“Sorp-Vection”: An Unusual Membrane-Based Separation

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A nonstandard membrane process is described that involves highly selective sorption of a compound “A” at a large absolute weight fraction ω_A, coupled with a significant diffusionally induced flux of a second component “B.” The flux of B convectively moves A from a dilute external mass fraction relative to component B upstream to an enriched mass fraction downstream. The general form of the process has potential applications involving dilute feeds where current membranes processes perform poorly for such removal as a result of excessive solubility of the smaller component B. The most important widespread application is expected to be the separation of small organic solutes from supercritical carbon dioxide to facilitate the recycling and reuse of CO_2 while minimizing costly and energy-intensive recompression steps. We consider the utility of this concept by modeling the separation efficiency of phenol from supercritical carbon dioxide. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 1396–1405, 2005

Keywords: separations, supercritical carbon dioxide, convection, bulk flow; condensables

Introduction

Separations of condensables from effluent streams can be achieved by low-temperature condensation or pressure swing adsorption. These technologies have the disadvantage that they are energy intensive and tend to have large footprints. Membranes, on the other hand, are compact, simple to operate, and economical. Development of membranes for separation of condensable components from effluent streams is being pursued and provides a potentially attractive separation avenue (Baker et al., 2002, 1994, 1998). If properly supported against mechanical deformation, polymer membranes can be used to separate dilute concentrations of highly condensable bulky components from smaller, less condensable components such as air. The highly condensable nature of heavier and polar hydrocarbons tends to make them sorb easily into rubbery or glassy polymers, whereas highly supercritical components such as N_2 exhibit low sorption uptakes, even at relatively high pressures of 10 bars or so (Mark et al., 1984). On the other hand, for rubbery polymers, the intrinsically higher diffusion coefficient for smaller vs. larger molecules tends to be much less extreme than that in glassy materials. Therefore, rubbery polymers are the preferred materials for such solubility-based separations where the sorption level of the small molecule is sufficiently low. An increasingly important class of systems, however, constitutes a sufficiently high intrinsic sorption coefficient that may prevent effective application of this simple solubility-controlled sorption–diffusion permeation mechanism of separation. This type of application is the focus of this article.

Separations involving supercritical carbon dioxide are of great interest, and development of CO_2 technology for use in industrial processing has become a research focal point. Worldwide, billions of pounds of organic solvents are used as processing tools, cleaning agents, and dispersants. Concern for workers’ safety and a drive to protect the environment have prompted industrial and academic research efforts to develop acceptable solvent alternatives (DeSimone 1998). Carbon dioxide has the potential to be the alternative of choice because it is nontoxic, inexpensive, nonflammable, widely available,

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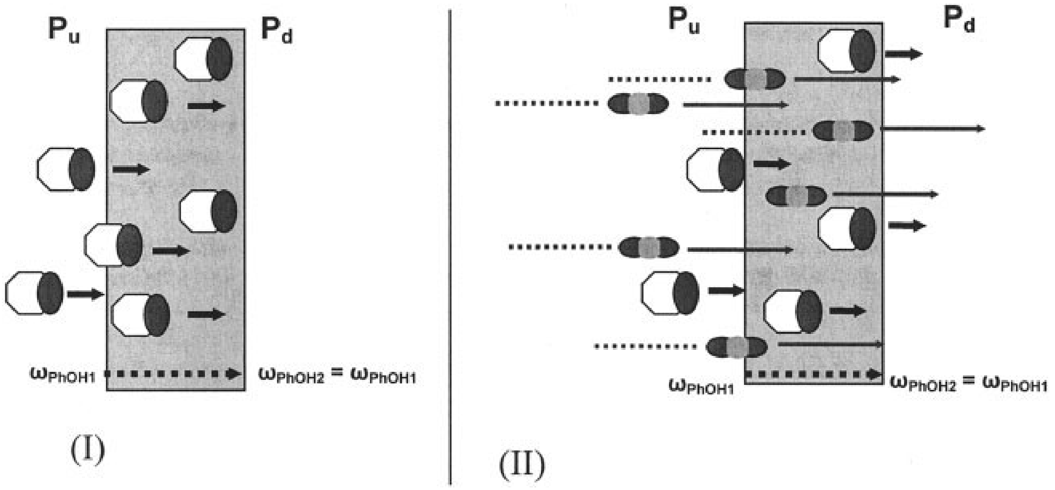

Figure 1. Representation of sorp-vection.

(I) Membrane acts to concentrate organic solute from feed into the membrane by means of a high partition coefficient. This results in a large weight fraction of the organic solute through the thickness of the material. (II) The flux of component B acts to sweep the solute into the downstream receiver, thereby concentrating the organic solute in the downstream relative to the upstream concentration. In the interest of clarity, this concept is depicted as a two-step process; however, it is important to note that the steps actually occur concurrently.

and has a broad range of dissolving power, especially in the supercritical region (Kazarian et al., 1999; McHugh and Krukonis, 1986). For the CO_2 to be recycled and reused in processing applications, separation of the CO_2 from bulkier organic solutes will be necessary. Membrane technology offers a potentially inexpensive and efficient method for this separation so that CO_2 can be recycled for use in further processing.

For condensable penetrants such as carbon dioxide, especially at high pressures such as those encountered in supercritical processing, the relative solubility differences tend to be less favorable than in the case of air-based separations mentioned above, and an alternative approach to selectively separate the larger component is attractive. Specifically, for the case that involves stripping of a dilute highly condensable component such as phenol from high pressure CO_2, a new process based on sorption induced convective transport—that is, *sorp-vection*—through the membrane appears particularly attractive. Given the increasing interest in supercritical processing, this topic is especially important. This paper describes a new type of membrane process as well as appropriate membrane and operating conditions to perform this process.

