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Prediction of Membrane Thickness in Hydrocarbon Permeation through Liquid Surfactant Membrane

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ABSTRACT

Separation of a mixture of toluene and heptane by means of a liquid surfactant membrane was studied. With the help of a membrane film model for mass transfer through a liquid membrane, the validity of the assumption made by Casamatta et al. in their study of hydrocarbon separation through a liquid water membrane was determined. This paper also proposes a novel method to determine the exact thickness of the liquid membrane through which permeation takes place, and thus eliminates any possibility of underprediction of the extraction rate as is made by other investigators considering the maximum membrane thickness.

INTRODUCTION

Separation of hydrocarbons by liquid membrane permeation (LMP) was first demonstrated by Li (1), and since then this highly selective membrane permeation process has become a challenging theme for the petroleum refinery industry as well as the chemical industry. Several other workers (2–9) have studied the fractionation of hydrocarbons by LMP and have suggested the enormous potential of this low cost separation technique in modern chemical engineering. The operation consists of interposing a

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water membrane stabilized by emulsification with a selected hydrophilic surfactant between a mixture of hydrocarbons to be separated and an organic solvent. The more soluble hydrocarbons in the feed-oil droplets permeate through the emulsion water membrane and leave behind the less permeable components. In short, transfer takes place between the emulsion drops and the solvent phase, and the interstitial membrane separates emulsified hydrocarbon droplets from each other and these droplets from the bulk hydrocarbon phase (Fig. 1a).

In the model developed by Casamatta et al. (5) this thickness was considered to be the maximum, assuming minimal close packing of emulsion droplets in the inner core of the emulsion drop. But in many situations of practical interest, where the resistance offered by the outer membrane layer is the controlling one, such assumptions may lead to an overprediction of actual membrane thickness and hence an error in calculation of the extraction rate. Therefore, in the present study a method is proposed for the correct evaluation of membrane thickness, and consequently the prediction of the actual extraction rate through the membrane.

In dealing with mass transfer into liquid membrane emulsion drops, it is advantageous to simplify the liquid membrane emulsion drop to the membrane film model as shown in Fig. 1b. In the membrane film model, all resistance to mass transfer is assumed to lie in a thin membrane film of constant thickness surrounding the emulsion drop. In many cases the

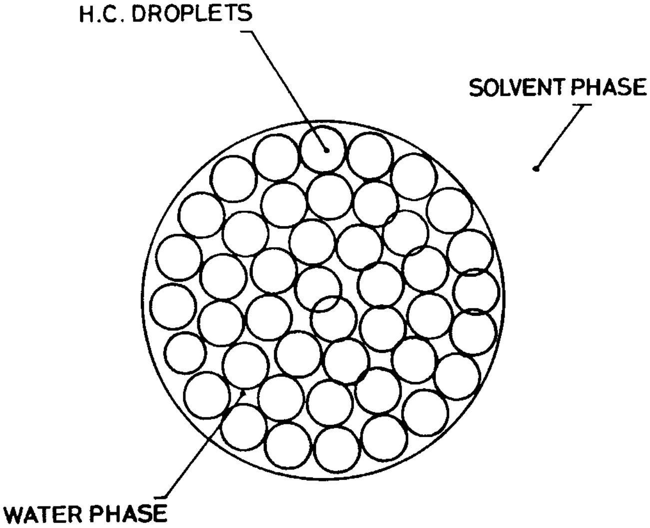

FIG. 1a Emulsion drop: homogeneous structure.

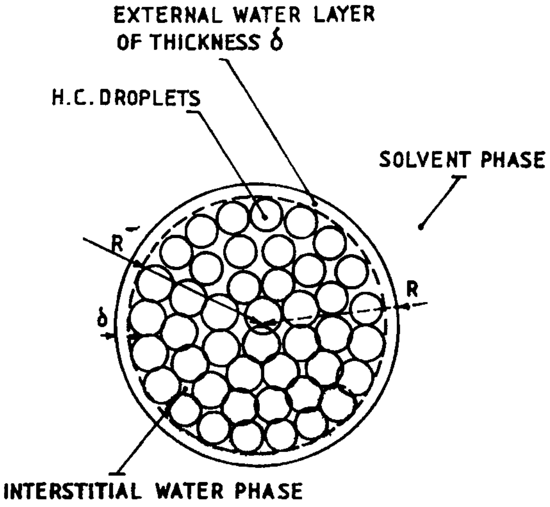

FIG. 1b Emulsion drop: flocculated structure.

membrane film model was found to be successful in explaining the transport processes (3–5) and it appears to be a reasonable physical approximation. In fact, the model has been found useful for rough process design and scale-up calculations.

