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Modeling of Carrier-Mediated Extraction

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Abstract

A two parametric mathematical model of carrier-mediated extraction is proposed for the case when emulsion technique is applied. Its simplified version, valid for diluted solutions, is solved analytically, and an implicit expression relating both parameters—rate of solute transfer and rate of emulsion destruction—is derived. Model parameters were evaluated from the experimental data obtained with two different three-phase systems: oil-in-water-in-oil and water-in-oil-in-water. In the first case, toluene and heptene were separated using water as an intermediate phase, and parameter evaluation was performed by means of an analog computer. In the second case, acetic, nitric, and hydrochloric acids were separated using a solution of tributylphosphate in carbon tetrachloride as a carrier phase. In this case the rate coefficients were found from the proposed implicit equation.

Carrier-mediated liquid–liquid extraction is a new, promising separational process suitable for many purposes, including wastewater treatment. Solute or solutes are transferred between two similar liquid phases A and B, separated by a third intermediate liquid phase C not miscible with A and B. The separational effect is based mainly on the different solubilities of the transferred components in the carrier phase C.

There are several techniques for practical realization of this process. The intermediate phase C can be introduced as a quasi-immobile medium

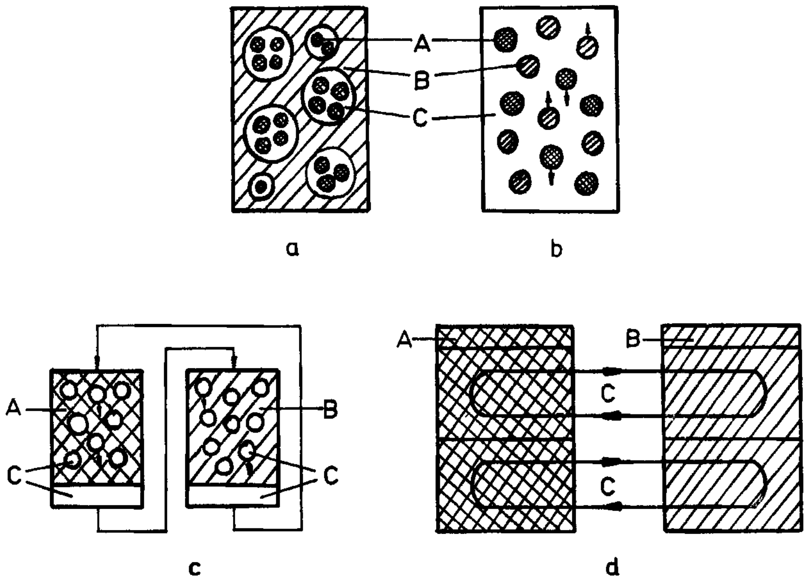

FIG. 1. Various techniques of carrier-mediated extraction.

or barrier between Phases A and B (Figs. 1a and 1b) or it may circulate continuously between two apparatuses containing the other two phases (Figs. 1c and 1d).

The first technique (Fig. 1a), proposed and successfully applied by Li (*1–3*) for separation of hydrocarbons and other materials, is known as "separation through liquid membrane" due to its similarity with the conventional separation through polymer membranes.

In the second case (Fig. 1b), Phases A and B are sprayed in countercurrent or cocurrent into the intermediate phase C, occupying the operational part of a properly packed extraction column (*4*). In both cases the droplet coalescence is prevented by addition of surface-active agents.

The last case shown in Fig. 1(d) represents the arrangement, proposed by Hartland (*5*), where the intermediate phase C circulates between the corresponding stages of two parallel multistage extraction columns.

The efficiency of carrier-mediated extraction is a time-dependent function. More soluble components are transferred faster than the less soluble ones, but finally, after a sufficiently long time, when the equilibrium is reached, the concentrations of each component in both Phases A and B become equal and hence the separation efficiency becomes zero. If, however, Phases A and B are not of the same type or some special conditions exist as a chemical reaction with the formation of a solid phase or insoluble in C product, a very efficient "pumping" of some of the components during a finite time period may be obtained.

By modifying the properties of the intermediate phase, several components may be consecutively extracted from the initial mixture.

Since the separational efficiency is a time-dependent function, the development of its rate models and their study is an important step toward better understanding and practical application of this process.

In this study the first case only will be considered, and a mathematical model of the process when Li's technique is applied will be proposed.

