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Sorption, desorption and diffusion processes in membrane permeation

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A majority of the anomalous permeation in the literature can be resolved if the solubility coefficient of the diffusion-solubility model is expanded into its component sorption and desorption processes.

Examples of these anomalies are (a) the permeability coefficient decreases with decreasing membrane thickness, (b) the membrane's selectivity changes with membrane thickness, (c) the surface concentrations are time dependent, and (d) the steady-state solubility and surface concentration are less than the equilibrium values. In the three parameter model, the sorption (K_1) and desorption (K_2) processes are included as part of the boundary conditions of the model. The permeability coefficient (K) becomes $DS/(1+2/B)$ where B, the thickness scaling parameter, is K_2L/D. L is the membrane thickness, D is the diffusion coefficient and S is the solubility coefficient. At equilibrium, S becomes S_{eq}. For large B, K approaches DS and the DS model is adequate. For some thin and ultrathin membranes where B is small, K approaches $K_1L/2$ and the normalized membrane flux (K/L) becomes independent of the thickness. In these cases, permeation looks more like a sorption and desorption process. These features are well described by the DK_1K_2 model but are anomalous for the DS model. For small B, the selectivity is determined by the relative values of K_1 which is the principal selection parameter for sorption processes. A simple method is reintroduced (first used over a half-century ago) to determine the three parameters from experimental permeability data. Experimental data are analyzed for liquid-membrane, vapor-membrane, gas-membrane and pervaporation systems. Values of D, K_1 and K_2 are given for these systems.

1. Introduction

It is widely accepted that gas permeation is an activated process of diffusion within the membrane and a partitioning process of the gas at the interfaces with the adjacent phases. As a prerequisite for the gas to diffuse through a nonporous membrane, the gas must first dissolve in the membrane. The gradient for permeation is the difference in the concentrations at the two surfaces for a given membrane thickness. In the DS model [1,2], this difference is defined at the equilibrium value. In some thin and ultrathin films, it may never reach the equilibrium value. $C(0,t)$ is fixed at $S_{eq}p_0$ and $C(L,t)$ is zero where $x=0$ and $x=L$ are the two surfaces and p_0 is the gas pressure at $x=0$.

By splitting S_{eq} into its two component processes of sorption and desorption and incorporating these rate processes in the boundary conditions, the surface concentrations can vary with time. Now the delay in the passage of gas through the membrane is due to both the diffusion process and the time to establish the steady-state concentrations at the surfaces. At steady state, S_{eq} always equals K_1 divided by K_2.

With K_1 and K_2 in the description of the surface concentrations, a finite limit for the gas flux is defined as the membrane thickness approaches zero. At some thickness, one of the surface processes is slower than the mass transfer for diffusion (D/L). For K_2, this event occurs when B is less than 1. Even before this condition is reached, however, the permeation rate gradually becomes less dependent on a decreasing L. Ultimately, the permeation rate is controlled by K_1 and independent of a decreasing L. In contrast, no finite limit is anticipated in the DS model.

1.1. Anomalies of membrane permeation

The reports of anomalous data in the DS model discussed here include: (a) losses in K with thinner membranes; (b) changing selectivity with changes in L; (c) time-dependent surface concentrations; and (d) solubilities and surface concentrations at steady state that differ from their equilibrium values. Anomalies (c) and (d) are related in that the observed S and $C(0,t)$ increase with time to their steady-state values. If the values are less than the equilibrium values,

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the data are anomalous in terms of the DS model. Anomaly (c) is implicit with this observation.

The author has observed (a) and (b) during his development of a production method to make continuous ultrathin membranes of silicone block copolymers [3]. The thicknesses of the ultrathin membranes (L_c) produced by this method were estimated from the normalized flux of oxygen and nitrogen and the corresponding permeability coefficients for thick membranes. The ultrathin membranes were intentionally made as multicolored (target yellow) membranes (of thickness L_u). Twice the calculated thickness was greater than the range for visible light. The calculated thickness would not provide a visible, constructive interference pattern. Hence, K for the ultrathin membrane (K_u) was less than K for a thick membrane (K_t), i.e., K_t/L_c equals K_u/L_u or K_u equals $K_t(L_u/L_c)$ where (L_u/L_c) is less than one. Also, the oxygen to nitrogen selectivity α_{ab} of the ultrathin membrane was larger than α_{ab} for a thick membrane (2.4 vs. 2.0). This observation is consistent with the DK_1K_2 model.

In Section 3, three cases of anomalous permeation are analyzed in detail: (1) studies of water soluble, basic dyes permeating through thin cellulose membranes by McGregor's group [4,5], (2) studies of oxygen, nitrogen and methane permeating through ultrathin polysulfone membranes by Rowe, et al. [6] and (3) a combined study of pervaporation and vapor permeability of 1-propanol permeating through low density, polyethylene (LDPE) membranes by Fialova et al. [7]. Two of the three cases demonstrate the three observable anomalies: (1) K trends with L, (2) α_{ab} changes with L, and (3) $C(0,ss)$ is less than C_{eq} (and the reduction in $C(0,ss)$ increases with decreasing L). The third case reports on a single vapor so the α_{ab} anomaly cannot be demonstrated. Some additional details about these cases are given in Section 1.2.