The mathematical development begins with Fick's law as it relates to the flux of permeating components. Using simplifications based on processing conditions specified herein, these equations are used to model the separation. To illustrate the general nature of the process, discussion will be couched in terms of "A" (phenol), "B" (CO_2), and "P" (polymer). In general, the process should work for selective sorption of any compound "A" at a significant (such as $>5\%$) absolute weight fraction (ω_A) coupled with a significant diffusionally induced flux of a second component "B" through a permeable polymer that is properly restrained from flow into a rigid support. As noted earlier, the flux of B *convectively* moves A, which selectively partitions into the polymer phase, across the membrane, rather than relying on diffusive transport of A to an enriched mass fraction downstream. In some respects, this process resembles an ideal continuous chromatograph. In its most general form the process could have many applications involving dilute feeds where current membrane processes perform poorly. Such current processes are limited by low transmembrane chemical potential, which is unable to strongly motivate component A between the upstream and downstream faces of the membrane. This problem is especially limiting when the molecular diffusion coefficient of A is low in the polymer matrix.

In this novel process (Figure 1), by proper selection of the composition of the membrane, the upstream side of the membrane acts as a "strong concentrator" of solute A from the solution. Component B, on the other hand, ideally should show a much lower sorption tendency than that of A in the upstream membrane. In this case, the local concentration at this point is highly enriched in A vs. B compared to the external upstream feed solution. For cases such as supercritical extraction, where component B has a high intrinsic diffusion coefficient in the A-swollen membrane, a significant steady-state diffusive flux occurs in B. By proper control of downstream conditions, the thermodynamic activity (or fugacity) of component A can be maintained high and essentially *constant* across the entire membrane. In this case, a small or nonexistent concentration profile of A exists, so negligible diffusion of A occurs. Nevertheless, the associated diffusive flux of component B provides an overall bulk flow within the membrane. The overall bulk flux moves component A at a greatly enriched mass fraction relative to the value in the feed into the downstream receiver. This coupled process produces a higher combined flux and selectivity of A vs. B than could be achieved with a conventional simple purely sorption–diffusion membrane. This paper develops the theoretical basis for the "sorp-vection" concept starting with Fick's law and uses the model separation of phenol, a byproduct of polycarbonate synthesis, from supercritical carbon dioxide using polymeric membranes to validate these phenomena.

Background

Separation of supercritical carbon dioxide containing effluent streams has been the focus of many researchers in the past

20 years (Afrane and Chimowitz, 1996; Chiu and Tan, 2001; Higashijima et al., 1994; Kulcke, 2001; Nakamura et al., 1993; Ohya et al., 1993; Sarrade et al., 2001; Semenova et al., 1992b). Much of the emphasis has been on ultrafiltration or nanofiltration membranes, which are either used in dense form or supported by a ceramic support. However, an interesting series of papers published by Ohya et al. (Higashijima et al., 1994; Semenova et al., 1992a,b) describes the successful separation of ethanol and iso-octane mixtures from supercritical carbon dioxide using asymmetric polymeric Kapton® membranes. These findings are highly unusual because preferential separations of larger components from smaller components are typically not easily achieved in glassy materials. These materials tend to separate based on size selectivity, with smaller molecules having the distinct advantage. That Ohya was successful in separating a multitude of larger hydrocarbons suggests that perhaps more is occurring than can be described with the simple solution–diffusion-based model of transport. Ohya briefly suggests that the mechanism of transport in not solution–diffusion, but rather that it follows more of a "pore flow model," which brings to mind transport by viscous flow through pores. However, this paper does not give supporting mathematical development for the model. It is actually quite likely that a modified solution diffusion model is still at the heart of this process, and that the separation effects can be described by taking into account frame of reference effects, which were first noted by Paul et al.[18-23] for single-component permeation, and then later expanded by Kammarudin et al. (1997) for mixtures.

The elimination of diffusive flux by constant organic penetrant concentration, proposed herein, has been observed by other researchers. Böddeker et al. (1990) were interested in the separation process of phenol from water. They detailed a separation of phenol from water where a nearly constant activity of the phenol across the thickness of the membrane, eliminating the activity gradient driven transport success of separation, is suggested to be attributed to *an intrinsically high flux* of organic substance through the material. These authors, however, note that the presence of a second component, water, whose flux was constant at all dilutions investigated, is only important to sweep phenol *already in the permeate reservoir* from the downstream face of the membrane to the condenser. Although some of Böddeker's ideas have similarities to those developed herein, the final application focus of this paper as well as the detailed development of a transport model, and corresponding manipulation of processing conditions, are quite different. The actual convection of "A" by "B" as a *useful* transport mechanism *within* the membrane is a key aspect not treated by previous researchers.

Theory

A membrane's material performance is defined in terms of penetrant transport properties, mainly permeability and selectivity. According to Fick's first law of diffusion, permeation flux of a permeant through a pore-free dense polymeric membrane with respect to a fixed frame of reference is equal to the sum of the bulk and diffusional flux as shown below:

$$n_A = n_A^{\mathrm{Diff}} + n_A^{\mathrm{Bulk}} \tag{1}$$

$$n_A^{\mathrm{Diff}} = -\rho D_{AM}\frac{\partial w_A}{\partial X} \tag{2}$$

$$n_A^{\mathrm{Bulk}} = w_A(n_A + n_B + n_P) \tag{3}$$

where n is the steady state flux of penetrants A and B, w_A is the average weight fraction of component A in the material, X is the thickness coordinate of the membrane, and D_{AM} is the effective binary diffusivity for diffusion of A in the mixture. For many common separations involving dense films, the process of selectively passing one component while rejecting the other occurs by a solution–diffusion mechanism. Penetrants on the upstream side of the membrane sorb into the polymer matrix and diffuse through the membrane to the downstream side, where they desorb. When the sorption of moieties is meager, the convective flow (or bulk flow) of components is neglected, and the flux of the component is described by the following (Mark et al., 1989)

$$n_A = n_A^{\mathrm{Diff}} = -\rho D_{AM}\frac{\partial w_A}{\partial X} \tag{4}$$

