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KINETIC STUDIES ON ORGANIC ACID EXTRACTION BY A SUPPORTED LIQUID MEMBRANE USING FUNCTIONALIZED POLYORGANOSILOXANES AS MOBILE AND FIXED-SITE CARRIERS

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ABSTRACT

A comprehensive model previously developed, which describes the kinetics and transport mechanism of a weak organic acid derivative through an integrated solvent-carrier supported liquid membrane (SLM), was used for the analysis of l-lactic acid ethyl ester and phenol transport by the SLM system through the use of functionalized polyorganosiloxanes as mobile and fixed site carriers. The model was verified with the transport experimental data of 2 organic acids. The acid transport parameters, which include the product of solute partition coefficient and diffusion coefficient (K_pD_s), the equilibrium extraction constant (K_{ex}), and the sum of effective diffusivity of the solute-carrier complex due to both mobile and jumping carrier mechanisms ($D_m + D_j$), was determined. Excellent agreement is achieved between predicted and experimental data in most of the

studies. Furthermore, the values of the effective diffusion coefficients ($D_m + D_j$), determined from experiments (curve-fitting), are in close agreement with the estimated values derived through the use of the Wilke-Chang and Lusis-Ratcliff correlations, and the values were also consistent in their orders of magnitude with the effective diffusion coefficients reported in the literature for various other substrates that were analyzed in similar systems.

Key Words: Effective diffusion coefficient; Supported liquid membrane; Functionalized polyorganosiloxane; Mobile and fixed-site carrier mechanisms; Phenol and l-lactic acid ethyl ester facilitated transport

INTRODUCTION

The chemical industry produces a large quantity of aqueous effluent that contains dissolved organic chemicals. Drinking and groundwater are vulnerable to contamination by these dissolved organic and volatile chemicals; aromatics and other dilute organics are of particular concern. Because of considerable pressure to reduce environmental pollution, the permissible levels of volatile organic compounds allowable within discharged water have been dramatically lowered. These requirements make the development of cheap, efficient recovery processes a priority. Because phenol and phenolic derivatives are highly toxic and resistant to biological treatment their removal from industrial and municipal wastewater is an approach to protect the environment from pollutants. Although phenols are exhausted from coke and petroleum industries and removed by various methods, they are often contained in water because of their high solubility in it. However, phenols are important starting materials for the production of phenolic resins, dyes, and antiseptics. Because phenolic-based products are inexpensive, the cost for the recovery of phenols must be cheap.

Lactic acid and its derivatives, such as l-lactic acid ethyl esters, are useful commodities with a myriad of uses ranging from acidulants and preservatives in the food industries to biodegradable sutures for medical applications (1). Although synthetic routes can be used to produce lactic acid and its derivatives, half of the world's requirement for lactic acid is fulfilled by fermentations (1–2). Such fermentations (biotransformations) are usually carried out in the aqueous phase, presenting a number of separation problems that are difficult and/or expensive to overcome. These problems arise because of low reactant and product concentrations, the presence of nutrients and extraneous salts, formation of metabolic products other than the desired compound, biomass or cell fragments in the aqueous phase.

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The separation/removal of phenol and phenolic derivatives from industrial waste effluents has been accomplished mainly through liquid solvent extraction and adsorption on polymeric resins (3–6). Other common techniques that have been used for product recovery (in systems such as the one described above) include ion exchange, affinity adsorption, and other forms of chromatography and conventional liquid membrane (CLM) techniques (1–3,7–13). With the exception of liquid membrane methods and affinity adsorption chromatography, all the existing techniques are only effective for components of significantly differing physical properties and when high selectivities are not required (7). Problems associated with fouling, capacity, regeneration, and nonspecific adsorption of components from the aqueous phase frequently beset affinity adsorption chromatography, and in the case of solvent extraction, inflammability and toxicity of the solvent, partitioning of the effluent between phases, poor selectivity, and inability to regenerate the solvent may all pose difficulties.

The CLM techniques based on carrier-containing hydrophobic organic solvents that combine the processes of extraction, diffusion, and stripping in a single step constitutes one of the cheapest separation techniques because of their relatively small inventory and low running costs. The CLM methodology offers an attractive alternative for removal of contaminants or organic acids directly from the wastewater effluent or fermentation broth, because high removal productivity and very selective separations are possible, and because only a small amount of carrier is required, expensive extractants can be used (7,14). Despite these advantages, stability and lifetimes of CLMs are too low to assure good commercial applications (15).

To alleviate the problems associated with problematic existing separation techniques, an integrated solvent-carrier supported liquid membrane (SLM)–based separation technique has recently been developed. It makes use of highly permeable, low-viscosity hydrophobic fluid polymers, polydimethylsiloxanes, chemically functionalized with suitably designed receptor functionalities and capable of molecular recognition as extractants (16–18). These SLMs do not suffer from several of the limitations that beset CLMs processes, but are similarly advantageous with regard to low energy costs, high enrichment factors, and environmentally acceptable operational procedures (19).

In this study, the comprehensive integrated model developed for the facilitated transport of species through an integrated solvent-carrier SLM system (20) that contains functionalized polyorganosiloxanes as mobile and fixed site carriers was used for the analysis of l-lactic acid ethyl ester and phenol transport. The model was verified with the organic acid transport experimental data, and it was used to determine the acid transport parameters, which include the product of solute partition coefficient and diffusion coefficient (K_pD_s), the equilibrium extraction constant (K_{ex}), and the sum of effective diffusivity of the solute-carrier complex caused by both mobile and jumping carrier mechanisms ($D_m + D_j$). The

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obtained ($D_m + D_j$) values were compared with those estimated from some commonly used empirical correlations.

THEORY AND TRANSPORT MECHANISMS OF ORGANIC ACIDS IN SILOXANE SLMS

Two primary mechanisms for facilitated transport are usually ascribed. The more common mechanism frequently found in SLMs, carrier-diffusion transport requires the complex to be mobile within the membrane for transport to occur. Another less well-understood mechanism involves the hopping (jumping) of permeate molecules between fixed-site carriers. In this latter process, adjacent carriers must pass a permeate between them; therefore, only local motion of carriers is required. Both mechanisms are expected to operate simultaneously in a functionalized siloxane system illustrated in Fig. 1, and the kinetic profiles for transport by carrier diffusion and fixed-site jumping are generally quite similar (21).

