

Hydraulic Permeation of Liquids Through Swollen Polymeric Networks. II. Liquid Mixtures

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Synopsis

The hydraulic permeation of toluene-cyclohexanone and isooctane- CCl_4 mixtures through a membrane, a rubber network, was studied. No separation of components occurred in this mode. The mixture flux data were successfully analyzed using a solution-diffusion theory by treating the mixture as if it were a single component with properties of the mixture. Diffusion coefficients determined in this way appear to be governed by frictional forces having a hydrodynamic origin. Slight separation of the components did occur when the pervaporation mode of operation was used. The significance of this is discussed.

INTRODUCTION

The objective of this series¹ is to examine hydraulic permeation in a wide range of polymeric network membranes using a solution-diffusion theory in order to understand better the mechanism of molecular diffusion in these situations. It has been shown earlier²⁻⁴ that pure organic liquids permeate a swollen rubber network at greatly different rates depending on the choice of liquid. The purpose here is to examine the transport of mixtures of organic liquids under the same circumstances. It will be shown that significant separation of the mixture components cannot be expected in the type of systems employed. However, it is of interest to explore the factors that govern the rate of transport of the mixture.

For pure liquids, the two most influential factors in the hydraulic transport rate are the degree to which the liquid swells the membrane and the viscosity of the liquid.²⁻⁵ Therefore, for this study of binary liquid mixtures, components were selected that would show significant variations in these two factors. The two systems used were toluene-cyclohexane and isooctane-carbon tetrachloride. Each pure component had been used in earlier work. Figure 1 shows the viscosity of mixtures of the first pair and the equilibrium swelling, v_{r0} = polymer volume fraction, of the gum rubber network from earlier studies,^{2,3} used as the membrane here, when immersed in these mixtures. This pair was selected because of the more than threefold range of viscosity that exists. Figure 2 shows the same parameters for the second pair which was selected mainly because of the twofold variation in equilibrium swelling. The two systems differ in an

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important way. In the first system, as the viscosity of the mixture increases, the equilibrium content of liquid in the membrane decreases. Both of these act to retard transport. In the second system, as the viscosity of the mixture increases, the equilibrium content of liquid in the membrane increases; thus, the

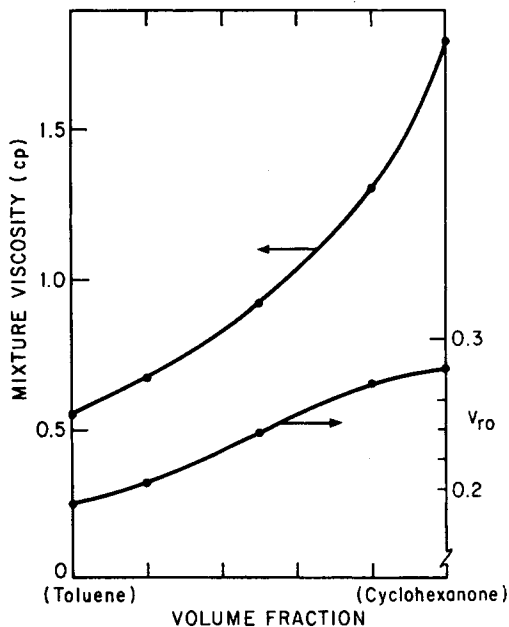


Fig. 1. Toluene-cyclohexanone system at 30°C. Upper curve gives viscosity of liquid mixtures. Lower curve gives the equilibrium swelling of gum rubber network (crosslink density = 1.06×10^{-4} moles/cc) used as the membrane in these mixtures.

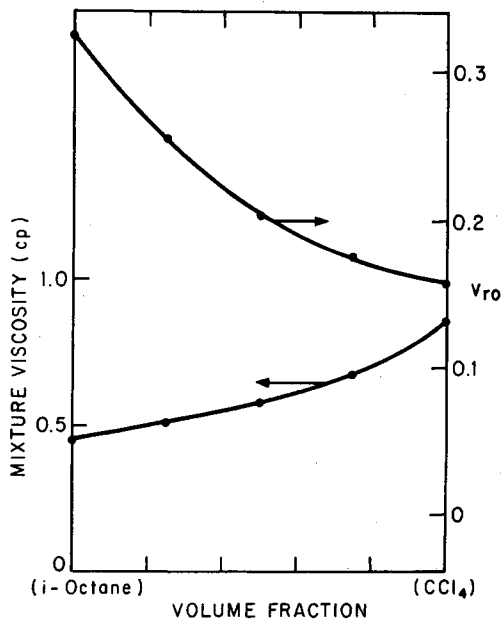


Fig. 2. Isooctane-carbon tetrachloride system at 30°C. Lower curve gives viscosity and upper curve equilibrium swelling.

two factors act in opposition with regard to their effect on transport rate. Note that in all cases here, volume fraction units are used to express the composition of the liquid mixture.