Productivity through a membrane is described in terms of the permeability of a specific component. The permeability, the flux of a penetrant normalized by pressure driving force and thickness, is shown by the following equation

$$P_A = \frac{n_A}{\Delta p_A/l} = D_A S_A \tag{5}$$

where P_A is the permeability of component A, Δp_A is the partial pressure driving force across the membrane, l is the thickness of the membrane, D_A is the diffusion coefficient of component A, and S_A is the solubility coefficient of component A. This general equation is valid for conditions where the components are considered ideal, which allows the driving force to be described by the difference in partial pressures. In nonideal situations, the difference in partial pressure of components is replaced with their corresponding fugacities.

Permeability values are typically reported in Barrers, where 1 Barrer = 10^{-10} cm^3(STP) cm^{-1}/cm^2 cmHg^{-1} s^{-1}.

As can be seen by Eq. 5, the calculation of productivity substantially depends on the method through which the flux is obtained. For feeds where the sorption of the components is not great and when the flux of two components is similar, neglecting bulk flow effects is appropriate. However, in the case where one of the components is highly sorbing and when the permeation flux of one of the permeants is much higher than that of the other, bulk flow effects must be taken into account (Kamaruddin et al., 1997). In fact, the effects of bulk flow are the crux of the method of separation proposed within this paper. If effects of bulk flow are considered, the following equations for the flux of the components A, B, and polymer P, are valid

$$n_A = -\rho D_{AM}\frac{dw_A}{dx} + w_A(n_A + n_B + n_p) \tag{6}$$

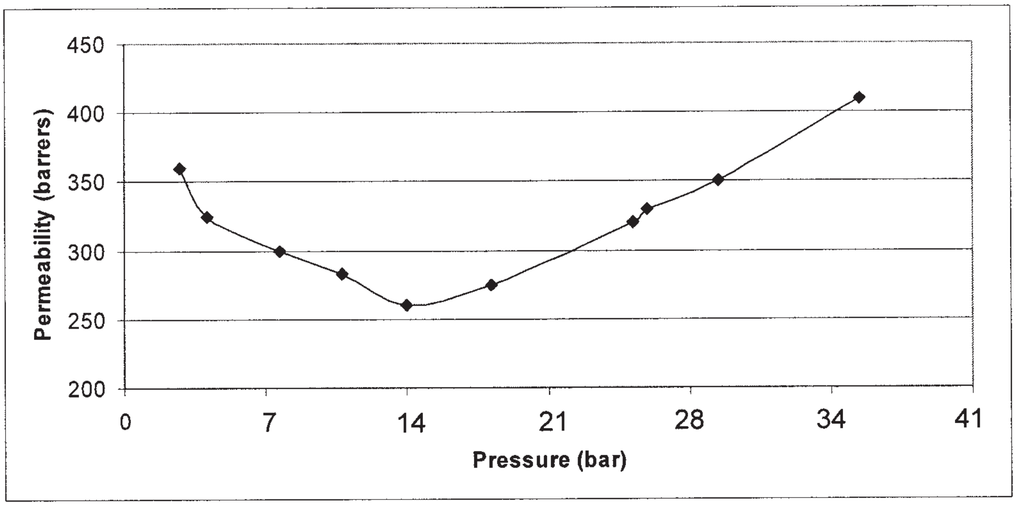

Figure 2. Plasticization effect displayed by polymer 6FDA [(4,4′-hexafluoroisopropylidene) diphthalic anhydride]–DAM (diaminomesitylene) in the presence of carbon dioxide.

Temperature: 35°C; Gas: CO_2.

$$n_B = -\rho D_{BM}\frac{dw_B}{dx} + w_B(n_A + n_B + n_p) \tag{7}$$

$$n_p = -\rho D_{pM}\frac{dw_p}{dx} + w_p(n_A + n_B + n_p) \tag{8}$$

The flux of the polymer n_p is zero at steady state because the center of mass of the membrane is stationary and thus will not be used in the following development. It is interesting to note, however, that because the polymer mass flux n_p is zero, given that the membrane is stationary, the diffusional flux of the polymer is equal in value and opposite in direction to the bulk term.

To understand the effects of bulk flow on the total flux through the membrane, the fraction of bulk flux through the membrane can be estimated following Kamarrudin et al. (1997) for each component

$$\Pi_A^{\text{Bulk}} = \frac{(n_A + n_B)w_A^{\text{Avg}}}{n_A} \tag{9}$$

$$\Pi_B^{\text{Bulk}} = \frac{(n_A + n_B)w_B^{\text{Avg}}}{n_B} \tag{10}$$

Obtaining the separation factor helps to understand the effects of bulk flow on material performance under mixed gas conditions. The separation factor, calculated using the mole fraction of components at the permeate and feed sides of the membrane, is

$$\alpha = \frac{(y_A/y_B)}{(x_A/x_B)} \tag{11}$$

where x refers to the mole fraction of component i on the feed side and y refers to component i in the permeate external stream. With only slight mathematical manipulation, Eq. 11 can be represented by the component mass fractions. The external mass fraction values will be represented by y^m and x^m.

