

# Liquid Transport Through Membranes Prepared by Grafting of Polar Monomers onto Poly(tetrafluoroethylene) Films. III. Steady-State Distribution in Membrane During Pervaporation

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## Synopsis

Steady-state concentration and composition gradients of pervaporating liquids inside the membrane were measured using stacks of membranes. The experimental results on pure components agree well with a simple mechanism of diffusion down a chemical potential gradient in a nonporous membrane. For mixtures, concentration gradients are similar to those obtained for pure liquids, and composition distribution shows that the selection between the two species does not take place at a given interface in the membrane but is progressive along the diffusional paths through the membrane. Data are also listed to show that solubility and diffusivity enhancements occur for components which are hydrogen bonded with the basic groups of the membrane.

## INTRODUCTION

The purpose of this third part of investigations on the pervaporation process is to give an insight into the principles of this fractionation method and discuss the theory with respect to experimental data, a part of which has been previously published.<sup>1,2</sup>

R. C. Binning et al.<sup>3</sup> suggested a qualitative model for the liquid permeation. These authors assumed the existence of two zones in the polymer film under pervaporation conditions: the upstream zone ("solution phase") is like a highly swollen gel and occupies the major portion of the membrane. The downstream zone ("vapor phase"), in which vaporization occurs, is practically the polymer in dry state. Selectivity may occur at the liquid-membrane interface, but probably most of the selectivity occurs at the interface between the "solution phase" and the "vapor phase." The diffusion in the latter zone is believed to be the rate-controlling step in the process.

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R. B. Long<sup>4</sup> has discussed a pure liquid permeation model based on diffusion concepts. The steady-state pervaporation process may be described by the form of Fick's law assuming an unidirectional diffusion:

$$\Phi = -D \frac{dC}{dx} \quad (1)$$

where  $\Phi$  = pervaporation rate (in g/cm<sup>2</sup>-sec),  $D$  = diffusion coefficient (in cm<sup>2</sup>/sec),  $x$  = distance along the direction of permeation (in cm), and  $C$  = liquid concentration in the membrane at the distance  $x$  (in g/cm<sup>3</sup> of swollen membrane).

The equation most widely accepted to relate  $D$  to the concentration  $C$  and to a diffusivity  $D_0$  at zero concentration of solvent in the membrane is

$$D = D_0 e^{\gamma C} \quad (2)$$

where  $D_0$  and  $\gamma$  are constant at a given temperature.

The integration of relation (1) taking into account relation (2) gives

$$\Phi = \frac{D_0}{\gamma l} [e^{\gamma C_1} - e^{\gamma C_0}] \quad (3)$$

where  $l$  = membrane thickness, and  $C_1$  and  $C_0$  = concentration of the pure component in the membrane at the liquid-membrane interface and at the vapor-membrane interface, respectively.

From the experimental values of  $\gamma$  and  $D_0$ , Long calculated the concentration gradient of *n*-heptane through polypropylene films; he showed, like Binning, that all the resistance to diffusion is essentially at the downstream zone of the membrane.

In the last papers published on the pervaporation process, it is assumed that pervaporation is a special case of ordinary diffusion; but only few papers enter upon the problem of selectivity. The sole interesting data, described by Kusnetzov and Maljoussov,<sup>5</sup> concluded that selectivity for the system ethyl alcohol/water/cellophane takes place at the liquid-membrane interface, which is not the case for the system isopropyl alcohol/water/cellophane.

So it is of great interest to evaluate by experiment the reliability of the diffusion model and discuss the problem of the origin of selectivity.

## EXPERIMENTAL

Poly(tetrafluoroethylene)-poly(4-vinylpyridine)- and poly(tetrafluoroethylene)-poly(*N*-vinylpyrrolidone)-grafted membranes (PTFE-P4VP and PTFE-PVP membranes) were prepared according to a previously described technique.<sup>1,2</sup>

Apparatus, chemicals products, analysis of binary mixtures, and measure of swelling ratio and membrane thickness have also been described.<sup>1,2</sup>

### Preferential Sorption

**Determination by Differential Refractometry.** The apparatus used was a Karl Zeiss differential refractometer. The two compartments of the

cell were filled with the binary liquid (A plus B) under test. A membrane sample was placed in one of the cell compartments, out of the path of the light beam. If preferential sorption occurs, the refractive index relative to the liquid in the reference compartment will change; this difference is measured at the sorption equilibrium.