Casamatta et al. (5), while developing a mathematical model for the case of mass transfer within an emulsion drop, explained the mechanism of forming such a spherical shell of constant thickness around the emulsion drop. They assumed that, due to a settling-out effect within the individual drops, regrouping of the hydrocarbon droplets occurs which makes them a closely packed structure within the drops. As a result, the excess aqueous phase is squeezed out from between these droplets and forms an external water layer surrounding the emulsion drop. The objective of the present study is to test the validity of the above assumption by carrying out experiments under two different operating conditions.

Some authors claimed that the stagnant liquid membrane film was the controlling resistance to mass transfer in their studies. Calculation of transfer rate thus largely depends on the correct evaluation of the thickness of this membrane film. But few attempts have been made to evaluate this membrane thickness. In fact, in the model developed by Cahn and Li (3), this membrane thickness was lumped into the permeation rate constant. These workers argued that they were forced to do so because it is difficult to measure the membrane thickness for a liquid membrane system. On the other hand, Matulevicius and Li (4) obtained good agreement between their experimental results and the model predictions through the judicious selection of this film thickness.

THEORY

It has been found that for a membrane film model, the concept of linear additivity of the mass transfer resistances can be applied. Accordingly, in the present work the following resistances to mass transfer are considered, just as by Casamatta et al. (5):

1. The resistance to mass transfer of the inner core of the emulsion drop which is governed by a mass transfer coefficient.
2. The resistance of the stagnant outer water membrane layer which is governed by another mass transfer coefficient that is related to its thickness.
3. The resistance to mass transfer from the liquid membrane interface to the continuous phase.

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

$$-\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 N_{ir}) = \frac{\partial C_i}{\partial t} \qquad (1)$$

Taking diffusivity of hydrocarbon through oil as 4 times larger than that through water, Casamatta et al. (5) obtained the following mass transfer coefficients for the three phases:

$$k_{i1} = \frac{4}{3}\frac{\pi^2}{R^-}\frac{\Phi}{m_i}D_{im} \qquad (2)$$

For a thin stagnant outer layer, that is, for $(R - R^-) = \delta \ll 1$:

$$k_{i2} = D_{im}/\delta \qquad (3)$$

and

$$k_{i3} = 4D_{im}/R \qquad (4)$$

The overall mass transfer coefficient for the emulsion drop was then written as

$$K = \frac{W_i}{4\pi R^2(C_{iR} - C_{iE})} = \frac{1}{\dfrac{1}{k_{i1}m_i} + \dfrac{1}{k_{i2}m_i} + \dfrac{1}{k_{i3}}} \qquad (5)$$

By combining Eqs. (2), (3), (4), and (5):

$$K = \frac{D_{im}m_i}{\delta}\left[\frac{1}{1 + \frac{3}{4\pi^2\Phi}\left(\frac{R}{\delta}\right)m_i + \frac{1}{4}\left(\frac{R}{\delta}\right)m_i}\right] \tag{6}$$

At infinite stirrer speed, $1/k_{i3} = 0$. Therefore

$$K = \frac{D_{im}m_i}{\delta}\left[\frac{1}{1 + \frac{3}{4\Phi\pi^2}\left(\frac{R}{\delta}\right)m_i}\right] \tag{7}$$

The symbols used above are defined in the Nomenclature Section.

EXPERIMENTAL

The inner oil phase of the emulsion consisted of a hydrocarbon feed of an equal volume mixture of toluene and heptane. The aqueous membrane solution was distilled water with 0.15% surfactant (sodium dodecyl sulfate). Experiments were carried out with two different ratios of the volume of aqueous surfactant solution to the volume of hydrocarbon feed: 0.6:1 and 0.7:1. Nitrobenzene was used as the solvent. The hydrocarbons were distilled before use. A high speed homogenizer was used as the emulsifier. A glass vessel of 80 mm diameter, 20 cm height, and fitted with four baffles was used as the extractor. The vessel was fitted with a stirrer having three sets of blades, each of 1.5 cm length and 1.1 cm width. The stirrer speed was measured by means of a digital hand tachometer. Samples drawn from the solvent phase were analyzed in a Hewlett-Packard 5840 AGC gas liquid chromatograph using a diethylene glycol succinate (DEGS) column. Membrane breakage was found to be negligible for both ratios.

