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A. F. Vetter[a]; S. N. Kim[a]
[a] UNIVERSITY OF IOWA, IOWA CITY, IOWA

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Liquid Permeation of Isopropanol and Water in a Silicone Rubber

A. F. VETTER and S. N. KIM
UNIVERSITY OF IOWA
IOWA CITY, IOWA

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Summary

The feasibility of using a silicone rubber membrane to separate mixtures of isopropyl alcohol and water, including the azeotropic composition, has been demonstrated and a quantitative measure of efficiency of separation has been developed.

One of the problem areas in studying liquid permeation is the variability in the polymer membrane structure. Such factors as the presence of solvents and plasticizers, previous thermal history, previous solvent history, and the degree of crystallinity of the polymer behavior affect membrane behavior. However, as the polymers are better understood, these drawbacks for the researcher may be of advantage to those tailoring a polymer to a specific use.

INTRODUCTION

Although the theory and application of gaseous phase separation through polymer membranes has been extensively studied, comparatively little work has been done in the area of liquid phase separation by this method. Azeotropes and mixtures whose components have close boiling-point temperatures have been studied by Binning and co-workers (*1*) and Sweeney and Rose (5), but few theoretical achievements or industrial applications have resulted. However, the rapid progress made in polymer membrane technology has created a number of strong candidates for successful selective permeation as a means of separating the components of liquid mixtures not amenable to treatment by more conventional methods. This paper is the report of an experimental investigation of the separation parameters of a liquid isopropyl alcohol–water mixture, using a silicone rubber membrane.

THEORY

Liquid permeation is defined as a permeation system in which the charge liquid is maintained in contact with the upstream side of the membrane and the permeate is removed as a vapor from the downstream side.

Binning has proposed a model in which, under liquid permeating conditions, the membrane can be assumed to consist of two zones—a solution phase zone and a vapor phase zone. The so-called solution zone may be visualized as a state of the polymer in which there is a high concentration of the permeating liquid in the polymer structure. The vapor phase zone may be considered as a region in which permeating molecules are much more dispersed and the polymer film corresponds to the membrane in ordinary gas permeation. Binning did not attempt to develop quantitative relation between the two phases.

The position of the interface between the two zones in a membrane under permeation conditions is characteristic of the polymer, permeating liquid, and the experimental conditions.

Long (*4*) showed that under conditions of liquid permeation, the concentration profile in a particular membrane in the direction of the movement of the fluid is independent of membrane thickness.

Binning and others have indicated that the resistance of the vapor phase zone is rate controlling in the permeation process. Therefore, the permeation rate through the membrane is inversely proportional to the thickness of the vapor phase zone and, from Long's observations as well as experimental evidence, proportional to the total membrane thickness.

Although in many respects liquid membrane permeation resembles gas permeation, there is a significant difference in that in liquid permeation the concentration of the permeating liquid on the upstream side of the membrane is much greater. It is not plausible to predict permeate composition on the basis of permeation rates of pure liquids and the composition of the charge mixture, as one can do in the case of gas permeation.

Using Binning's model of a two-zone membrane, an equation for the permeability of a membrane can be developed from Fig. 1.

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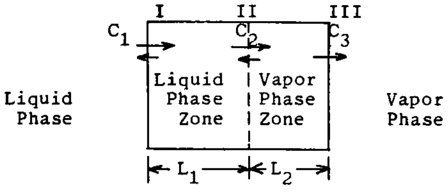

FIG. 1.

At steady-state conditions, Fick's first law for mass transport through the membrane can be written:

$$Q = -D\Delta C/\Delta L \tag{1}$$

where Q is the mass diffusion flux, D the diffusivity constant, C the concentration, and L the thickness of the membrane.

One can then write the equations for the diffusion flux in the two zones as

$$Q_1 = \frac{K(SC_1 - C_2)}{L_1}$$

$$Q_2 = \frac{D(C_2 - C_3)}{L_2}$$

where Q_1 and Q_2 are the respective mass transfer fluxes, C_1 the charge concentration, SC_1 the concentration of permeate in the polymer film at interface I, C_2 the concentration of permeate at interface II, C_3 the concentration of permeate at interface III, K the diffusion coefficient in the solution phase zone, D the diffusion coefficient in the vapor phase zone, and L_1 and L_2 the respective zone thicknesses.

