

MASS TRANSFER OF PHENOL THROUGH SUPPORTED LIQUID MEMBRANE

Sang Wook Park[†], Christiawaty Ferania Kaseger, Jin Bok Moon and Jong Hyun Kim*

Dept. of Chem. Eng., College of Eng., Pusan National University, Pusan 609-735, Korea

*Dept. of Chem. Eng., Dong Seo University, Pusan 616-010, Korea

(Received 10 April 1996 • accepted 4 October 1996)

Abstract – The separation of phenol from the aqueous solution was carried out at 25°C in a supported liquid membrane of batch type using benzene or dibenzo-18-crown-6 as carrier in the phenol-NaOH system. The mass transfer of phenol was investigated with a theoretical model based on the mass transfer with or without chemical reaction in the stripping side. Pseudo-first-order reaction type was used to measure overall and individual mass transfer coefficients of phenol. The influence of initial concentration of carrier on overall mass transfer coefficient was found to be more significant than those of agitation speed and initial concentrations of phenol and NaOH solutions. The numerical analysis of facilitated transport of phenol through liquid membrane gave a result that the chemical reversible reaction between phenol and carrier in the liquid membrane side was fallen into the region between fast and slow reaction with the tendency to be much closer to the slow reaction region.

Key words: Supported Liquid Membrane, Pseudo-first Order Reaction, Dibenzo-18-Crown-6, Facilitated Transport, Mass Transfer Coefficients

INTRODUCTION

Phenol and phenolic derivatives in the aqueous effluent from many chemical industries are usually recovered by means of liquid-liquid solvent extraction or adsorption using polymeric resins [Crook et al., 1975].

In view of selective separation and treating dilute solutions, a liquid membrane technique which can be made in two different forms namely, supported liquid membrane (SLM) and emulsion liquid membrane (ELM), become an attractive alternative to the solvent extraction because it comprise the processes of extraction, stripping and regeneration in a single step. Liquid membrane technique were widely applied to gas transport. Recently, metal ions separation has also received considerable interest in order to recover metal, as well as to control pollution. Finally, biotechnological applications and recovery of other products, such as acetic acid and phenols, have also been reported. An extensive review including industrial applications has been published [Noble et al., 1988].

The liquid membrane for the recovery of phenol uses a solubility difference of the phenol in an aqueous phase and an organic phase. Works on the recovery of phenol by emulsion liquid membrane (ELM) have been reported by several authors in which NaOH solutions is used as stripping solution for the phenol in an encapsulated form of W/O (water in oil) [Halwachs et al., 1980; Teramoto and Matsuyama, 1986; Noble et al., 1988]. Unfortunately, the stability of ELM is considered to be inferior for a long term operation due to the breakage of emulsions. This problem can be overcome by means of supported liquid membrane (SLM).

In the case of supported liquid membrane (SLM), an organic extractive phase is immobilized by capillary forces in the mi-

cro pores of a polymer membrane which separates a feed solution containing the phenol from the caustic stripping solution [Danesi, 1985; Prasad and Sirkar, 1988; Sengupta et al., 1988; Basu et al., 1988]. The first order reaction model based on the film theory is usually used to estimate the overall mass transfer coefficient of a solute when the concentration gradient of solute in the stripping side is neglected. On the other hand, in case that the concentration gradient of phenol in the stripping side was significant, the first order reaction form should be modified to be applicable to the system.

The mass transfer rate of a solute within the supported liquid membrane increases when an appropriate solvent with a high distribution coefficient to the solute is used, or when chemical reaction occurs at the interfaces between membrane side and feed side and/or between the membrane side and stripping side. Further enhancement can be accomplished by the addition of an active carrier into the liquid membrane which leads to a facilitated transport.

The facilitated transport process is a transport of solute through liquid membrane where an active carrier immobilized in liquid membrane reacts with the solute under interest, transport it across the film, and releases it at the other boundary. Those reversible reactions increase the flux of solute across the liquid membrane and enhance selectivity. There are several articles which describe facilitated transport in detail [Ward, 1970; Schultz et al., 1974; Smith et al., 1977; Goddard, 1977].

As described above, the observation on the recovery of phenol using liquid membrane were done by means of emulsion liquid membrane and no observation was done in supported liquid membrane. The aim of the present work are the development of kinetics model on facilitated transport of phenol separation in a flat-type SLM separator for phenol-benzene-H₂O, phenol-benzene-NaOH, phenol-benzene+DBC-H₂O and phenol-benzene+DBC-NaOH systems. The facilitated transport mechanism was

[†]To whom all correspondences should be addressed.

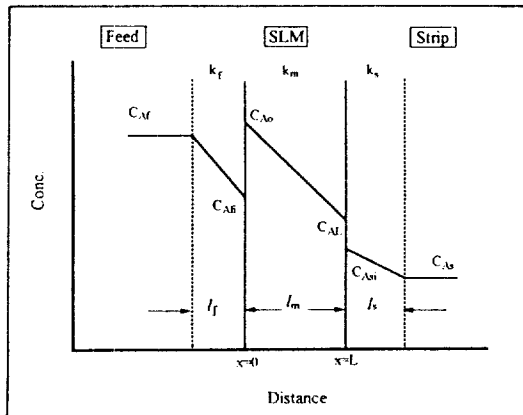


Fig. 1. Concentration profiles of phenol in the bulk solutions, aqueous boundary layers and SLM at steady state by film theory.

analyzed from the comparison of experimentally measured values of solute flux with the calculated values from the facilitated transport mechanism with the addition of carrier such as crown ether into the system.

THEORY

The schematic transport mechanism of phenol from an aqueous feed side to an aqueous stripping side through an organic phase in the microporous polymeric membrane support is shown in Fig. 1. At steady-state, the flux of phenol at each step of feed side, liquid membrane and stripping side can be expressed by the film theory as follows

$$N^o = K^o(C_{Af} - C_{As}) = k_f(C_{Af} - C_{Af,i}) = k_m(C_{A0} - C_{AL}) = k_s(C_{As,i} - C_{As}) \quad (1)$$

The distribution coefficient of phenol, E is defined as the ratio of concentration in the organic phase to that in the aqueous phase at equilibrium

$$E = \frac{\bar{C}_A}{C_A} \quad (2)$$

From Eq. (1) and Eq. (2), the relationship of overall and local mass transfer resistances can be rearranged to be

$$\frac{1}{K^o} = \frac{1}{k_f} + \frac{1}{k_m E} + \frac{1}{k_s} \quad (3)$$

If the agitation speed and diffusivity of phenol of both feed and stripping sides are equal, which leads to the assumption of an equal mass transfer coefficient between the two sides. Eq. (3) reduces as follows

$$\frac{1}{K^o} = \frac{2}{k_f} + \frac{1}{k_m E} \quad (4)$$

The differential mass balance of phenol can be expressed as follows

$$-\frac{V}{a} \frac{dC_{Af}}{dt} = \frac{V}{a} \frac{dC_{As}}{dt} = K^o(C_{Af} - C_{As}) \quad (5)$$