RESULTS AND DISCUSSION

In the present study the values of diffusivity through the membrane phase, D_{im}, and the distribution coefficient, m_i, are taken from the work of Casamatta et al. (5) as 1×10^{-5} cm^2/s and 6×10^{-4}, respectively. The volume fractions of the dispersed phase, Φ, for the two ratios of aqueous surfactant solution to hydrocarbon feed of 0.6:1 and 0.7:1 are 0.62 and 0.59, respectively.

The rate equation describing the mass transfer in this study may be expressed as

$$\ln \frac{C_I}{C_I - C_{T,t}} = \frac{KA}{V} t \tag{8}$$

A plot of the left-hand side of Eq. (8) against time, *t*, will give a straight line (as shown in Figs. 2 and 3) with a slope of KA/V or Ka, where $a = A/V$. Thus, different values of the mass transfer capacity coefficient, Ka, are obtained for different stirrer speeds from these figures for the two volume ratios of aqueous surfactant solution to hydrocarbon feed.

Effect of Volume Ratio of Aqueous Surfactant Solution to Hydrocarbon Feed

Figures 2 and 3 show the variation of concentration of permeated toluene in the solvent phase with time at different stirrer speeds. As is seen

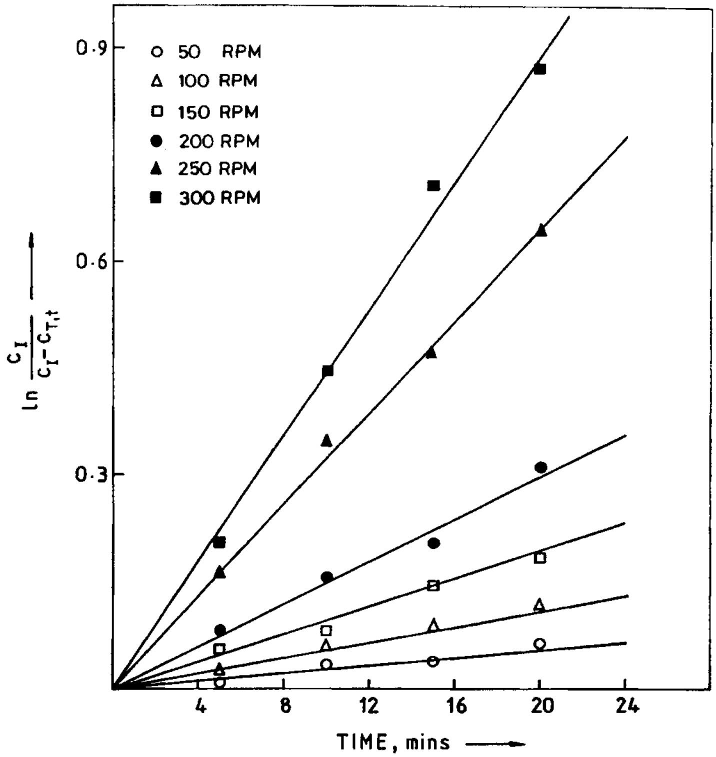

FIG. 2 Concentration of toluene vs time at different stirrer speeds for $\Phi = 0.62$.

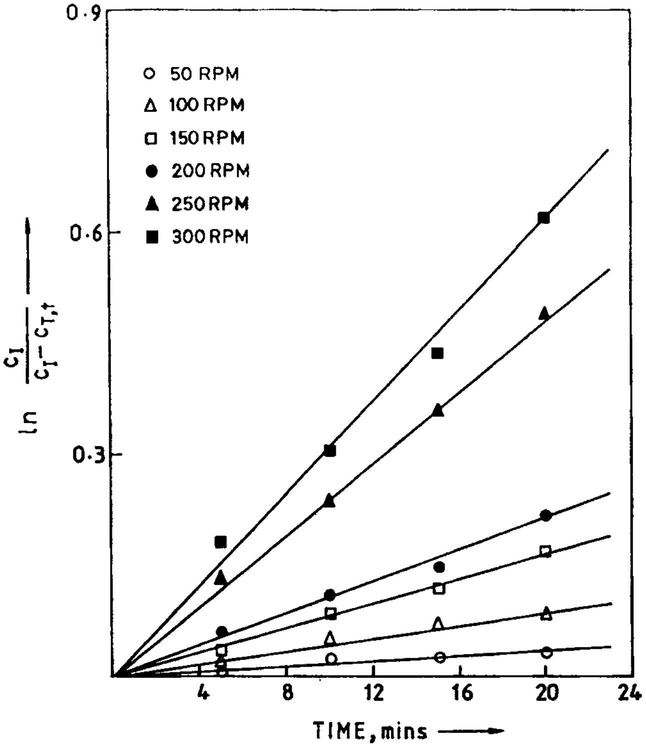

FIG. 3 Concentration of toluene vs time at different stirrer speeds for $\Phi = 0.59$.