Detailed descriptions of l-lactic acid ethyl ester transport mechanisms by an amine functionalized polyorganosiloxane SLMs are available in (20). Similar

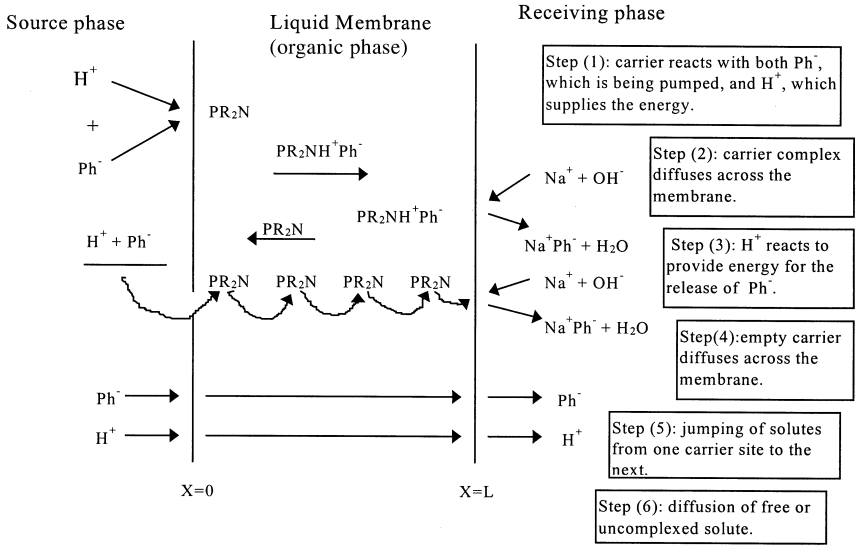

Figure 1. Mass transfer mechanism (cotransport) of phenol facilitated permeation by an SLM using amine functionalized polyorganosiloxane (PR_2N) as both mobile and fixed site carriers (Ph^- = phenate; $PR_2NH^+Ph^-$ = quaternary ammonium salt (complex) formed in the complexing reaction).

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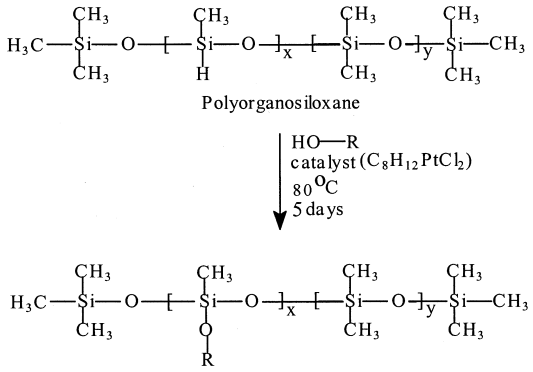

Figure 2. Reaction scheme and molecular structure of functionalized polyorganosiloxanes (16,17).

mechanisms can be described for acid transport by ether functionalized polyorganosiloxane SLMs used in this study.

An amine functionalized polyorganosiloxane fluid illustrated in Fig. 2 is one of the integrated solvent-carriers considered in our study of phenol transport mechanisms. The capacity of amines to act as extractants is related to their basicity, i.e., to the fact that their nitrogen atom has a lone pair of electrons capable of forming weak bonds with cations or weakly acidic polar molecules. Some noted the suitability of amine-functionalized siloxanes for extraction of phenol from the aqueous phase (22). The transport of phenol in a siloxane SLM with amine functionalized groups (PR_2N) as a mobile and fixed-site carrier is illustrated in Fig. 1 and represented in Eqs. (1–3). Tertiary amines (PR_2N) can extract organic acids by neutralization reactions, resulting in salt formation, and can extract specific polar organics via hydrogen-bonding interactions between the electronegative nitrogen center of the amine and an electron pair (i.e., the acidic) center of the solute. The solute in

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the source phase diffuses toward the interface $x = 0$, where the solute-PR_2N salt complex forms. At the interface ($x = 0$) between the source and the membrane phases, the first step of the reaction series is protonation of the amine carrier, i.e.,

$$(PR_2N)_{org} + (H^+)_{aq} \leftrightarrow (PR_2NH^+)_{org} \quad (1)$$

where PR_2N is $Me_3SiO(MeSi[O\{(CH_2)_3N(CH_3)_2\}]O)_x(Me_2SiO)_ySiMe_3$. The proton transfer reaction occurs because of the low pH of the source phase, which results from phenol being in its mainly ionized form. The anion will interact with the protonated amine residue to form an acid-base pair (complex) that is soluble in the membrane phase and will diffuse and/or jump from carrier site to carrier site across the membrane. Hence, the overall reaction for the extraction of phenol by the carrier is

$$(H^+)_{aq} + (Ph^-)_{aq} + (PR_2N)_{org} \leftrightarrow (PR_2NH^+Ph^-)_{org} \quad (2)$$

where Ph^- represents the anion of phenol (phenate); PR_2N represents the tertiary amine functionalized carrier; and $PR_2NH^+Ph^-$ is the quaternary ammonium salt (complex) formed in the complexing reaction.

At the interface of the membrane phase and the stripping medium, the complex ($PR_2NH^+Ph^-$) reacts with OH^- and releases Ph^- into the stripping medium. Thus, both hydrogen and phenate are transferred from the feed to the stripping medium and PR_2N is again available for further transport of hydrogen ions and phenate. The pH gradient between the source and receiving phases and the copermeation of protons result in phenol being transported only in one direction. Thus, phenol stripping occurs by the following reaction:

$$(PR_2NH^+Ph^-)_{org} + (Na^+)_{aq} + (OH^-)_{aq} \leftrightarrow (PR_2N)_{org} + (Na^+)_{aq} + (Ph^-)_{aq} + (H_2O)_{aq} \quad (3)$$

MODELS FOR TRANSPORT RATES OF ORGANIC ACIDS IN SILOXANE SLMS

The diffusion processes occurring in the studied system can involve both mobile and chained (fixed-site) carrier mechanisms (Fig. 1). Both mechanisms can operate simultaneously because each carrier is chemically linked onto the backbone of the organosiloxane polymer (Fig. 2). Although the polymer itself is completely mobile, the receptors are not. The solute-carrier complexes can be transported by the mobility of the whole polymer chain, but the solute can also jump from one carrier site to another on the same polymer molecule or/and between adjacent polymer molecules if the carrier is of a sufficient concentration (Fig. 1). Models for the facilitated transport of a weak organic acid through an integrated solvent-carrier SLM have previously been developed for 4 different lev-

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els of carrier concentrations, i.e., low, relatively high, very high, and extremely high carrier concentrations (20).

