Determining the Rate Constant of Diffusion-Controlled Oxygen Scavenging Reaction in Polymer Membranes by Transient Permeability Measurements

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Received: June 29, 2004; In Final Form: July 30, 2004

A new method for determining the effective rate constant of diffusion-controlled oxygen scavenging reactions in reactive polymer membranes with finite reactive capacity is proposed. The method is based on rapid homogeneous scavenger activation throughout the membrane and measurement of transient oxygen flux through the membrane with fixed boundary conditions according to standardized testing procedures. After the steady state flux is established across the initially passive membrane the reactive species are activated throughout the membrane thickness by an external source. The transient permeability tests are separately performed on two activated reactive films with preselected different thicknesses, scavenger loadings, and/or scavenger activities, and the minimum transient fluxes through the films are compared. The ratio of these fluxes is related to the reaction rate constant using the analytical results for the effective flux through the catalytic reactive membrane. To account for noninstantaneous and potentially inhomogeneous scavenger activation, the asymptotic behavior of the effective flux growth around the activation time is analyzed in two limiting cases. On the basis of the derived asymptotic expressions, the correction procedures for adjusting the measured minimum fluxes are proposed. The method validity is supported by numerical simulations that demonstrated excellent agreement between the analytical and numerical results for a variety of scavenger activation mechanisms.

Introduction

Polymeric and other barrier materials, routinely used in packaging as passive barriers to gas permeation, work by restricting the rate of ordinary concentration diffusion through the barrier that is usually produced as a uniform thin membrane. While metals and inorganic glasses are thought to be nearly absolute barriers to permeation of atmospheric gases, plastics currently dominate the modern packaging marketplace due to a number of well-documented advantages over metals and glass. High permeability coefficients of permanent atmospheric gases in most commercially important polymers constitute a major drawback of such materials for packaging applications. Active packaging is a relatively new development field, aiming among other things at improving barrier properties of polymeric films through chemical reaction.[1−5] Reactive barrier materials work by scavenging the undesirable solute during its diffusion across the membrane either by binding it in the course of irreversible chemical reaction or by chemically converting it into other (neutral) species. A major current direction in active packaging market for food, beverage, and pharmaceutical applications is the development of reactive barriers to oxygen permeation focused mostly on incorporation of oxygen scavengers into a packaging structure. Utilization of irreversible oxidative reactions to lower oxygen transmission rates through plastic packaging and to reduce oxygen amount present in a package after sealing is seen as an attractive alternative to developing high passive barrier solutions for extending the shelf life of oxygen-sensitive products. Most scavenging reactions involving irreversible binding of permeating permanent gases like oxygen by oxidizable reactive substrates are inherently noncatalytic

(NCR) at ambient conditions even if they are catalyzed by a third species; i.e., they always involve consumption of the reactive substrate. As a result, irrespective of the chemical nature of the oxygen scavenging system, its total reactive capacity to consume oxygen is always finite. While several methods for evaluating the reactive capacity of scavengers and scavenging packaging structures are available, determining the rate constant of the oxygen scavenging reaction in polymer matrix remains the most problematic part of reactive barrier characterization. For fast scavenging reactions that are strongly diffusion-controlled, the oxygen diffusion in polymer matrix is the rate-limiting step; hence, the exact knowledge of the scavenging reaction rate is often unnecessary for practical applications.[6,7] For commercially important reactions with intermediate rates that are weakly diffusion-controlled (the quantitative difference between strong and weak diffusion control is explained in text), the scavenging rate can have a dramatic effect on scavenger consumption dynamics and transient oxygen ingress into the package.[8−10] Therefore, determining the scavenging reaction rate is critical for the systems with weak diffusion control and may still be essential for characterization, comparison, and optimization of strongly diffusion-controlled systems. The activation-controlled systems with slow reaction rates are of no practical importance for packaging since the improvement of membrane barrier function due to a slow scavenging reaction is negligible on the time scale comparable to the expected shelf life of the packaged product.[10]

Various oxygen-scavenging systems and chemistries have been proposed to date for active packaging applications.[3−5] Some of them involve dispersion of reactive inorganic particulates like ferrous iron in the nonreactive polymer matrix while others involve placement of metal-based catalysts for accelerated

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oxidation of double bonds that may be present in the matrix polymer molecules or in dispersed reactive additives susceptible to oxidation such as ascorbic and unsaturated fatty acids. Newer scavenging systems incorporate ring-opening oxidation of specially designed polymers containing heterocycles like ethylene−methyl acrylate−cyclohexene−methyl acrylate copolymer (EMCM).[11,12] The advantage of such systems is that oxygen removal occurs without formation of low molecular weight oxidation byproducts. Such byproducts are often undesirable in packaging due to their potential migration into a packaged product and related regulatory issues. Thus, in many instances the scavenger becomes inseparable from the matrix material. That fact leads to difficulties in determining its reaction rates with permeating oxygen since the scavenger cannot be analyzed in "pure" form, but in the polymer matrix the analysis is complicated by often present diffusion control of the overall reaction rate, leading to falsified measured kinetics. Moreover, even if the scavenger is available in pure form and its reaction rate can be determined by measurements of oxygen consumption kinetics in oxygen atmosphere, the simple ratio of oxygen diffusivities in a vacuum and in polymer matrix may not account for structural inhomogeneities and corresponding diffusivity differences present around dispersed active binding sites.[13,14] The access of oxygen to binding sites embedded in a polymer matrix may also be limited due to potential matrix chemical, morphological, and crystalline structure changes around the embedded scavenger and molecular interactions of matrix polymer with the scavenger. These facts may affect the effective scavenging rate constant in the reactive membrane as well as its scavenging reactive capacity.

Another challenge for the reaction rate measurement is that the scavenger has to be activated before the reactive barrier starts to work. Some scavenger chemistries may be immediately active upon manufacture and that presents a problem for their storage and distribution since preservation of their reactive capacity before it is actually needed can be cost-inefficient and difficult to achieve. Therefore, it is preferred to have a simple and reliable "on-demand" activation method for the scavenger to be commercially successful. While activation mechanisms differ widely depending on the particular scavenging chemistry, in many instances the scavenger cannot be instantly and homogeneously activated throughout the membrane. For example, oxygen scavenging systems based on ferrous iron are activated by a combination of moisture and heat diffusion through the matrix, and obviously, the humidity and temperature levels required for scavenger activation throughout film thickness cannot be achieved instantly. The EMCM-based scavengers with photoinitiators, on the other hand, can be nearly instantly activated by film exposure to UV radiation; however, the degree of activation and the corresponding reaction rate and even the activated reactive capacity strongly depend on the exposure time and UV light intensity.[12]

Considering the points made above, a general method for determining the effective reaction rate constants in polymer-based reactive films is clearly needed, especially when standard spectroscopic methods are not applicable due to a lack of measurable fluorescence emissions in many scavenging systems and spatiotemporal inhomogeneity of concurrent scavenger and solute consumption in the reactive-diffusive systems far from equilibrium. The method has to be applicable to analysis of various scavenging chemistries, and it has to address the scavenger activation kinetics. One such method is proposed in the presented work.

Theoretical Background

Diffusion of gaseous permeating species (concentration [C] of the solute in the membrane material) through an essentially planar homogeneous isotropic polymeric membrane with thickness L and its isothermal homogeneous noncatalytic reaction with immobile reactive species (concentration [R] of the anchored active sites) uniformly dispersed within the polymer matrix are considered. The irreversible bimolecular reaction between C and R of the second order with the stoichiometric coefficient μ, the reaction rate ν, and the apparent effective rate constant K representing common oxygen scavenging systems in polymeric barrier membranes is chosen for the method development:

$$\mu C + R \xrightarrow{K} products \tag{1}$$

$$\nu = K[C][R] \tag{2}$$

The stoichiometric coefficient μ in mol/mol or cm^3 (STP)/g represents the maximum amount of the solute consumed by a particular weight or molar load of the scavenger in the membrane material before the scavenger is completely deactivated or consumed by the reaction. Since many oxidative reactions of transition metals and unsaturated organic compounds proceed on the exposed (possibly catalyzed) active sites and the solute often may not penetrate the oxidized surface of the reactive particle, not all embedded reactive sites may be available for the reaction. The corresponding activity $a = a(x,t)$ of the scavenger will also depend on the reactive particle morphology, dispersion, shape, and size distribution. The reaction mechanism then may look like

$$\mu^* a C + R \xrightarrow{K} products \tag{3}$$

where μ^* represents the true stoichiometry of the reaction. The fundamental Smoluchowsky rate constant[15] $K_{Smol} = 4\pi R_{AB} D_{AB}$ for diffusion of particle A to particle B through a three-dimensional sphere with the collision radius $R_{AB} = R_A + R_B$ and the diffusivity $D_{AB} = D_A + D_B$ determines the upper limit of the apparent reaction rate constant K. For the reactive particles B embedded in the immobile polymer matrix M, $D_B = 0$, and the diffusivity of solute A in the solid matrix is $D = D_{AM}$. The rate constant K may be concentration and time dependent if the embedded reactive particles are porous or the reaction products are permeable and the solute is allowed to penetrate through the reacted particle surface with potentially very different mobility of the solute molecules within the particulate (similar to processes in permeable catalysts). However, because of the difficulty of determining the reactive particle parameters, the noncatalytic nature of the oxygen scavenging reactions and generally nonporous nature of commercially available oxygen scavengers we will not address this possibility. Moreover, if there is a transition from the reaction initially taking place on the surfaces of scavenger particulate to the reaction inside the particles or particle pores,[7] only the rate constant for the initial reaction on particle surfaces can be determined by the proposed methodology as well as by most other methods if at all applicable. Also as mentioned, many modern oxygen scavenging systems rely on oxidation of double bonds in the matrix polymer in the presence of metal salt based catalysts and do not involve reactive consumption of dispersed inorganic particulates. On the other hand, the effective stoichiometric coefficient $\mu = \mu^* a$ can be easily determined by the standard reactive capacity

measurement techniques, e.g., by measuring the total amount of oxygen consumed by the activated reactive membrane with known scavenger loading placed in a closed chamber filled with oxygen.