MATHEMATICAL MODEL

Let us consider the following physical model: Phase A containing the transferable components is emulsified into intermediate Phase C in such a way that a stable, very fine emulsion with a mean droplet diameter, $d_A = 10^{-6}$ to 10^{-5} m, is formed. This emulsion is spread and kept dispersed into the third phase (the Solvent B) where the size of the emulsion globules is within the range of $d_e \approx 10^{-3}$ to 10^{-2} m. This situation is shown schematically in Fig. 2. The components are transferred from Phase A into the washing liquid B by two mechanisms—a diffusional and a mechanical one due to the slow but inevitable emulsion destruction. The transfer in the opposite direction, from Phase B to Phase A, is diffusional only. Assuming that component accumulation in Phase C is negligible compared with their amounts in the principal phases A and B, the first mechanism is described by

$$\frac{dQ'_{y,i}}{dt} = -\frac{dQ'_{x,i}}{dt} = K_{1,i}a_1\left(x_i - \frac{z_i}{m_{1,i}}\right) = K_{2,i}a_2\left(\frac{z_i}{m_{2,i}} - y_i\right) \tag{1}$$

where the overall mass transfer coefficients $K_{1,i}$ and $K_{2,i}$ are defined as

$$\frac{1}{K_{1,i}} = \frac{1}{K_{x,i}} + \frac{1}{m_{1,i}K_{z,i}}, \quad \frac{1}{K_{2,i}} = \frac{1}{m_{2,i}K_{z,i}} + \frac{1}{K_{y,i}}, \qquad i = 1, 2, \ldots, n \tag{2}$$

$K_{x,i}$, $K_{z,i}$, and $K_{y,i}$ are the phase mass transfer coefficients of *i*th component in the small droplets, intermediate phase, and washing solvent, respectively.

$m_{1,i}$ and $m_{2,i}$ are the distribution coefficients of transferable component

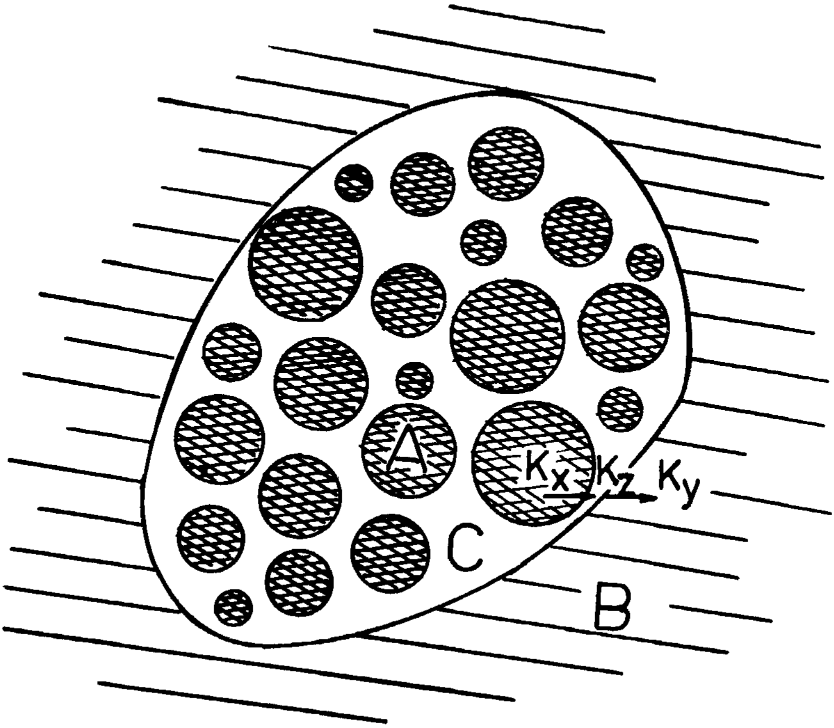

FIG. 2. Scheme of solute transfer from encapsulated Phase A into Phase B through the intermediate, "membrane" Phase C.

i defined as

$$m_{1,i} = \left(\frac{z_i}{x_i}\right)_{\text{equil}}, \qquad m_{2,i} = \left(\frac{z_i}{y_i}\right)_{\text{equil}}$$