The swelling ratio  $S$  (g solvent per 100 g dry membrane), the sample weight, and the volume and composition of the mixture in the compartment allow us to calculate the quantity  $z_A$ , which is the volume fraction of A in the sorbed liquid:

$$z_A = \frac{v_A}{v_A + v_B}$$

where  $v_A, v_B$  = volume of A and B (in ml per 100 g dry polymer).

If  $d_A$  and  $d_B$  are the densities of the two compounds,

$$S = v_A d_A + v_B d_B.$$

A good precision was reached by using a relatively high sample weight (0.1 g) and a small mixture volume (0.5 ml).

**Determination by Desorption Technique.** A dry membrane was soaked in the A-B mixture at constant temperature. When the swelling equilibrium was reached, the sample was rapidly taken out of the bath, blotted free of surface liquid, and placed in a glass reactor initially dried by a stream of  $N_2$ . The reactor was then connected to a vacuum pump. Two traps, cooled by liquid air, collected the liquid sorbed by the polymer. The time necessary to reach the total desorption could be decreased by heating the reactor. By weighing the liquid collected in the traps and the membrane sample, we could ensure that the whole of the sorbed liquid was collected and that the polymer sample was dry.

This technique is advantageous when the swelling ratio is low because a high sample weight could be used. The values of  $z_A$  obtained by the two methods are in good agreement (less than 5%).

### Concentration and Composition Gradients

The use in pervaporation of a stack of identical membranes has been previously reported.<sup>2</sup> It has been shown that the resistance at the interfaces between two membranes could be considered as a negligible quantity because the pervaporation results obtained with a stack of membranes are the same as those obtained with a single membrane of the same thickness. We can then assume that the stack of identical membranes is a good model for a single membrane.

When steady-state pervaporation was reached, the cell connected to the apparatus with a flexible pipe was reversed so that the liquid did not remain in contact with the membrane, and the cell was taken to pieces. The upper side of the stack was then blotted free of surface liquid and the membranes were rapidly separated. Each individual membrane was

weighed to determine its solvent content. In the case of a liquid mixture, the volume fraction  $z_A$  of compound A was measured by the desorption technique.

### Membrane Density

The density  $d_m$  of the dry membrane was determined with a sample of known weight by pycnometry or by measuring the thickness and the surface. The precision was about 5%.

## RESULTS AND DISCUSSION

### Pervaporation of Pure Compounds

Our purpose is to show whether Fick's law may be used to describe the pervaporation of a pure compound or, in other words, if relation (3) is valid.

We will assume that the concentration  $C_0$  at the vapor-membrane interface is zero because the downstream compartment of the pervaporation cell is maintained at very low pressure and that the concentration  $C_l$ , at the liquid-membrane interface, is the concentration of solvent determined at the swelling equilibrium. With these assumptions, eq. (3) can be simplified to

$$\Phi = \frac{D_0}{\gamma l} (e^{\gamma C_l} - 1) \quad (4)$$

**Effect of Membrane Thickness.** The results obtained from the pervaporation of water through PTFE-P4VP membranes (Fig. 1) of dif-

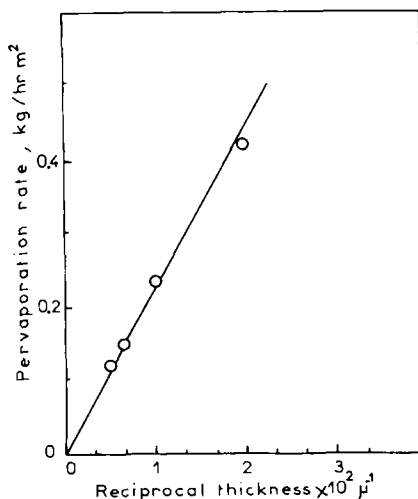


Fig. 1. Effect of membrane thickness on pervaporation rate of water at 25°C. PTFE-P4VP membranes, 150% grafting.

ferent thickness show that the transport rate  $\Phi$  is inversely proportional to  $l$  as predicted by Fick's law.