In the following discussion the square brackets denoting concentrations of the species C and R are dropped for convenience. Then the dynamics of the outlined reaction−diffusion process is described by the one-dimensional material balance across the membrane thickness ($0 < x < L$), assuming the concentration-independent effective diffusivity D of the solute in the matrix and neglecting both accumulation of the reaction products in the membrane and matrix polymer transport property changes due to reaction (generally valid assumptions for small volumetric scavenger loadings in commercial reactive films)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \mu KRC \qquad (4)$$

$$\frac{\partial R}{\partial t} = -KRC \qquad (5)$$

for $C = C(x,t)$, $R = R(x,t)$ and the irreversible reaction with the reaction rate constant $K = K(T)$ to be determined. Most currently available commercial oxygen scavenging systems involve irreversible oxidation reactions,[1−5] while the first order by both reactants is a common feature of bimolecular reactions in liquids and gases and by extension on activated solid surfaces. In the case of catalyzed oxidation of the scavenging species the effective rate of threemolecular diffusion-controlled reaction has a much more complex form,[16] and it can be concentration and time dependent even without structural inhomogeneities around the embedded active sites.[17]

The proposed method is based on combination of the steady-state permeation with catalytic scavenging reaction (CR) and the asymptotic analysis around the time of scavenger activation. The method can still be applied if the reaction is not of the second order; however, some modification of the derived results will be required: this case is not considered here. It is also assumed that solute diffusivity D is not affected by the scavenger presence or the reaction products. If the scavenger presence strongly affects D, e.g., due to high solid loadings or electrostatic interactions between polar species, the corresponding effective value of D_{AM} for the solute in a polymeric matrix loaded with the inactivated scavenger has to be evaluated using standard techniques[18−21] before the proposed method can be used. Diffusivity of gases in any polymer is a strong function of temperature; hence, the isothermal reaction is commonly assumed when slowly reacting scavengers are present in the membrane at low concentrations and thermal equilibrium is rapidly established across the thin membrane in contact with the unlimited environments at a fixed temperature. For the method development purposes we initially assume the scavenger to be instantly and fully activated and at 100% of its reactive capacity by the time $t = 0$; thus, after the activation the scavenger concentration R is affected only by its reaction with C, and it no longer depends on interactions with the external fields. The scavenger activation mechanism and the effect of induction period of the scavenger on the transient transmission rate will be taken into account later. The induction period refers to the duration of the scavenger activation process throughout the membrane by some external source: it should not be confused with the lag time that is a measure of the asymptotic delay before establishing the steady state permeation pattern across a (passive) membrane initially free of the solute in the presence of the fixed solute concentration difference at the membrane interfaces.
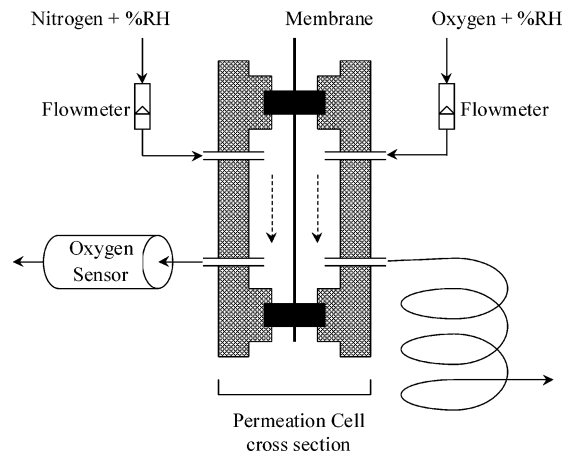

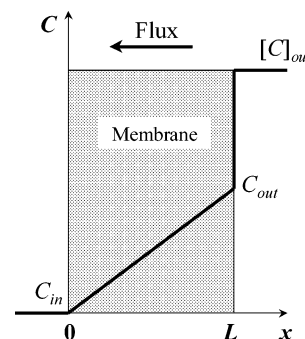**Figure 1.** Experimental setup schematic for isothermal film permeability measurement.

Figure 2. Steady-state solute concentration profile in the passive homogeneous membrane.

Fixed boundary conditions outside the film corresponding to gaseous permeant equilibrium on the film surfaces and representing the standard oxygen transmission rate test conditions[22] commonly used for plastic packaging materials are set as

downstream: $x < 0$, oxygen partial pressure $p(0) = p_{in}$ (6)

upstream: $x > L$, oxygen partial pressure $p(L) = p_{out} > p_{in}$ (7)

Equilibrium boundary concentrations C_{in} and C_{out} of the permeant within the film are then found from Henry's law for dilute solutions, assuming linearity of sorption isotherm for the membrane material within solute pressure range of interest (<1 atm in ambient packaging):

downstream film boundary: $x = 0$, $C(0,t) \equiv C_{in} = Sp_{in}$ (8)

upstream film boundary: $x = L$, $C(L,t) \equiv C_{out} = Sp_{out}$ (9)

Here S is the equilibrium solubility coefficient of the particular permeant in the particular film material. A schematic of the standard experimental setup for permeability measurements is shown in Figure 1. Figure 2 shows the steady state solute concentration profile across an initially passive membrane before the scavenger activation and after the exhaustion of the scavenger reactive capacity by the reaction with the solute.

The standard method of film permeability testing,[22] e.g., using MOCON oxygen sensory and transmission rate measuring equipment, involves continuous removal of the species permeated through the film by a carrier gas flow (usually nitrogen or nitrogen/oxygen mixture with preset relative humidity level if
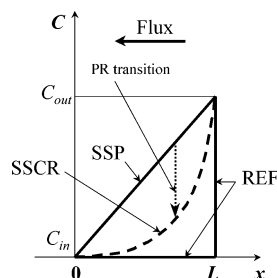
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Figure 3. Three types of common initial conditions in reactive membranes: REF = reference; SSP = steady-state passive; SSCR = steady-state catalytic reaction.

desired), thus maintaining a fixed partial oxygen pressure at the inner membrane boundary and serving as a perfect sink for the permeated oxygen. Preset zero oxygen concentration $C_{in} = 0$ at the downstream boundary $x = 0$ is the common choice, but any other value may be used. At the upstream membrane boundary the constant partial pressure of oxygen is maintained by a controlled flow of pure oxygen or atmospheric air of desired humidity through the permeation cell as shown in Figure 1. The relevance of this test setup for packaging applications stems from the fact that barrier polymeric materials and structures are routinely used for packaging oxygen-sensitive products (containing easily oxidizable vitamins C and E for example). Therefore, we can usually assume that nearly all permeated oxygen will immediately react with the packaged product, preventing any significant free oxygen accumulation in the package headspace and in the product.

The initial conditions for the solute within the membrane around scavenger activation time can be difficult to determine, but they are critical to know if experimental data for transient permeation are to be utilized. We consider the initial conditions of the following general form

$$C(x,0) = C_0(x) \qquad (10)$$

$$R(x,0) = R_0 \qquad (11)$$

Here $C_0(x)$ is the oxygen concentration profile chosen from three alternatives shown in Figure 3:

reference conditions: $C_0^{REF}(x) = 0 \qquad (12)$

steady state passive permeation:

$$C_0^{SSP}(x) = C_{in} + (C_{out} - C_{in})\frac{x}{L} \qquad (13)$$

steady state catalytic reaction:

$$C_0^{SSCR}(x) = \frac{C_{out}}{e^\phi - e^{-\phi}}(e^{\phi x/L} - e^{-\phi x/L}) \qquad (14)$$

where ϕ is the Thiele modulus for the catalytic homogeneously reactive monolayer described below. The SSCR concentration profile in condition (14) corresponds to the boundary condition $C_{in} = 0$. Although the SSCR solutions are available for any fixed boundary conditions, we will focus only on the downstream condition $C_{in} = 0$ in order to avoid potential solute scavenging from the downstream membrane side. The instantaneous scavenger activation at the time $t = 0$ can be formally expressed as

$$K(t) = K_A h(t) \qquad (15)$$

where $h(t)$ is the Heaviside step function. As mentioned earlier, such systems are commercially available, e.g., EMCM copolymer with photoinitiator activated by UV source. Thus, for the method development purposes we initially deal with the passive film with steady-state permeation pattern defined by the boundary conditions (8) and (9) and then start considering the system behavior from the moment of complete scavenger activation according to (15) while maintaining the same fixed boundary conditions.

