

## Time Lag and Permeation Rate in Liquid/Liquid Dialysis

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### Synopsis

Time lag and permeation rate in liquid/liquid dialysis in general are found different from those in pervaporation. Theoretical treatments of time lag in liquid/liquid dialysis indicate that time lag, in certain cases, may be correlated to the "relaxation time" of the membrane, defined as the time required for the membrane to relax, or as the change of the permeation flux of diffusible species from initial flux to steady state due to the long time required for the dialysis solvent to reach steady state in the membrane. The permeation of dichlorobenzene in a Teflon-FEP membrane for both the operations of liquid/liquid dialysis and pervaporation was measured as an example. It was found that the time lag in liquid/liquid dialysis is much longer than that calculated from a diffusion constant calculated from pervaporation. Permeation rate and activation energy are also different in both operations.

### INTRODUCTION

Transport through a polymer membrane has been extensively studied in recent years. It is known that polymer membranes can be subjected to varieties of driving force gradients such as concentration, pressure, and electric field, and the corresponding flux of permeants can be utilized to facilitate the separation or concentration of component(s) in a mixture. The general permeation equations for various transport operations such as liquid/liquid dialysis, liquid/gas pervaporation, gas/gas permeation, and reverse osmosis have been correlated according to the solution-diffusion theory.<sup>1</sup>

In this paper, we will try to compare the permeability constant and time lags in two different transport operations, liquid/liquid dialysis and liquid/gas pervaporation. In the case of liquid/liquid dialysis, the membrane will be exposed to both dialysis solvent and feed species, while only feed species exist in the membrane in pervaporation. Therefore, the permeation properties of liquid/liquid dialysis and liquid/gas pervaporation cannot be compared directly in some cases. In other words, the dialysis solvent may play an important role in the membrane permeation process besides creating the thermodynamic driving force difference.

The time lag in diffusion through the membrane has been extensively studied before.<sup>2-4</sup> However, no experimental data about the time lag in liquid/liquid dialysis and its comparison with that in pervaporation have been published. It is also the purpose of this paper to discuss the time lag in liquid/liquid dialysis and its significance.

## EXPERIMENTAL

The pervaporation equipment is similar to that described previously.<sup>5</sup> It consists of a permeation cell, a temperature control system, a permeate collection system, and a vacuum pumping system, all connected in series. For the dialysis cell, there are two halves of a cell and "O" rings. The membrane held between the "O" rings partitions the two halves of the cell. The cell can be rotated. Periodic samples are taken for analysis. The total available surface area for both pervaporation and dialysis is about 11 cm<sup>2</sup>.

Solubilities of ortho- and para-dichlorobenzene in a Teflon-FEP membrane were obtained from the ratio of the increased weight of the membrane, which was exposed to dichlorobenzene (50 ortho/50 para by weight) until the equilibrium of solution in the membrane was reached, to the weight of the dry membrane. The concentration of dichlorobenzene in the membrane was calculated from the v.p.c. analysis of the concentration of dichlorobenzene in the hexadecane solution, which was obtained by extracting out the dichlorobenzene in the membrane with hexadecane.

The Teflon-FEP membrane [fluorinated copoly(ethylene/propylene)] (thickness 1 mil) was obtained from Cadillac Plastic Company. Dichlorobenzene and hexadecane were purchased from Fisher Scientific Company. Analysis of dichlorobenzene in hexadecane was conducted on a Hewlett Packard Series 5750 gas chromatograph equipped with a thermal conductivity detector.

## THEORY

It is known that the time lag in diffusion can give some information about the diffusion constants of permeating molecules.<sup>2,3</sup> Ash, Baker, and Barrer<sup>4</sup> have derived the general expressions for the time lag in transport through membranes where the diffusion constants of permeating molecules are considered as a function of concentration, distance, and/or time. The time lag in transport through membranes has been studied in the case of gas permeation. However, no experimental facts about the time lag in liquid/liquid dialysis have ever been published.

The general equation for the time lag,  $L$ , is given by<sup>3</sup>

$$L = \left\{ \int_0^l x C(x) dx + \int_0^\infty \int_0^l [J_\infty(C_0) - J(x, t)] dx dt \right\} / l J_\infty(C_0) \quad (1)$$

and the boundary conditions for the above expression are

$$\begin{aligned} C(0, t) &= C_0 & \text{for all } t > 0 \\ C(l, t) &= 0 & \text{for all } t > 0 \\ C(x, 0) &= 0 & \text{for all } 0 < x < l \end{aligned}$$

$C(x, t)$  and  $J(x, t)$  are, respectively, concentration and fluxes of diffusible species at a time  $t$  and position  $x$  in the membrane;  $J_\infty(C_0)$  is the flux when the steady state has been established;  $l$  is the thickness of the membrane.

If the diffusion constant  $D$  is a constant or a function of concentration only, the last integral in the numerator of eq. (1) is zero, and the time lag will be some kind of concentration average of the diffusion constant.<sup>2</sup> However,

when  $D$  depends on time and position in the membrane, the last integral will not be zero, and the time lag will not be a simple concentration average of the diffusion constant of the diffusable species.