The material's response to high pressure is quite important to consider when dealing with supercritical carbon dioxide. Under high pressure carbon dioxide conditions, most membrane materials tend to "plasticize." Specifically, the presence of the sorbed carbon dioxide at high pressures softens and dilates the membrane material, thereby causing D_A and P_A in Eq. 5 to increase sharply with increasing feed pressure. A typical plasticization curve for permeability is presented in Figure 2 (Wind, 2002). Initially the permeability declines with an increase in pressure as the nonequilibrium microvoids present in the glassy material become saturated (Koros et al., 1981). The permeability reaches a minimum before it begins to increase with increasing pressure. This minimum in the permeability vs. pressure is usually defined as the "plasticization pressure" of the material. Plasticization is caused by an increase in the segmental motion of the polymer chain arising from the presence of a highly condensable component. The increased mobility of the segments increases both the frequency and the average size of transient gaps that enable diffusion, thereby increasing the permeability. In conventional systems, this upswing in permeability following the minimum is usually accompanied by a decline in selectivity as the material loses its ability to distinguish between molecules of similar sizes. However, in the separation of larger condensable solutes from smaller components using glassy materials, this is a *favorable* response because it reduces the membrane's intrinsic size discrimination ability that would give the smaller component the advantage.

Bulk Flow Effects on PhOH/CO_2 System

The transport process specific for the phenol/carbon dioxide separation is included in Figure 3. For cases such as supercritical extraction, where the supercritical carbon dioxide (component B) has a high intrinsic diffusion coefficient in the solute-swollen membrane, a large steady-state diffusive flux occurs of the solute. By proper control of downstream conditions, the

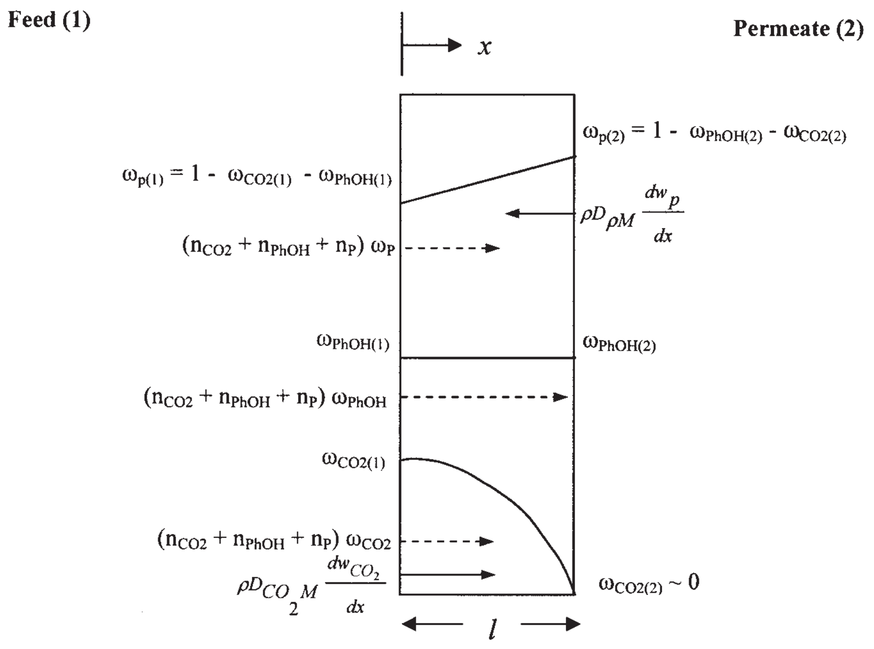

Figure 3. Transport process of phenol and carbon dioxide.

thermodynamic activity (or fugacity) of the solute, in our case phenol (component A), can be maintained high and essentially constant across the entire membrane. In this case, a small or nonexistent concentration profile of phenol exists (Figure 3), so negligible diffusion occurs. The detailed attainment of such a condition requires accounting for pressure-dependent partitioning behavior under supercritical conditions. Moreover, accounting for the well-known effect of hydrostatic pressure on penetrant in the polymer in equilibrium with this downstream sweep stream and the pressure discontinuity, explained by the fact that the membrane is supported on a rigid support, complicates the situation (Paul and Ebra-Lima, 1971). Nevertheless, by increasing the downstream phenol partial pressure in a flowing sweep stream, the activity and thus the sorption within the downstream face of the membrane can be increased to produce a negligible concentration profile of phenol. This is discussed in more detail in Appendix B, but by accepting this fact now and taking these conditions into account, Eq. 6 can be rewritten as

$$n_{\mathrm{PhOH}} = w_{\mathrm{PhOH}}(n_{\mathrm{PhOH}} + n_{\mathrm{CO_2}}) \qquad (12)$$

where w_{PhOH} is the weight fraction of phenol in the membrane. Solving for n_{PhOH} yields

$$n_{\mathrm{PhOH}} = \frac{w_{\mathrm{PhOH}}}{1 - w_{\mathrm{PhOH}}} n_{\mathrm{CO_2}} \qquad (13)$$

For the case of carbon dioxide, a concentration gradient does exist across the membrane (see Figure 3), and therefore both convective and diffusive transport should be occurring. The flux of CO_2 through the membrane is represented by rewriting Eq. 7 as

$$n_{\mathrm{CO_2}} = -\rho D_{\mathrm{CO_2}} \frac{\partial w_{\mathrm{CO_2}}}{\partial X} + w_{\mathrm{CO_2}}(n_{\mathrm{PhOH}} + n_{\mathrm{CO_2}}) \qquad (14)$$

Solving for $n_{\mathrm{CO_2}}$ results in the expression

$$n_{\mathrm{CO_2}} = \frac{w_{\mathrm{CO_2}}}{1 - w_{\mathrm{CO_2}}} n_{\mathrm{PhOH}} - \frac{\rho D_{\mathrm{CO_{2M}}}}{1 - w_{\mathrm{CO_2}}} \frac{dw_{\mathrm{CO_2}}}{dx} \qquad (15)$$

For the following analysis, it is assumed that the density throughout the polymer is constant, and that the diffusion coefficient is independent of concentration. The density of the membrane will indeed vary in the thickness direction because of the difference in sorption from the upstream to downstream portions of the membrane. However, if desired, this fluctuation in density can be reasonably accounted for by taking an average of the upstream and downstream densities. Because the diffusion coefficient can be a strong function of local concentration, the average diffusion coefficient of the permeant is used.