Effective Flux with Catalytic Scavenger

We consider the following simplifying assumption to be able to reduce the system of eqs 4 and 5 to an analytically solvable steady-state reaction−diffusion problem: the concentration of active scavenging sites R is in excess of stoichiometric amount of oxygen present anywhere within a film, and the active site concentration available for reaction is changing slowly (not necessarily due to slow reaction rate: morphology of scavenger particles may provide sufficiently high reactivity on particle surface only; then when the surface layer reacted completely, the permeant has a chance of reacting within untapped inner layers, provided the reaction products do not interfere with permeant access to active sites). This assumption is similar to scavenger acting as a catalyst without active site depletion, i.e., $R(x,t) = R_0$. We also postulated earlier that reaction products do not affect transport properties of the membrane matrix such as permeant diffusivity and solubility in it as well as the membrane geometric dimensions. Then we can make a substitution:

$$k = \mu K R_0 \qquad (16)$$

After introducing dimensionless x coordinate $\xi = [0...1]$

$$\xi = \frac{x}{L} \qquad (17)$$

we rewrite material balance (4) with the apparent rate constant k for the pseudo-first-order reaction:

$$\frac{L^2}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial \xi^2} - \phi^2 C \qquad (18)$$

where ϕ is a dimensionless complex called the Thiele modulus. The ϕ^2 complex is also known as the second Damköhler number Da^{II} representing the ratio of characteristic time of solute diffusion to characteristic time of its reaction within the membrane:

$$\phi \equiv \sqrt{Da^{II}} = L\sqrt{\frac{k}{D}} \qquad (19)$$

The overall reaction rate is said to be diffusion-controlled at some time moment t if the transient Thiele modulus of the reactive membrane $\phi(t) > 1$. Obviously for the catalytic scavenger the Thiele modulus $\phi = $ const if the rate constant K, the membrane thickness L, and the solute diffusivity D are not affected by the potential matrix morphology, transport property, or temperature changes. For the noncatalytic scavenger at the same conditions the spatially averaged transient Thiele modulus may be used:

$$\bar{\phi}(t) = L\sqrt{\frac{\mu K}{DL}\int_0^L R(x,t)\,dx} \qquad (20)$$

The strong diffusion control of the overall reaction rate is exercised when $\bar{\phi}(t) \gg 1$. For practical purposes $\bar{\phi}(t) > 100$ can be used as an approximate boundary separating weak and strong diffusion control cases. Then the weak diffusion control is present when $1 < \bar{\phi}(t) < 100$. The latter case is characterized by a potentially significant "leakage" of the solute through the reactive membrane during the transient permeation period even when its reactive capacity is not yet close to being exhausted. The amount of leakage during the scavenger capacity exhaustion time was quantified by us elsewhere.[10] Meanwhile, the strong diffusion control case is associated with the "fast" reaction limit, resulting in nearly zero transient permeation rates before the so-called "breakthrough time". Breakthrough time[7] corresponds to the time when the scavenger reactive capacity is nearly exhausted by the localized reaction−diffusion wave front propagating through the membrane thickness, and the solute starts to emerge (leak) from the downstream membrane boundary. The numerical simulations[6,10] of the solute ingress dynamics through the noncatalytic reactive membrane also demonstrated continuous solute leakage through the membrane in the weak diffusion control case and the breakthrough time phenomenon when the strong diffusion control is present. It should be noted that the difference between the solute leakage and solute breakthrough is quantitative rather than qualitative: when the perfect sink condition $C_{in} = 0$ is maintained at the downstream boundary, the solute leakage is present for any value $\bar{\phi}(t) < \infty$ from the scavenger activation instant $t = 0$ and with the SSP initial condition in use, although the rate of leakage, i.e., the effective flux through the membrane, is the exponentially vanishing function of $\bar{\phi}(t)$ as demonstrated below.

We initially focus on a steady-state solution for eq 18 with the boundary conditions (8) and (9), i.e., consider the equation

$$\frac{\partial^2 C}{\partial \xi^2} = \phi^2 C \qquad (21)$$

The general solution of (21) is found as

$$C(\xi) = \alpha_1 \cosh(\phi\xi) + \alpha_2 \sinh(\phi\xi) = \beta_1 e^{\phi\xi} + \beta_2 e^{-\phi\xi} \quad (22)$$

where

$$\alpha_1 = \beta_1 + \beta_2 \qquad (23)$$

$$\alpha_2 = \beta_1 - \beta_2 \qquad (24)$$

Constants β_1 and β_2 are determined from the boundary conditions (8) and (9) as

$$\beta_1 = \frac{C_{out} - C_{in}e^{-\phi}}{e^{\phi} - e^{-\phi}} \qquad (25)$$

$$\beta_2 = \frac{C_{in}e^{\phi} - C_{out}}{e^{\phi} - e^{-\phi}} \qquad (26)$$

In the standard permeability test method the downstream solute concentration is commonly maintained at zero utilizing constant removal of the permeated solute by the carrier flow and resulting in $C_{in} = 0$, hence

$$\beta_1 = -\beta_2 = \frac{C_{out}}{e^{\phi} - e^{-\phi}} \qquad (27)$$

Then the steady-state solution for catalytic reaction that was given as the SSCR initial condition (14) has a form:

$$C^{SSCR}(\xi) \equiv C_0^{SSCR}(\xi) = \frac{C_{out}}{e^{\phi} - e^{-\phi}}(e^{\phi\xi} - e^{-\phi\xi}) \qquad (28)$$

The material flux J_x of a species across any membrane plane $x = X$ normal to its thickness direction is determined from Fick's first law of diffusion as

$$-J_x = D\frac{dC}{dx}\bigg|_{x=X} = \frac{D}{L}\frac{dC}{d\xi}\bigg|_{\xi=X/L} \qquad (29)$$

After differentiating (22) by ξ, we obtain the local flux J_x at $x = \xi L$ as

$$-J_x = \frac{D}{L}\phi(\beta_1 e^{\phi\xi} - \beta_2 e^{-\phi\xi}) \qquad (30)$$

At the downstream membrane boundary $\xi = 0$, the effective SSCR flux J_0 is

$$-J_0 = \frac{D}{L}\phi(C_{out}\,\text{csch}(\phi) - C_{in}\,\text{coth}(\phi)) \qquad (31)$$

and for $C_{in} = 0$

$$-J_0 = \frac{DC_{out}}{L}\frac{\phi}{\sinh(\phi)} \qquad (32)$$

These are known results from standard treatment of diffusive mass transport coupled with catalytic scavenging reaction. Note that the transient effective flux $J_0(t)$ through the exposed test film area is the actual quantity recorded during standardized permeability measurements. The ASTM permeability testing procedure[22] for passive membranes suggests using only the steady-state experimental values of J_0 for measuring gas transmission rates through uniform membranes and determining permeabilities of homogeneous isotropic materials. Our method proposed for the NCR membranes intends to utilize transient flux values $J_0(t)$ measured and recorded during and after scavenger activation at the preset time intervals to determine the flux dependence on ϕ. We also note that solutions (22) and (30)−(32) are applicable only when $\phi > 0$, i.e., when the reaction constant $K > 0$. For $K \equiv 0$ the coefficients in (25) and (26) become degenerate due to 0/0 singularity, although in this case the result (32) asymptotically converges to the passive barrier solution (13) as $K \rightarrow 0$.

The Method

If we measure transient solute permeation through a reactive membrane with the fixed boundary conditions (8) and (9) and the initial conditions (11) and (13), i.e., using the initial solute concentration profile $C_0^{SSP}(x)$, performing instantaneous scavenger activation throughout the membrane, and neglecting the PR transition shown in Figure 3 (an ideal case), then the measured effective flux $J_0(t)$ will evolve as shown in Figure 4a. For comparison, Figure 4b demonstrates the actual experimental data clearly showing the effects of noninstantaneous scavenger activation with the activation rate comparable to the rate of oxygen diffusion. In the ideal case, the minimum measured effective flux J_0^{min} will be equal to the effective SSCR flux J_0 from (32) where $\phi = \phi_0$ (the initial Thiele modulus

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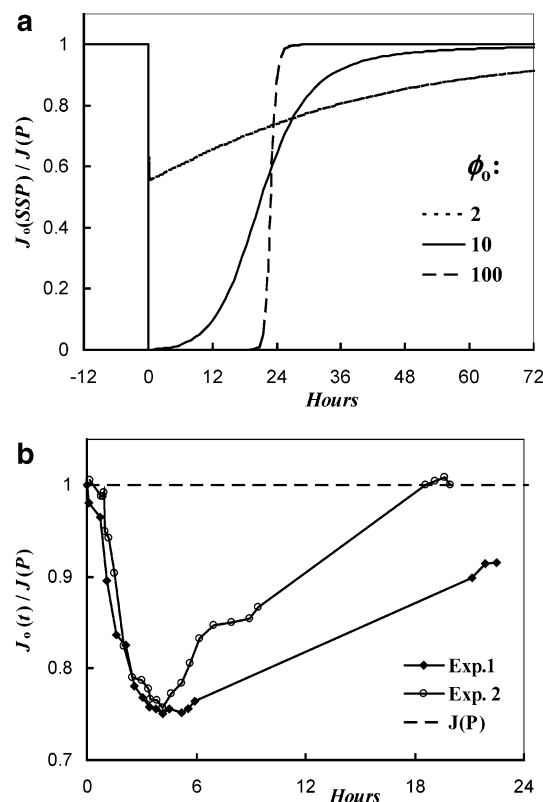*J. Phys. Chem. B, Vol. 108, No. 40, 2004* **15623**

Figure 4. (a) Evolution of the effective flux through the NCR membrane with instantaneous and homogeneous scavenger activation at $t = 0$ and instant PR transition for three initial Thiele moduli ϕ_0 and a constant relative scavenging capacity $\Psi = 50$. (b) Evolution of the experimental transient flux through the moisture activated NCR membrane with unquantified reactive capacity and reactivity (courtesy of Dr. A. Goldman, Alcoa CSI).