**Concentration Gradient of Pure Compound through Membrane.** With the preceding assumptions, we can calculate a relation between the concentration  $C_x$  of a pure compound and the distance  $x$  to the downstream face of the membrane. Relations (1) and (2) may be written as follows:

$$\Phi_x = + D_x \frac{dC_x}{dx} \quad (1a)$$

$$D_x = D_0 e^{\gamma C_x} \quad (2a)$$

where the index  $x$  means that  $\Phi$ ,  $D$ , and  $C$  depend on the distance  $x$ . When steady-state pervaporation is reached, the derivatives of relations (1a) and (2a) give

$$\frac{d\Phi_x}{dx} = \frac{dD_x}{dx} \cdot \frac{dC_x}{dx} + D_x \frac{d^2 C_x}{dx^2} = 0 \quad (5)$$

and

$$\frac{dD_x}{dx} = D_0 \gamma \frac{dC_x}{dx} e^{\gamma C_x}. \quad (6)$$

The substitution of relations (6) and (2a) into eq. (5) leads to

$$\gamma \left( \frac{dC_x}{dx} \right)^2 + \frac{d^2 C_x}{dx^2} = 0. \quad (7)$$

With the boundary conditions

$$\begin{aligned} x = 0 & \quad C_x = 0 \\ x = l & \quad C_x = C_l \end{aligned}$$

the integration of relation (7) gives

$$C_x = \frac{1}{\gamma} \ln \left[ 1 + \frac{x}{l} (e^{\gamma C_l} - 1) \right]. \quad (8)$$

The experimental values of the concentration ( $S_x$ ) were expressed in grams per 100 grams dry polymer. To express the concentration in grams per cubic centimeter of swollen polymer ( $C_x$ ), the following relation was used:

$$C_x = k S_x. \quad (9)$$

The volume increase of the swollen membrane is essentially due to the volume of the sorbed liquid because the density of the grafted membranes is constant in the different used liquids, so  $k$  can be calculated with the following relation:

$$\frac{1}{k} = \frac{S}{d_s} + \frac{100}{d_m} \quad (10)$$

where  $d_m$  and  $d_s$  are the densities of the grafted membrane and of the sorbed liquid, respectively, and  $S$  is the swelling ratio of the membrane in the

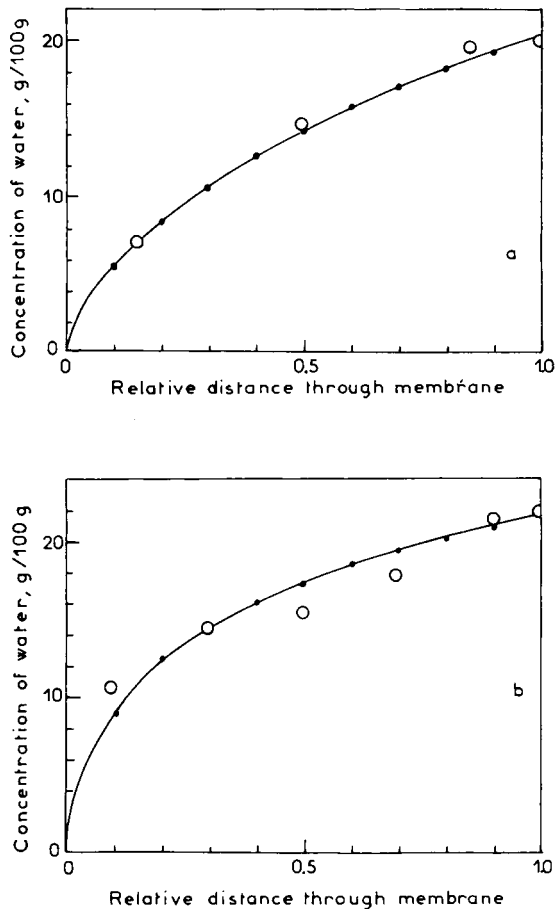


Fig. 2. Concentration gradient of water in PTFE-P4VP membranes: (a) stack of three membranes (PTFE thickness,  $17 \mu$ ; 150% grafting); (b) stack of five membranes (PTFE thickness,  $50 \mu$ ; 160% grafting); (O) experimental average values; (●) calculated values: (a)  $\gamma = 10$ ; (b)  $\gamma = 16$ .

liquid, which is experimentally determined at the swelling equilibrium. Relations (8) and (9) give

$$S_x = \frac{1}{k\gamma} \ln \left[ 1 + \frac{x}{l} (e^{\gamma ks} - 1) \right]. \quad (11)$$

By using a stack of identical membranes, we determined the average concentration  $\bar{S}_x$  of the sorbed liquid in each membrane. A quantitative comparison between the experimental values of  $\bar{S}_x$  and the values of  $S_x$  calculated from relation (11) is shown for water/PTFE-P4VP in Figures 2a and 2b and for the system N,N-dimethylformamide/PTFE-P4VP in Figure 3. The penetrants were selected because of their low volatility and diffusion constant; PTFE-P4VP membranes, because of their relatively