The rate of material transfer due to the emulsion breakage is

$$\frac{dQ''_{y,i}}{dt} = \alpha x_i V_x \tag{3}$$

Adding the component balance equations,

$$V_x x_i + V_y y_i + V_z z_i = Q_i, \qquad i = 1, 2, \ldots, n \tag{4}$$

and the phase balance equations,

$$\sum_{i=1}^{n} x_i = 1, \qquad \sum_{i=1}^{n} y_i = 1, \qquad \sum_{i=1}^{n} z_i = 1 \tag{5}$$

we obtain the general form of the mathematical model for the case being considered. Introducing (2) into (1) and taking into account that

$$\frac{dQ_{y,i}}{dt} = \frac{dQ'_{y,i}}{dt} + \frac{dQ''_{y,i}}{dt} \tag{6}$$

the rate equation takes the form

$$\frac{dQ_{y,i}}{dt} = \frac{K_{x,i}K_{y,i}K_{z,i}a_1a_2(m_{1,i}x_i - m_{2,i}y_i)}{K_{x,i}a_1(K_{y,i} + m_{2,i}K_{z,i}) + K_{y,i}a_2(K_{x,i} + m_{1,i}K_{z,i})} + \alpha x_i V_x \tag{7}$$

Following some physical considerations, we are able to introduce the assumptions that

$$a_2 \ll a_1, \qquad m_{1,i} \approx m_{2,i} = m_i \ll 1,$$

$$V_z z_i \ll V_x x_i, \qquad K_{y,i} > K_{z,i} > K_{x,i}$$

and therefore Eqs. (7), (4), and (5) could be simplified to

$$\frac{dQ_{y,i}}{dt} = \frac{d(V_y y_i)}{dt} = K_{z,i}m_i a_2(x_i - y_i) + \alpha x_i V_x \tag{8}$$

$$V_x x_i + V_y y_i = Q_i, \qquad i = 1, 2, \ldots, n \tag{9}$$

$$\sum_{i=1}^{n} x_i = 1 \tag{10}$$

$$\sum_{i=1}^{n} y_i = 1 \tag{11}$$

with initial conditions

$$|V_y|_{t=0} = V_y^\circ, \qquad |y_i|_{t=0} = y_i^\circ \tag{12}$$

The process model consists of $2N + 2$ equations and contains $2N + 2$ unknowns—V_x, V_y, x_i, y_i—and therefore could be solved numerically.

In many particular cases, especially when water-in-oil-in-water dispersions are considered and the concentrations of the transferable components are sufficiently low, the change of the phase volumes is due to the emulsion break-up only, e.g.,

$$-\frac{dV_x}{dt} = \frac{dV_y}{dt} = \alpha V_x \tag{13}$$

which further simplifies the model.

Replacing the mole fractions x_i and y_i with their mass per volume analogies—the concentrations X_i and Y_i—Eq. (8) becomes

$$\frac{dY_i}{dt} = \frac{1}{V_Y}\left[\beta_i(X_i - Y_i) + \alpha X_i V_X - Y_i \frac{dV_Y}{dt}\right] \tag{14}$$

where

$$\beta_i = K_{z,i} m_i a_2$$

Eq. (9) is modified into:

$$X_i V_X + Y_i V_Y = G_i \tag{15}$$

Applying the initial conditions, analogous to Eq. (12),

$$|Y_i|_{t=0} = Y_i^\circ = 0, \qquad |V_Y|_{t=0} = V_Y^\circ \tag{16}$$

the solution of (14) is

$$Y_i = \frac{G_i}{V^\circ}\left[1 - \exp\left(\frac{\beta_i}{\alpha V_X^\circ}(1 - \exp\alpha t)\right)\left(\frac{V^\circ - V_X^\circ}{V^\circ \exp\alpha t - V_X^\circ}\right)^{(1+\beta_i/\alpha V^\circ)}\right] \tag{17}$$

Equation (17) presents in an implicit form the relationship between the component concentrations Y_i and the model parameters β_i and α. It follows from (17) that at $t = 0$, $Y_i = 0$, and $t \to \infty$, $Y_i = G_i/V^\circ = X_i$, e.g., the final concentrations of component in both phases become equal.

EVALUATION OF MODEL PARAMETERS α AND β_i

The model parameters α and β_i, controlling the separational efficiency, may be evaluated from the experimentally obtained curves $x_i = \varphi(t)$ or $y_i = f(t)$. Two examples of such evaluations will be shown here; separation of binary mixture of hydrocarbons applying the model equations (8) to (12), and separation of inorganic acids applying the solution (17).