Unlike in the chained carrier mechanism (21), a positive solute flux will be created across the membrane at low carrier concentration because solute can be transported across the membrane by the mobility of the whole fluid polymer-linked solute-carrier complex. However, if chain movement is extensive, some overlapping of solute-carrier complex with adjacent uncomplexed carriers may occur. This is likely to be negligible at low carrier loadings (concentrations) and thus we assumed that it contributes zero flux to the transport processes. Therefore, at very low carrier concentration, diffusion processes in the SLM can be described essentially by the mobile carrier mechanism only, and this can be represented by the equation previously reported (20,21):

$$J_s + J_F = \frac{K_p D_s}{L}(S_0 - S_L) + \frac{D_m}{L}\left(\frac{K_{ex} C_o (S_0 - S_L)}{(1 + K_{ex} S_0)(1 + K_{ex} S_L)}\right) \tag{4}$$

At higher carrier concentrations, some of the solute can be transported across the membrane by the mobile solute-carrier complex formed by the complexation reaction at the interface, and some can also be transported via a solute jumping mechanism within the membrane. Under these conditions, some of the solutes molecules can pass from one carrier site to the next, as enough carrier is present to bring carrier sites sufficiently close for a jumping mechanism to occur. Thus, for relatively high carrier concentration, the model can be described by both mobile and chain carrier mechanisms operating simultaneously, and it can be represented by the equation previously developed (20):

For a model based on an assumption of fast-reaction, i.e., diffusion controlling:

$$J_{Total} = \frac{K_p D_s}{L}(S_0 - S_L) + \left(\frac{K_{ex} C_o (S_0 - S_L)}{L(1 + K_{ex} S_0)(1 + K_{ex} S_L)}\right) \times \left[D_m + X D_j \left(\frac{2l/l_o}{3 - l_o/l}\right)\right] \tag{5}$$

and for the assumption of fast diffusion, i.e., reaction equilibrium:

$$J_{Total} = \frac{K_p D_s}{L}(S_0 - S_L) + \left(\frac{K_{ex} C_o (S_0 - S_L)}{L(1 + K_{ex} S_0)(1 + K_{ex} S_L)}\right) \times \left\{D_m + X \left[\frac{k C_o l^3 (l_o - l)}{l_o^2}\right]\right\} \tag{6}$$

For very high carrier concentrations, a substantial fraction of the solute molecules will be transported across the membrane by the jumping mechanism.

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At the same time some solute molecules will be transported by the mobile mechanism. As carriers in high concentration are on average much closer to each other than they are in lower concentration, a lot of solute jumping can occur. Thus, as for high carrier concentrations, the model can be described by both mechanisms operating simultaneously and by reported equation (20):

For a model based on an assumption of fast-reaction, i.e., diffusion controlling:

$$J_{\text{Total}} = \frac{K_{\text{p}} D_{\text{s}}}{L}(S_0 - S_{\text{L}}) + \left(\frac{K_{\text{ex}} C_{\text{o}}(S_0 - S_{\text{L}})}{L(1 + K_{\text{ex}} S_0)(1 + K_{\text{ex}} S_{\text{L}})}\right) \times \left[D_{\text{m}} + D_{\text{j}}\left(\frac{2l/l_{\text{o}}}{3 - l_{\text{o}}/l}\right)\right] \tag{7}$$

and for the assumption of fast diffusion, i.e., reaction equilibrium:

$$J_{\text{Total}} = \frac{K_{\text{p}} D_{\text{s}}}{L}(S_0 - S_{\text{L}}) + \left(\frac{K_{\text{ex}} C_{\text{o}}(S_0 - S_{\text{L}})}{L(1 + K_{\text{ex}} S_0)(1 + K_{\text{ex}} S_{\text{L}})}\right) \times \left\{D_{\text{m}} + \left[\frac{kC_{\text{o}} l^3 (l_{\text{o}} - l)}{l_{\text{o}}^2}\right]\right\} \tag{8}$$

For extremely high (infinite) carrier concentrations, all solute molecules will be transported by a jumping mechanism. None will be transported by the mobile carrier mechanism. The jumping process will occur quickly so the system behaves as a mobile one. Thus, the model for extremely high carrier concentrations has been described by the chain carrier mechanism and is reported as (20):

$$J = \frac{D}{L}\left(\frac{K_{\text{ex}} C_{\text{o}}}{(1 + K_{\text{ex}} S_0)(1 + K_{\text{ex}} S_{\text{L}})}\right)(S_0 - S_{\text{L}}) \tag{9}$$

These models can be used for the analysis of phenol and l-lactic acid ethyl transport experiments as they were conducted on the same integrated solvent-carrier SLM (16,22,23) used in the development of the models. Thus, the transport rate (flux) of the substrate (phenol or ethyl lactate) through the studied SLM systems may be represented by either Eq. (6) or Eq. (8), as they both account for both mobile and chained carrier mechanisms. One's choice of these 2 equations can also be justified from a previous study (21) that showed that fast diffusion occurs much more frequently in chained carrier mechanisms than in the mobile carrier mechanism.