TABLE I  
Parameters of Relation (11)

| System                              | PTFE membrane            |                         | $S$ ,<br>g/100 g | $d_m$ | $k \times 10^3$ ,<br>g/cm <sup>3</sup> | $\gamma$ ,<br>cm <sup>3</sup> /g |
|-------------------------------------|--------------------------|-------------------------|------------------|-------|--|----------------------------------|
|                                     | Thick-<br>ness,<br>$\mu$ | Grafting<br>ratio,<br>% |                  |       |  |                                  |
| Water/PTFE-P4VP                     | 17                       | 150                     | 20               | 1.20  | 9.70                                   | 10                               |
| Water/PTFE-P4VP                     | 50                       | 160                     | 22               | 1.15  | 9.17                                   | 16                               |
| N,N-Dimethylformamide/<br>PTFE-P4VP | 17                       | 150                     | 50               | 1.20  | 7.35                                   | 8                                |

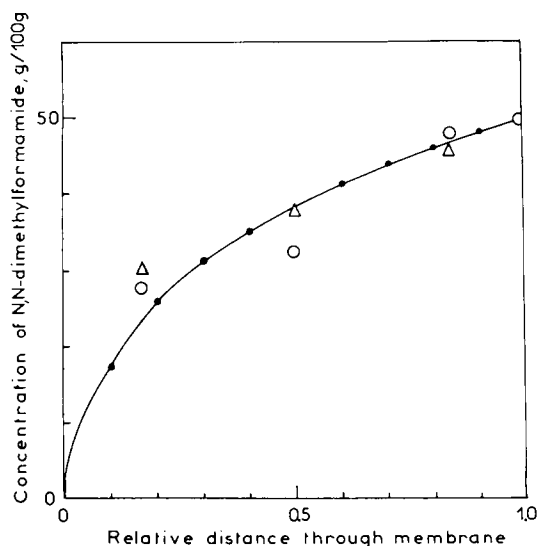


Fig. 3. Concentration gradient of N,N-dimethylformamide in PTFE-P4VP membrane, stack of three membranes (PTFE thickness, 17  $\mu$ ; 150% grafting): ( $\Delta$ ) experimental values; ( $\bullet$ ) calculated values ( $\gamma = 8$ ).

high swelling ratio. In Table I, the values of the parameters used to calculate  $S_z$  are reported.

In Figures 2 and 3, the solid line, which is the predicted concentration gradient, passes through the experimental points. The  $\gamma$  values allowing to plot the theoretical graphs are low (Table I). As the value of this parameter is characteristic of the effect of the solvent concentration on polymer segmental motion, the plasticizing effect of the used penetrants is relatively low. Moreover, the structure of the initial PTFE films<sup>2</sup> may explain the difference between the  $\gamma$  values for water in the PTFE-P4VP membranes prepared with PTFE films 17 and 50  $\mu$  thick.

According to the results about the thickness and the concentration gradient, it can be concluded that for a pure compound, the pervaporation process is well described by Fick's diffusion law.

TABLE II  
Pure Compounds in PTFE-PVP Membranes:  
Pervaporation Rate and Swelling Ratio at 25°C<sup>a</sup>

| Compound           | $\Phi$ ,<br>kg/hr-m <sup>2</sup> | $S$ ,<br>g/100 g | Compound              | $\Phi$ ,<br>kg/hr-m <sup>2</sup> | $S$ ,<br>g/100 g |
|--------------------|----------------------------------|------------------|-----------------------|----------------------------------|------------------|
| Water              | 0.56                             | 17.0             | Tetrahydro-           |                                  |                  |
| Methanol           | 2.18                             | 15.0             | furan                 | 0.26                             | 4.5              |
| Ethanol            | 0.74                             | 16.5             | Dioxane               | 0.05                             | 9.0              |
| <i>n</i> -Propanol | 0.34                             | 20.5             | <i>N,N</i> -Dimethyl- |                                  |                  |
| <i>n</i> -Butanol  | 0.36                             | 21.5             | formamide             | 0.18                             | 7.0              |
| Chloroform         | 2.76                             | 32.0             | Pentane               | 0.00                             | 0.0              |

<sup>a</sup> PTFE thickness, 50  $\mu$ ; 38% grafting.