Example 1

An equivolumetric mixture of toluene and heptene with an initial volume of 29 cm^3 was emulsified in 11 cm^3 water containing 2% Saponine. The emulsion was continuously washed by 50 cm^3 kerosene, measuring at the same time the concentrations of the toluene (Y_T), heptene (Y_H), and kerosene (Y_K) in this phase. Details on the experimental technique may be found elsewhere (*6*). The kinetics of the separational process is shown on Fig. 3 as a series of experimental points for Y_T and Y_H. The evaluation of the parameters α and β_i was performed by the simultaneous solution of

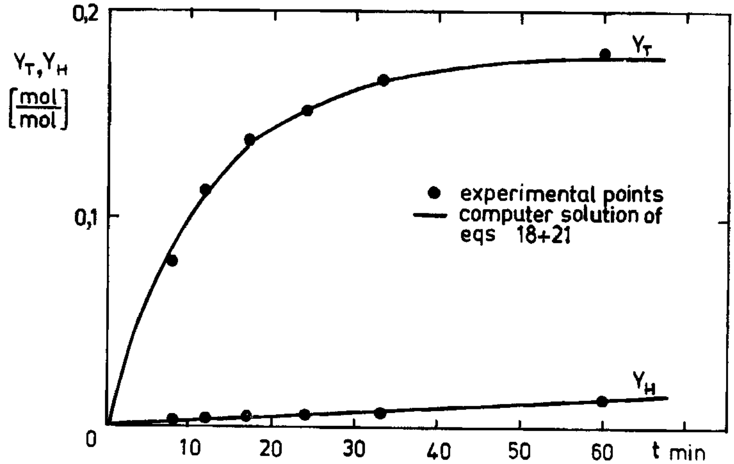

FIG. 3. Change of toluene and heptene concentrations in kerosene phase (Phase B). Transfer direction A → C → B.

the model equations, presented for this case in the following form:

$$\frac{dy_T}{dt} = \frac{1}{V_y}\left[\beta_T(V - V_y)\frac{Q_T - y_T Q}{Q - V_y} + \alpha(Q_T - y_T V_y) - y_T\frac{dV_y}{dt}\right] \quad (18)$$

$$\frac{dy_H}{dt} = \frac{1}{V_y}\left[\beta_H(V - V_y)\frac{Q_H - y_H Q}{Q - V_y} + \alpha(Q_H - y_H V_y) - y_H\frac{dV_y}{dt}\right] \quad (19)$$

$$\frac{dy_K}{dt} = \frac{1}{V_y}\left[-\beta_K(V - V_y)\frac{Q_K - y_K Q}{Q - V_y} + \alpha(Q_K - y_K V_y) - y_K\frac{dV_y}{dt}\right] \quad (20)$$

$$\frac{dV_y}{dt} = (V - V_y)\left[\beta_T\frac{Q_T - y_T Q}{Q - V_y} + \beta_H\frac{Q_H - y_H Q}{Q - V_y} + \beta_K\frac{Q_K - y_K Q}{Q - V_y}\right] + \alpha(Q - V_y) \quad (21)$$

The solution was performed on an analog computer MEDA 80T, using an adaptive iterational technique, equivalent to the trial-and-error method in numerical computation. The initial conductions were $y_T^\circ = 0$, $y_H^\circ = 0$, $y_K^\circ = 1$, and $V_y^\circ = 50$.

The best fit between the experimental and computed curves was searched by varying the model parameters α, β_T, β_H, and β_K incorporated in the analog scheme. The solutions obtained in this way are shown in Fig. 3, and they correspond to the following values: $\beta_T = 7.5 \times 10^{-4}\ \text{sec}^{-1}$, $\beta_H = 4.5 \times 10^{-6}\ \text{sec}^{-1}$, $\beta_K < 10^{-6}\ \text{sec}^{-1}$, and $\alpha = 5 \times 10^{-6}\ \text{sec}^{-1}$

As a result of the model simulation and its computer solution, it was found that the ratio $\beta_T/\beta_H = K_T m_T/K_H m_H$ is 167, which is close to the ratio of $m_T/m_H = 176$ according to the available data, which was discussed earlier (7).

Example 2

In the second example the simultaneous transfer of nitric hydrochloric and acetic acids to distilled water through a 1% solution of tri-iso-butylphosphate in carbon tetrachloride was performed. The stabilization of the emulsion of the acid solution in the organic phase was obtained by addition of 2% sorbitane monooleate (Span 80) emulsifier. The phase ratio of initial mixture to the organic intermediate phase was 1.5:1, and the ratio of the water phase in the emulsion to the washing phase was 1:20. The change of the acid concentrations in the washing liquid was measured during the experiment. Some details on the experimental technique are given elsewhere (7). The results of these experiments, presented as X_{HCl}, X_{HNO_3}, X_{CH_3COOH}, Y_{HCl}, Y_{HNO_3}, and Y_{CH_3COOH} evolution with time, are shown in Fig. 4.