EXPERIMENTAL

Detailed descriptions of the experimental procedure, including functional

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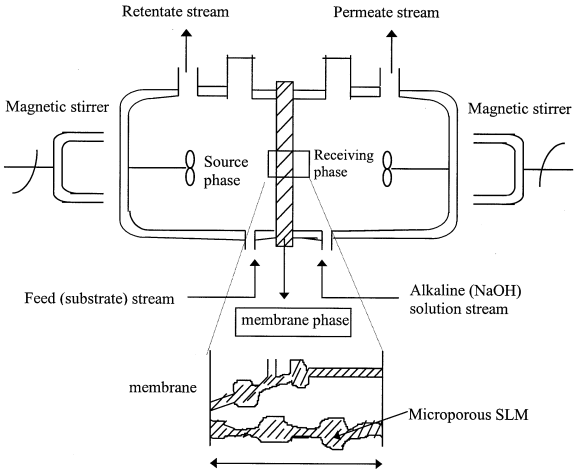

Figure 3. Schematic representation of an experimental setup of the supported liquid membrane (SLM)-based separation cell.

fluid siloxane preparations, analytical methods, SLM preparation, and transport experiments are available in our previous publications (16–17,20,23). The transport experiments were carried out at 25°C in a permeation cell shown in Fig. 3. The supported liquid membrane consisted of Celgard K-273, a microporous polypropylene film with porosity of 0.33 and membrane thickness of 25 μm (Hoechst Celanese Corporation, Separation Products Division, USA), supporting the functionalized fluid polymer. An aqueous solution of known concentration of the required substrate (l-lactic acid ethyl ester or phenol) was used as the source phase, and 0.1 mol/L NaOH solution was used as the receiving phase. The feed and stripping solutions were fed to the cell by peristaltic pumps. The flow rate through each compartment was controlled by an individual pump at 1.4 mL/min. Both compartments were stirred continuously with magnetic stirrers driven by synchronous motors. The amount (concentration) of each substrate transported through the membrane was monitored continuously through alkaline outflow (permeate or receiving phase) collection in an autosampler at measured time intervals. Each sample was analyzed quantitatively by methods described elsewhere (16,22).

RESULTS AND DISCUSSION

The experimental data obtained for the facilitated transport studies of l-lactic acid ethyl ester through an SLM that consists of ether-functionalized polyorganosiloxane with different ether loadings (carrier concentrations, such as x in

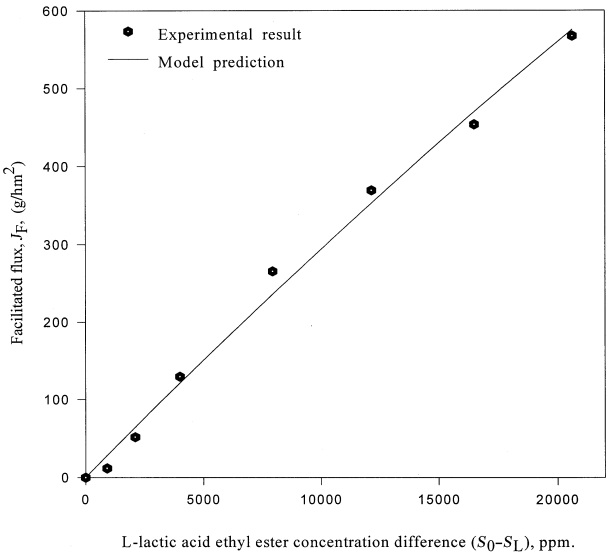

Figure 4. Effect of the L-lactic acid ethyl ester concentration gradient on the facilitated flux through 11% (mol) ether functionalized polyorganosiloxane-Celgard K-273 SLM and comparison of the measured and predicted values. The solid line is calculated from the transport model (Eq. 10) and the symbols are measured values.

Eq. (1)) (16) and the one obtained for the facilitated transport studies of phenol by the integrated SLM at different loadings (carrier concentrations, such as x as in Eq. (1)) of amine and ether functionalized polyorganosiloxane as a mobile-fixed site carrier (22) were used to verify the proposed transport models (20).As predicted by the model and shown in Figs. 4–9, the experimentally obtained facilitated fluxes of the substrates vary almost linearly at low substrate concentrations, but they are almost independent of high solute concentrations. Figures 10 and 11 indicate that the flux increases greatly at low carrier concentrations and then approaches a plateau value at higher concentrations. This result is consistent with the model.

From the experimental data (16,22), the transport parameters, K_pD_s, K_{ex}, $(D_m + D_j)$ were determined through the use of Eqs. (6 or 8). The quantity in square brackets in the 2 equations i.e., $[kC_ol^3(l_o–l)/l_o^2]$ describes D_j. The diffusivity coefficient can be described by $D_j = 0$ when $l \geq l_o$. This result conforms to the limit of conventional facilitated diffusion (Eq. 4) (20,21). Furthermore, researchers had previously assumed that the membrane contained chained carrier molecules that could move a distance l_o (20,21). The quantity l_o is a physical property of the membrane polymer. In this sense, it is like the diffusion coefficient D or the rate con-

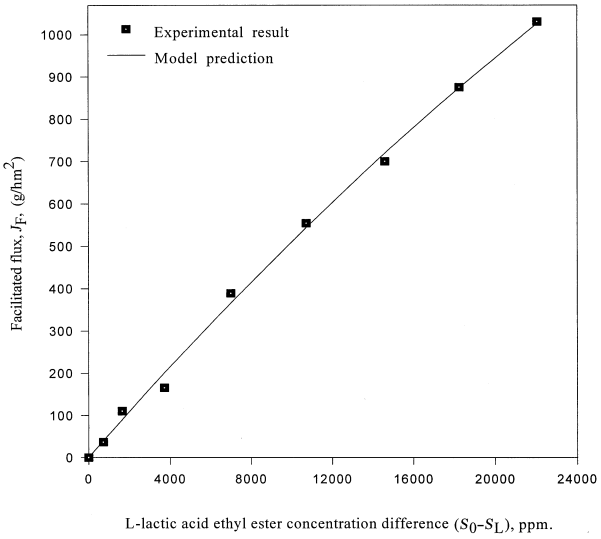

Figure 5. Effect of the L-lactic acid ethyl ester concentration gradient on the facilitated flux through 30% (mol) ether functionalized polyorganosiloxane-Celgard K-273 SLM and comparison of the measured and predicted values. The solid line is calculated from the transport model (Eq. 10) and the symbols are measured values.