Experimentally it will be shown that virtually no separation occurs when these mixtures are caused to permeate the highly swollen membrane by the action of a hydraulic force. The permeation rate can be analyzed by treating the mixture as a pure fluid with the properties of the mixture. By contrast, one of the mixtures, isooctane- CCl_4 , was examined in the pervaporation mode of transport where selective transport of the smaller molecule, CCl_4 , did occur.

Hydraulic Permeation Results for Liquid Mixtures

The membrane used in this work was a lightly crosslinked natural rubber identical to that described and characterized earlier.^{2,3} The equipment and procedures used to determine the hydraulic permeation were also the same as used earlier,^{1,3} except that here a continuously stirred liquid mixture was fed to the upstream side of the apparatus. After application of the pressure differential ($p_0 - p_i$), enough time was allowed to flush out the downstream compartment of the permeation cell several times before data were collected. For each condition, the total volumetric flux through the membrane was measured, and a sample of the effluent liquid was collected and analyzed by refractometry. In no case was there a significant difference in composition between the permeate and the feed. The flux- Δp relations for the mixtures were nonlinear as found previously for pure liquids. Pure toluene permeates this membrane about five times faster than pure cyclohexanone. Flux- Δp data for the mixtures of these two (not shown here, but the fluxes are presented in another form in Fig. 4) were found to form a simple family of curves falling intermediate and in order of their composition between the pure component curves.

Figure 3 shows the flux- Δp data for the isooctane- CCl_4 system. The results are somewhat similar to that of the toluene-cyclohexanone system, but the

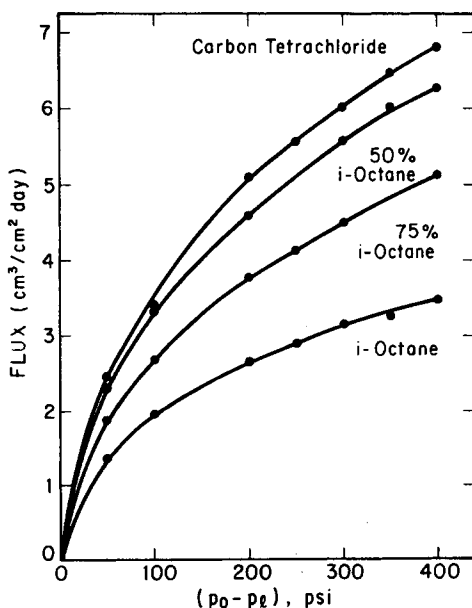


Fig. 3. Total flux vs. applied pressure differential for the isooctane- CCl_4 system at 30°C.

mixture curves do not fall between those of the pure components with the same regularity. For example, the 50% mixture curve falls closer to the CCl_4 curve than a simple rule of additivity would suggest. For reasons of clarity, it was necessary to omit the 25% isooctane curve. It was almost coincident with the CCl_4 curve at low pressures and actually slightly above it at higher pressures. The analysis to be discussed next shows that this is in no way anomalous but results from the opposition in the trends of swelling v_{r0} and mixture viscosity η , shown in Figure 2.

Solution-Diffusion Analysis Using Single-Fluid Approximation

The solution-diffusion theory developed earlier² can be extended to multi-component systems, and the rudiments of this extension are outlined here. If we designate the two liquids as components 1 and 2, their activities in the upstream surface of the membrane are related to their activities in the feed solution as follows²:

$$\begin{aligned} a_{10}^m &= a_{10}^s \\ a_{20}^m &= a_{20}^s. \end{aligned} \quad (1)$$

Activities in the membrane at its downstream surface are related to the activities in the permeate solution by

$$\begin{aligned} a_{1l}^m &= a_{1l}^s e^{-V_1(p_0 - p_l)/RT} \\ a_{2l}^m &= a_{2l}^s e^{-V_2(p_0 - p_l)/RT}. \end{aligned} \quad (2)$$

To complete the model, one needs (1) solution activity data to relate a_i^s to feed and permeate composition; (2) a ternary thermodynamic model for the membrane that can relate a_i^m to composition in the membrane—a simple example is described by Krigbaum and Carpenter,⁶ which requires three interaction parameters, χ_{ij} ; and (3) a multicomponent diffusion rate equation to replace Fick's law for binary systems, which would require at least two diffusion coefficients and possibly more. Implementation of these into a composite calculation for the flux of each component is complicated by the fact that the thermodynamics which provide the boundary conditions for the transport equations are coupled with the transport equations, i.e., the a_{il}^m depend on the a_{il}^s , which depend on the ratio of fluxes.