Figure 5. (a) Plot of function $f(\phi) = \phi/\sinh(\phi)$. (b) Range of the initial Thiele modulus ϕ_0 of the NCR reactive film recommended for method implementation with corresponding steady-state CR to passive (P) flux ratio (boxed).

for the instantly and homogeneously activated NCR membrane). The ϕ_0 value can be found if we compare measured $J_0^{\min}$ with the steady-state effective flux $J_0(P)$ through the passive film with the same thickness and matrix material:

$$\frac{J_0(SSCR)}{J_0(P)} = \frac{\phi_0}{\sinh(\phi_0)} \tag{33}$$

Note that in steady-state permeation through passive homogeneous membranes the flux $J_x(P)$ through any cross section $x = X$ normal to membrane thickness direction is equal to the effective flux $J_0(P)$ across the downstream boundary. Therefore, it will be referred to simply as $J(P)$ in further discussions. Figure 5 demonstrates that $\phi_0/\sinh(\phi_0)$ is a monotonic function of ϕ_0; therefore, the solution of (33) is unique. However, usefulness of (33) is limited since the passive membrane without the scavenger may not have the same effective kinetic (D) and thermodynamic (S) transport properties as a reactive membrane loaded with scavenger. Even if this difference can be neglected in practice, the use of (33) may be limited by the sensitivity range of oxygen sensory equipment. Figure 5b exemplifies that fact by showing that for a reasonably large ϕ_0 the ratio (33) goes to zero, rapidly exceeding the sensitivity range of the oxygen sensor. A better way to use the result (33) is to compare two nearly identical reactive films with different initial Thiele moduli that are not very large. Rephrasing this statement, weakening the diffusion control of the overall reaction rate provides a way to improve the method resolution, which is not at all surprising. The selection of the scavenger loading, the
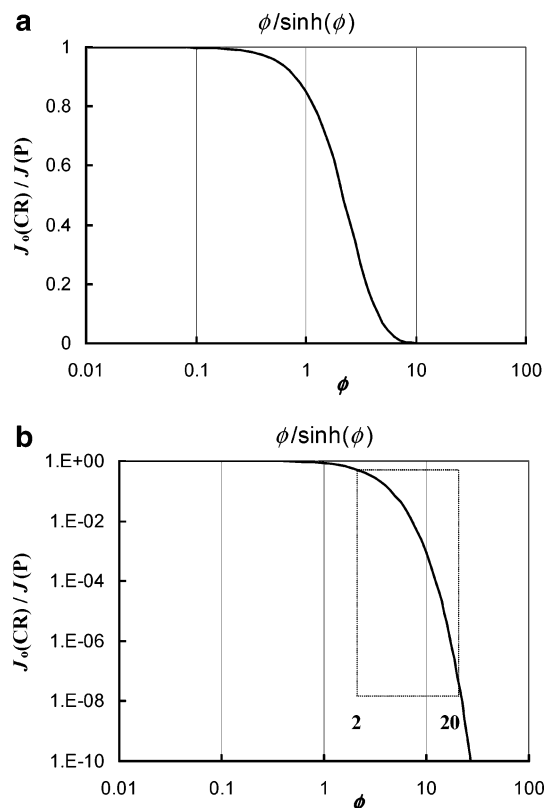
degree of its activation, and the film thickness to satisfy the practical criterion

$$2 < \phi_0 < 20 \tag{34}$$

shown in Figure 5b depends on the transport properties of the membrane material and the specific scavenger system in question. This information should be readily available to the reactive barrier system developer.

Controlled variation in the film properties for testing can be achieved by varying the loaded scavenger amount (the initial concentration R_0) and the initial activity of the scavenger (equivalent to altering the loaded amount of the fully activated scavenger), by changing the test film thickness, or by any combination of the above. Since manufacturing of very thin, uniform, and homogeneous films to increase their measurable transmission rates may be problematic in the case of highly reactive barriers, a slight variation of the scavenger loading and/or its initial activity (in the case of scavengers with controlled activation) may serve as a practical remedy for problems arising in thin film processing. Then the ratio of the measured minimum transient fluxes through such NCR films denoted 1 and 2 corresponding to the steady-state fluxes through the respective hypothetical CR films is found from (32) as

$$\frac{\min(J_{01}(t))}{\min(J_{02}(t))} \approx \frac{J_{01}(CR)}{J_{02}(CR)} = \frac{L_2}{L_1}\frac{\phi_1}{\phi_2}\frac{\sinh(\phi_2)}{\sinh(\phi_1)} \tag{35}$$

where ϕ_1 and ϕ_2 denote the initial Thiele moduli ϕ_{01} and ϕ_{02} of the instantly activated NCR films 1 and 2, respectively. Note that the minimum of the transient flux $J_0(t)$ will be observed only when the SSP initial condition with $J_0(0) = J(P)$ is used as shown in Figure 6. In further discussions we will drop the
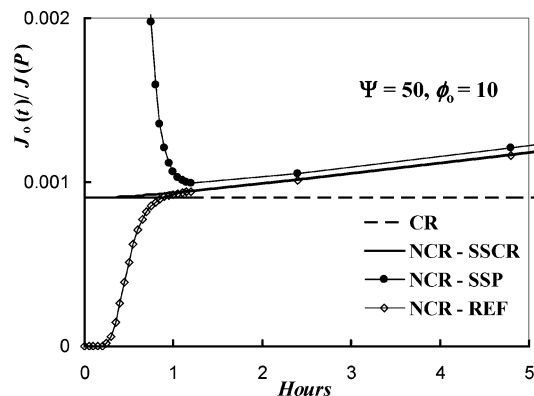
Figure 6. Steady-state effective flux J_0 in the CR membrane and evolution of the effective flux in the NCR membrane for the REF, SSP, and SSCR initial conditions with $\phi_0 = 10$ obtained by numerical simulations. The initial transient phase for the REF and SSP conditions represents two types of reference-to-reactive and passive-to-reactive transitions.

qualifier (*CR*) in denoting the steady-state CR fluxes J_{01} and J_{02} for convenience.

Since the matrix polymer is the same in both films and the volumetric scavenger loading is generally low, we can assume that the effective diffusivity of the membrane matrix is not affected by the loaded scavenger and $D_1 = D_2 = D$. If that is determined not to be the case, the corresponding diffusivity values have to be evaluated in separate experiments for each test film with altered initial concentration R_0 and then substituted into ϕ_1 and ϕ_2. The variation in the other film properties can be expressed by two independent constants α and β known a priori:

$$L_2 = \alpha L_1 \tag{36}$$

$$R_{02} = \beta R_{01} \tag{37}$$

Then the result (35) can be rewritten as

$$\frac{J_{01}}{J_{02}} = \frac{1}{\sqrt{\beta}} \frac{\sinh(\phi_1 \alpha \sqrt{\beta})}{\sinh(\phi_1)} \tag{38}$$

The value of ϕ_1 for film 1 can be determined from (38) by comparing the minimum transient fluxes through both test films. For the special case of changing only the film thickness by factor α, $L_2 = \alpha L_1$, and keeping the same initial scavenger concentration and its activity a in both films, $R_{01} = R_{02} = \text{const}$, we obtain for the CR flux ratio $j(L/\alpha L)$:

$$j(L/\alpha L) \equiv \frac{J_0(L_1)}{J_0(\alpha L_1)} = \frac{\sinh(\alpha \phi_1)}{\sinh(\phi_1)} \tag{39}$$

For the case of changing the initial scavenger concentration R_0 in the membrane by factor β (or varying scavenger activity a when a controlled activation method is available), $R_{02} = \beta R_{01}$, and keeping the thickness of both test films the same, $L_1 = L_2 = \text{const}$, we obtain for the CR flux ratio $j(R/\beta R)$:

$$j(R/\beta R) \equiv \frac{J_0(R_{01})}{J_0(\beta R_{01})} = \frac{\sinh(\phi_1 \sqrt{\beta})}{\sqrt{\beta} \sinh(\phi_1)} \tag{40}$$

If we incorporate the same scavenger amount M in two films with different thicknesses

$$M = R_{01} A L_1 = R_{02} A L_2 \tag{41}$$

where A is the sample area and $L_2 = \alpha L_1$, then $R_{02} = \alpha^{-1} R_{01}$ with the corresponding CR flux ratio

$$j(L/\alpha L, R/\alpha^{-1} R) \equiv \frac{J_0(L_1, R_{01})}{J_0(\alpha L_1, \alpha^{-1} R_{01})} = \sqrt{\alpha} \frac{\sinh(\phi_1 \sqrt{\alpha})}{\sinh(\phi_1)} \tag{42}$$

Using variation in the film thickness and/or the scavenger concentration as well as a suitable film sample area for the measured flux to fall within the oxygen sensor sensitivity range, the result (38) provides a general method to evaluate the initial Thiele modulus ϕ_1 of the reactive membrane 1 and hence the reaction rate constant K if the oxygen diffusivity D in the membrane matrix material and the effective stoichiometric coefficient μ of the reaction are known. The standard time lag method can be used to determine the value of D.[18–21] It is interesting to note that neither the thermodynamic solubility coefficient S of the solute in the membrane material nor the permeability coefficient $P = DS$ of the matrix material is needed for implementation of the proposed method, provided the effective diffusivity D of the solute in the matrix material is known. There is also no need to wait for the establishment of the steady-state permeation pattern upon the scavenger capacity exhaustion that can be a very long time in reactive barriers with a large solute scavenging capacity. The eq 38 and its derivatives (39), (40), and (42) have to be solved numerically to find the corresponding initial Thiele modulus ϕ_1; however, in several simple to implement practical cases it is possible to obtain analytical formulas.