Taking into account the following mathematical equality

$$w_P + w_{\mathrm{PhOH}} + w_{\mathrm{CO_2}} = 1 \qquad (16)$$

using Eq. 13 for the flux of phenol, and integrating to solve for the flux of carbon dioxide through the membrane, the following expression is obtained

$$n_{\mathrm{CO_2}} = \frac{\rho D_{\mathrm{CO_{2M}}}}{l} \left\{ (1 - w_{\mathrm{PhOH}}) \ln \left[\frac{1 - w_{\mathrm{PhOH}}}{1 - w_{\mathrm{PhOH}} - w_{\mathrm{CO_{2(0)}}}} \right] \right\} \qquad (17)$$

A detailed, step-by-step progression of the calculations used to derive Eq. 17 is included in Appendix A.

As stated previously

$$n_p = 0 \tag{18}$$

Although the diffusive flux of phenol is negligible, the associated diffusive flux of the supercritical carbon dioxide (n_{CO_2}) provides an overall bulk flow within the membrane. This overall convective flow combined with the large weight fraction of sorbed phenol (phenol uptake by membrane shown below in Figure 6) carries the phenol into the downstream receiver. In this special case, the coupled process produces a higher combined flux and selectivity of the phenol vs. carbon dioxide than could be achieved with a conventional, purely sorption–diffusion membrane approach. Sorption of carbon dioxide within the membrane is significant and thus it also experiences a small convective enhancement; however, the fraction of flux arising from bulk flow effects is typically small compared to that of the phenol, and does not significantly alter the selectivity of the material. Solving Eq. 13 for the ratio of phenol to carbon dioxide flux results in

$$\frac{n_{\mathrm{PhOH}}}{n_{\mathrm{CO_2}}} = \frac{w_{\mathrm{PhOH}}}{1 - w_{\mathrm{PhOH}}} \tag{19}$$

which indicates that the ratio of fluxes, which determines the material selectivity, is controlled by the *sorbed concentration of phenol* in the membrane, and is independent of the productivity of the material. Of course, for this separation process to be industrially viable, fluxes through the membrane should be reasonably high, although the intrinsic selectivity achievable is distinct from this productivity issue.

The fraction of bulk flux through the membrane can be calculated for each component using the following equations

$$\Pi^{\mathrm{Bulk}}_{\mathrm{PhOH}} = \frac{(n_{\mathrm{PhOH}} + n_{\mathrm{CO_2}})w^{\mathrm{Avg}}_{\mathrm{PhOH}}}{n_{\mathrm{PhOH}}} \tag{20}$$

$$\Pi^{\mathrm{Bulk}}_{\mathrm{CO_2}} = \frac{(n_{\mathrm{PhOH}} + n_{\mathrm{CO_2}})w^{\mathrm{Avg}}_{\mathrm{CO_2}}}{n_{\mathrm{CO_2}}} \tag{21}$$

Because the weight fraction of phenol throughout the membrane is constant in this idealized illustrative case (see discussion before Eq. 12), the only movement of phenol is by convective flow, resulting in a simplification of Eq. 20 to

$$\Pi^{\mathrm{Bulk}}_{\mathrm{PhOH}} = 1 \tag{22}$$

By substituting Eq. 19 into Eq. 21 and rearranging, one finds

$$\Pi^{\mathrm{Bulk}}_{\mathrm{CO_2}} = w^{\mathrm{Avg}}_{\mathrm{CO_2}} + \frac{w_{\mathrm{PhOH}}}{1 - w_{\mathrm{PhOH}}} w^{\mathrm{Avg}}_{\mathrm{CO_2}} \tag{23}$$

To describe bulk flow effects on the transport of carbon dioxide through the membrane, an expression for the average concentration through the membrane is required and the following definition for average concentration is reasonable

$$w^{\mathrm{Avg}}_{\mathrm{CO_2}} = \frac{\displaystyle\int_0^l w_{\mathrm{CO_2}}(x)dx}{\displaystyle\int_0^l dx} \tag{24}$$

Solving for w_{CO_2}, an average concentration for CO_2 in the membrane can be defined. Details of this calculation are detailed elsewhere (Kamaruddin et al., 1997); however, the resulting expression is given by the following equation

$$w^{\mathrm{Avg}}_{\mathrm{CO_2}} = \frac{1}{1 + \dfrac{n_{\mathrm{PhOH}}}{n_{\mathrm{CO_2}}}} - \frac{w_{\mathrm{CO_2(0)}}}{\ln\left\{1\Big/\left[1 - w_{\mathrm{CO_2(0)}}\left(1 + \dfrac{n_{\mathrm{PhOH}}}{n_{\mathrm{CO_2}}}\right)\right]\right\}} \tag{25}$$

The subscript 0 refers to the weight fraction of sorbed carbon dioxide at the upstream face of the membrane. The weight fraction of CO_2 sorbed at the downstream face of the membrane was assumed to be negligible [that is, $w_{\mathrm{CO_{2(litel)}}} = 0$]. This is a reasonable initial assumption given the typical operating conditions for which this process is suited. Upstream pressures will reach 1500–2000 psi, whereas the downstream pressure remains <14 psi. The true concentration of CO_2 in the downstream portion of the membrane will not be zero; however, it will be negligible compared to the concentration on the upstream face. Substituting Eq. 19 into the above expression and simplifying results in the following equation

$$w^{\mathrm{Avg}}_{\mathrm{CO_2}} = 1 - w_{\mathrm{PhOH}} - \frac{w_{\mathrm{CO_2(0)}}}{\ln\left\{\left[\dfrac{1 - w_{\mathrm{PhOH}}}{1 - w_{\mathrm{PhOH}} - w_{\mathrm{CO_2(0)}}}\right]\right\}} \tag{26}$$

This average weight fraction of sorbed CO_2 can be used in conjunction with Eq. 23 to determine fractional bulk flow effects on the flux of CO_2 and will be discussed later.