C_{Ao} can be expressed as the sum of phenol concentrations in the feed and stripping sides because the total volume of the organic extractant within the micropores of the polymeric membrane is extremely small, compared with those of aqueous phases in the feed and stripping sides. Taking this condition into consideration Eq. (5) is integrated with initial condition $t=0$, $C_{Af} = C_{Ao}$ as follows

$$\ln \left(2 \frac{C_{Af}}{C_{Ao}} - 1 \right) = -\frac{2K^o a}{V} t \quad (6)$$

On the other hand, when the stripping side solution is NaOH, the phenol is consumed by an instantaneous acid-base reaction which causes the mass transfer resistance of stripping side to be zero so that the Eq. (1) is simplified as follows

$$\frac{1}{K} = \frac{1}{k_f} + \frac{1}{k_m E} \quad (7)$$

Then, the integration result of Eq. (5) can be obtained as follows

$$\ln \left(\frac{C_{Af}}{C_{Ao}} \right) = -\frac{Ka}{V} t \quad (8)$$

In the facilitated transport, an active chemical carrier will selectively bind with a solute to form a carrier-solute complex at a feed side, and the complex transfers across a film, releases the solute at the stripping side, and then the carrier returns to the feed side boundary for further reaction repeatedly.

The reaction by the facilitated transport system in the liquid membrane film is postulated as follows



where A is the component being transported across the membrane, B the active chemical carrier, and AB the solute-carrier complex.

At steady-state, differential mass balance can be expressed for each component in one-dimensional transport as follows

$$D_A \frac{d^2 C_A}{dx^2} - k_1 C_A C_B + k_{-1} C_{AB} = 0 \quad (10)$$

$$D_B \frac{d^2 C_B}{dx^2} - k_1 C_A C_B + k_{-1} C_{AB} = 0 \quad (11)$$

$$D_{AB} \frac{d^2 C_{AB}}{dx^2} + k_1 C_A C_B - k_{-1} C_{AB} = 0 \quad (12)$$

Where it is assumed that each diffusion coefficient is a constant, the molecular weight of the solute is usually much smaller than that of the carrier so that the carrier and solute-carrier complex are roughly equivalent in size. This allows us to assume that $D_B = D_{AB}$ [Cussler, 1984]. We can state

$$C_T = C_B + C_{AB} \quad (13)$$

where C_T is the amount of carrier initially present in the system. The boundary conditions of Eqs. (10)-(12) are :

$$\text{at } x=0, C_A = C_{A0}, \quad \frac{dC_B}{dx} = \frac{dC_{AB}}{dx} = 0 \quad (14)$$

$$\text{at } x=L, C_A = C_{AL}, \quad \frac{dC_B}{dx} = \frac{dC_{AB}}{dx} = 0 \quad (15)$$

The boundary conditions on B and AB represent that the carrier and the carrier-solute complex are immiscible in the aqueous phase and constrained to stay within the liquid membrane system. The boundary conditions of A means that there is a constant source of A at one boundary and that A is removed from the opposite boundary so that the concentration of A at that point is a constant [Ward, 1970]. This was explained well in determining the interfacial concentrations of phenol at the feed and stripping side boundaries of the liquid membrane which can be calculated from Eq. (1) and Eq. (2) as follows

$$C_{A0} = \frac{k_f C_{Af} \left(1 + k_m C_{As} + \frac{k_m}{k_s} E \right)}{k_m + \frac{k_f}{E} + \frac{k_m k_f}{k_s}} \quad (16)$$

$$C_{AL} = \frac{k_m C_{A0} + \frac{k_f C_{As}}{E}}{k_m + \frac{k_s}{E}} \quad (17)$$

Since the phenol does not exist initially in the stripping side due to the acid-base reaction, the value of C_{AL} can be taken as zero, Eq. (16) can be rewritten in Eq. (18) as follows

$$C_{A0} = \frac{k_f C_{Af}}{k_m + \frac{k_f}{E}} \quad (18)$$

The total flux of A across the membrane is

$$N_{AT} = -D_A \frac{dC_A}{dx} - D_{AB} \frac{dC_{AB}}{dx} \quad (19)$$

The following dimensionless variables are defined

$$\varepsilon = \frac{D_{AB}}{k_{-1} L^2}, \quad R = \frac{k_1 C_{A0}}{k_{-1}}, \quad \alpha = \frac{D_{AB} C_T}{D_A C_{A0}}, \quad X = \frac{x}{L}$$

$$C_A^* = \frac{C_A}{C_{A0}}, \quad C_B^* = \frac{C_B}{C_T}, \quad C_{AB}^* = \frac{C_{AB}}{C_T}$$

To aid in characterizing the facilitation effect in this system, the above equations and boundary conditions are solved in dimensionless forms

$$\frac{d^2 C_A^*}{dX^2} + \frac{\alpha}{\varepsilon} (1 - C_B^*) - \frac{\alpha R}{\varepsilon} C_A^* C_B^* = 0 \quad (20)$$

$$\frac{d^2 C_B^*}{dX^2} + \frac{1}{\varepsilon} (1 - C_B^*) - \frac{R}{\varepsilon} C_A^* C_B^* = 0 \quad (21)$$

$$\frac{d^2 C_{AB}^*}{dX^2} + \frac{R}{\varepsilon} (C_A^* C_B^*) - \frac{1}{\varepsilon} C_{AB}^* = 0 \quad (22)$$

$$1 = C_B^* + C_{AB}^* \quad (23)$$

$$\text{at } X=0, C_A^* = 1, \quad \frac{dC_B^*}{dX} = \frac{dC_{AB}^*}{dX} = 0 \quad (24)$$

$$\text{at } X=1, C_A^* = \frac{C_{AL}}{C_{A0}}, \quad \frac{dC_B^*}{dX} = \frac{dC_{AB}^*}{dX} = 0 \quad (25)$$

where ε is the inverse of a Damköhler number which gives a measure of the relationship between diffusion and the reverse reaction rate. A small value of ε means a rapid reaction step and the system is diffusion-controlled. On the other hand, a large value of ε means a rapid diffusion and the system is reaction-controlled. R is a dimensionless equilibrium constant and α is a dimensionless variable directly proportional to the amount of carrier initially present in the system.