Let ϕ_0 correspond to the reactive film with the thickness L and the initial weight or molar scavenger loading $M_0 = R_0 A L$. By doubling the thickness and keeping $R_0 = \text{const}$, we find from (39)

$$j(L/2L) = \frac{\sinh(2\phi_0)}{\sinh(\phi_0)} = 2 \cosh(\phi_0) \tag{43}$$

then

$$K = \frac{D}{L^2 \mu R_0} \left(\cosh^{-1}\left(\frac{j(L/2L)}{2} \right) \right)^2 \tag{44}$$

The following identity can be used to simplify calculation of $\cosh^{-1}$ if needed:

$$\cosh^{-1}(z) = \ln(z + \sqrt{z^2 - 1}) \tag{45}$$

Note that the minimum possible value $j(L/2L) = 2$ is obtained for the case of steady-state flux through two passive films. (Transient flux values smaller than the steady-state values during the diffusive time lag for the reference initial condition (12) are excluded.) Equation 44 handles this situation correctly by predicting $K = 0$.

We can increase the membrane thickness to $1.5L$ to improve the measurement accuracy if the $J_0(2L)$ value is too small or close to the sensitivity limit of the oxygen sensor in the fast reaction case:

$$j(L/1.5L) = \frac{\sinh(1.5\phi_0)}{\sinh(\phi_0)} = 2 \cosh(0.5\phi_0) - \frac{1}{2 \cosh(0.5\phi_0)} \tag{46}$$

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then

$$K = \frac{4D}{L^2 \mu R_0}\left(\cosh^{-1}\left(\frac{j(L/1.5L) + \sqrt{[j(L/1.5L)]^2 + 4}}{4}\right)\right)^2 \quad (47)$$

Increasing the initial scavenger loading into the matrix material by 4 times (resulting in $R_{01} = 4R_0$) and producing the test film of the same thickness L, we obtain

$$j(R/4R) = \frac{\sinh(2\phi_0)}{2\sinh(\phi_0)} = \cosh(\phi_0) \quad (48)$$

then

$$K = \frac{D}{L^2 \mu R_0}(\cosh^{-1}(j(R/4R)))^2 \quad (49)$$

Using the scavenger loading ratio of 2.25 instead of 4 allows utilization of the algebraic result (46) to express $j(R/2.25R)$. Finally, if we keep the scavenger amount in the film constant and increase its thickness 4 times with corresponding 4 time reduction in the scavenger concentration, the following result is obtained by applying (42):

$$j(L/4L, R/{}^1/_4 R) = \frac{2\sinh(2\phi_0)}{\sinh(\phi_0)} = 4\cosh(\phi_0) \quad (50)$$

then

$$K = \frac{D}{L^2 \mu R_0}\left(\cosh^{-1}\left(\frac{1}{4}j(L/4L, R/{}^1/_4 R)\right)\right)^2 \quad (51)$$

Correction for the Passive-to-Reactive Transition

Because of inevitable use of some initial condition for oxygen concentration in the membrane other than the SSCR profile at the instant of the scavenger activation, the nonzero delay will always exist before the minimum of the effective flux $J_0(t)$, corresponding to the SSCR flux, is reached in the experiment as shown in Figure 4b. This minimum flux may also be higher than J_0(SSCR) due to partial inhomogeneous consumption of the scavenger reactive capacity through the thickness during the induction period: that issue is addressed in the following section. Even at nearly instantaneous scavenger activation by a penetrating source like UV radiation it will take an instantaneous reaction rate ($K = \infty$) to realize the instant transition from the SSP (likely present before the scavenger activation) to the SSCR oxygen concentration profile, provided the reactive capacity of the scavenger is not affected by the transition. This passive-to-reactive transition (PRT) was described by us earlier.[10] The PRT, the reference-to-reactive transition, and their effects on the $J_0(t)$ are shown in Figure 6 as predicted by numerical simulations for the corresponding initial conditions. Clearly, for any sufficiently large initial Thiele modulus ϕ_0 the minimum transient flux could be very small, and the error in determining it could be unacceptably large if the practically important SSP initial condition was present at the onset of scavenger activation. The reference initial condition (12) commonly used in the asymptotic analysis[7,21,23] of permeation at infinite times is even less useful for practical purposes since it requires precisely controlled simultaneous introduction of the solute upstream of the initially degassed membrane and instantaneous homogeneous

activation of the scavenger throughout the membrane. Nonetheless, if such combination of the environmental change and instantaneous activation were realized in the experiment, the determination of J_0(SSCR) would be greatly simplified due to the lack of the PRT interference distorting the short-term asymptotic behavior of $J_0(t)$. The following analytical technique describes how the $J_0(t)$ asymptote can be obtained at $t \geq 0$ from the moment of complete scavenger activation.

After the SSCR solute concentration profile is established throughout the activated membrane with a large relative reactive capacity $\Psi \gg 1$ of the membrane material:[9]

$$\Psi = \frac{\mu R_0}{C_{out}} = \frac{\mu R_0}{Sp_{out}} \quad (52)$$

the permeation dynamics is determined by the transient Thiele modulus $\bar{\phi}(t)$. Large $\bar{\phi}(t) \gg 1$ (>100 for practical purposes) will result in a sharp reaction–diffusion wave front propagating downstream across the membrane thickness and consuming the scavenger.[6-10] Decreasing $\bar{\phi}(t)$ below 100 weakens diffusion control of the overall rate and eventually leads to transition to the homogeneous reaction in the activation-controlled limit at $\bar{\phi}(t) < 1$. Around the scavenger activation time $t = 0$ the major difference between the cases of weak and strong diffusion control will be at the upstream boundary and its vicinity: the asymptotic form of $J_0(t)$ growth will not be affected by rapid changes upstream although the kinetics of $J_0(t)$ growth will be different. To demonstrate that we rewrite (4) as

$$\frac{\partial C}{\partial t} = \frac{D}{L^2}\frac{\partial^2 C}{\partial \xi^2} - \mu KRC \quad (53)$$

and hypothesize the time–space separability of the solution $C(\xi,t)$ around time $t \to 0$:

$$C \equiv C(\xi,t) = C(\xi)\,C(t) \quad (54)$$

Using the SSCR solution (28) in (54) and substituting it into (53), we obtain asymptotically at $t \to 0$ after dividing both sides on $C(\xi)$:

$$\frac{\partial C(t)}{\partial t} = C(t)\left(\frac{D\phi_0^2}{L^2} - \mu KR\right) \quad (55)$$

For the NCR membranes with the large value of $\Psi \gg 1$ meaning the initial excess of the scavenger throughout the membrane thickness, the pseudo-steady concentration R of the reactive species will exist in the vicinity of the downstream boundary $\xi = 0$ due to small initial SSCR concentration of the solute available for reaction when the downstream boundary condition $C_{in} = 0$ is in effect:

$$R \equiv R(\xi,t) = R(\xi)|_{t \to 0} \neq R_0 \quad (56)$$

where $t \Rightarrow 0$ means $t \to t^{1\circ} > 0$ and t° is a small fixed positive time. After substituting (56) into (55), separating variables, integrating, and multiplying it back on $C(\xi)$, we obtain

$$C(\xi,t)|_{t \to 0} = C_0^{SSCR}(\xi)\{1 + t\mu K(R_0 - R(\xi)|_{t \to 0})\} \quad (57)$$

Applying Fick's first law (29) at the downstream boundary, after routine manipulations and Taylor series expansion of $C_0^{SSCR}(\xi)$

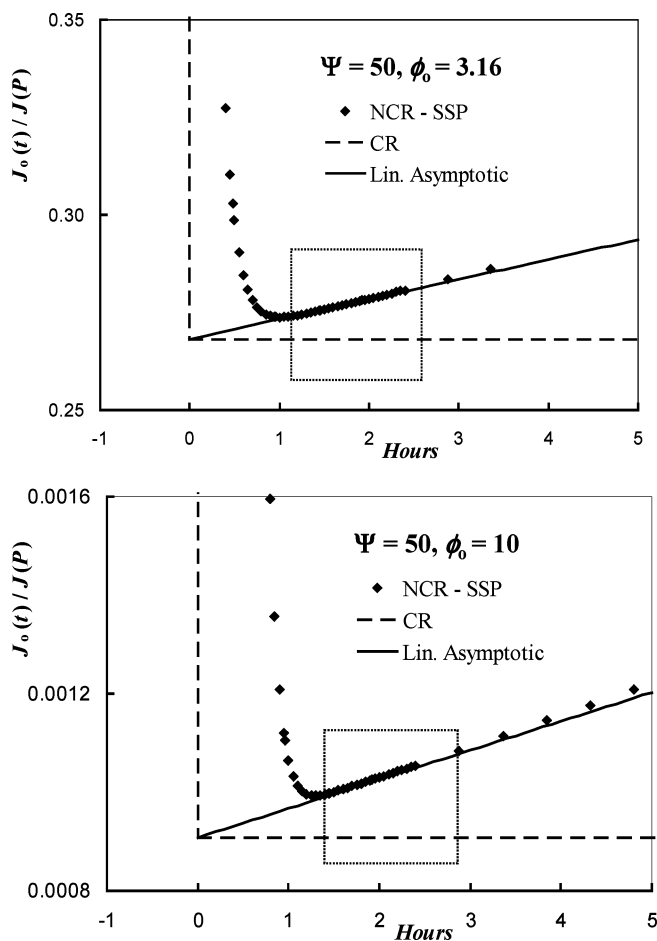**Figure 7.** Extrapolation of the measured transient flux through the NCR membrane by applying asymptotic solution (62) to obtain J_0^{SSCR}. The dotted box shows the location of the linear asymptotic part of $J_0(t)$ curve. (a, top) $\Psi = 50$, $\phi_0 = 3.16$; (b, bottom) $\Psi = 50$, $\phi_0 = 10$.