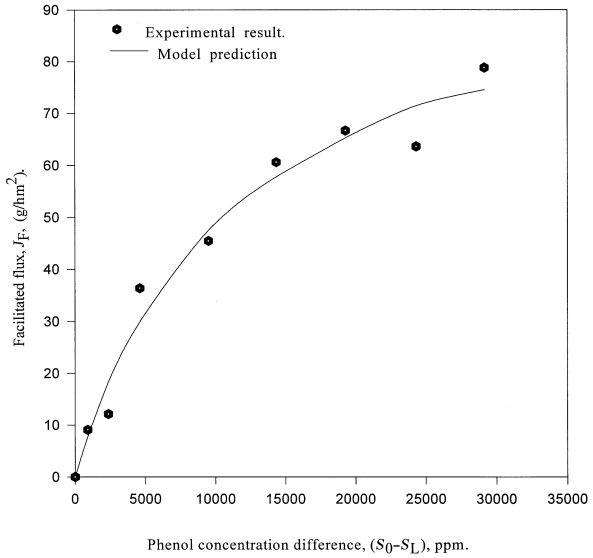

Figure 6. Effect of the phenol concentration gradient on the facilitated flux through 4 % (mol) amine functionalized polyorganosiloxane-Celgard K-273 SLM and comparison of the measured and predicted values. The solid line is calculated from the transport model (Eq. 10) and the symbols are measured values.

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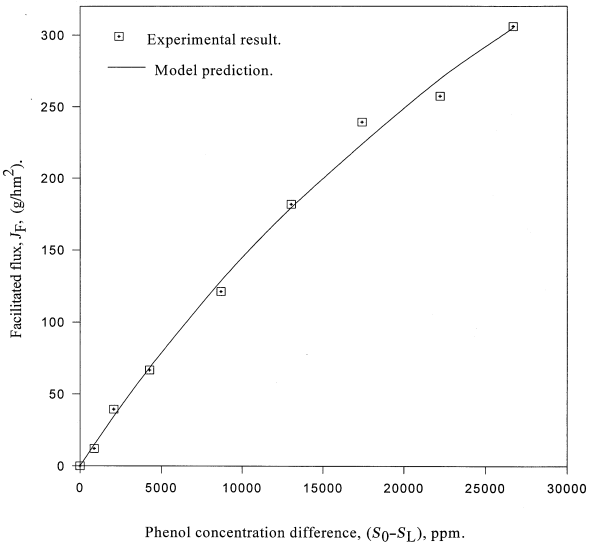

Figure 7. Effect of the phenol concentration gradient on the facilitated flux through 11 % (mol) amine functionalized polyorganosiloxane-Celgard K-273 SLM and comparison of the measured and predicted values. The solid line is calculated from the transport model (Eq. 10) and the symbols are measured values.

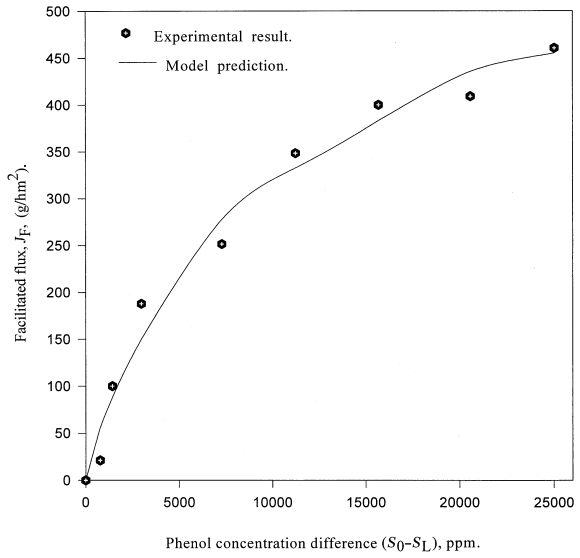

Figure 8. Effect of the phenol concentration gradient on the facilitated flux through 30% (mol) amine functionalized polyorganosiloxane-Celgard K-273 SLM and comparison of the measured and predicted values. The solid line is calculated from the transport model (Eq. 10) and the symbols are measured values.

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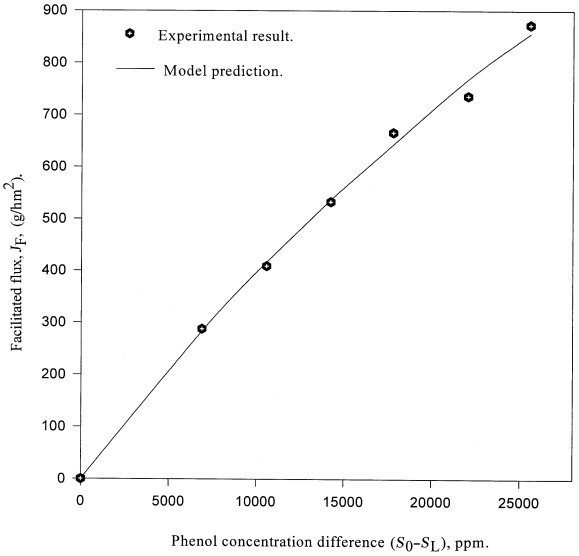

Figure 9. Effect of the phenol concentration gradient on the facilitated flux through 30% (mol) ether functionalized polyorganosiloxane-Celgard K-273 SLM and comparison of the measured and predicted values. The solid line is calculated from the transport model (Eq. 10) and the symbols are measured values.