To measure the extent of the flux enhancement due to the reversible chemical complexation, a facilitated factor, F , is defined

$$F = \frac{N_{AT}}{N_{A0}} \quad (26)$$

where N_{A0} is the diffusional flux of A and N_{AT} is the diffusional flux of A accompanied by the chemical reaction. Therefore, F is a measure of the increased selectivity of the separation of A from a mixture. A large value of F does not necessarily imply a larger total flux. This facilitated factor can also be defined in terms of concentration gradients as follows

$$F = \frac{\left(-\frac{dC_A^*}{dX} \right)_{X=1, \alpha}}{\left(-\frac{dC_A^*}{dX} \right)_{X=1, \alpha=0}} \quad (27)$$

EXPERIMENTAL

1. Materials

Reagent grade phenol, benzene and dibenzo-18-Crown-6 were used as solute, organic extractant and carrier, respectively. Poly-tetrafluoroethylene (nominal thickness: 7×10^{-5} m, nominal area: 6.95×10^{-3} m², porosity: 61%, tortuosity: 2.18) was used as polymeric microporous membrane support.

2. Apparatus and Procedure

The flat-type membrane separator module shown in Fig. 2 was made of pyrex with inside diameter of 1×10^{-1} m and height of 3×10^{-2} m. The impregnation of organic extractant into the polymeric membrane support was carried out by immersing the support in organic extractant for 24 hr. After fixing the impregnated support at the center of the module, 1.85×10^{-4} m³ of aqueous phenol solution was put into the lower part of the module which was called as the feed side and the same volume of distilled water or aqueous NaOH solution was put into the upper part of the module called as the stripping side. The feed side was agitated by magnetic bar and the stripping side was agitated by an impeller connected to motor. The experiment was carried out under atmospheric circumstances and room temperature. The concentration of phenol and sodium phenolate were analysed by UV-visible spectrophotometry. From the measured concentration of phenol in the feed side, the mass transfer coefficients of the phenol was calculated, from which the enhancement factor for phenol flux by the carrier was ob-

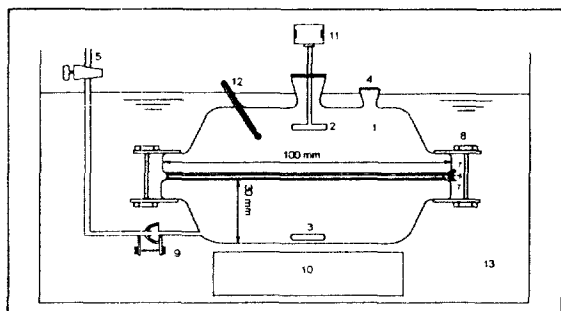


Fig. 2. Schematic diagram of batch-type experimental apparatus.

- | | |
|----------------------------|------------------------------|
| 1. Agitate vessel | 8. Joint |
| 2. Stirring impeller | 9. Ball joint |
| 3. Magnetic bar | 10. Immersion stirring plate |
| 4. Sample inlet | 11. Motor |
| 5. Aqueous phase injection | 12. Thermometer |
| 6. Membrane | 13. Water bath |
| 7. Teflon supporter | |

tained.

RESULTS AND DISCUSSION

1. Distribution Coefficient of Phenol

Distribution coefficient of phenol between water and benzene was obtained by using conventional equilibrium experimental method. The mass balance of phenol in terms of equilibrium concentration can be formulated as follows

$$C_{Ao} = C_A + \bar{C}_A \quad (28)$$

where, C_{Ao} is the initial concentration of phenol in aqueous phase or in benzene phase. Combining Eqs. (2) and (28) the following equation is obtained

$$C_{Ao} = C_A (1 + E) \quad (29)$$

The initial concentrations of phenol in aqueous and organic solution used to get E value were 0.028, 0.054, and 0.10 kmol/m³, respectively.

The measured equilibrium concentration of phenol in aqueous phase, C_A , was plotted against its initial concentration in Fig. 3, which shows that the experimental data agree to the Eq. (29) passing through origin. The value of distribution coefficient obtained was 2.08.

2. Mass Transfer Coefficients

The changes of phenol concentration in the systems with and without NaOH in the stripping side are shown in Fig. 4. The initial phenol concentration in feed solution was 0.054 kmol/m³ and the system was agitated at 500 rpm. The stripping side solutions were distilled water and 0.5 kmol/m³ NaOH, respectively. The change of phenol concentration with NaOH in the stripping side was faster than that of without NaOH. This is due to the instantaneous reaction between phenol and NaOH at the interface of the stripping side.

With reference to Eq. (6) and Eq. (8), the phenol concentration data in Fig. 4 were replotted in Fig. 5 in terms of

$\ln \left(2 \frac{C_{Af}}{C_o} - 1 \right)$ and $\ln \left(\frac{C_{Af}}{C_o} \right)$ vs. time, t . Linear relationship of

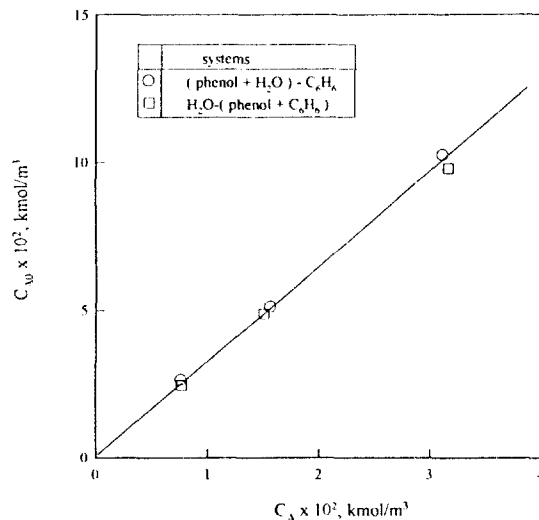


Fig. 3. The initial concentration of phenol in organic and aqueous phase, C_{Ao} as a function of its equilibrium concentration in aqueous phase, C_A for the distribution coefficient of phenol between H₂O and benzene.