around $\xi = 0$, the effective transient flux $J_0(t)$ is obtained in the double asymptotic limit as

$$-J_0(t)|_{t\to 0} =$$
$$\frac{DC_{\text{out}}}{L}\frac{2\phi_0}{e^{\phi_0} - e^{-\phi_0}}\left\{1 + t\mu K\left[R_0 - R(0)|_{t\to 0} - \xi\frac{dR(\xi)}{d\xi}\Big|_{\xi\to 0}^{t\to 0}\right]\right\}$$
$$= \frac{DC_{\text{out}}}{L}\phi_0\,\text{csch}(\phi_0)\left\{1 - t\mu K\frac{dR(\xi)}{d\ln\xi}\Big|_{\xi\to 0}^{t\to 0}\right\} \quad (58)$$

After denoting the SSCR flux J_0 in (32) as J_0^{SSCR}, the result (58) can be rewritten as

$$J_0(t)|_{t\to 0} = J_0^{\text{SSCR}}(1 + B_1 t) \quad (59)$$

where the parameter B_1

$$B_1 = -\mu K\frac{dR(\xi)}{d\ln\xi}\Big|_{\xi\to 0}^{t\to 0} > 0 \quad (60)$$

can be considered the test specific experimental constant. B_1 is positive due negativity of $dR(\xi)/d\xi$ everywhere on $\xi = [0...1]$ (at least until the scavenger capacity is exhausted), resulting from the preset relationship between the boundary conditions $C_{\text{in}} < C_{\text{out}}$. After the linear asymptotic growth of $J_0(t)$ is resolved from the experimental transient flux data, the result (59) can be used to extrapolate $J_0(t)$ to the time $t = 0$ of the scavenger activation so that the minimum transient flux corresponding to

the CR flux could be calculated. Figure 7a,b demonstrates an excellent agreement of result (59) with the effective flux profiles obtained by numerical simulations for instantaneous activation with the SSP initial condition on the solute and large Ψ values ($\Psi = 50$ was used as an example). We note that only the short time asymptotic (boxed in the figures) should be used to apply this correction technique. To extend the linear asymptotic time scale and to account for noninstantaneous scavenger activation, another correction of the measured transient flux data should be implemented.

Correction for the Noninstantaneous Inhomogeneous Scavenger Activation

The PRT as well as noninstantaneous scavenger activation kinetics may shift the intersection point of (59) with the zero time axis requiring a time correction to that asymptotic solution. The correction, thereafter called the time shift t_0, can be thought of as a hypothetical time averaged instant of the complete scavenger activation in the presence of PR transition from the SSP initial condition to satisfy a modified version of (59):

$$J_0(t) = J_0^{\text{SSCR}}(1 + B_1(t - t_0)) \quad (61)$$

The flux J_0^{SSCR} can still be found from the experimental data by solving (61) if the time shift t_0 is known for the pairs of experimental data points $(t_i, J_0(t_i))$ belonging to the linear part of the transient flux growth curve. Obviously, the time shift itself cannot be resolved from the linear asymptotic solution (61). To work around this problem we consider transient permeability testing of the second reactive membrane with a low scavenger loading, insisting, however, that the same kinetics of the scavenger activation by the external fields were implemented as for the original test membrane in order to ensure the same apparent time shift in both tests. The reason for this method to work is that for low values of the relative reactive capacity $\Psi \approx 1$ or less a different asymptotic expression for the $J_0(t)$ growth can be derived in the strong diffusion control limit $\phi_0 \gg 1$.

Our goals are twofold: (1) to determine the nonlinear functional form of the $J_0(t)$ asymptote at $t \to t_0$ and $\phi_0 \gg 1$ and by applying it; (2) to correct the measured minimum of the flux $J_0(t)$ in order to obtain the true $J_0(\text{SSCR})$ value. The time t_0 coincides with the activation time $t = 0$ only if activation is instantaneous, and the SSCR oxygen concentration profile is already present in the membrane upon activation. As noted earlier that is next to impossible to achieve in practice. When the relative reactive capacity of the membrane material is low, the scavenger concentration will be affected by the reaction with the solute throughout the film thickness even in the asymptotic limit $t \to 0$, resulting in the nonlinear $J_0(t)$ growth. In other words, the lack of the pseudo-steady-state behavior of R in the vicinity of the downstream boundary for low Ψ values can be utilized to improve the accuracy of the transient permeability method. Low Ψ values for the same scavenger chemistry may be obtained by introducing a low scavenger loading in the membrane material, by activating only a part of the available reactive sites or by increasing the external solute pressure p_{out} although the first two options may not always produce the desired effect. Namely, lowering the activated scavenger concentration R_0 will simultaneously reduce the initial Thiele modulus ϕ_0 of the reactive membrane, resulting in much higher corresponding transient fluxes comparable to the SSP flux $J(P)$ and short scavenger exhaustion times. Because of that the asymptotic behavior of $J_0(t)$ growth will be suppressed and

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overshadowed by the dynamics of the transient flux approaching the steady-state $J(P)$ value. To strengthen the diffusion control of the overall reaction rate after reducing R_0, the initial Thiele modulus ϕ_0 has to be raised by the respective increase of the membrane thickness L as demonstrated below by our numerical simulation results. The L increase will also result in the increase in the total loaded scavenger amount M per unit membrane area, but it will keep the scavenger concentration R_0 constant. From processing viewpoint we just need to extrude a thicker film from the same material with the fixed scavenger letdown ratio. An additional benefit of using low Ψ values will be a shorter scavenger exhaustion time, resulting in reduction of the experimental test time for establishing the nonlinear $J_0(t)$ asymptote.

For the low relative scavenging capacity Ψ of the membrane material, the pseudo-steady-state solute concentration $C(\xi)$ will exist in the vicinity of the downstream boundary $\xi = 0$ after PRT. Then eq 5 for the scavenger consumption can be decoupled from the solute mass balance (4) and solved analytically around the time shift t_0, when the hypothetical SSCR or another slowly changing solute concentration profile $C(\xi)$ is established. For presentation clarity we will derive the asymptotic expression for $J_0(t)$ at $t^* \to 0$ where the new time variable $t^* = t - t_0$ already incorporates the time shift; however, in the following derivations the star superscript will be dropped for convenience, meaning the derivation will be apparently performed for the instantaneous scavenger activation. The solution of the decoupled eq 5 is

$$R(\xi,t) = R_0(\xi) \exp(-KC(\xi)t) \qquad (62)$$

or

$$R(\xi,t) \approx R_0(\xi)\left(1 - Kt\,\frac{2\phi_0\xi C_{\text{out}}}{e^{\phi_0} - e^{-\phi_0}}\right) \qquad (63)$$

in the vicinity of the downstream boundary $\xi = 0$ if the SSCR solution (28) is substituted into (62) as the initial condition. Once again assuming the time−space separability of the $C(\xi,t)$ solution and using the SSCR solution C_0^{SSCR} for $C(\xi)$, we obtain in the $t \to 0$ limit after substituting (63) into (53)

$$\frac{\partial C}{\partial t} = \frac{D}{L^2}\phi_0{}^2 C_0^{\text{SSCR}} - \mu K R C_0^{\text{SSCR}} = \mu K C_0^{\text{SSCR}}(R_0 - R) \quad (64)$$

Note that after transforming (53), the analogue of the diffusive term in (64) operates on R_0 since the condition $C_{\text{in}} = 0$ is in effect, and the pseudo-steady-state solute concentration $C(\xi,t)$ exists around $\xi = 0$. By making the variational transition in (64) from C_0^{SSCR} to $C(\xi,t)$ in the double asymptotic limit $t{\to}0$, $\xi \Rightarrow 0$ ($\xi \Rightarrow 0$ meaning $\xi \to \xi^\circ > 0$) and substituting (63) into the resulting equation, we obtain

$$\frac{\partial C}{\partial t} = \frac{2C_{\text{out}}\phi_0\xi}{e^{\phi_0} - e^{-\phi_0}}\mu R_0 K^2 C t \qquad (65)$$

After solving (65) by separating variables, we arrive at the solution for the SSCR initial condition (14)

$$C(\xi,t) = C_0^{\text{SSCR}}(\xi) \exp\left(\frac{\mu R_0 K^2 C_{\text{out}}\phi_0\xi}{e^{\phi_0} - e^{-\phi_0}}\,t^2\right) \qquad (66)$$

Expanding the exponent in (66) into Taylor series in the double asymptotic limit gives

$$C(\xi,t) = C_0^{\text{SSCR}}(\xi)(1 + B_2\xi t^2) \qquad (67)$$

where

$$B_2 = \frac{\mu R_0 K^2 C_{\text{out}}\phi_0}{e^{\phi_0} - e^{-\phi_0}} \qquad (68)$$

and substituting (67) into Fick's first law expression (29), we obtain for the effective flux asymptote

$$-J_0(t)|_{t\to 0} = \frac{DC_{\text{out}}}{L}\frac{2\phi_0}{e^{\phi_0} - e^{-\phi_0}}(1 + 2B_2\xi t^2) \qquad (69)$$