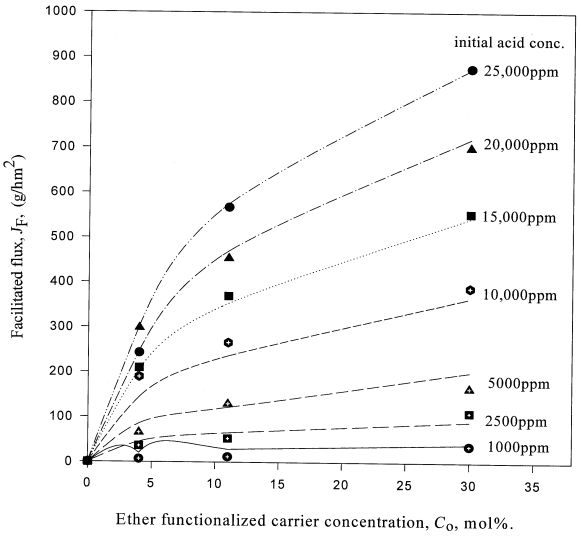

Figure 10. Effect of carrier concentration on the facilitated flux of different initial concentrations of L-lactic acid ethyl ester through ether functionalized polyorganosiloxane-Celgard K-273 SLM and comparison of the measured and predicted values. The lines drawn are calculated from the transport model (Eq. 10) and the symbols are experimentally measured values.

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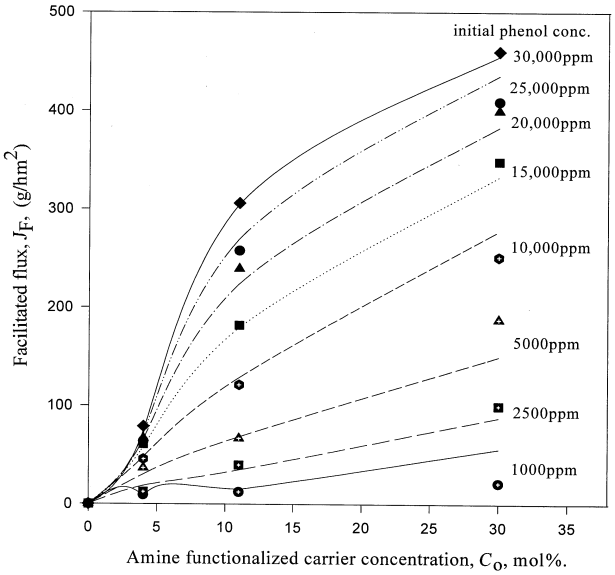

Figure 11. Effect of carrier concentration on the facilitated flux of different initial concentrations of phenol through amine functionalized polyorganosiloxane-Celgard K-273 SLM, and comparison of the measured and predicted values. The lines drawn are calculated from the transport model (Eq. 10) and the symbols are experimentally measured values.

stant K. It has less resemblance to the distance between reactive sites l, which can be varied by changing the total carrier concentration C_o. The quantity in brackets in Eq. (5 and 7), i.e., $[(2l/l_o) / (3–l_o/l)]$, can also be regarded as D_j because as the mobility in the chained carriers is incorporated into parameter l_o and when $l \geq l_o$, the equations are identical to the limit of conventional facilitated diffusion (Eq. 4) (20,21). Thus, the quantity in the bracket can be incorporated into the existing diffusion coefficient due to the jumping mechanism, and it can thus be represented as D_j.

With the above modifications in the chain carrier mechanisms of the model, the transport model equation can now be written as

$$J_{\text{Total}} = \frac{K_p D_s}{L}(S_0 - S_L) + \frac{K_{ex} C_o (S_0 - S_L)}{L(1 + K_{ex} S_0)(1 + K_{ex} S_L)}(D_m + D_j) \qquad (10)$$

where D_j is the diffusion coefficient due to the jumping mechanism obtained from incorporation of the mobility term l_o in the chained carriers. The important difference between D_j and D_m is the physical basis for D_j and its dependence on the fixed-site carrier.

Simple curve-fitting and iteration procedures using the model (Eq. 10) were

applied to obtain accurate values of K_pD_s, K_{ex}, and $(D_m + D_j)$ as shown in Tables 1 and 2. K_pD_s was obtained from the plot of J_s vs. $(S_0–S_L)$ and K_{ex} and $(D_m + D_j)$ were determined from the plot of J_F vs. $K_{ex}(S_0–S_L)/[(1 + K_{ex}S_0)(1 + K_{ex}S_L)]$. The facilitated flux J_F was obtained by subtracting the unfacilitated flux J_s from the total flux J_{Total}, which was obtained from the transport experimental data (16,22). As shown in Fig. 12 for phenol transport through 11% (mol) amine-functionalized polyorganosiloxane-Celgard K-273 SLM, the expected linear correlation was obtained. The same procedure was applied to the 2 acids with other carrier concentrations. Very good curve-fitting iterations were achieved as indicated by the values of regression coefficients obtained for each case (Table 1).

With these parameters, the observed fluxes can be simulated very well as shown in Figs. 4–11, and as can be observed from the figures, the agreement between theory (Eq. 10) and experimental data is excellent for almost all the carrier concentrations considered.

Estimation of Effective Diffusion Coefficients D_m and D_j

Table 1. Values of Equilibrium Extraction Constant and Transport Parameters Determined from Curve-Fitting Procedures and Used for the Model Calculation

Transport Parameters for Phenol Transport by the Integrated Solvent-Carrier SLM			
Unfunctionalized PDMS in the Celgard K-273 SLM	K_PD_S (cm^2/s) 5.0×10^{-7}	Regression Coefficient (r^2) 1.0	
Functionalized SLM (x as in Eq. 1)	K_{ex} (m^2/g)	$(D_m + D_j)$, cm^2/s	Regression Coefficient (r^2)
4% (mol) amine	81.78×10^{-6}	1.62×10^{-7}	0.973
11 % (mol) amine	14.82×10^{-6}	6.44×10^{-7}	0.995
30 % (mol) amine	73.07×10^{-6}	2.62×10^{-7}	0.980
30 % (mol) ether	7.47×10^{-6}	16.11×10^{-7}	0.996
Transport Parameters for L-Lactic Acid Ethyl Ester Transport by the Integrated Solvent-Carrier SLM			
Unfunctionalized PDMS in the Celgard K-273 SLM	K_PD_S (cm^2/s) 9.7×10^{-6}	Regression Coefficient (r^2) 1.0	
Functionalized SLM (x as in Eq. 1)	K_{ex} (m^2/g)	$(D_m + D_j)$, cm^2/s	Regression Coefficient (r^2)
11% (mol) ether	3.85×10^{-6}	50.09×10^{-7}	0.994
30% (mol) ether	5.04×10^{-6}	2.94×10^{-7}	0.998