TABLE III  
Pure Compounds in PTFE-P4VP Membranes:  
Pervaporation Rate and Swelling Ratio at 25°C<sup>a</sup>

| Compound   | $\Phi$ ,<br>kg/hr-m <sup>2</sup> | $S$ ,<br>g/100 g | Compound              | $\Phi$ ,<br>kg/hr-m <sup>2</sup> | $S$ ,<br>g/100 g |
|------------|----------------------------------|------------------|-----------------------|----------------------------------|------------------|
| Water      | 0.29                             | 22               | Tetrahydro-           |                                  |                  |
| Ethanol    | 0.60                             | 57               | furan                 | 0.45                             | 18               |
| Chloroform | 5.25                             | 110              | Dioxane               | 0.05                             | 10               |
|            |                                  |                  | <i>N,N</i> -Dimethyl- |                                  |                  |
|            |                                  |                  | formamide             | 0.40                             | 76               |
|            |                                  |                  | <i>N,N</i> -Dimethyl- |                                  |                  |
|            |                                  |                  | acetamide             | 0.36                             | 64               |
|            |                                  |                  | Pentane               | 0                                | 0                |

<sup>a</sup> PTFE thickness, 50  $\mu$ ; 200% grafting. THF: tetrafulan; DMF: *N,N*-dimethylformamide; DMA: *N,N*-dimethylacetamide.

**Correlation Between Swelling Ratio and Pervaporation Rate.** By integrating relation (2), we can obtain the average value of the diffusion coefficient  $\bar{D}$ :

$$\bar{D} = \frac{D_i - D_0}{\ln D_i/D_0} \quad (12)$$

where  $D_i$  is the  $D$  value at the upstream face of the membrane:

$$D_i = D_0 e^{\gamma C_i} \quad (13)$$

Combination of relations (4), (9), (12), and (13) gives

$$\Phi = \frac{\bar{D} C_i}{l} = \frac{\bar{D} k S}{l} \quad (14)$$

So both solubility and diffusion factors ( $S$  and  $\bar{D}$ ) play an important role in the transport rate.

The experimental data of the pervaporation rate and the swelling ratio for different compounds are listed in Table II (PTFE-PVP membranes) and in Table III (PTFE-P4VP membranes). The penetrants are solvents of PVP and P4VP, except water, which is a nonsolvent of P4VP.



TABLE IV  
Viscosity<sup>a</sup> of Pure Compounds and Diffusion Coefficient in PTFE-PVP<sup>a</sup> and PTFE-P4VP<sup>b</sup> Membranes

| Compound              | Viscosity<br>at 25°C, cp | $\bar{D} \times 10^7, \text{cm}^2/\text{s}$ |           |
|-----------------------|--------------------------|---|-----------|
|                       |                          | PTFE-PVP                                    | PTFE-P4VP |
| Methanol              | 0.544                    | 18.0  |           |
| Chloroform            | 0.545                    | 10.4  | 23.0      |
| Water                 | 0.890                    | 3.8   | 4.4       |
| Ethanol               | 1.078                    | 5.7   | 5.0       |
| <i>n</i> -Propanol    | 2.988                    | 2.2   |           |
| <i>n</i> -Butanol     | 2.573                    | 2.3   |           |
| Tetrahydrofuran       | 0.460                    | 5.7   | 8.3       |
| N,N-Dimethylformamide | 0.802                    | 2.7   | 2.6       |
| N,N-Dimethylacetamide | 0.919 <sup>c</sup>       |   | 2.6       |
| Dioxane               | 1.204                    | 0.5   | 1.5       |

<sup>a</sup> PTFE thickness: 50 $\mu$ ; 38% grafting.

<sup>b</sup> PTFE thickness: 50 $\mu$ ; 20% grafting.

<sup>c</sup> From Lester et al.<sup>7</sup>

The results listed in Table II clearly show that compounds which are hydrogen bonded with the polymer basic units (water, alcohols, chloroform) swell the membrane more than the nucleophilic solvents (ethers, amides). Moreover, the former have a higher pervaporation rate than the latter. In the case of PTFE-P4VP membrane (Table III), the relatively high swelling ratio of amides compared with ethers can be explained by the fact that the solubility power of these amides for P4VP is higher than those of the ethers.

