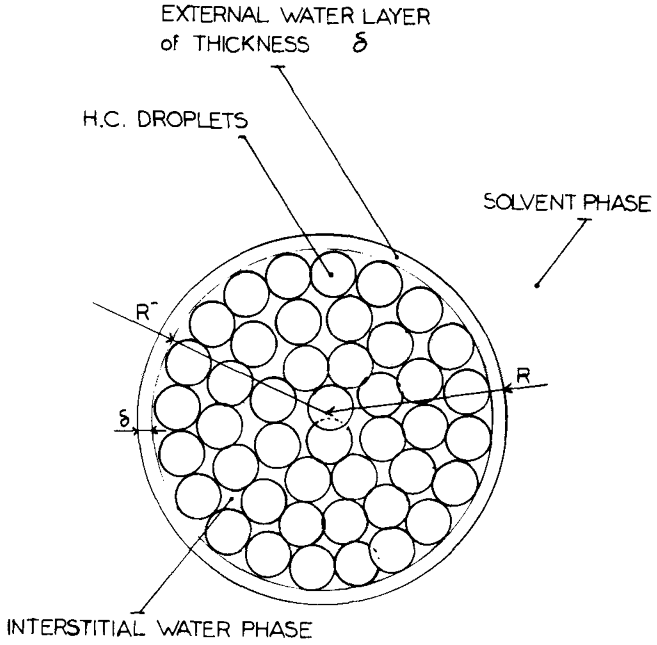

Fig. 3. Emulsion drop: flocculated structure.

As a rough estimate, we assume that each emulsion drop is 1 mm in radius and that the organic phase is distributed in n_μ droplets of 1 μm in radius. In the experimental program, prepared emulsions typically contained 70% of hydrocarbons, and under such conditions, $A\mu/A$ would be around 700. It therefore seems very likely that at each point within the drop, and at any time, the aqueous and the organic phases have reached partition equilibrium.

3. The hydrocarbon species dissolved in the aqueous phase migrate from the inner core of the emulsion drop through a network of stagnant aqueous interstices between the droplets. The effective radial mass transfer area may then be assumed to be proportional to the water volumetric fraction $(1 - \phi)$ in the emulsion. Indeed, it has been reported (Fitreman, 1972) that if β_r is the ratio between the aqueous transfer area and the total surface area at a given radius in an emulsion drop, then the following is valid:

$$\int_0^R \beta_r 4\pi r^2\, dr = (1 - \phi)\frac{4}{3}\pi R^3 \tag{6}$$

If β_r has a constant value β for any r, then β is equal to $(1 - \phi)$. The expression $(1 - \phi)$ appears as the average value of β_r. When, for any r, β_r is replaced by its mean value, it signifies only that an emulsion drop is assumed to be an isotropic homogeneous medium, or, in other words, that the probability of presence of one phase is the same at each point of the drop.

4. The hydrocarbon diffusion through the aqueous phase of the inner core imposes a concentration gradient across each emulsion droplet. This results in a concentration gradient inside each droplet due to the bias of the postulated equilibrium process. Diffusion consequently also occurs across each droplet. It is proposed that this phenomenon can be treated as a continuous permeation through the organic phase in parallel with the aqueous phase.

5. Molecular diffusivities are assumed to be constant, independent of the surfactant presence, independent of the nature of the hydrocarbon species considered, and of the order of magnitude of the binary molecular diffusivity of an hydrocarbon in water. A reduction by a factor of four is assumed for the diffusion of a hydrocarbon in an organic phase. For example, while the binary diffusivity of toluene in water is of the order of 10^{-5} cm^2/s, Perry et al. (1973) report a value of 3.7×10^{-5} cm^2/s for toluene in heptane.