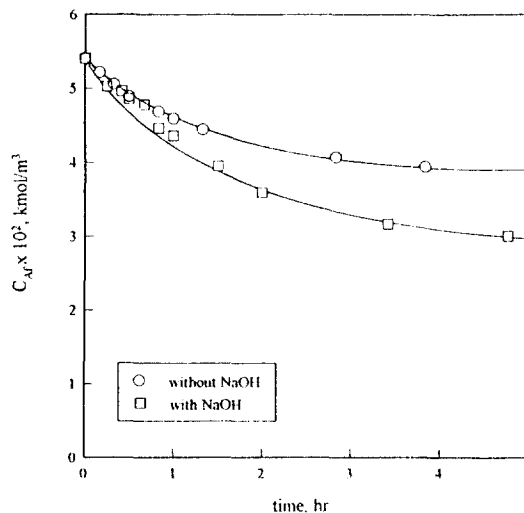


Fig. 4. Change of phenol concentration of feed side, C_{Af} in the systems with and without NaOH in the stripping side.

the experimental data through origin was observed. This means Eq. (6) and Eq. (8) express well the concentration change of phenol in feed side in the systems with and without NaOH, respectively. The gradients in Fig. 5 gave 9.35×10^{-6} m/s value of the overall mass transfer coefficient, K' , for phenol-benzene-water system and 1.33×10^{-5} m/s value of overall mass transfer coefficient, K , for phenol-benzene-NaOH system. Furthermore the local mass transfer coefficients of each side, k_f , k_m , k_s , where k_f is equal to k_s , were calculated by substituting the overall mass transfer coefficient of each system into Eqs. (4) and (7). The values of k_f , k_m and k_s were found to be 3.15×10^{-5} , 1.1×10^{-5} and 3.15×10^{-5} m/s respectively. The value of k_m was considered to be reasonable since it was close enough to the theoretical value of k_m , 1.22×10^{-5} m/s, calculated from film-theory as follows [Danckwerts, 1970]

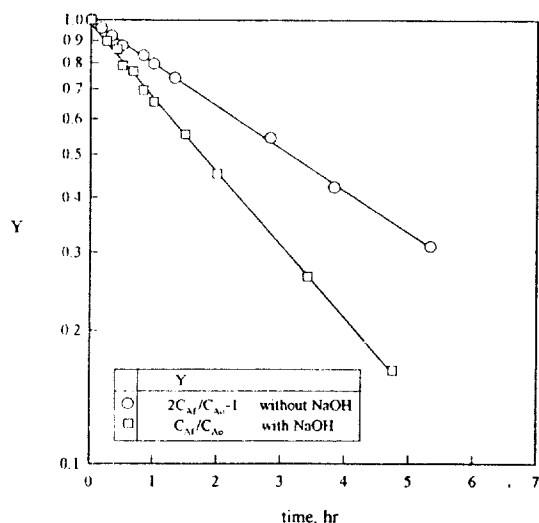


Fig. 5. Change of left hand side of Eq. (6) and (8) as a function of time.

$$k_m = \frac{D}{\delta_{ff}} \quad (30)$$

where D is the diffusivity of phenol in benzene calculated from Wilke-Chang equation, $1.86 \times 10^{-9} \text{ m}^2/\text{s}$ and δ_{ff} is the effective thickness of membrane, $1.526 \times 10^{-5} \text{ m}$ which was obtained from separate experiment to measure the tortuosity of the polymeric membrane [Park et al., 1994].

The characteristic of mass transfer coefficient of phenol in the liquid membrane side, k_m , was observed by varying the agitation speed of both feed and stripping sides simultaneously from 300 to 900 rpm. The values of k_m observed from the plot of the measured concentration of phenol in the feed side against stream time and use of Eq. (6) and (8) were plotted in Fig. 6. The change of agitation speed shows no influence on k_m . It can, therefore, be concluded that the mass transfer coefficient of phenol in the liquid membrane side was stable because it was irrelevant to the hydrodynamic variation of both feed and stripping sides.

The concentration gradient existence of phenol in the stripping side was confirmed by varying the agitation speed of the stripping side from 300 to 900 rpm while the agitation speed of feed side was fixed at 500 rpm in phenol-benzene-water system. The result was plotted in Fig. 7. The plot of Eq. (8) does not satisfy linear relationship for phenol-benzene-water system. The overall mass transfer coefficient can not, therefore, be obtained with these non-linearity. This result gives a conclusion that the concentration gradient of phenol in the stripping side can not be ignored and the change of phenol concentration is represented by the pseudo-first-order equation of Eq. (6) rather than by the first order reaction equation of Eq. (8).

The values of k , was plotted in Fig. 8 with the variation of agitation speed in the stripping side. This figure shows no significant influence of stripping side agitation speed on k .

The influences of initial concentrations of phenol in the feed side and NaOH in the stripping side on the overall mass transfer coefficient, K were studied by varying the concentration of phenol from 0.05 to 0.2 kmol/m^3 at a fixed concentration of

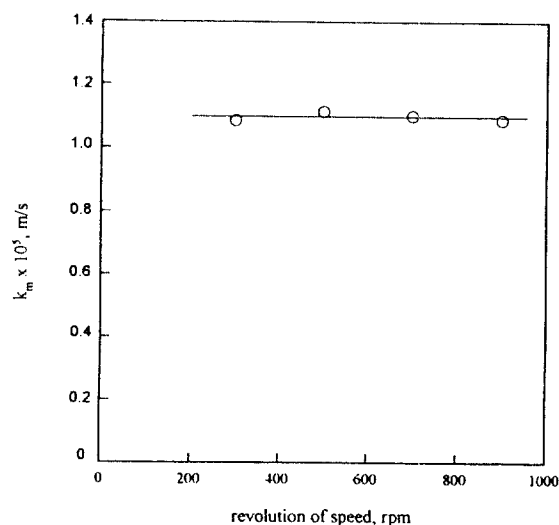


Fig. 6. Effect of revolution of speed on liquid membrane side mass transfer coefficient (k_m) in the system without NaOH in the stripping side.

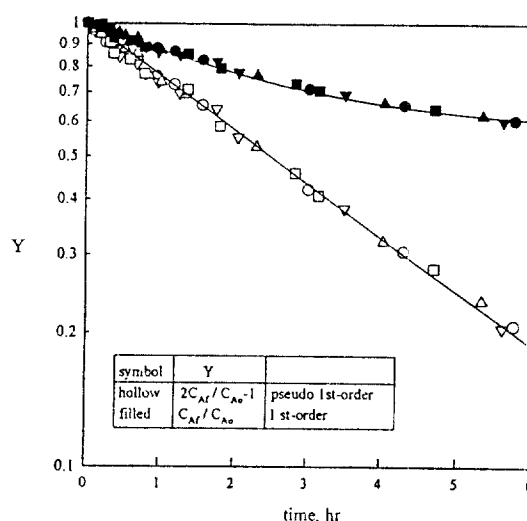


Fig. 7. Effect of revolution of speed on the plot of pseudo 1st-order and 1st-order reaction forms, Y as a function of time in the system without NaOH in the stripping side. (\square : 300, \circ : 500, \triangle : 700, ∇ : 900).