The conventional definition of material selectivity for the separation of phenol from carbon dioxide is shown in mass fractions as

$$\alpha_{\mathrm{PhOH/CO_2}} = \frac{(y^m_{\mathrm{PhOH}}/y^m_{\mathrm{CO_2}})}{(x^m_{\mathrm{PhOH}}/x^m_{\mathrm{CO_2}})} \tag{27}$$

For convenience, in the present illustrative case, a negligible "stage cut" can be assumed to apply, so that essentially a constant mass fraction of phenol exist on the feed side of the membrane. This limiting case can be achieved by maintaining a high crossflow feed rate relative to the transmembrane flow rate. The mass fraction composition of the feed is fixed and therefore needs no further discussion. Rather than basing the discussions of the separation effectiveness in terms of Eq. 27, a more meaningful figure of merit for the sweep stream situation is to consider α' defined in terms of the fluxes of individual components, normalized by the upstream composition ratios.

Therefore, expression for the effective separation factor is

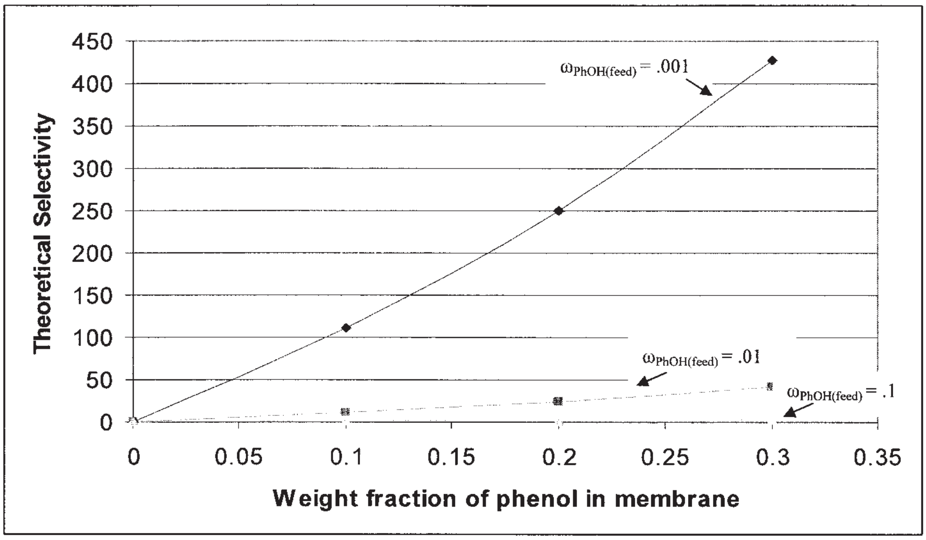

Figure 4. Plot of theoretical selectivity vs. sorbed phenol concentration for different phenol feed compositions.

$$\alpha' = \frac{n_{PhOH}/n_{CO_2}}{x^m_{PhOH}/x^m_{CO_2}} \tag{28}$$

Using Eq. 19 to put fluxes in terms of measurable quantities, the selectivity term becomes

$$\alpha' = \frac{w_{PhOH(M)}}{(1 - w_{PhOH(M)}) \cdot x^m_{PhOH(G)}/x^m_{CO_2(G)}} \tag{29}$$

where $w_{PhOH(M)}$ values represent the weight fractions of phenol sorbed into the membrane and $x_{(G)}$ values represent mass fractions of components in the gas phase of the feed.

Discussion

Based on the above development, several salient points should be discussed. Equation 13 shows that the ratio of phenol to carbon dioxide flux is fixed by the weight fraction of phenol sorbed into the membrane, and does not depend on the "fastness" of the faster permeating species. However, for industrial relevance, productivities are quite important and must be considered. Equation 29, which defines selectivity based on phenol weight fraction, suggests that selectivity for the organic solute—in our case, phenol—is guaranteed only for dilute solutions when conditions are present in which constant solute composition is achieved throughout the membrane. Figure 4 presents a graph of selectivity vs. the amount of sorbed phenol for various feed compositions, based on Eq. 29. This plot shows a significant decrease in selectivity from 438 to 3, at a fixed sorbed phenol weight fraction of 0.3, as weight fractions of phenol in the feed increase from 0.1 to 1.0 wt %, a result that emphasizes the relevance of this process for the stripping of dilute components from feed streams. It is also apparent that higher sorbed phenol concentrations—the crux of the model developed herein—result in significantly higher selectivities. A note of caution is relevant here. Although significant sorption of phenol in the material is desired, care must be taken to ensure mechanical robustness of the separation polymer. Tailoring the materials for specific phenol interactions and further stabilizing the polymer by integrated crosslinking might be necessary for realistic use of this concept.

Bulk flux contributions are the only driving force for phenol flux through the membrane under the conditions studied here. However, these contributions also serve to promote the flux of carbon dioxide. Equation 23 and Figure 5 show that bulk flux effects depend on both the sorbed fraction of phenol and carbon dioxide in the polymer. However, this self-acceleration of carbon dioxide does not adversely affect the overall selectivity of the polymer.