In a particular case,  $J(x,t)$  may be assumed to be an exponential function of time only as follows:

$$J(x,t) = J(t) = J_0(C_0) + [J_\infty(C_0) - J_0(C_0)][1 - e^{-t/\tau}] \quad (2)$$

where  $J_0(C_0)$  is the permeation flux at time zero and  $J_\infty(C_0)$  is that at infinite time. If

$$\int_0^\infty \int_0^l [J_\infty(C_0) - J(x,t)] dx dt \gg \int_0^l x C(x) dx \quad (3)$$

then

$$L = \frac{J_\infty(C_0) - J_0(C_0)}{J_\infty(C_0)} \tau. \quad (4)$$

Thus, the time lag in liquid/liquid dialysis will be as follows in the two extreme cases:

Case I:  $D = \text{constant}$

$$L = \frac{l^2}{6D}$$

Case II: If the assumptions in eq. (2) and (3) hold, the time lag will be given by eq. (4).

Thus, the time lag in liquid/liquid dialysis does not always reflect only the diffusion constant of diffusable species.  $L$  may be a function of the "relaxation time"  $\tau$  of the membrane, defined as the time of the membrane to relax or change the permeation flux of diffusable species from initial flux  $J_0(C_0)$  to steady-state flux  $J_\infty(C_0)$  due to the long time needed for the dialysis solvent to reach steady state.

## RESULTS AND DISCUSSION

It is known that a membrane plasticized by organic solvents might give higher permeation rates. Table I indicates the permeation rate of dichlorobenzene in a FEP membrane with liquid/liquid mode increases as much as twice of that in pervaporation. Also, the activation energy for the permeation of dichlorobenzene through a FEP membrane is 11 kcal for dialysis and 15 kcal for pervaporation. These data indicate that the dialysis solvent hexadecane indeed plasticizes the FEP membrane and, therefore, increases the permeation rate and decreases the activation energy.

The calculated time lag and measured time lag are shown in Table II. The calculated time lag is derived from the diffusion constant, which is assumed to be the ratio of the permeability constant and the solubility constant in the pervaporation.<sup>1</sup> It is shown in Table II that the measured time lags in dialysis, for both para- and ortho-dichlorobenzene, are the same and are much longer than the calculated time lag in pervaporation. This result indicates that the assumption in eq. (3) may be true. Thus, the significance of eq. (4) is based on the assumption that permeation flux is an exponential function of time and is independent of position in the membrane. The fact that the per-

TABLE I  
Permeation Rates of Dichlorobenzene Through Teflon-FEP Membrane  
at Various Temperatures<sup>a</sup>

Mode of operation	Temp., °C	Rate, g/hr-11 cm <sup>2</sup>
Pervaporation	80	$4.8 \times 10^{-3}$
Pervaporation	72	$2.7 \times 10^{-3}$
Pervaporation	50	$6.2 \times 10^{-4}$
Liquid/liquid dialysis using hexadecane as dialysis solvent	82	$6.2 \times 10^{-3}$
Liquid/liquid dialysis using hexadecane as dialysis solvent	72	$4.6 \times 10^{-3}$
Liquid/liquid dialysis using hexadecane as dialysis solvent	62	$2.4 \times 10^{-3}$

<sup>a</sup> (Feed composition: 50% para-dichlorobenzene, 50% ortho-dichlorobenzene.)

meation rate for the dialysis solvent hexadecane is about 100 times less than that for dichlorobenzene indicates that the permeation flux in liquid/liquid dialysis at the nonsteady state is strongly time dependent. Therefore, the assumption in eq.(3) may not be deviated from greatly.

If the assumption in eq. (2) holds, the relaxation time calculated from eq. (4) is about 24 hr. The longer time required for the dialysis solvent hexadecane to reach the steady state may explain the longer relaxation time for the membrane to reach the steady state compared with the time lag in diffusion through the membrane for pervaporation.

In conclusion, we have shown that the dialysis solvent may play an important role in the membrane permeation process besides creating the thermodynamic driving force difference. Also, the time lag in liquid/liquid dialysis may be positive or negative, dependent on the dialysis solvent and whether it

TABLE II  
Time Lag Measured for Dichlorobenzene in Liquid/Liquid Dialysis and Time Lag  
Calculated from Diffusion Constant of Dichlorobenzene Isomers Through FEP  
Membrane in Pervaporation at 72°C

	Permeant	$L^a$ , hr	$P^b$	$S^c$	$D^d$	$\frac{l^{2e}}{6D}$ , sec
<i>p</i> -Dichlorobenzene	<i>p</i> -DCB	$10 \pm 2$	$2.05 \times 10^{-10}$	0.02	$1.02 \times 10^{-8}$	102
<i>o</i> -Dichlorobenzene	<i>o</i> -DCB	$10 \pm 2$	$1.05 \times 10^{-10}$	0.014	$0.75 \times 10^{-8}$	148

<sup>a</sup> Measured time lag<sup>(6)</sup> in liquid/liquid dialysis using hexadecane as dialysis solvent. Feed composition same as in Table I.

<sup>b</sup> Permeability constant of dichlorobenzene in FEP in pervaporation; corrected to units of g-cm/cm<sup>2</sup>-sec- $\Delta VF$  ( $\Delta VF$  is volume fraction).

<sup>c</sup> Solubility constant, obtained as described in experimental section and corrected to g/cm<sup>3</sup>.

<sup>d</sup>  $D$  is diffusion constant for pervaporation; obtained from the ratio of  $P/S$  (unit: cm<sup>2</sup>/sec).

<sup>e</sup>  $l$  is the thickness of membrane (1 mil).

plasticizes or antiplasticizes the membrane. Thus, the time lag may reflect only the effects of the dialysis solvent on the membrane instead of the diffusion constant of permeating molecules.

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