Since the permeate is removed as a vapor from interface III as fast as it approaches this interface, $C_2 \gg C_3$.

Neglecting film resistances on both sides of the membrane and equating Q_1 to Q_2 (steady state),

$$C_2 = \frac{SC_1}{(L_1D/L_2K) + 1} \tag{2}$$

If, as Binning stated, the permeation in the vapor phase zone is rate controlling,

$$P = Q_2 = \frac{DC_2}{L_2}$$

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And in terms of C_1:

$$P = \frac{DSC_1}{[(L_1D/L_2K) + 1]L_2} = \frac{DSC_1}{(L_1D/K) + L_2} \tag{3}$$

This is the general equation for permeation for the Binning model.

Li et al. (3) showed that the value of diffusivity depends strongly on the concentration of the permeate in the membrane. Therefore, it can be assumed that for all cases $K > D$ in Eq. (3). In general, the position of interface II within the membrane is not known so that the values of L_1 and L_2 are also not known. Therefore, unless this interface position can be determined independently, we are restricted to two limiting cases:

1. If the liquid phase zone is only a very short distance into the membrane, $L_2 \gg L_1$ and L_2 is essentially the same as L. The general equation then reduces to

$$P = \frac{DSC_1}{L} \tag{4}$$

2. If the liquid phase zone includes almost the entire membrane, $L_1 \gg L_2$, $L_1/L_2 \gg K/D$, and L_1 is essentially the same as L.

Since $L_1D/L_2K \gg 1$, the general equation reduces to

$$P = \frac{KSC_1}{L} \tag{5}$$

The solubility coefficient S is defined by the Arrhenius equation:

$$S = S_0 \exp(-\Delta H/RT) \tag{6}$$

where ΔH is the heat of solution, R the gas constant, and T the absolute temperature.

The diffusion coefficient is defined by

$$D = D_0 \exp(-\Delta E/RT) \tag{7}$$

where ΔE is the activation energy of diffusion.

Substituting Eqs. (6) and (7) into Eq. (4) and letting $P_0 = S_0D_0C_1/L$ and $E_p = \Delta H + \Delta E$,

$$P = P_0 \exp(-E_p/RT)$$

or in logarithmic form,

$$\log P = -E_p/2.303RT + \log P_0 \tag{8}$$

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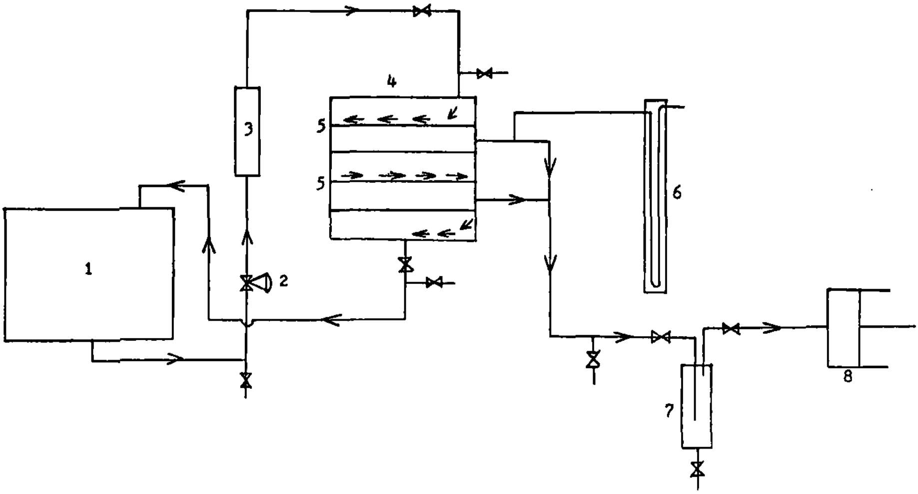

FIG. 2. Schematic diagram of apparatus. 1, Constant temperature bath (12,000 cc); 2, valve for flow control (manually operated); 3, rotameter; 4, permeation cell; 5, membranes; 6, mercury manometer; 7, cold trap; 8, vacuum pump.