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Table 2. Effective Diffusion Coefficients of Phenol and l-Lactic Acid Ethyl Ester in the Unfunctionalized PDMS and Functionalized Polyorganosiloxanes Supported in Celgard K-273 SLMs

Effective Diffusion Coefficients for Phenol Transport by the Integrated Solvent-Carrier SLM				
Unfunctionalized Polydimethyl Siloxanes (PDMS) Supported by Celgard K-273 SLM				
Experimental	Wilke-Chang		Lusis-Ratcliff	
K_pD_s (cm^2/s)	D_{AB} (cm^2/s)	D_s (cm^2/s)	D_{AB} (cm^2/s)	D_s (cm^2/s)
5.0×10^{-7}	31.88×10^{-7}	3.47×10^{-7}	28.28×10^{-7}	3.08×10^{-7}

Functionalized Polyorganosiloxanes as Mobile and Fixed-Site Carriers Supported by Celgard K-273 SLM							
Functionalized SLM (x as in Eq. 1)	Experimental $(D_m+D_j) \times 10^7$ (cm^2/s)	Wilke-Chang $D_{AB} \times 10^7$ (cm^2/s)	Wilke-Chang $D_m \times 10^7$ (cm^2/s)	Wilke-Chang $(D_m + D_j) \times 10^7$ (cm^2/s)	Lusis-Ratcliff $D_{AB} \times 10^7$ (cm^2/s)	Lusis-Ratcliff $D_m \times 10^7$ cm^2/s	Lusis-Ratcliff $(D_m + D_j) \times 10^7$ (cm^2/s)
4% (mol) amine	1.62	5.52	0.60	1.20	6.07	0.66	1.32
11% (mol) amine	6.44	10.14	1.10	2.21	9.11	1.00	1.98
30% (mol) amine	2.62	5.61	0.61	1.22	5.14	0.56	1.12
30% (mol) ether	16.10	7.57	0.82	1.65	2.29	0.25	0.50

Effective Diffusion Coefficients for L-Lactic Acid Ethyl Ester Transport by the Integrated Solvent-Carrier SLM				
Unfunctionalized Polydimethyl Siloxanes (PDMS) Supported by Celgard K-273 SLM				
Experimental	Wilke-Chang		Lusis-Ratcliff	
K_pD_s (cm^2/s)	D_{AB} (cm^2/s)	D_s (cm^2/s)	D_{AB} (cm^2/s)	D_s (cm^2/s)
9.70×10^{-6}	25.38×10^{-7}	2.76×10^{-7}	20.10×10^{-7}	2.19×10^{-7}

Functionalized Polyorganosiloxanes as Mobile and Fixed-Site Carriers Supported by Celgard K-273 SLM							
Functionalized SLM (x as in Eq. 1)	Experimental $(D_m+D_j) \times 10^7$ (cm^2/s)	Wilke-Chang $D_{AB} \times 10^7$ (cm^2/s)	Wilke-Chang $D_m \times 10^7$ (cm^2/s)	Wilke-Chang $(D_m + D_j) \times 10^7$ (cm^2/s)	Lusis-Ratcliff $D_{AB} \times 10^7$ (cm^2/s)	Lusis-Ratcliff $D_m \times 10^7$ cm^2/s	Lusis-Ratcliff $(D_m + D_j) \times 10^7$ (cm^2/s)
11% (mol) ether	50.09	8.15	0.89	1.78	6.47	0.71	1.41
30% (mol) ether	2.94	6.02	0.66	1.31	4.81	0.52	1.05

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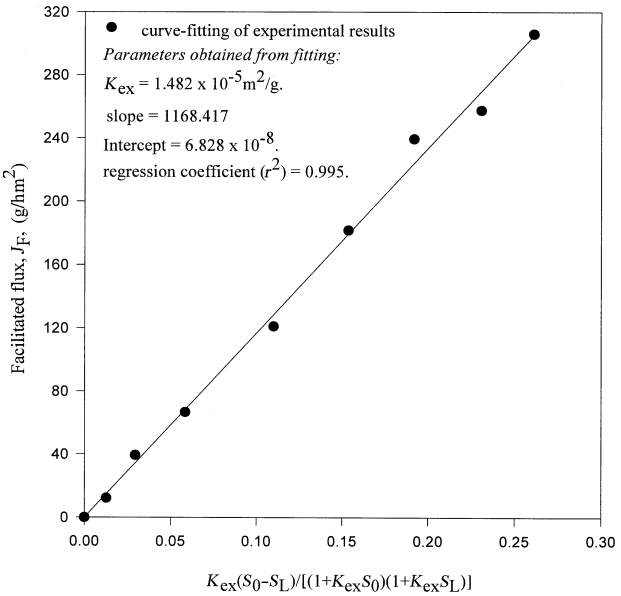

Figure 12. Curve-fitting of facilitated flux with $K_{ex}(S_0 - S_L)/[(1 + K_{ex}S_0)(1 + K_{ex}S_L)]$ obtained from transport data of phenol through 11% (mol) amine functionalized polyorganosiloxane-Celgard K-273 through use of the transport model.

To estimate the effective diffusion coefficients ($D_m + D_j$) of l-lactic acid ethyl ester and phenol in the functionalized polyorganosiloxanes or unfunctionalized polydimethylsiloxane (PDMS) immobilized in the membrane (Celgard K-273) pores, the SLM systems studied, which have been described in our previous publication (20), can operate simultaneously by both mobile and fixed-site carrier mechanisms. Thus, to make possible a comparison between the experimentally determined ($D_m + D_j$) with those estimated from empirical correlations, the 2 diffusion coefficients D_{mobile} and D_{jump} involved simultaneously in the SLM systems must be considered independently.