NaOH in the stripping side of $0.5 \text{ kmol}/\text{m}^3$ and NaOH from 0.25 to $1.0 \text{ kmol}/\text{m}^3$ at a fixed concentration of phenol in the feed side of $0.054 \text{ kmol}/\text{m}^3$. The result was plotted in Fig. 9 which also shows that no significant influences of phenol and NaOH concentrations on overall mass transfer coefficient.

Another alternative was used to increase the mass transfer coefficient of phenol, i.e. addition of crown ether, a cation catcher catalyst into liquid membrane side. The crown ether used in this study was a chemical reagent of dibenzo-18-Crown-6 (DBC). The influence of this substance was observed by carrying out an experiment in phenol-benzene+DBC-water and phenol-benzene+DBC-NaOH system with the initial concentration of phenol in the feed side, NaOH in the stripping side and DBC in the liquid membrane side at $0.054 \text{ kmol}/\text{m}^3$, $0.51 \text{ kmol}/\text{m}^3$ and $0.01 \text{ kmol}/\text{m}^3$, respectively. Fig. 10 shows that the con-

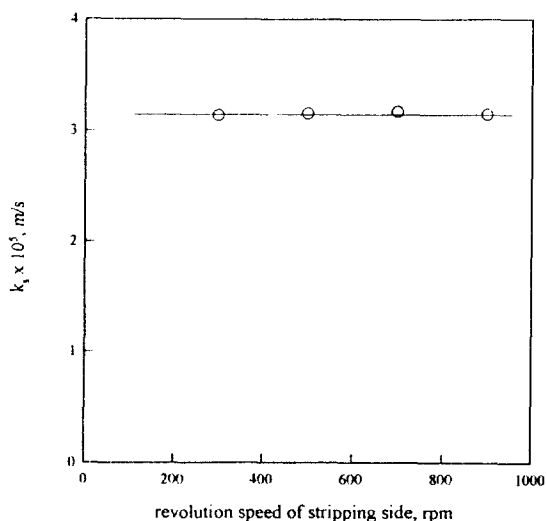


Fig. 8. Effect of revolution speed of stripping side on strip side mass transfer coefficient (k_s) in phenol-benzene- H_2O system.

centration of phenol in the feed side was decreased faster than those without the addition of DBC. The overall mass transfer coefficients of phenol-benzene+DBC-water and phenol-benzene+DBC-NaOH systems, K^o and K calculated from Fig. (10) were found to be 1.36×10^{-5} and 2.38×10^{-5} m/s, respectively. These values are higher than those obtained in phenol-benzene-water and phenol-benzene-NaOH systems, it means that the influence of DBC addition in the liquid membrane side is stronger than that of NaOH addition in the stripping side. The local mass transfer of phenol in the feed, liquid membrane and stripping sides were obtained from Eq. (4) and Eq. (7) with the same procedure as that in phenol-benzene-water and phenol-benzene-NaOH systems and their values were found to be 3.15×10^{-5} , 4.7×10^{-5} and 3.15×10^{-5} m/s, respectively. The values of k_f and k_r were equal to those without DBC while k_m was found to be four times higher than that obtained without DBC. It could be explained that phenol dissolved from the feed side into the liquid membrane side chemically reacted with DBC to produce a phenol-DBC complex, which diffused to the stripping side boundary to release phenol into the stripping side and DBC returned to the feed side boundary for further cycle of reaction as a carrier.

The influence of initial concentration of DBC in the liquid membrane side on k_m was studied by varying of the concentration of DBC from 0.001 to 0.015 kmol/m³ while the initial concentration of phenol in the feed side was fixed at 0.054 kmol/m³. The result plotted in Fig. 11 shows that the k_m was increased linearly as the concentration of DBC was increased according to the following empirical equation and its regression coefficient was 0.976

$$k_m = 3.5 \times 10^{-3} C_{\text{DBC}} + 1.15 \times 10^{-5} \quad (31)$$

The forward- and backward-reaction rate constants, and the physical properties such as diffusivities of A and AB and effective thickness of liquid membrane, and the experimental variables like concentrations of phenol and NaOH should be obtained in order to calculate the facilitated coefficient of phenol

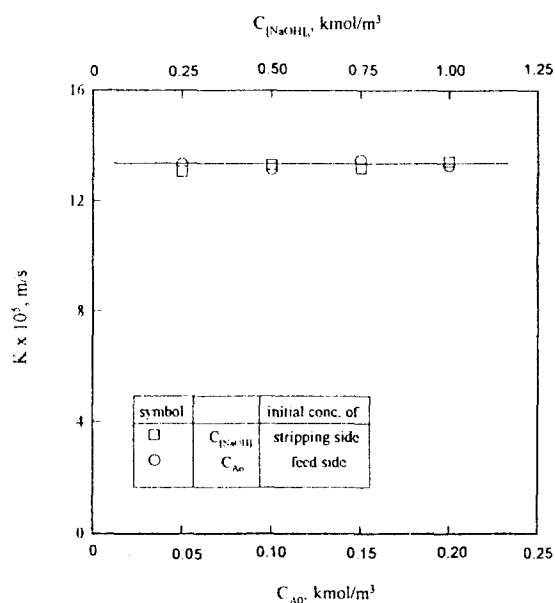


Fig. 9. Effect of initial concentration of phenol in feed side (C_{A0}) and NaOH ($C_{\text{NaOH}0}$) in stripping side on overall mass transfer coefficient (K) in the system with NaOH in stripping side.

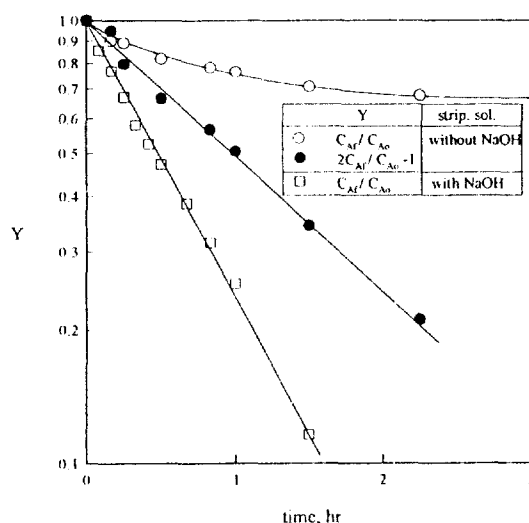


Fig. 10. Change of left hand side of Eq. (6) and Eq. (8) as a function of time in phenol-benzene+DBC- H_2O and phenol-benzene+DBC-NaOH systems. ($C_{A0}=0.054$ kmol/m³, $C_{\text{DBC}}=0.01$ kmol/m³).