Since the acid transfer does not provoke practical changes of phase volumes and no transfer of the third component occurs due to the fact that

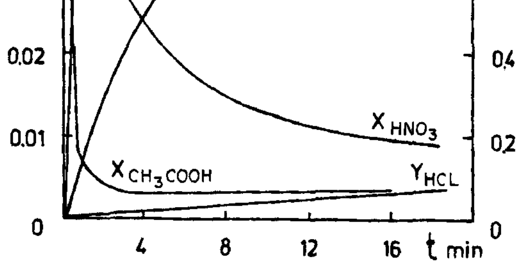

FIG. 4. Change of acid concentrations in Phase A (X_i) and Phase B (Y_i). Transfer direction A → C → B.

TABLE 1

No.	Transferred solute	α (sec^{-1})	β_i (m^{3}sec^{-1})	m_i
1	Acetic acid	2.5×10^{-5}	0.62	0.60
2	Nitric acid	2.5×10^{-5}	0.029	0.025
3	Hydrochloric acid	2.5×10^{-5}	0.0002	~0.0001

$X_{H_2O} \approx Y_{H_2O}$, the simplified model (14 and 16) and its analytical solution (17) could be applied.

The parameters α and β_i were found for each component separately by solving a set of two equations for the concentrations Y_i:$Y_{i,1}$ and $Y_{i,2}$ obtained after t_1 and t_2 seconds agitation of the dispersion. The results are presented in Table 1.

In the last column of Table 1 the experimentally obtained distribution coefficients

$$m_i = \frac{\text{equilibrium concentration in the organic phase}}{\text{equilibrium concentration in the aqueous phase}}$$

are given for initial acid concentration $x_i^\circ = 1$ gmole/liter. Comparing these values and "rate" coefficients β_i, it is obvious that the rate of transfer and therefore the separational efficiency is practically controlled by the component solubility in the intermediate phase C.

In order to prove the validity of the proposed model, another experiment was carried out. It introduced an insoluble in an organic phase dyestuff—methylene blue—in Phase A and measured its concentration in the washing liquid B colorimetrically. Since the coefficient β of this component is virtually zero ($m_d = 0$), the rate of emulsion destruction α could be directly measured. Proceeding in this manner, it was found that α is between 1.8 and $1.8 + 2.1 \times 10^{-5}$ sec^{-1}, a value quite close to the coefficient obtained by the above-mentioned evaluation of α and β_i.

CONCLUSION

The proposed and experimentally verified model of the carrier-mediated extraction represented by Eqs. (8) and (11) and its simplified version (Eqs. 14 and 15) enable an adequate description of the transfer kinetics in double emulsified liquid systems including partial emulsion destruction. Using these models, the optimum process efficiency could be predicted. The models can be used in further development of the process theory as well as in its practical application to mixture separation, which is to be the subject of our further studies.

SYMBOLS

a	contact area between A and C phases (m^2)
A	dispersed, internal phase
B	external, solvent phase
C	intermediate (carrier) phase
d_e	mean diameter of A-phase droplets (m)
G	amount of transferred solute (m^3 or kg)
K	coefficient of mass transfer (m/sec)
m	distribution coefficient (X_c/Z_a) equilibrium
Q	total amount of the component (m^3)
V	phase volume (m^3)
x	solute concentration in the A phase (m^3/m^3)
X	solute mass concentration in the A phase (kg/m^3)
y	solute concentration in the B phase (m^3/m^3)
Y	solute mass concentration in the B phase (kg/m^3)
z	solute concentration in the C phase (m^3/m^3)
α	rate coefficient of emulsion destruction (sec^{-1})
β	overall (diffusional) mass transfer coefficient (sec^{-1})

Subscripts

H	refers to heptene
i	refers to the *i*th component
K	refers to kerosene
T	refers to toluene
x	refers to the A phase
y	refers to the B phase
z	refers to the C phase

REFERENCES

1. N. N. Li, *AIChE J.*, *17*(2), 459 (1971).

2. N. N. Li, *Ind. Eng. Chem., Process Des. Dev.*, *10*(2), 215 (1971).

3. N. N. Li, and A. L. Shrier, ***Recent Developments in Separation Sciences***, Vol. 1, CRC Press, Cleveland, 1972.

4. L. Boyadzhiev, E. Bezenshek, and G. Kyuchoukov, ***Rep. IX 003.05/1975***, CLChE-BAS, 1975.

5. S. Hartland, *Trans. Inst. Chem. Eng.*, *45*(2), 90 (1967).
6. G. Casamatta, L. Boyadzhiev, and H. Angelino, *Chem. Eng. Sci.*, *29*, 2005 (1974).
7. L. Boyadzhiev and E. Bezenshek, *C. R. Acad. Bulg. Sci.*, *28*(4), 559 (1975).

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