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Since tests of the membrane by long-period submersion in both isopropanol and water indicated negligible swelling, Eqs. (4) and (8) were used in this investigation. Equation (8) predicts a linear relationship between log P and temperature, as in Fig. 3. The slope of the straight line in such a plot can be used to calculate E_p in the temperature range where no transition in the polymer structure occurs.

PROCEDURE

A schematic diagram of the apparatus is shown in Fig. 2. The membranes were silicone rubber prepared from Dow Corning's Silastic RTV-501. Two sets of membranes of two membranes per set were used. The total effective permeation area for the two membranes was 866.6 cm^2. Thickness of the membranes was determined by a series of 12 measurements over the surface and the average thickness was used. The membranes in the first set averaged 0.0246 cm and those in the other set averaged 0.0340 cm thick.

The charge liquids were water, isopropyl alcohol, and mixtures of various concentrations of the two, with particular attention given to the azeotrope which consists of 31.46 mole % water and boils at 80.37°C.

Upstream pressure was at ambient conditions, approximately 740 mm Hg. Downstream pressure was kept below 5 mm Hg. Trap temperature was kept at −80°C for permeation of water and at −195°C for permeation of pure isopropanol and all mixtures.

The 12,000-cc constant temperature bath and the flow system of the charge liquid assured that any change in the composition of the charge due to selective permeation could be neglected. Furthermore, the flow was maintained at turbulent conditions so that the film resistance at the liquid side of the membrane was negligible. Temperature was held to within ±0.5°C of the desired value. The temperature range was from room temperature, 25°C, to the boiling point of the azeotrope, 80°C.

RESULTS

Figure 3 illustrates the relation of permeability with temperature for both pure liquids and the azeotropic mixture in both membrane sets. By comparing the two curves for the same charge liquid, the effect of membrane thickness on permeation rate can be seen. Within experimental error, the product of permeability flux P and membrane thickness L proved to be the same for both membranes at each temperature. This supports the thesis that P is inversely proportional to L.

A quantity called a selectivity factor has been used by several investigators as follows:

$$S_F = \left(\frac{x}{100 - x}\right)\left(\frac{100 - y}{y}\right)$$

where S_F is the selectivity factor and is an indicator of the effectiveness of the system for selective permeation, x the weight per cent of water in the feed liquid, and y the weight per cent of water in the permeate.

Figure 4 illustrates the variations of the selectivity factor and the composition of the permeate with varying compositions of the charge liquid.

Calculations of the selectivity factor for the azeotropic mixture as a function of temperature and membrane thickness yielded values within the range of 1.60 and 1.94 over the temperature range of 25 to 70°C for both membrane thicknesses. Compared to the variation of the selectivity factor as a function of the composition