The possible separation effectiveness for a supercritical fluid mixture containing phenol and carbon dioxide can be estimated using Eq. 29 and a phenol feed activity of 0.1. To estimate sorption of phenol into the polymer, dip tests were performed at different phenol activities. Figure 6 presents dip test sorption data for phenol in various polyimides. To ensure mechanical integrity of the uncrosslinked polymers, the percentage of phenol uptake by the membrane of <40% was desired. 6FDA–DAM, which sorbs about 20% phenol by weight between phenol activities of 0–0.2, was chosen as a test case. Hexane was used as a solvent for the phenol in these dip sorption tests. Because it has negligible interaction with the polymer, essentially all sorption was assumed to be from phenol. Detailed explanations of the materials, methodology, and assumptions for these measurements are discussed elsewhere (Damle, 2004). At an activity of 0.1, the phenol uptake in the polymer was about 6%; the proposed feed composition was 0.08 wt % phenol, and thus a selectivity of 79 is predicted. As can be seen from the form of Eq. 29, the selectivities are substantially dependent on both the solute sorption into the polymer and the composition of the feed. Assuming that most feed concentrations are fixed, the single most important determinant of separation efficiency is the affinity of the solute for the polymer. However, care must also be taken to ensure that the swelling caused by the phenol is not enough to cause deformation and subsequent failure of the membrane. The need for this delicate

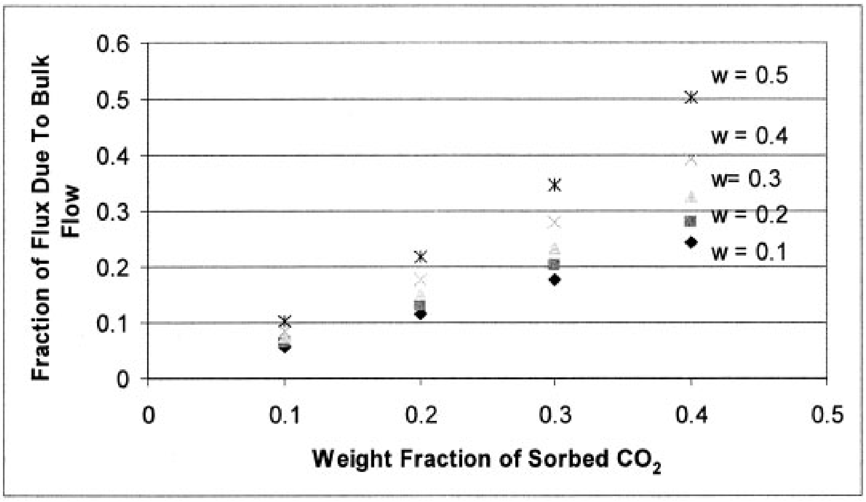

Figure 5. Fraction of flux attributed to bulk flow for carbon dioxide.

This is displayed as a function of sorbed carbon dioxide concentration for different weight fractions of sorbed phenol.

balance emphasizes the need for careful material development in these separation processes.

As stated previously, the development of the "sorp-vection" concept was achieved using Fick's law as a platform. It is important to note that an alternate development of this concept can be achieved by means of the Maxwell–Stephan approach.

Conclusions

This article has described a novel separation process, based on fundamental transport phenomena, and has developed the theoretical background and foundations for the separation. The most salient conclusions are as follows:

(1) Separation of organic solutes from supercritical carbon dioxide is possible and, because of their mechanical stability, preferred, using glassy materials when sorption enhanced convective transfer is used.

(2) For optimum separation effectiveness, conditions should be engineered to ensure a constant activity of dilute organic solute A (phenol).

(3) The flux of component B, in this case CO_2, then *convectively* moves A (phenol), which has selectively partitioned into the polymer phase, across the membrane, rather than relying on diffusive transport of A to an enriched mass fraction downstream.

(4) Although large inherent fluxes of components are desired for high throughput, the ratio of A to B in the downstream receiver is only a function of the amount of A sorbed into the polymer (Eq. 19). Therefore, careful material selection and

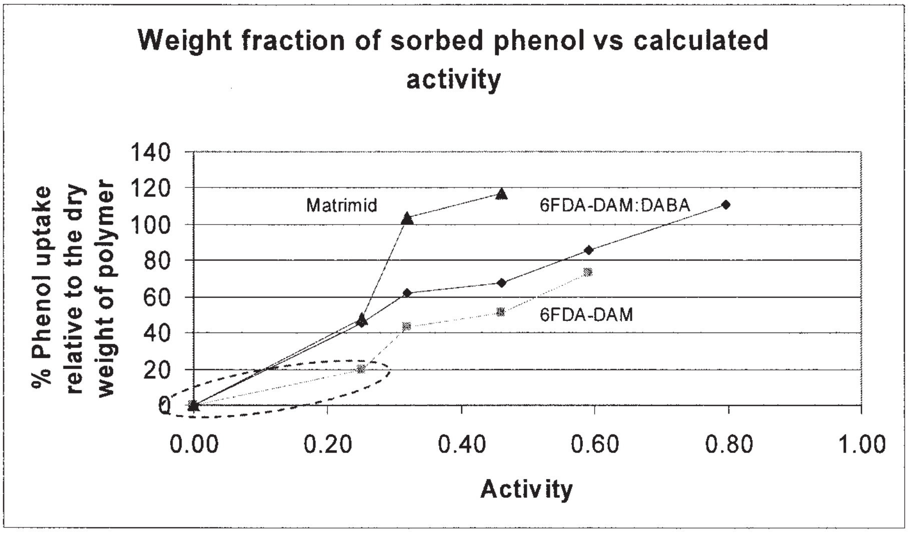

Figure 6. Plot of weight fraction of sorbed phenol vs. phenol solution concentration for three different polymers: 6FDA [(4,4′-hexafluoroisopropylidene) diphthalic anhydride]–DAM (diaminomesitylene), 6FDA [(4,4′-hexafluoroisopropylidene) diphthalic anhydride]–DAM (diaminomesitylene):DABA (3,5-diaminobenzoic acid), and Matrimid®.

Circle marks region of interest for 6FDA–DAM.

development are necessary for optimum separation effectiveness.