in this system. The forward- and backward-reaction rate constants of the Eq. (9) can be obtained by assuming that the reaction between A and B was progressed stoichiometrically in which 1 mol of A reacted with 1 mol of B to produce 1 mol of AB. The following equation can be derived by conventional reaction kinetics and the assumption of stoichiometric reaction between phenol and DBC leads to a second order reaction

$$-\frac{dX_A}{dt} = k_1 C_{A0} (1 - X_A)^2 - k_{-1} X_A \quad (32)$$

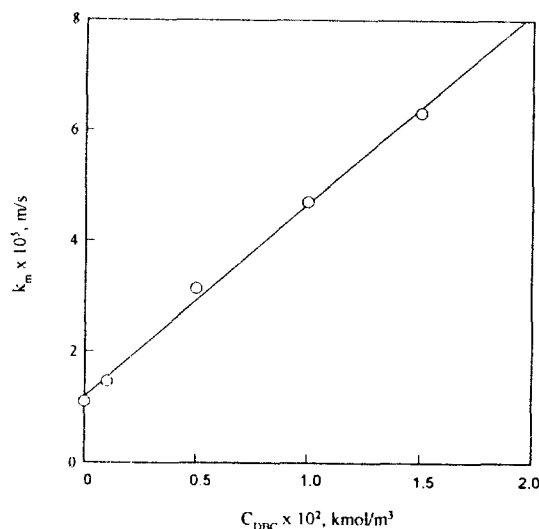


Fig. 11. Effect of carrier concentration on liquid membrane side mass transfer coefficient (k_m) for phenol-benzene+DBC- H_2O .

($C_{A0}=0.054$ kmol/ m^3).

Backward-reaction rate constant from the equilibrium condition can be written as follows:

$$k_{-1} = k_1 C_{A0} \frac{(1 - X_{Ae})^2}{X_{Ae}} \quad (33)$$

where

$$X_{Ae} = \frac{C_{A0} - C_{Ae}}{C_{A0}} \quad (34)$$

Defining K_c from Eq. (33) as follows

$$K_c = \frac{(1 - X_{Ae})^2}{X_{Ae}} = \frac{k_{-1}}{k_1 C_{A0}} \quad (35)$$

The following equation was derived with Eqs. (33), (34) and (35)

$$\ln \frac{[2 + K_c - \sqrt{4K_c + K_c^2}]X_A - 2}{[2 + K_c + \sqrt{4K_c + K_c^2}]X_A - 2} = k_1 C_{A0} \sqrt{4K_c + K_c^2} t \quad (36)$$

The stoichiometrical reaction of phenol and DBC in benzene solution was carried out in the round-bottom flask at 500 rpm and 25°C. The concentrations of unreacted phenol was measured as a function of reaction time using GC-FID chromatography. The value of K_c was obtained by substituting the equilibrium concentration of phenol, C_{Ae} into Eq. (34) and Eq. (35). Using these measured concentrations, the left-hand side of Eq. (36) was plotted as a function of time as shown in Fig. 12. The forward- and backward-reaction rate constants were obtained from the slope of the straight line in the Fig. 12 and the value of equilibrium conversion.

3. Physical Properties

Diffusivities of A and AB, D_A and D_{AB} were calculated from Wilke-Chang equation. The physical properties and experimental variables in phenol-benzene+DBC-NaOH system are shown in Table 1.

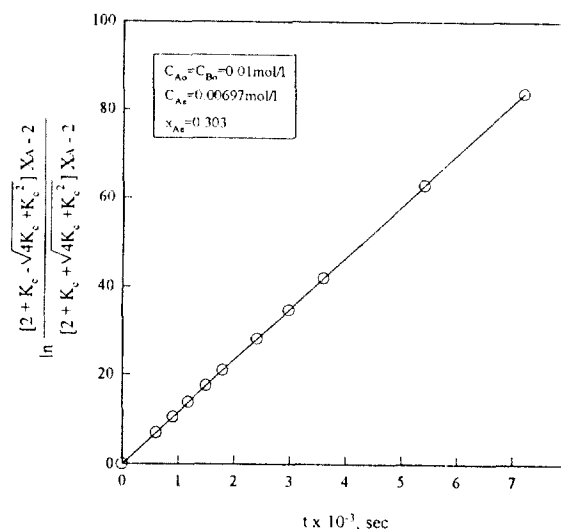


Fig. 12. Calculation result of k_1 and k_{-1} obtained from equilibria condition of phenol-DBC in benzene solution.

Table 1. Physical properties and experimental variables in phenol-benzene+DBC-NaOH system

Forward-reaction rate constant (k_1) obtained from experimental data plotted in Fig. 12:	1318.71 m ³ /kmol·sec
Backward-reaction rate constant (k_{-1}) obtained from experimental data plotted in Fig. 12:	0.341 s ⁻¹
Effective thickness of polymeric membrane (L):	1.526×10^{-2} m
Diffusivity of phenol in benzene (D_A):	1.862×10^{-5} m ² /s
Diffusivity of DBC in benzene (D_{AB}):	7.994×10^{-6} m ² /s
Initial concentration range of phenol in water:	0.05-0.2 kmol/m ³
Initial concentration range of DBC in benzene:	0.001-0.015 kmol/m ³
Initial concentration range of NaOH in water:	0.25-1.0 kmol/m ³

4. Facilitated Factor

Discussion on the overall and local mass transfer coefficients of phenol in phenol-benzene-water and phenol-benzene-NaOH systems with or without the addition of DBC gave a conclusion that the addition of DBC was more significant in increasing the mass transfer coefficient of phenol through liquid membrane than that without DBC. The phenol-benzene+DBC-water is, therefore, chosen for the numerical discussion of phenol transport.

The calculated value of F was obtained by finite difference method using the dimensionless Eq. (20)-(23) with the values of L , C_{A0} , k_1 , k_{-1} , D_A and D_{AB} . The experimental value of F was obtained from the ratio of mass transfer coefficient of phenol in the liquid membrane with DBC to that without DBC by changing the initial concentration of DBC from 0 to 0.015 mol/L. The result was plotted in Fig. 13. This figure shows that the experimental and calculated values of F vs. initial concentration of DBC are mostly equal to each other. It means that the analysis of facilitated transport of phenol in this system is appropriate.