**Diffusion Coefficient.** According to relation (14), we can calculate the average diffusion coefficient  $\bar{D}$ . For each class of compounds (electrophilic and nucleophilic), the less viscous liquids have a higher diffusivity (Table IV); this is in agreement with the classical Stokes-Einstein equation of the diffusion coefficient. If we compare compounds of similar viscosity, it can be seen that the electrophilic ones have a higher diffusion coefficient than the nucleophilic ones. That is, the diffusivity of compounds which are H bonded with the polymer basic units does not decrease as has been suggested.<sup>8</sup>

### Pervaporation of Mixtures

The different relations established for the pervaporation of pure compounds cannot be extended to the cases of mixtures without assuming that the solvent A/solvent B/membrane system is ideal. But for polar liquids and membranes, the high interactions between the three components do not permit such simplifications. However, it was possible to show that the theoretical laws are also qualitatively valid for mixtures and to discuss the problem of the selectivity.

TABLE V  
Preferential Sorption and Pervaporation Selectivity

| Membrane               | Liquid mixture |                       | A, vol-%  |                  |                |
|------------------------|----------------|-----------------------|-----------|------------------|----------------|
|                        |                |                       | in liquid | in sorbed liquid | in pervaporate |
|                        | A              | B                     | $x_A$     | $z_A$            | $y_A$          |
| PTFE-P4VP <sup>a</sup> | water          | N,N-dimethylacetamide | 70        | 75               | 100            |
|                        | water          | N,N-dimethylacetamide | 6         | 20               | 77             |
|                        | water          | N,N-dimethylformamide | 50        | 50               | 98             |
| PTFE-PVP <sup>b</sup>  | water          | Dioxane               | 50        | 60               | 90             |
|                        | water          | N,N-dimethylformamide | 50        | 56               | 96             |
| PTFE-PVP <sup>c</sup>  | water          | Dioxane               | 17.4      | 23               | 73             |

<sup>a</sup> PTFE thickness, 50  $\mu$ ; 200% grafting.

<sup>b</sup> PTFE thickness, 50  $\mu$ ; 87% grafting.

<sup>c</sup> PTFE thickness, 50  $\mu$ ; 55% grafting.

**Effect of Membrane Thickness.** It has previously been shown<sup>2</sup> that the pervaporation rate of mixtures was inversely proportional to the thickness as is the case for pure compounds.

**Selectivity Due to Preferential Sorption.** The problem was to know if selectivity would take place at the liquid-membrane interface. In Table V, we have reported the values of the volume per cent of the preferential pervaporated component (A) in the initial mixture ( $x_A$ ), in the membrane at the liquid interface ( $z_A$ ), and in the pervaporate ( $y_A$ ), respectively. The difference between  $z_A$  and  $x_A$  is much lower than that between  $y_A$  and  $x_A$ . Especially in the case of the system water/N,N-dimethylformamide/PTFE-P4VP, there is no sorption selectivity. These results show that the selection between the two species A and B occurs essentially during their transport through the membrane. Thus, it was interesting to measure the composition gradient through the membrane.

**Concentration and Composition Gradients of a Mixture through the Membrane.** By using a stack of membranes, it was possible to evaluate the average quantity and composition of the liquid mixture within the membrane at various distances from the faces. Before discussing the results, some remarks on the precision of the experiments are necessary. Just before the separation of the membranes from the cell, we may assume that the steady state of the pervaporation is always established because some liquid remains in contact with the upper membrane, whereas the downstream face is always under vacuum. But a slight reequilibration can change the concentration and composition gradients during the time (roughly 1.5 min) necessary to separate and to place all the membranes in the reactors. However, experiments show that less than 10% of the

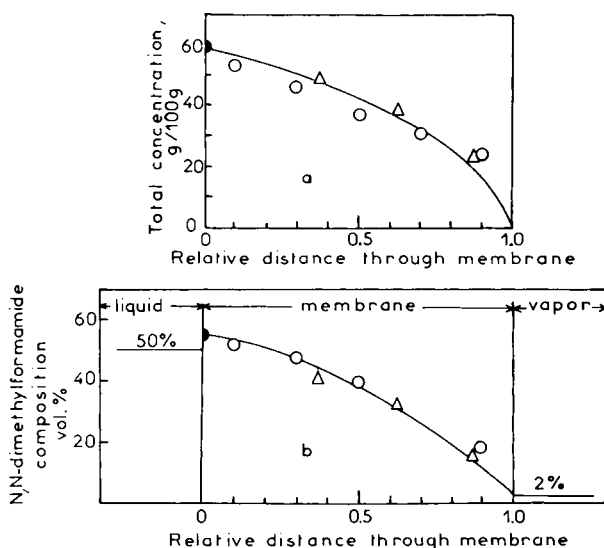


Fig. 4. Concentration (a) and composition (b) gradients of water-N,N-dimethylformamide mixture in PTFE-P4VP membrane (PTFE thickness,  $17 \mu$ ; 150% grafting): (O) stack of five membranes; ( $\Delta$ ) stack of four membranes.

total liquid can be desorbed in 1.5 min when the membrane is swollen with a very volatile solvent.