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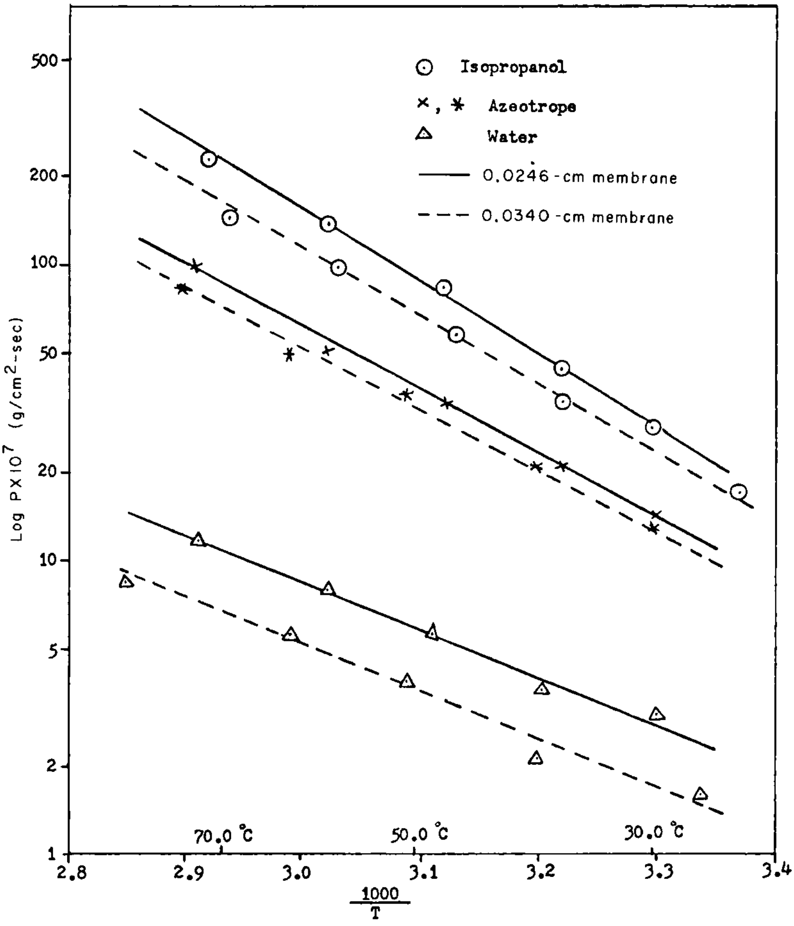

FIG. 3. Log of permeability versus 1000/*T*.

of the charge liquid, the variations with temperature and thickness are very small and are considered within experimental error. Binning also found only a very small change in selectivity as a function of temperature and membrane thickness in a 50 vol. % mixture of normal heptane in isooctane charge liquid.

Using Eq. (8) and the data depicted in Fig. 3, values of the activation energy of permeation were calculated and the results are given in Table 1. The higher value of E_p for isopropanol indicates a

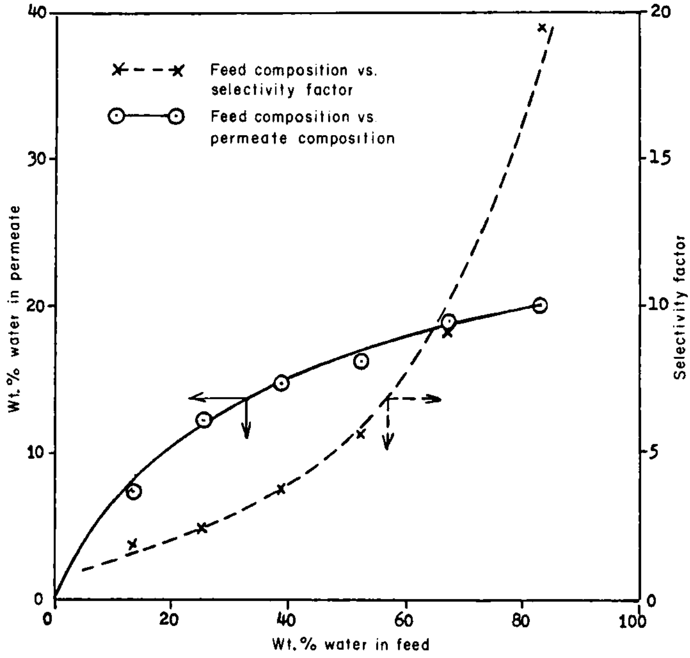

FIG. 4. Feed compositions vs. permeate compositions and selectivity factors at 48.5°C; membrane thickness, 0.0246 cm.

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greater sensitivity of permeability to temperature compared to water and the azeotropic mixture.

If, as Binning and others have indicated, the permeation rate is inversely proportional to membrane thickness, E_p should be independent of thickness. The differences in the values of E_p in Table 1

TABLE 1

Charge liquid	Film thickness, cm	E_p, kcal/ gram mole
Water	0.0246	7.146
Water	0.0340	7.535
Isopropanol	0.0246	11.10
Isopropanol	0.0340	10.02
Azeotrope	0.0246	9.495
Azeotrope	0.0340	9.171

for the same charge liquid and different membrane thicknesses probably represents an indication of experimental error.

Acknowledgment

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