Further, the concentration profile of each component inside the liquid membrane can easily be calculated in the same manner and the profile was plotted in Fig. 14. This figure shows that phenol and phenol-DBC complex are more concentrated at

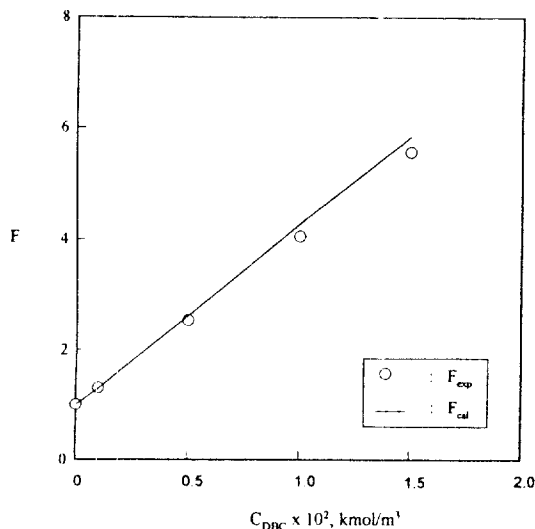


Fig. 13. Effect of carrier concentration on facilitated factor (F).

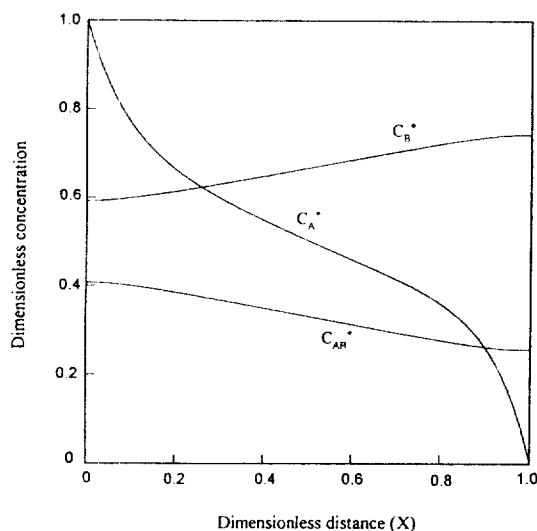


Fig. 14. Dimensionless concentration profile inside the SLM.

the feed side boundary while DBC concentration is higher at the stripping side boundary than at the feed side boundary. This is agreed with the model of reversible reaction between A and B.

Mass transfer system which is accompanied by chemical reaction are usually classified according to their limiting-steps as very fast and very slow reactions. In this study the system was also analysed to find the most appropriate reaction region.

Two kinds of assumption are used here. The first one is that the reaction (9) is sufficiently fast so that reacting species are present in equilibrium concentrations. In this case, it is useful to solve Eqs. (10)-(12) by adding Eqs. (10) and (12) to get the flux of A since the reaction terms as follows.

$$D_A \frac{d^2 C_A}{dx^2} + D_{AB} \frac{d^2 C_{AB}}{dx^2} = 0 \quad (37)$$

The solution of Eq. (37) is

$$D_A C_A + D_{AB} C_{AB} = a_1 x + a_2 \quad (38)$$

where a_1 and a_2 are constants.

The equilibrium condition leads to following equations.

$$C_{Be} + C_{ABe} = C_T \quad (39)$$

$$C_{ABe} = \frac{k_1 C_{Ac} C_T}{k_1 C_{Ac} + k_2} \quad (40)$$

The total flux of A is

$$N_A^T = -D_A \frac{dC_A}{dx} - D_{AB} \frac{dC_{AB}}{dx} \quad (41)$$

Eq. (41) is valid at all points in the film, and it is seen from Eq. (38) that

$$N_A^T = -a_1 \quad (42)$$

Applying the condition of $D_B = D_{AB}$ which leads to Eq. (13), the final expression for the total flux of A is

$$N_A^T = \frac{D_A}{L} (C_{Ao} - C_{AL}) + \frac{D_{AB} K_{eq} C_T (C_{Ao} - C_{AL})}{L(1 + K_{eq} C_{Ao})(1 + K_{eq} C_{AL})} \quad (43)$$

$$\text{where } K_{eq} = \frac{k_1}{k_2}$$

And the facilitated factor, F, for fast reaction assumption case is

$$F = 1 + \frac{D_{AB}}{D_A} \frac{K_{eq} C_T}{(1 + K_{eq} C_{Ao})(1 + K_{eq} C_{AL})} \quad (44)$$

The other assumption is that the reaction (9) is sufficiently slow that the concentration of B and AB are essentially constant through the film. In this case, Eq. (10) can be solved with the result

$$C_A = \frac{B_1}{K_1} \sinh(\sqrt{K_3} x) + \frac{B_2}{K_1} \cosh(\sqrt{K_3} x) + \frac{K_2}{K_1} \quad (45)$$

where the relationship of the symbols used in Eq. (45) are as follows:

$$\bar{C}_{AB} = \frac{k_1 C_T (C_{AL} + C_{Ao})}{2k_{-1} + k_1 (C_{AL} + C_{Ao})}$$

$$\bar{C}_B = C_T - \bar{C}_{AB}$$

$$K_1 = k_1 \bar{C}_B$$

$$K_2 = k_{-1} \bar{C}_{AB}$$

$$K_3 = \frac{K_1}{D_A}$$

$$B_1 = \frac{K_1 C_{AL} - K_2 - B_2 \cosh \sqrt{K_3} L}{\sinh \sqrt{K_3} L}$$

$$B_2 = K_1 C_{Ao} - K_2$$

The useful relationship to calculate C_A is as follows:

$$\left. \frac{dC_A}{dx} \right|_{x=L} = \frac{B_1}{K_1} \sqrt{K_3} \cosh(\sqrt{K_3} L) + \frac{B_2}{K_1} \sqrt{K_3} \sinh(\sqrt{K_3} L) \quad (46)$$

The expression for total flux of A is

$$N_A^T \Big|_{x=L} = -D_A \left[\frac{B_1}{K_1} \sqrt{K_3} \cosh(\sqrt{K_3} L) + \frac{B_2}{K_1} \sqrt{K_3} \sinh(\sqrt{K_3} L) \right] \quad (47)$$

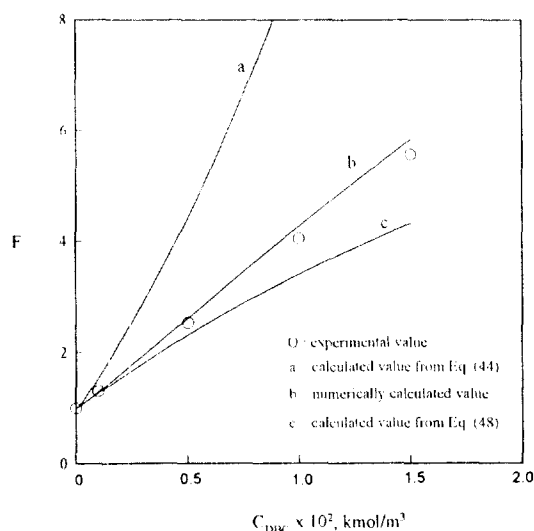


Fig. 15. Effect of carrier concentration on facilitated factor (F) according to reaction region.