Figures 4 and 5 are related to the system water/N,N-dimethylformamide/PTFE-P4VP and water/dioxane/PTFE-P4VP, respectively. When the components pass from the upstream side ( $x/l = 0$ ) to the downstream side ( $x/l = 1$ ), we can see, first, the decrease in total concentration  $\bar{S}_x$  (Figs. 4a and 5a), and secondly, the decrease in the composition of the less easily pervaporated component (Figs. 4b and 5b).

The general form of the graphs  $S_x$  versus  $x/l$  is similar to that found for a pure compound, and, as was suggested by Long,<sup>4</sup> the chief resistance to diffusion is at the downstream zone of the membrane. We must also note that the results obtained with a stack of four membranes are in agreement with those obtained with five membranes; this means that the concentration  $S_x$  only depends on the ratio  $x/l$  as is the case for a pure compound, relation (11).

On the other hand, the almost linear decrease of the composition of dioxane or N,N-dimethylformamide as the mixture passes up through the membrane does not agree with Binning's assumption<sup>3</sup> that selectivity occurs at an interface placed between two different phases in the membrane. Moreover, as observed for concentration, the composition in the membrane depends only on the ratio  $x/l$ . Then, the composition at a given point inside the membrane is dependent on the swelling state of the polymer at this point. These last results explain that the selectivity factor has been found to be independent of membrane thickness.<sup>2</sup>

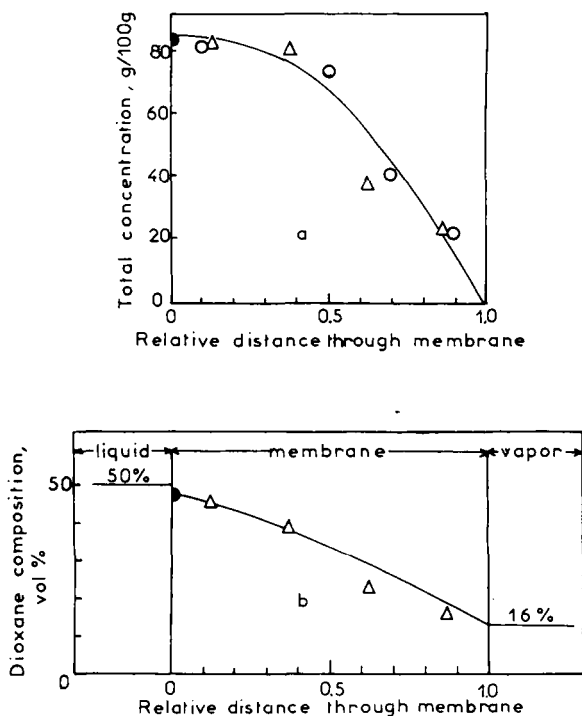


Fig. 5. Concentration (a) and composition (b) gradients of water-dioxane mixture in PFTE-P4VP membrane (PTFE thickness,  $17 \mu$ ; 160% grafting): (O) stack of five membranes; ( $\Delta$ ) stack of four membranes.

### Some Qualitative Correlations Between Selectivity and Physicochemical Properties of the Ternary Mixtures Solvent A/Solvent B/Membrane.

The transport through the membrane of component A or B of a mixture is due, as has been seen, to a chemical potential difference existing on both sides of the membranes. Under this driving force, each molecule diffuses at its specific rate. This rate can be very different from that of the pure compounds and can vary greatly with the composition of the mixture.<sup>9,10</sup> It was not the subject of this paper to give a complete study of this problem, but below we give some important general trends to show that the origins of selectivity must be found in the different interactions which take place in the ternary system solvent A/solvent B/membrane.

From the data previously obtained,<sup>1,2</sup> it may be seen that in all cases, the H-bonded component with the nucleophilic sites VP or 4VP pervaporates selectively through modified PTFE films. This remains true even when the hydrogen-donor component is associated with a better swelling component which has a higher pervaporation rate. This is the case particularly for systems water/amide/PTFE-P4VP (Table VI).