Transport Equation

A material balance on component i within a spherical differential element in the inner core of the emulsion drop yields

$$\frac{-1}{r^2}\frac{\partial}{\partial r}(r^2 N_{i_r}) = \frac{\partial C_i}{\partial t} \tag{7}$$

Assumptions 1 to 5 lead to

$$N_{i_r} = N_{i_m}(1 - \phi) + N_{i_R}\phi = -D_{i_m}(1 - \phi)\frac{\partial C_{i_m}}{\partial r} - D_{i_r}\phi\frac{\partial C_{i_R}}{\partial r} \tag{8}$$

$$N_{i_r} = -D_{i_m}(1 - \phi + 4\phi/m_i)\frac{\partial C_{i_m}}{\partial r} \tag{9}$$

while

$$C_i = (1 - \phi)C_{i_m} + C_{i_R}\phi \tag{10}$$

$$C_i = \left(1 - \phi + \frac{\phi}{m_i}\right)C_{i_m} \tag{11}$$

Equation (7) can then be rewritten as

$$D_{i_m}\frac{(1 - \phi + 4\phi/m_i)}{(1 - \phi + \phi/m_i)}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{i_m}}{\partial r}\right) = \frac{\partial C_{i_m}}{\partial t} \tag{12}$$

or simply

$$D_i\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{i_m}}{\partial r}\right) = \frac{\partial C_{i_m}}{\partial t} \tag{13}$$

TRANSFER THROUGH THE PERIPHERAL WATER LAYER

Considering the hindered mobility of the inner core of the emulsion drop, and in view of the observed thinness of the peripheral water layer, it seems likely that for all practical purposes the aqueous outer region of the emulsion drop is stagnant.

The material balance in this region is then simply identical to Equation (13), with $D_i = D_{i_m}$.

MODELING OF PERMEATION THROUGH THE EMULSION DROP

The mass transfer through an emulsion drop can be described by Equation (13) with the following conditions:

$$D_i = D_{i_m}\frac{(1 - \phi + 4\phi/m_i)}{(1 - \phi + \phi/m_i)} \quad \text{for} \quad r < R^- \tag{14}$$

$$D_i = D_{i_m} \quad \text{for} \quad R^- < r < R \tag{15}$$

for $t < 0$ and all values of r

$$C_{i_m} = C_{i_m}{}^0 \tag{16}$$

for $t \geqq 0$

$$\text{at} \quad r = 0, \quad \frac{\partial C_{i_m}}{\partial r} = 0 \tag{17}$$

$$\text{at} \quad r = R^-, \quad C_{i_{m_1}} = C_{i_{m_2}} \tag{18}$$

and

$$(1 - \phi)\frac{\partial C_{i_{m_1}}}{\partial r} = \frac{\partial C_{i_{m_2}}}{\partial r}$$

and at $r = R$

$$-D_{i_m}\frac{\partial C_{i_{m_2}}}{\partial r} = \alpha\left(\frac{C_{i_{m_2}}}{m_i} - \overline{C}_{i_E}\right) \tag{19}$$

Unsteady state diffusion into a composite sphere comprised of an inner core and an outer shell has been considered by Carslaw and Jaeger (1959). The complexity of the solution, particularly with the inclusion of an external mass transfer conductance α, does not readily lend itself to a versatile and practical model.

On the other hand, the observed experimental behavior of the system (Casamatta et al., 1975) suggests some plausible simplifying assumptions. For example, it has been shown that a single overall mass transfer parameter Γ_i, independent of time, is sufficient to describe the process. This then strongly suggests that the controlling resistances rapidly become time independent and that the process is sufficiently slow that it is in a quasi steady state regime.

When we consider the above, the linear additivity of the mass transfer resistances can be applied to this problem. Furthermore, to evaluate the controlling influence of the various transfer steps, each resistance can be allowed to reach its maximum value.

The solution (Carslaw, 1959) of Equation (13) for the inner core of the emulsion with a constant interface concentration C_{im_s} (which is permissible in view of the relative slow rate of the process) is given by

$$\frac{C_{im} - C_{im_s}}{C_{im}{}^0 - C_{im_s}} = \frac{2R^-}{\pi} \sum_{n=1}^{\infty} - \frac{(-1)^n}{n} e^{-\theta n^2} \sin \frac{n\pi r}{R} \tag{20}$$

The mean value of C_{im} can be expressed by

$$\frac{\overline{C}_{im} - C_{im_s}}{C_{im}{}^0 - C_{im_s}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-\theta n^2}}{n^2} \tag{21}$$