By comparing the result (69) with the result (32) for J_0^{SSCR}, we can write

$$J_0(t)|_{t\to 0} = J_0^{\text{SSCR}}(1 + \lambda t^2) \qquad (70)$$

where the parameter $\lambda = 2B_2\xi$ is the test specific experimental constant. Now the transient flux data can be used to determine the time shift t_0. Conversion of (70) back to the original time scale with the inhomogeneous scavenger activation results in the expression suitable for fitting the experimental data

$$J_0(t)|_{t\to 0} = J_0^{\text{SSCR}}(1 + j_0 + \lambda(t - t_0)^2) \qquad (71)$$

where j_0 is an experimental constant correcting for the potential difference between J_0^{SSCR} and the extrapolated J_0^{min} value at $t = t_0$ stemming from the PRT interference. Since the PRT of the $C(\xi,t)$ profile from the SSP initial condition to the SSCR profile may result in a rapid drop of the measured flux by several orders of magnitude especially for large ϕ_0 as follows from (33), it is not surprising that the small (relative to $J(P)$) parameter such as J_0^{SSCR} is highly sensitive to the initial scavenger distribution $R_0(\xi)$, and it may not be accurately reproduced in the experiment. Rearranging (71) into

$$J_0(t)|_{t\to 0} = E + F(t - t_0)^2 \qquad (72)$$

where $E \equiv J_0^{\text{SSCR}}(1 + j_0)$ and $F \equiv \lambda J_0^{\text{SSCR}}$ and isolating the quadratic part of the $J_0(t)$ growth asymptote with at least four experimental data points $(t_i, J_0(t_i))$, the three unknowns t_0, E, and F can be found by a fitting technique. Alternatively, the extrapolation of the linear part of the time derivative $dJ_0(t)/dt$ to intersection with the time axis immediately establishes the time shift t_0 value:

$$\frac{dJ_0(t)}{dt} = 2F(t - t_0) \qquad (73)$$

After that, determining two remaining unknown complexes E and F from (72) is trivial. The J_0^{SSCR} value still cannot be resolved from E and F; however, it can be determined indirectly by comparing the asymptotes of transient fluxes in two membranes with low and high Ψ but with the same ϕ_0 value. Since the same scavenger activation kinetics by the external field independent of solute diffusion are required to be used for transient permeability measurements (e.g., using the boundary conditions for diffusion of the scavenger activating species adjusted for the membrane thicknesses or using controlled rapid activation by a penetrating source) and the same initial conditions are imposed, the time shifts are expected to be the same in both tests. Hence, J_0^{SSCR} values can be accurately determined for both test films by substituting the t_0 value from (72) into
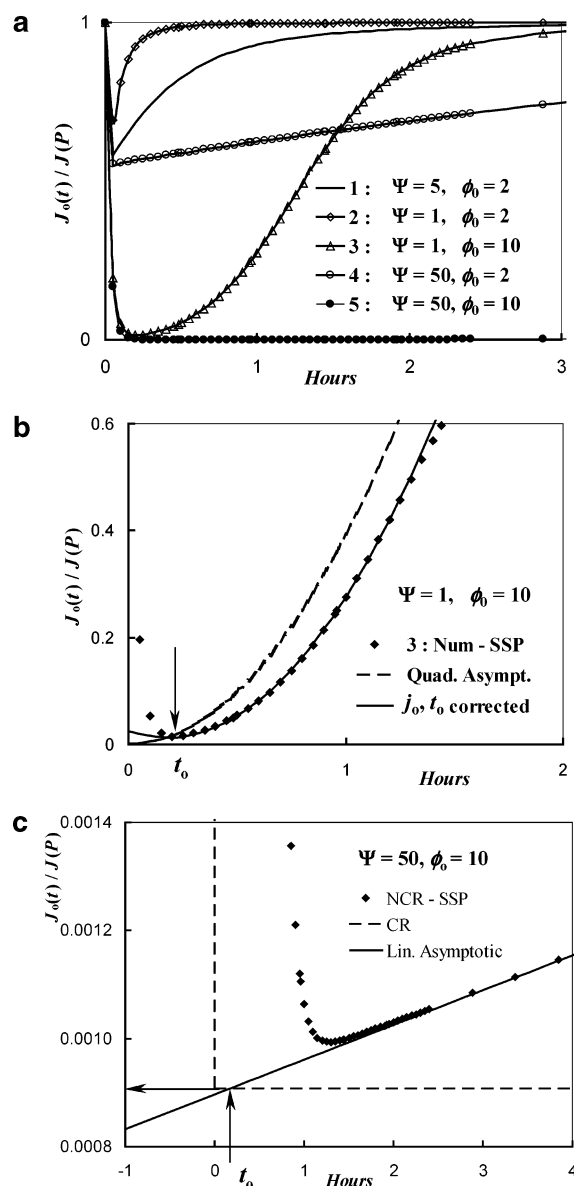
Figure 9. Effect of the SSCR and SSP initial conditions and the PR transition on the quadratic $J_0(t)$ growth asymptote.

Figure 8. (a) Effect of the relative scavenging capacity Ψ and the initial Thiele modulus ϕ_0 on the initial $J_0(t)$ growth asymptote with the SSP initial condition for the solute concentration and instantaneous scavenger activation. (b) Numerically simulated transient flux $J_0(t)$ for the SSP initial condition with $\Psi = 1$, $\phi_0 = 10$ and its original and corrected quadratic asymptotes. The minimum of the corrected asymptote corresponds to the time shift parameter t_0 shown by arrow. (c) Using the time shift t_0 from (b) and the linear $J_0(t)$ growth asymptote for the membrane with large $\Psi = 50$ to obtain correct J_0^{SSCR} value (shown by arrows).

(61) with the linear $J_0(t)$ growth asymptote obtained for large values of $\Psi \gg 1$.

It must be stressed that the same ϕ_0 value should be used for transferring t_0 obtained for the low Ψ membrane to the membranes with high Ψ. The reason is that the time shift t_0 is a strong function of ϕ_0 since it characterizes the PRT duration that in turn depends on the solute amount to be scavenged in the membrane during PRT and the apparent reaction rate constant K. Varying external solute pressure p_{out} allows one to control the parameter Ψ without affecting the initial Thiele modulus ϕ_0. If the nonlinear sorption isotherm of some known form exists for the particular matrix material at higher solute pressures, the pressure p_{out} has to be adjusted accordingly to allow accurate control of the sorbed solute concentration C_{out} within the upstream membrane boundary.
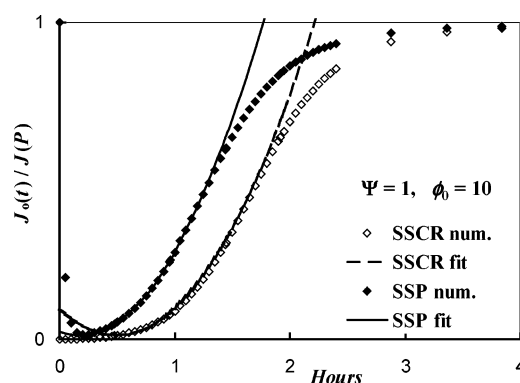
Figure 8a demonstrates that in the base case 1 with intermediate $\Psi = 5$ and a weak diffusion control by $\phi_0 = 2$, the quadratic $J_0(t)$ asymptote is not observed as expected. In case 2 when the relative capacity Ψ is respectively reduced by the 5 times increase in the external solute pressure p_{out}, the low ϕ_0 value results in higher transient flux $J_0(t)$ and again prevents the formation of the nonlinear transient flux asymptote. In case 3 when the membrane thickness is increased 5 times vs case 2 while keeping the scavenger concentration R_0 constant, the low Ψ value of the membrane is not affected, but the diffusion control is increased by the respectively higher $\phi_0 = 10$ value, resulting in the observed quadratic $J_0(t)$ asymptote as predicted by (71) and shown in Figure 8b. The corrected quadratic asymptote in the figure shows an excellent fit with the numerically simulated transient flux data; however, it does not help in determining J_0^{SSCR} as previously noted. Figure 8c demonstrates how to use the time shift t_0 obtained by fitting from Figure 8b in order to predict J_0^{SSCR} for larger Ψ values, resulting in the linear asymptotic behavior of $J_0(t)$. Comparing Figure 8c with Figure 7b, we note that the use of the time shift correction allows one to utilize a longer term asymptotic behavior of the transient flux to predict J_0^{SSCR} and as a result to improve the accuracy of the method by using a larger number of data points for fitting. For comparison, cases 4 and 5 in Figure 8a demonstrate that membranes with the large relative scavenging capacity $\Psi = 50 \gg 1$ exhibit the linear $J_0(t)$ asymptote (59) after PRT for any level of diffusion control of the overall reaction rate. Case 5 with large Ψ and ϕ_0 parameter values permits the direct determination of (a very small) J_0^{SSCR} value by applying the linear asymptote (59) but only if the test equipment sensitivity is high enough to allow that. Case 4 with smaller ϕ_0 does not have such sensitivity issues, and it can also be used for the analysis in the linear asymptotic limit. However, both cases 4 and 5 cannot be used for determining the time shifts which are critical for the analysis of reactive membranes with inhomogeneous scavenger activation coupled to PRT.