When the preferential pervaporated compounds (A) are taken in a homologous series and associated with a like compound, the pervaporation

TABLE VI  
Pervaporation Properties at 25°C of Water, Amides, and Mixtures of Water and Amide Through PTFE-P4VP<sup>a</sup> Membranes

|                               | Pure compound |               |               | Mixture A plus B    |                     |
|-------------------------------|---------------|---------------|---------------|---------------------|---------------------|
|                               | Water         | N,N-Dimethyl- | N,N-Dimethyl- | Water-N,N-Dimethyl- | Water-N,N-Dimethyl- |
|                               |               | formamide     | acetamide     | formamide           | acetamide           |
| <i>S</i> , g/100 g            | 22            | 76            | 64            | 50                  | 40                  |
| $\Phi$ , kg/hr-m <sup>2</sup> | 0.29          | 0.40          | 0.36          | 0.45                | 0.21                |
| Water in liquid mixture       |               |               |               |                     |                     |
| <i>x</i> <sub>A</sub> , vol-% |               |               |               | 50                  | 70                  |
| Water in pervaporate          |               |               |               |                     |                     |
| <i>y</i> <sub>A</sub> , vol-% |               |               |               | 98                  | 100                 |

<sup>a</sup> PTFE thickness, 50  $\mu$ ; 200% grafting.

TABLE VII  
Pervaporation Properties of Alcohol/N,N-Dimethylformamide Mixtures<sup>a</sup> through PTFE-PVP<sup>b</sup> Membranes (temperature 25°C)

| Mixture            |                  | Pervaporation                 |          |
|--------------------|------------------|-------------------------------|----------|
| A                  | B                | $\Phi$ , l./hr-m <sup>2</sup> | $\alpha$ |
| Methanol           | DMF <sup>c</sup> | 0.48                          | 4        |
| Ethanol            | DMF              | 0.30                          | 2.3      |
| <i>n</i> -Propanol | DMF              | 0.21                          | 1.7      |
| <i>n</i> -Butanol  | DMF              | 0.16                          | 1.4      |

<sup>a</sup> Molar fraction of A, 0.5.

<sup>b</sup> PTFE thickness, 50  $\mu$ ; 30% grafting.

<sup>c</sup> N,N-Dimethylformamide.

TABLE VIII  
Examples of Mixtures Which Cannot Be Fractionated by Pervaporation Through Modified PTFE Membranes (Temperature, 20°C)

| Mixture         |                      |   | Pervaporation          |                               |          |
|-----------------|----------------------|---|------------------------|-------------------------------|----------|
| A               | B                    | A in liquid <i>x</i> <sub>A</sub> , vol-% | Membrane               | $\Phi$ , kg/hr-m <sup>2</sup> | $\alpha$ |
| Chloroform      | methanol             | 36  | PTFE-P4VP <sup>a</sup> | 6.2                           | 1.1      |
| Chloroform      | methanol             | 66  | PTFE-PVP <sup>b</sup>  | 3.8                           | 1.4      |
| Chloroform      | ethanol              | 90  | PTFE-PVP <sup>c</sup>  | 2.5                           | 1.0      |
| Chloroform      | <i>d</i> -chloroform | 50  | PTFE-PVP <sup>b</sup>  | 1.2                           | 1.0      |
| Tetrahydrofuran | dioxane              | 55  | PTFE-PVP <sup>b</sup>  | 0.3                           | 1.2      |
| Acetone         | carbon disulfide     | 33  | PTFE-PVP <sup>c</sup>  | 0.7                           | 1.0      |

<sup>a</sup> PTFE thickness, 50  $\mu$ ; 250% grafting.

<sup>b</sup> PTFE thickness, 50  $\mu$ ; 38% grafting.

<sup>c</sup> PTFE thickness, 50  $\mu$ ; 70% grafting.

rate and the selectivity decrease with increasing molecular weight of A (Table VII).

Practically no fractionation occurs between two species of similar size which present similar affinities with the polar sites of the membrane (Table VIII).

### CONCLUSIONS

Pervaporation is a special case of ordinary diffusion and can be explained by a model using classical Fick's laws. In the case of pervaporation of pure compounds, the experimental data agree with the theoretical relations. For mixtures, the global concentration gradient of the species in the membrane is similar to that found for pure compounds; the increase of the composition of the preferentially pervaporated component through the membrane shows that the selection of the transported species is progressive and does not occur at an interface in the membrane. These results are in agreement with the fact that the pervaporation rate is inversely proportional to the membrane thickness and that the selectivity remains constant when the thickness decreases.

It was also established that the hydrogen bonds, between a compound and the polar sites, carried by the membrane enhance the solubility and the diffusivity of this compound and that this latter is always selectively pervaporated when it is associated with a nonhydrogen donor component.

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