If we define the mass transfer coefficient for the inner core by

$$k_{i1} = \frac{W_i}{4\pi (R^-)^2 (\overline{C}_{im} - C_{im_s})} \tag{22}$$

and use the quasi steady state approach, whereby

$$W_i = \frac{-4}{3} \pi (R^-)^3 \phi \frac{\partial \overline{C}_{iR}}{\partial t} = \frac{-4\pi}{3} (R^-)^3 \frac{\phi}{m_i} \frac{\partial \overline{C}_{im}}{\partial t} \tag{23}$$

Equations (21), (22), and (23) can be combined to yield

$$k_{i1} = \frac{\pi^2 D_{i1} \phi}{3R^- m_i} \frac{\sum_{n=1}^{\infty} e^{-\theta n^2}}{\sum_{n=1}^{\infty} \frac{e^{-\theta n^2}}{n^2}} \tag{24}$$

Higher-order terms for the above series rapidly become negligible with time, and k_{i1} quickly reaches a minimum value (maximum resistance) of

$$k_{i1} = \frac{\pi^2}{3R^-} D_{i1} \frac{\phi}{m_i} \tag{25}$$

which, with the aid of Equation (14) and the fact that $m_i << 1$, can be simplified to

$$k_{i1} = \frac{4}{3} \frac{\pi^2}{R^-} \frac{\phi}{m_i} D_{im} \tag{26}$$

For the experimental condition of this work ($D_{im} \simeq 10^{-5}$ cm²/s and $R^- \simeq 10^{-1}$ cm), k_{i1} becomes constant and equal to Equation (26) within the first minute of the process.

On the other hand, it can be easily shown for a thin stagnant outer layer, that is, for

$$(R - R^-) = \delta << 1 \tag{27}$$

that

$$k_{i2} = \frac{D_{im}}{\delta} \tag{28}$$

while

$$k_{i3} = \frac{D_{iE}}{R} \simeq 4 \frac{D_{im}}{R} \tag{29}$$

The overall mass transfer coefficient for the emulsion drop can be obtained from

$$K_i = \frac{W_i}{4\pi R^2 (\overline{C}_{iR} - \overline{C}_{iE})} = \frac{1}{\frac{1}{k_{i1} m_i} + \frac{1}{k_{i2} m_i} + \frac{1}{k_{i3}}} \tag{30}$$

and using Equations (26) to (29), we get

$$K_i = \frac{1}{\frac{3R}{4\pi^2 \phi D_{im}} + \frac{\delta}{D_{im}\, m_i} + \frac{R}{4D_{im}}} \tag{31}$$

$$K_i = \frac{D_{im}\, m_i}{\delta} \left[1 + \frac{3}{4\pi^2 \phi} \left(\frac{R}{\delta} \right) m_i + \frac{1}{4} \left(\frac{R}{\delta} \right) m_i \right] \tag{32}$$

If we use the following order of magnitude

$$\frac{R}{\delta} \simeq 10^3; \quad m_i \simeq 6 \times 10^{-4}; \quad \phi = 0.7 \tag{33}$$

Equation (32) becomes

$$K_i = \frac{D_{im}\, m_i}{\delta} (1 + 0.07 + 0.15) \tag{34}$$

which shows that 85% of the overall resistance lies in the outer water membrane of the emulsion drop. Considering that the slightest natural or forced mixing will rapidly increase the conductance of the third step of the diffusion process manyfold without disturbing the inner permeation steps, the controlling influence of nearly 95% can actually be attributed to the water membrane.

COMPARISON BETWEEN MODEL AND EXPERIMENTAL VALUES

Assuming that all emulsion drops are of the same size and that perfect mixing exists in the solvent phase, we get

$$\Gamma_i = \frac{V_e}{4/3\pi R^3} 4\pi R^2 K_i \tag{35}$$

and hence

$$\Gamma_i = \frac{3V_e\, D_{im}\, m_i}{R\, \delta} \tag{36}$$

We notice that for any two hydrocarbon species, under the conditions of Equation (36) and assumption (5), our model does indeed predict that the ratio of the overall mass transfer coefficients directly follows from the ratio of the partition coefficients of each individual species in the water phase as reported in Equation (2).