The initial condition $C(\xi)$ for the solute present in the membrane around the scavenger activation time may also affect the parameters of the quadratic $J_0(t)$ asymptote as shown in Figure 9. The results of numerical simulations for the membrane parameters corresponding to case 3 in Figure 8a with the SSP and SSCR initial conditions are plotted in Figure 9 along with their $J_0(t)$ asymptotes obtained using (72). To recall, the SSCR condition corresponds to the initial solute concentration profile with catalytic reaction that does not consume the scavenger. An apparent nonzero time shift observed for the SSCR asymptotic in Figure 9 is an artifact of a practical impossibility of coexistence of the initial SSCR solute concentration profile (where PRT is artificially eliminated) with the constant initial
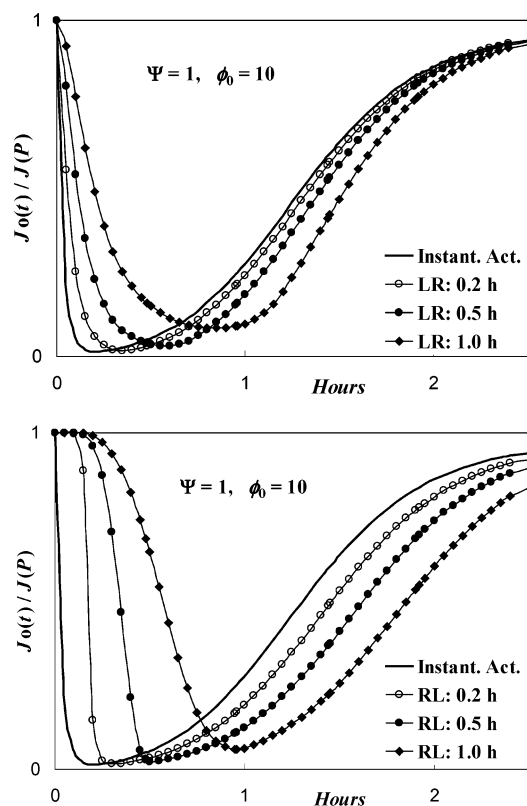
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Figure 10. Numerical simulations of the transient effective flux through the NCR membrane with a constant speed (a, top) "left-to-right" and (b, bottom) "right-to-left" scavenger activation through the membrane thickness of the denoted duration.

Figure 11. Numerical simulations of the transient effective flux through the NCR membrane with a constant speed (a, top) "left-to-right" and (b, bottom) "right-to-left" scavenger activation of the denoted duration. The arrows show how to use time shifts from Figure 10 and linear $J_0(t)$ growth asymptote to obtain J_0^{SSCR}.

$R(\xi) = R_0$ profile of the homogeneously activated noncatalytic scavenger. As a result of PRT coupled to the scavenger consumption taking place when the SSP initial condition is used, a significant difference is observed between simulated transient fluxes, namely, in the time shift t_0 value and the coefficients of the second-order fitting polynomial (72). Nonetheless, the longer term quadratic form of the $J_0(t)$ asymptote is not affected by the initial conditions in a case of instantaneous scavenger activation, and it can be used for determination of the time shifts due to PRT.

Application of the proposed method to the analysis of the numerically simulated $J_0(t)$ with inhomogeneous activation of the scavenger and the SSP initial condition is demonstrated in Figure 10 for the membrane parameters corresponding to the case of the quadratic $J_0(t)$ asymptote. The "left-to-right" (LR) scavenger activation of various durations with the constant activation speeds ϵ is simulated as a sharp activation front $x_f(t) = \epsilon t$ initiated at $t = 0$ and propagating in the direction $x_f = [0 \rightarrow L]$ across the membrane with $R(x,t) = R_0\delta(x_f(t))$ ahead of the front for $x \geq x_f$ and the evolving $R(x,t)$ behind the front for $x < x_f$ where $\delta(z)$ is the symbolic Dirac delta function. The $J_0(t)$ evolution for the LR activation case is shown in Figure 10a. In Figure 10b the direction of the activation front is reversed to "right-to-left" (RL) described by the front position $x_f(t) = L - \epsilon t$. In the RL activation case the apparent time shift t_0 appears to be well correlated with the duration of the scavenger activation which is not surprising since the asymptotic behavior of $J_0(t)$ may not be triggered until the scavenger has been activated at the downstream (left) membrane boundary $x = 0$. In this case the time shift simply reflects the completion of PRT for inhomogeneous activation. In the LR activation case the PRT proceeds faster initially, but it is not being completed until the scavenger is activated throughout the membrane. Thus, in both
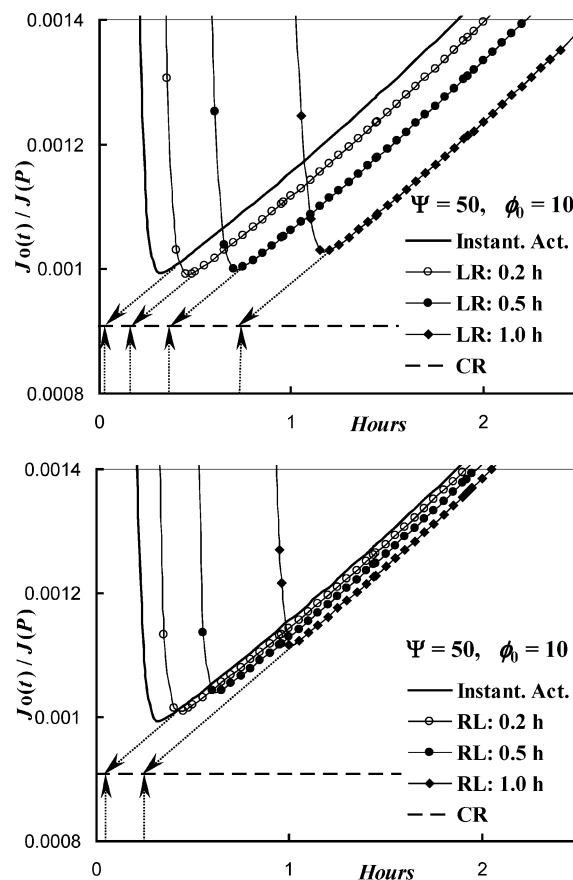
LR and RL activation cases the corresponding time shift can be determined from the quadratic asymptote despite the different quadratic polynomial coefficients for this asymptote. Provided the duration of the complete scavenger activation is much shorter than the time of its deactivation (i.e., its reactive capacity exhaustion) by NCR, the proposed correction results in an accurate prediction of the time shifts that are later used to determine the SSCR flux values from the linear $J_0(t)$ asymptote for membranes with large $\Psi \gg 1$. Figure 11 demonstrates that for large $\Psi = 50$ and the same $\phi_0 = 10$ as in Figure 10 with the apparent linear asymptote that does not appear to be affected by the scavenger activation kinetics.

To summarize the results presented in this section, in a case of slow and potentially inhomogeneous scavenger activation in the reactive membrane the method accuracy may be improved if the transient flux measurements are separately performed on two membranes with fixed intermediate to strong diffusion control of the overall reaction rate (e.g., with fixed $\phi_0 > 5$) but differing in their relative reactive capacity (low $\Psi \approx 1$ and high $\Psi \gg 1$) achieved by the respective adjustment of control parameters L, R_0, and p_{out} for the same scavenger chemistry and spatiotemporal activation kinetics. That allows one to observe the quadratic asymptote of the measured transient flux growth in the case of low Ψ values and correlate it with the time delay (time shift t_0) after which the minimum of the transient flux would have been observed in the case of instantaneous scavenger activation. This time shift estimate can be used for calculating J_0^{SSCR} from the corresponding linear $J_0(t)$ asymptote existing in the membranes with high $\Psi \gg 1$.

Conclusions

The proposed method allows the straightforward experimental evaluation of the effective reaction rate constant of the diffusion-controlled solute scavenging reaction in permeable polymeric barrier membranes. It is based on the transient permeability measurement technique using standard test equipment and properly modified experimental procedures. The method can be applied to a variety of available and novel scavenging chemistries where direct measurement of the reaction kinetics may be impossible or where interactions between the scavenger and the polymer matrix strongly affect such kinetics thus making the analysis of the solute reaction with a pure scavenging species outside the polymer matrix impractical. The experimental technique utilizes the results of asymptotic analysis of the transient effective flux through the membrane around the scavenger activation time. The method heavily relies on the nearly instantaneous scavenger activation throughout the membrane. While the experimental error cannot be completely eliminated if slow and potentially inhomogeneous scavenger activation takes place in the membrane, it can be dramatically reduced by the proposed correction technique for extrapolation of the transient flux to the moment of hypothetical homogeneous scavenger activation in the diffusion-controlled limit with the low scavenging reactive capacity $\Psi \approx 1$. A high scavenging capacity $\Psi \gg 1$ of the film material is required to guarantee the pseudo-steady-state concentration of the scavenger downstream in the diffusion-controlled limit, resulting in a linear asymptotic behavior. Low values of $\Psi \approx 1$ accompanied by a high initial Thiele modulus ϕ_0 obtained by a low scavenger loading into a thicker membrane result in the quadratic asymptote of the transient flux growth around the activation time. This asymptote may be used to determine the time shift correction accounting for inhomogeneous activation kinetics and the passive-to-reactive transition.

The method can be applied to rapid characterization and screening of a variety of diffusion-controlled scavenging reactions in permeable reactive membranes that are actively studied and commercialized in the area of active packaging for food, beverage, and microelectronic packaging as well as for pharmaceutical applications.

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