from the figures, there is a steady increase in toluene concentration in the solvent phase with time in both cases. It is further seen that the rate of permeation of toluene is higher when the ratio of aqueous surfactant solution to hydrocarbon feed is 0.6:1 than when it is 0.7:1. This may be explained as due to an increase in the volume of the aqueous surfactant solution when the ratio is 0.7:1 as compared to 0.6:1. This excess aqueous phase, which normally settles out under gravity, spreads around the drop, which in turn increases the membrane thickness (Table 1) and offers greater resistance to mass transfer through the membrane. This observation clearly supports the assumption made by Casamatta et al. that when emulsion drops move through the solvent phase, the excess aqueous phase, which normally settles out under gravity, is squeezed out from between the droplets and spreads around the drops in an uniform manner to form a water layer around the emulsion drop. Thus it may be concluded that when the ratio is increased from 0.6:1 to 0.7:1, there is an increase

TABLE 1

Φ	K (cm/s) at infinite stirrer speed	Membrane thickness (μm), present study	Maximum membrane thickness (μm), Casamatta et al.'s method
0.62	1.89×10^{-5}	3.15	4.12
0.59	1.206×10^{-5}	4.86	5.0

in the volume of the aqueous surfactant solution which in turn increases the membrane thickness and offers greater resistance to mass transfer through the membrane.

Calculation of Liquid Membrane Thickness

Figure 4 shows plots of $1/KA$ vs stirrer speed for the above two cases. It is seen from Fig. 4 that the overall resistance decreases with an increase in stirrer speeds, and at higher stirrer speeds the resistance almost be-

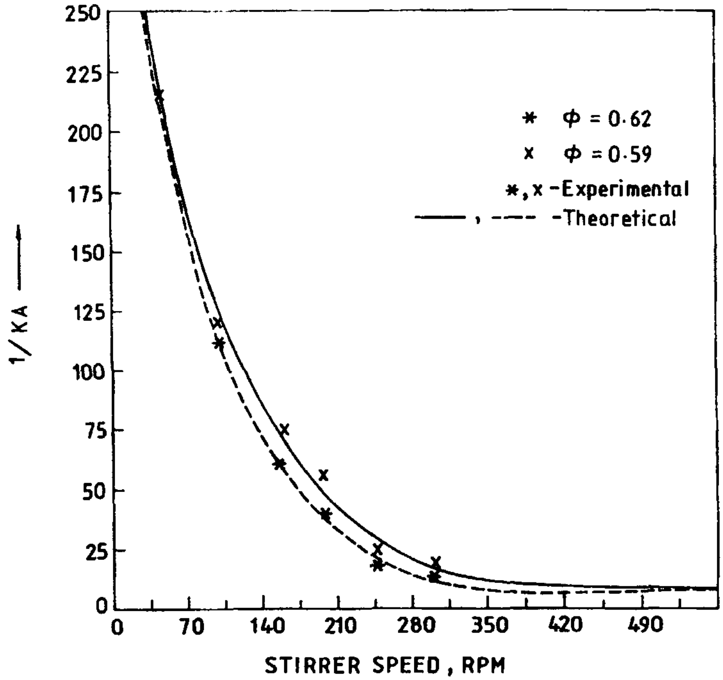

FIG. 4 Variation of permeation resistance with stirrer speed.

comes constant. Since the stirrer speed can influence only the continuous phase resistance, an equation is proposed based on the above observation in order to compare the theoretical results with the experimental ones:

$$R_o = C_1 e^{-MN} + R_\infty \tag{9}$$

Equation (9) was fitted through all experimental $1/KA$–N data by the least-squares method, and the following values were obtained from the curve-fitting results. For $\Phi = 0.62$:

$M = 0.0116$, $C_1 = 353.62$, and $R_\infty = 1.760313$

For $\Phi = 0.59$:

$M = 0.01025$, $C_1 = 349.35$, and $R_\infty = 2.769226$

The overall mass transfer coefficient (KA) at infinite stirrer speed is obtained from the inverse of R_∞ because at infinite stirrer speed the resistance offered by the continuous phase is equal to zero. Since it has often been reported in the literature that the emulsion drop size varies from 0.2 to 2 mm, the overall mass transfer coefficient (K) at infinite stirrer speed is determined by taking the lowest value of the drop size, i.e., 0.2 mm. The calculated values of the mass transfer coefficient at infinite stirrer speed for $\Phi = 0.62$ and for $\Phi = 0.59$ are given in Table 1. Values of the membrane film thickness, δ, are then obtained from Eq. (7) by substituting the mass transfer coefficient values at infinite stirrer speed. The calculated values of δ are 3.15×10^{-4} and 4.86×10^{-4} cm for $\Phi = 0.62$ and 0.59, respectively. These values agree well with the view of Li and Shrier (10) that the outer water layer membrane thickness is of the order of a few micrometers. Moreover, the corresponding values of the maximum membrane thicknesses were calculated from the equation proposed by Casamatta et al. and found to be 4.12 and 5.0 μm, respectively. Thus the thicknesses calculated by this method were also found to be within the range of the maximum value predicted. It is further interesting to note that the method proposed by Casamatta et al. (5) overpredicts the membrane thickness by as much as 25% in the first case and by 3% in the second case (Table 1).

CONCLUSION

A study of the separation of toluene from a mixture of toluene and heptane was made in order to develop a method for the determination of liquid membrane thickness. Experimental results from two different operating conditions justify Casamatta et al.'s view that excess water from the membrane settles out under gravity and is also pressed out from between the droplets to create a water layer around the emulsion drops. It is this water layer that offers the major resistance to mass transfer when emulsion drops move through the solvent. Membrane thickness was determined when the mass transfer resistance of the continuous phase is zero, and it was found to be in good agreement with the data given by Li and Shrier and also well within the maximum thickness predicted by the equation proposed by Casamatta et al.

NOMENCLATURE

C_i	concentration of Component *i* (mol/cm^3)
D_i	diffusivity (cm^2/s)
k_i	local mass transfer coefficient (cm/s)
K	overall mass transfer coefficient (cm/s)
m_i	distribution coefficient of Component *i* between the aqueous and the organic phase
N_i	molar flux of Component *i* (mol/s·cm^2)
R	radius of an emulsion drop (cm)
R^-	radius of the inner core of an emulsion drop (cm)
t	time (s)
V	total volume of the emulsion (cm^3)
W_i	molar rate of transfer of Component *i* (mol/s)
δ	thickness of the peripheral water layer
Φ	volumetric percentage of the dispersed phase of an emulsion
r	radial coordinate
A	mass transfer area through the emulsion droplets (cm^2)
C_{I}	initial concentration of toluene (the more permeating component) in the emulsion (mol/cm^3)
$C_{\mathrm{T,t}}$	concentration of toluene in the continuous phase after time *t* (mol/cm^3)
R_{o}	overall mass transfer resistance at any stirrer speed *N* (s/cm)
C_1	a constant in Eq. (9)
M	another constant in Eq. (9)
N	stirrer speed (rpm)
R_∞	mass transfer resistance at infinite stirrer speed (s/cm)

Subscripts

E	solvent phase (extract)
m	aqueous phase
R	hydrocarbon phase (raffinate)
r	radial

REFERENCES

1. N. N. Li, US Patent 3,410,794 (1968).
2. N. D. Shah and T. C. Owens, *Ind. Eng. Chem., Process Des. Dev.*, *11*, 58 (1972).
3. R. P. Cahn and N. N. Li, *J. Membr. Sci.*, *1*, 129 (1976).
4. E. S. Matulevicius and N. N. Li, *Sep. Purif. Methods*, *4*, 73 (1975).
5. G. Casamatta, C. Chavarie, and H. Angelino, *AIChE J.*, *24*, 945 (1978).
6. P. Alessi, L. Kikic, and M. Orlandini-Visalberghi, *Chem. Eng. J.*, *19*, 221 (1980).
7. W. Halwachs, E. Flaschel, and K. Schugerl, *J. Membr. Sci.*, *6*, 33 (1980).
8. M. Ulbrich, R. J. Marr, and J. Draxler, *Ibid.*, *59*, 189 (1991).
9. N. Garti and A. Kovacs, *Ibid.*, *56*, 239 (1991).
10. N. N. Li and A. L. Shrier, *Recent Developments in Separation Science*, Vol. 1, Chemical Rubber Co., Cleveland, Ohio, 1972, p. 163.

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