In previous work (Casamatta et al., 1975), it has been shown that

ϕ = 0.73
m_i = 6×10^{-4}
V_e = 80 cm³

$$R \simeq 1 \times 10^{-1}\ \text{cm}$$
$$D_{im} = 10^{-5}\ \text{cm}^2/\text{s}$$
$$\Gamma_i = 0.048\ \text{cm}^3/\text{s} \qquad (37)$$

Under the same conditions, Equation (36) predicts an outer water membrane thickness of 3 μm. This value is in agreement with Li's indication that in an emulsion drop, the water membrane is reduced to a peripheral layer of a few micrometers thickness (Li and Shirer, 1972).

Furthermore, considering that the existence of the water layer is based upon the regrouping of the hydrocarbon droplets, for a uniform droplet size, this can only be achieved with an excess of water, that is, if ϕ is less than the maximum void fraction $\phi_{\max}$ corresponding to the closest packing of undeformable spheres. $\phi_{\max}$ can be calculated from the geometry of close packed hexagonal spherical network (Becher, 1965); that is $\phi_{\max} = 0.74$. For an emulsion prepared with ϕ percent hydrocarbon in water, the water volume content of an emulsion drop of radius R is given by

$$V_m = 4/3\pi R^3(1 - \phi) \qquad (38)$$

After a regrouping or flocculation of the droplets within the drop, the same volume of water is distributed between the inner core and the aqueous water outer layer so that

$$V_m = (1 - \phi_{\max})\frac{4}{3}\pi(R - \delta_{\max})^3 + \frac{4}{3}\pi[R^3 - (R - \delta_{\max})^3] \qquad (39)$$

Equations (37) and (38) give

$$\left(1 - \frac{\delta_{\max}}{R}\right)^{1/3} = \frac{\phi}{\phi_{\max}} \qquad (40)$$

Using the experimental values reported above, we find

$$\delta_{\max} = 4.5\ \mu\text{m} \qquad (41)$$

Hence, the value of δ predicted by our model also respects the macroscopic conservation constraints of the physical system.

CONCLUSION

The model developed clearly identifies the outer water membrane of an emulsion drop as the controlling mass transfer resistance for the conditions of this work. A reasonable estimate of the mass transfer rate is obtained if the thickness of the outer layer is taken to be the maximum thickness predicted from the geometry of close packed solid spheres.

It is believed that this analysis will allow a better understanding of liquid membrane behavior. The model developed not only supports the conclusions of previous work (Casamatta et al., 1974, 1975) but may help through the various assumptions required to explain deviations from the generally observed behavior of the system such as reported by Alessi et al. (1976). For example, the nature of the emulsion may slow down the transfer rate within the inner core of the drop enough to change the general feature of the process and seriously change the direct relationship between selectivity and the relative solubilities of the various hydrocarbon species in water.

NOTATION

A = surface area of an emulsion drop
$A\mu$ = surface area of all emulsified hydrocarbon droplet
C_i = concentration of component i
D_i = diffusivity
k_i = local mass transfer coefficient
K_i = overall mass transfer coefficient
m_i = partition coefficient of component i between the aqueous and the organic phase
N_i = molar flux of component i, moles/s/cm^2
$n\mu$ = number of emulsified droplets in an emulsion drop
R = radius on an emulsion drop
R^- = radius of the inner core of an emulsion drop
$R\mu$ = radius of an emulsified droplet
t = time
V = volume
W_i = molar rate of transfer of component i, mole/s
α = external mass transfer conductance from an emulsion drop
β_r = ratio of the aqueous transfer area over the total surface area at a given radius in an emulsion drop
Γ_i = total mass transfer parameter from a given emulsion
δ = thickness of the peripheral water layer
$\delta_{\max}$ = maximum value for δ
θ = dimensionless time, $\pi^2 D_i\, t/R^2$
ϕ = volumetric percentage of the dispersed phase of an emulsion
$\phi_{\max}$ = maximum value for ϕ

Superscripts

0 = initial
— = average

Subscripts

1, 2, 3 = identification of the inner core, the outer water layer, and the exterior surroundings of an emulsion drop
A, B, i = components
e = identifies the whole of the emulsion
E = solvent phase (extract)
m = aqueous phase
R = hydrocarbon phase (raffinate)
r = radial
s = at an interface

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