1.2. *Historical perspective*

Following William Henry's discovery in 1855 [8] that different gases have unique S_{eq} in water, Sigmund von Wroblewski suggested in 1879 [1] that gas permeability through a membrane could be described as the product of S_{eq} and the diffusion coefficient (D). If S_{eq} is determined from an equilibrium solubility experiment and K is determined from a permeability experiment at the same conditions, D equals K/S_{eq}. von Wroblewski performed both experiments with hydrogen, carbon dioxide and nitrous oxide through a rubber membrane and determined the corresponding diffusion coefficients by this method.

Daynes [2] used the 1906 solution of Carslaw [9] for the one dimensional, heat conduction problem to describe the concentration of the gas within the membrane as a function of time. His effort provided a mathematical basis for the DS model and for the Daynes' time lag method to determine D. Earlier, Adolph Fick [10] proposed a similar equivalence in mathematical form for the problem of diffusion of water in a membrane and the problem of heat conduction in a solid analyzed by Fourier [11].

To evaluate von Wroblewski's suggestion, one can start with Fick's first law [10]:

$$J = -D\frac{dC}{dx} \quad 0 < x < L \quad t > 0 \tag{1}$$

where J defines the flux, in moles/cm^2 s, at location x in the membrane and $C(x,t)$ is the concentration of the gas at location x and time t. The first law requires

$$\frac{dC(x,t)}{dt} = 0 \quad \text{so} \quad C(x,t) = C(x) = A1 + A2x. \tag{2}$$

$A1$ and $A2$ are determined from the boundary conditions for a Fickian system. The simplest case is when both are zero, for example when a membrane is being degassed under vacuum, then after steady state is achieved,

$$C(x) = 0 \quad 0 < x < L \tag{3}$$

The next level of complexity is when the concentration at one boundary is set to zero and the other is a constant. For the boundary conditions proposed by von Wroblewski and used by Daynes, $C(0,t)$ equals $S_{eq}p_0$ (or $S_{eq}C_o$ where C_o is the solute concentration in the adjacent phase) and $C(L,t)$ is set to zero (with a gas pressure p_l (or concentration) equal zero adjacent to the $x=L$ boundary). At steady state, $C(x)$ becomes

$$C(x) = S_{eq}p_o\left(1 - \frac{x}{L}\right) \quad \text{and} \quad \frac{dC(x)}{dx} = -S_{eq}\frac{p_o}{L}. \tag{4}$$

For these boundary conditions, the permeability coefficient is defined as

$$K = J\frac{L}{p_o} = (-D)\left(-S_{eq}\frac{p_o}{L}\right)\left(\frac{L}{p_0}\right) = DS_{eq} \quad \text{as suggested by von Wroblewski.} \tag{5}$$

Eq. (5) is the significant equation of the DS model for permeation. The anomalies of the DS model are experimental evidence that the boundary conditions are too restrictive. The most frequent anomaly is the thickness dependent K.

1.2.1. *L dependent K*

In his 1960 review, Jost [12] dedicated a section to permeation anomalies. The key feature he associated with the anomalies was an increase in K with an increase in L. Later reviewers associated anomalous permeability with the polymer's structure. Rogers [13] in his 1965 review related anomalous permeability to experimental temperatures below the glass transition temperature (T_g) of the polymer. Fujita [14] in a 1968 review described anomalies in the vicinity of T_g. Park [15] described other anomalies at experimental temperatures well above T_g when fillers were present. He related these anomalies to microheterogeneities in the polymer structure. It is clear that anomalous permeability can occur at any temperature relative to T_g and the causes can be different. Park's heterogeneous structure leads to an increasing K with a decreasing L (by providing a second diffusion path or even multiple paths). Rogers' anomaly leads to pinhole defects (and the creation of multiple diffusion paths) where K increases with decreasing L. The presence of crystallites can also lead to defects and multiple diffusion paths.

McGregor et al. [4,5] reported in 1962 and 1965 on the thickness dependent permeability of certain cellulose membranes (tens of micrometers (μm) thick, regenerated from cellulose triacetate). They used basic dyes in water at 75 and 90 °C. Like von Wroblewski's method for the DS model [1], their method requires the independent determination of S_{eq} for the DK_1K_2 model. Data from their studies are analyzed in Section 3.

Rowe et al. [6], as part of their effort to capture higher free volume fractions (FFV or f) in quenched, glassy polymer membranes, observed thickness dependent values of K for thinner polysulfone (PSF) films. Perhaps the first report of time-dependent values of K in physical aging was by Kapur and Rogers [16] in 1972. They quenched isotactic polypropylene from above its melt temperature into an ice bath. The T_g for isotactic polypropylene is 0 °C [17]. The permeabilities at 25 °C for helium and neon exhibited some physical aging for a period of days, whereas K for argon was unchanged by the T_m quench process over the same period. They used a film thickness of 10 mils (254 μm). Pfromm and Koros observed thickness dependent aging (accelerated aging) as early as 1995 [18] with T_g quenched films.

Since K in the DS model is neither L dependent nor time dependent, the data are anomalous. Rowe reported on the permeability of oxygen, nitrogen and methane through PSF membranes. The technique used to capture higher values of f consisted of elevating the temperature of the polymer above its T_g, allowing it