(5) As noted above, the selectivity of the material depends to a large extent on the sorbed solute concentration in the polymer. This in turn depends on the partitioning of the solute from the gas to the polymer phase. For optimum selectivity, large partitioning between gas and polymer is desired and can be tuned through material development.

Clearly, the general form of the process could have many applications involving dilute feeds where current membranes processes perform poorly for such removal because of excessive solubility of the smaller component B. Nevertheless, probably the most important widespread application is expected to be the separation of small organic solutes from supercritical carbon dioxide to facilitate the recycling and reuse of CO_2 while bypassing the costly and energy-intensive recompression step. The model proposed herein is currently being investigated experimentally in the laboratory.

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Appendix A

Starting with Eq. 15, the following details the development leading to Eq. 17.

$$n_{CO_2} = \frac{w_{CO_2}}{1 - w_{CO_2}} n_{PhOH} - \frac{\rho D_{CO_2M}}{1 - w_{CO_2}} \frac{dw_{CO_2}}{dx} \tag{15}$$

Substituting Eq. 13 for the flux of phenol,

$$n_{CO_2} = \frac{w_{CO_2}}{1 - w_{CO_2}} \frac{w_{PhOH}}{1 - w_{PhOH}} n_{CO_2} - \frac{\rho D_{CO_2M}}{1 - w_{CO_2}} \frac{dw_{CO_2}}{dx} \tag{A1}$$

Collection of n_{CO_2} on the left-hand side of the equation and consolidation of terms yields

$$n_{CO_2}\left[\frac{1 - w_{CO_2} - w_{PhOH}}{(1 - w_{PhOH})(1 - w_{CO_2})}\right] = -\frac{\rho D_{CO_2M}}{1 - w_{CO_2}} \frac{dw_{CO_2}}{dx} \tag{A2}$$

$$n_{\mathrm{CO_2}} = -\frac{\rho D_{\mathrm{CO_2}M}(1 - w_{\mathrm{PhOH}})}{1 - w_{\mathrm{CO_2}} - w_{\mathrm{PhOH}}}\frac{dw_{\mathrm{CO_2}}}{dx} \tag{A3}$$

After separating variables, the following integral is formed

$$\int_0^l n_{\mathrm{CO_2}}dx = -\int_{w_{\mathrm{CO_2(0)}}}^{w_{\mathrm{CO_2}(l)}} \frac{\rho D_{\mathrm{CO_2}M} w_{\mathrm{CO_2}}}{1 - w_{\mathrm{CO_2}} - w_{\mathrm{PhOH}}} dw_{\mathrm{CO_2}} - \int_{w_{\mathrm{CO_2(0)}}}^{w_{\mathrm{CO_2}(l)}} \rho D_{\mathrm{CO_2}(M)} dw_{\mathrm{CO_2}} \tag{A4}$$

The limits of integration are as follows

$$l = 0 \qquad w_{\mathrm{CO_2}} = w_{\mathrm{CO_2(0)}}$$

$$l = l \qquad w_{\mathrm{CO_2}} = 0 \tag{A5}$$

Integration and collection of terms yield the following expression

$$n_{\mathrm{CO_2}} = \frac{\rho D_{\mathrm{CO_2}M}}{l}\left\{(1 - w_{\mathrm{PhOH}})\ln\left[\frac{1 - w_{\mathrm{PhOH}}}{1 - w_{\mathrm{PhOH}} - w_{\mathrm{CO_2(0)}}}\right]\right\} \tag{A6}$$

which is Eq. 17.

Appendix B

Two key issues to address when establishing the activities of minor components in both the upstream and downstream reservoirs are as follows:

(1) The use of activity to describe the thermodynamic potential of components in the membrane is possible, if the reference state fugacity used in each activity calculation is the same for both upstream and downstream faces of the membrane. As well cited in the literature,

$$a = \frac{f}{f^0}$$

where a is the activity, f is the fugacity of component i in the mixture, and f^0 is the reference state fugacity. In the above equation, f^0 used should be the same for both upstream and downstream faces of the membrane. In the supercritical community, a common choice for the solute reference state is the pure compound as a condensed state at the temperature and pressure of the system (50°C and 1500 psia in this case).

(2) The well-known effect of hydrostatic pressure on penetrant in the polymer in equilibrium with the downstream sweep stream and the pressure discontinuity, attributed to the fact that the membrane is supported on a rigid support, should also be accounted for.

Using Paul's equation, which shows the reduction on component activity in the membrane arising from hydrostatic effects, the following calculation was performed to estimate the hydrostatic pressure effects on the component activity in the membrane's downstream face:

$$a_i^{\mathrm{membrane}} = a_i^{\mathrm{reservoir}}\exp\left[-\frac{\bar{V}_i(P_u - P_d)}{RT}\right]$$

For this calculation, a theoretical supercritical phenol/CO_2 mixture was used as an example, where the upstream pressure is 1500 psi, with the downstream pressure near vacuum. The partial molar volume of phenol in the membrane is estimated by its liquid partial molar volume, 89 cm^3/mol. The following parameters were used in the calculation:

V_i = 89 cm^3/mol
P_u = 1500 psi
P_d = 0 psi
R = 82.05 (gmol K)/(cm^3 atm)
T = 323.15

The results show that hydrostatic pressures affects are present and do lower the activity of the phenol in the membrane by about 30%.

$$a_i^{\mathrm{membrane}} = a_i^{\mathrm{reservoir}}0.71$$

This decrease in activity can be accounted for by merely increasing the mol fraction of phenol in the downstream reservoir until a constant activity throughout the thickness of the membrane is attained. Therefore, one can clearly still attain a condition in which any net swelling differences in phenol uptake between the upstream and downstream sides of the membrane can be made negligible, consistent with the conditions assumed to apply in the present discussion.

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