As previously reported (20), D_m is the effective diffusion coefficient of the substrate in the SLM due to the mobile carrier mechanism, and D_j is the diffusion coefficient of the substrate in the SLM due to the jumping mechanism. However, the diffusion process through an SLM is affected by the porosity (ε) and tortuosity (τ) of the polymeric membrane support. Thus, to estimate D_m, corrections must be made for the morphological characteristics of the membrane support. The effective diffusion coefficient, D_m or D_{app} (diffusivity in a microporous membrane) is related to the molecular or true diffusivity D_{AB} (diffusivity of a species in the

bulk organic solution) through the porosity (ε) and tortuosity factor (τ) of the membrane support (24,25) and is given as

$$D_m = \frac{D_{AB}\varepsilon}{\tau} \tag{11}$$

Researchers customarily assume D_{AB} to be the diffusion coefficient of species in bulk solution. By relying on this assumption, one can comfortably estimate D_{AB} by the most widely used empirical correlations in the literature such as those by Wilke-Chang (1955) (Eq. 12) and Lusis-Ratcliff (1968) (Eq. 13) (26):

$$D_{AB} = \frac{7.4 \times 10^{-8} T (\phi M_B)^{1/2}}{\mu_{AB} V_{bA}^{0.6}} \tag{12}$$

$$D_{AB} = 8.52 \times 10^{-8} \frac{T V_{bB}^{-1/3}}{\mu_B} \left\{ 1.4 \left(\frac{V_{bB}}{V_{bA}} \right)^{1/3} + \frac{V_{bB}}{V_{bA}} \right\} \tag{13}$$

where A is the substrate (phenol or ethyl lactate permeate) and B is the functionalized or unfunctionalized PDMS in the SLM Celgard K-273 membrane pores. Based on these correlations, D_{AB} of phenol or ethyl lactate substrate in PDMS and in different concentrations of amine and ether functionalized polyorganosiloxanes immobilized in the pores of the membrane support (Celgard K-273), is estimated and the results are shown in Table 2.

With the D_{AB} values noted in Table, D_m can be estimated from Eq. (11). Tortuosity values have been estimated (27) using the equation

$$\tau = \frac{1}{1 - V_p} = \frac{1}{\varepsilon} \tag{14}$$

where $V_p = 1–\varepsilon$.

τ values estimated through use of Eq. (14) are in close agreement with the values reported in most studies. Thus, tortuosity of the membrane (Celgard K-273) support was estimated from Eq. (14). The τ value of 3.03 estimated from Eq. (14) was used in Eq. (11) for the Celgard K-273 ($\varepsilon = 0.33$) membrane support, and the D_m values for phenol and l-lactic acid ethyl ester substrates were obtained (Table 2).

The value of D_j can also be estimated (20). In our current case, species jump from one receptor site to the next. This jumping can be imagined to mimic diffusion of species to various carrier sites. Because the results of jumping are similar to those found through the mobile carriers mechanism (D_m), values of D_j will be approximately the same as those of D_m. D_m and D_j values of some species transporting through SLMs with different carriers have been determined and found to be within the same range (21,28). Hence, D_j is assumed to be equal to D_m. Therefore,

$$D_m + D_j = 2D_m \tag{15}$$

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Thus, by multiplying the values of D_m by 2, one obtains ($D_m + D_j$) as shown in Table 2.

As depicted in Table 2, the values of effective diffusion coefficients ($D_m + D_j$) in PDMS and in different concentrations of carriers determined from experimental (curve-fitting) data for the 2 substrates are in close agreement with the estimated values obtained through the use of Wilke-Chang and Lusis-Ratcliff correlations. Furthermore, the experimental results of the effective diffusion coefficients obtained for the substrates in each solvent are consistent in their orders of magnitude with the effective diffusion coefficients reported for various other substrates in conventional facilitated liquid membranes (21,28).

CONCLUSION

Analysis of phenol and l-lactic acid ethyl ester transport by an SLM system that contains functionalized polyorganosiloxanes as mobile-fixed site carriers has been conducted with a comprehensive transport model, previously developed for transport of a weak organic acid derivative through integrated solvent-carrier SLMs. The model is based upon simultaneous occurrence of both mobile and chained (fixed-site) jumping carrier mechanisms. An overall transport mechanism based upon the 2 mechanisms operating simultaneously in this SLM has also been developed for the phenol separation. Through transport experimental data obtained through amine and ether functionalized polyorganosiloxane-Celgard K-273 SLMs, the transport model was verified and then used to determine the transport parameters, K_pD_s, K_{ex}, and ($D_m + D_j$) of the 2 substrates. The agreement between the theoretical model and experimental data was found to be excellent for almost all carrier concentrations considered for the 2 acids. Furthermore, the values of effective diffusion coefficients ($D_m + D_j$) determined from experiments (curve-fitting) are in close agreement with the estimated values using Wilke-Chang and Lusis-Ratcliff correlations, and they are also consistent in their orders of magnitude with the effective diffusion coefficients reported in the literature for various other substrates in similar systems.

NOMENCLATURE

D	diffusion coefficient (cm^2/s)
D_{AB}	diffusivity of a species in the bulk organic solution (cm^2/s)
D_j	effective diffusivity of solute-carrier complex due to jumping carrier mechanism (cm^2/s)
D_m	effective diffusivity of solute-carrier complex due to mobile carrier mechanism (cm^2/s)

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D_s	solute diffusion coefficient (cm^2/s)
J_F	flux due to carrier-assisted diffusion (g/hm^2)
J_s	flux due to free, uncomplexed solute (g/hm^2)
J_{Total}	total flux caused by both mobile and jumping carriers mechanism (g/hm^2)
K_{ex}	equilibrium extraction constant (m^3/g)
K_p	solute partition coefficient = (external-phase concentration)/(membrane-phase concentration)
L	membrane thickness (m)
l	distance between 2 adjacent chained carriers
l_o	Distance allowed for each chained carrier to move around its equilibrium position within a layer
M_B	molecular weight of solvent
S_0	solute concentration in the aqueous phase (mol/m^3)
S_L	solute concentration in the receiving phase (mol/m^3)
V_{bA}	the molal volume of the solute at its normal boiling point
V_{bB}	the molal volume of the solvent at its normal boiling point
X	fraction of overlap occurring
μ_{AB}	the viscosity of the solution
μ_B	the viscosity of the solvent
ϕ	Association parameter

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