And the facilitated factor, F , for slow reaction assumption case is

$$F = \frac{\left[\frac{B_1}{K_1} \sqrt{K_3} \cosh(\sqrt{K_3} L) + \frac{B_2}{K_1} \sqrt{K_3} \sinh(\sqrt{K_3} L) \right]}{\frac{(C_{A0} - C_{AL})}{L}} \quad (48)$$

The calculated facilitated factor for each case was plotted in Fig. 15, giving a conclusion that the system under interest can be classified into the region between fast and slow reaction with the tendency to be more closer to the slow reaction region.

CONCLUSION

It is possible to carry out the separation-concentration of aqueous phenol in agitated-batch liquid membrane separator at 25°C using microporous polymeric polytetrafluoroethylene membrane as liquid membrane support. The experimental results showed that the pseudo-first order reaction form based on film theory was applicable to the system without NaOH in the stripping side. It was also observed that the influence of dibenzo-18-Crown-6, DBC addition on mass transfer coefficient of phenol was more significant than that without DBC.

The numerical analysis of facilitated transport of phenol through liquid membrane due to the addition of DBC in phenol-benzene- H_2O system gave a result that the system under interest was fallen into the region between fast and slow reaction with the tendency to be closer to the slow reaction region.

NOMENCLATURE

- A : phenol
 a : membrane area [m^2]
 B : dibenzo-18-Crown-6 (DBC)
 AB : phenol-DBC complex
 C : concentration [$kmol/m^3$]

- C_{A0} : initial concentration of phenol [$kmol/m^3$]
 C_{A0} : phenol concentration at $x=0$ [$kmol/m^3$]
 C_{Ae} : equilibrium concentration of phenol in the reaction between phenol and DBC [$kmol/m^3$]
 C_{AL} : phenol concentration at $x=L$ [$kmol/m^3$]
 C_A^* : dimensionless concentration of phenol
 C_B^* : dimensionless concentration of DBC
 C_{AB}^* : dimensionless concentration of phenol-DBC complex
 D : diffusivity [m^2/s]
 E : distribution coefficient,
 F : facilitated factor, as defined in Eq. (26)
 R : dimensionless variable
 K : overall mass transfer coefficient with chemical reaction [m/s]
 K^o : overall mass transfer coefficient without chemical reaction [m/s]
 K_c : constant, as defined in Eq. (35)
 k : local (individual) mass transfer coefficient, m/s
 k_1 : forward reaction rate constant [$m^3/kmol \cdot s$]
 k_{-1} : backward reaction rate constant [s^{-1}]
 L : liquid membrane thickness [m]
 N : mass transfer rate [$kmol/m^2 \cdot s$]
 N_{A0} : flux of phenol through liquid membrane without enhancement [$kmol/m^2 \cdot s$]
 N_{A7} : flux of phenol through liquid membrane with enhancement [$kmol/m^2 \cdot s$]
 t : time [s]
 V : volume of cell [m^3]
 X : dimensionless thickness
 X_A : conversion of phenol
 X_{Ae} : conversion of phenol (A) at equilibrium

Greek Letters

- α : dimensionless variable
 δ : membrane thickness [m]
 ϵ : inverse Damköhler number
 τ : tortuosity

Superscripts

- eff : effective
 - : organic phase

Subscripts

- f : feed side
 L : stripping side boundary ($x=L$)
 m : membrane side
 i : interface
 o : initial
 0 : feed side boundary ($x=0$)
 s : stripping side
 T : total

REFERENCES

- Basu, R., Prasad, R. and Sirkar, K. K., "Non Dispersive Membrane Solvent Back Extraction of Phenol", *AIChE J.*, **36**, 450 (1990).
 Crook, E. H., McDonnel, R. P. and McNulty J. T., "Removal

- and Recovery of Phenols from Industrial Waste Effluents with Amberlite XAD Polymeric Adsorbent", *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 113 (1975).
- Cussler, E. L., "Diffusion: Mass Transfer in Fluid Systems", Cambridge Univ. Press, p. 389 (1984).
- Danckwerts, P. V., "Gas-Liquid Reactions", Eq. (5-3), Mc-Graw-Hill Book Co., 98 (1970).
- Danesi, P. R., "Separation of Metal Species by Supported Liquid Membranes", *Sep. Sci. Technol.*, **19**, 857 (1985).
- Goddard, J. D., "Further Application of Carrier-Mediated Transport Theory. Survey", *Chem. Eng. Sci.*, **32**, 795 (1977).
- Halwachs, W., Flaschel, E. and Schugerl, K., "Liquid Membrane Transport-A Highly Selective Separation Process for Organic Solutes", *J. Mem. Sci.*, **6**, 33 (1980).
- Noble, R. D., Way, J. D. and Bunge, A. L., "Liquid Membranes", *Ion Exch. Solvent. Extr.*, **10**, 63 (1988).
- Park, S. W., Moon, J. B., Jung, Y. H., Park, D. W. and Shin, J. H., "Alkaline Hydrolysis of n-Butyl Acetate with Aliquat 336 in a Membrane Reactor-II. Experimental Study", *HWAHAK KONGHAK*, **32**(2), 233 (1994).
- Prasad, R. and Sirkar, K. K., "Dispersion-free Solvent Extraction with Microporous Hollow-fiber Modules", *AIChE J.*, **34**, 177 (1988).
- Schultz, J. S., Goddard, J. D. and Suchdeo, S. R., "Facilitated Diffusion via Carrier-Mediated Diffusion in Membranes, Part I. Mechanistic Aspects, Experimental Systems and Characteristic Regimes", *AIChE J.*, **20**, 417 (1974).
- Schultz, J. S., Goddard, J. D. and Suchdeo, S. R., "Facilitated Diffusion via Carrier-Mediated Diffusion in Membranes, Part II. Mathematical Aspects and Analysis", *AIChE J.*, **20**, 625 (1974).
- Sengupta, A., Basu, R. and Sirkar, K. K., "Separation of Solutes from Aqueous Solutions by Contained Liquid Membranes", *AIChE J.*, **34**, 1698 (1988).
- Smith, D. R., Lander, R. J. and Quinn, J. A., "Carrier-Mediated Transport in Synthetic Membranes", *Recent Dev. Sep. Sci.*, **3**, 225 (1977).
- Teramoto, M. and Matsuyama, H., "Effect of Facilitated Diffusion in Internal Aqueous Droplets on Effective Diffusivity and Extraction Rate of Phenol in Emulsion Liquid Membranes", *J. Chem. Eng. Japan*, **19**, 469 (1986).
- Ward, W. J., III., "Analytical and Experimental Studies of Facilitated Transport", *AIChE J.*, **16**, 405 (1970).