No attempt will be made here to develop further the details of such a model since experimentally we already know that, to within the precision of our measurements, the ratio of fluxes is equal to the proportion of components 1 and 2 in the feed mixture. This knowledge could be easily anticipated in advance, as the following shows. The difference in chemical potential for species 1 between the upstream and downstream solutions is given² by

$$\mu_{10}^s - \mu_{1l}^s = V_1(p_0 - p_l) - RT \ln \frac{a_{1l}^s}{a_{10}^s}. \quad (3)$$

In order for species 1 to spontaneously transfer from the upstream to the downstream solution, $\mu_{10}^s - \mu_{1l}^s$ must be positive. For $V_1 \sim 100$ cc/mole, this means that a_{1l}^s/a_{10}^s must be less than 1.03 when $\Delta p = 100$ psi or less than 1.13 when $\Delta p = 400$ psi. Stated another way, if the membrane were totally impermeable to species 2, then the osmotic pressure differential between the two compartments when $a_{1l}^s/a_{10}^s = 1.03$ would be 100 psi, and species 1 could not be transported to the downstream compartment until a pressure differential larger than

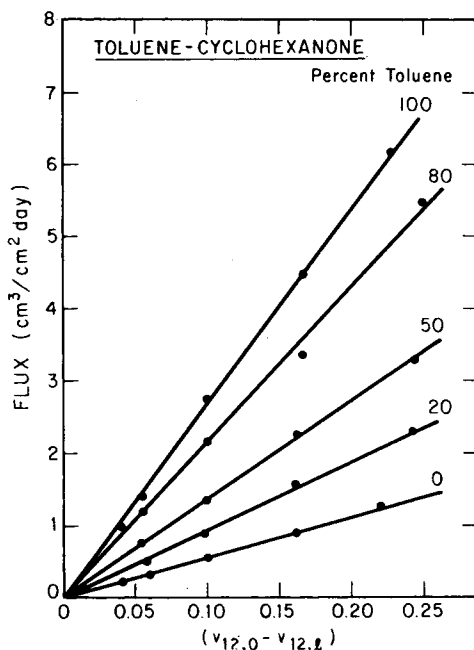


Fig. 4. Total flux for the toluene-cyclohexanone system at 30°C against liquid volume fraction differential across membrane.

this is applied. The fact is that the membrane in this case is not impermeable to either species, and the very large osmotic effects ensure that the two components move together as one fluid without any separation. The effect is similar to diffusion of electrolytes where cations and anions move at the same rate owing to the large electrical forces that would result if they did not.

With this background, it is reasonable now to treat the feed mixture as if it were a pseudopure fluid; however, in doing this, it should be remembered that in general the composition of the fluid imbibed into the membrane need not be the same composition as the feed mixture,^{6,7} even though no separation occurs. We will ignore this complication for now. In this approach we treat the mixture as a single fluid whose volume fraction in the membrane is defined as

$$v_{12} = v_1 + v_2 = 1 - v_r. \quad (4)$$

At the upstream membrane surface, the volume fraction of liquid is $v_{12,0} = 1 - v_{r0}$. During hydraulic transport, the volume fraction of liquid at the downstream membrane surface is $v_{12,l}$ and can be calculated as follows. First, the "activity" of this pseudosingle fluid in the membrane at its downstream surface is calculated² from the following:

$$a_{12,l}^m = e^{-V_{12}(p_0 - p_l)/RT} \quad (5)$$

where V_{12} is the volume of 1 mole of the mixture. Second, this value is inserted into the binary Flory-Huggins equation² (where v_{12} is used instead of v_1) to obtain value of $v_{12,l}$. The Flory-Huggins interaction parameter can be evaluated for each mixture using the v_{r0} data shown in Figures 1 and 2.

In this way, the liquid concentration differential $v_{12,0} - v_{12,l}$ was computed for each $p_0 - p_l$, as described previously for pure fluids. The flux data can now be plotted versus this concentration differential as illustrated in Figure 4 for the

TABLE I
 Mixture Results at 30°C

Liquid	V_{12} , cc/mole	$D_0 \times 10^6$, cm ² /sec	$D_m \times 10^6$, cm ² /sec
Toluene 100%	106	21.3	2.75
Toluene 80%	104	17.7	2.32
Toluene 50%	102	13.0	1.62
Toluene 20%	100	9.24	1.18
Cyclohexanone 100%	98.4	6.76	0.74
Isooctane 100%	167	22.7	1.95
Isooctane 75%	142	20.9	2.52
Isooctane 50%	124	19.3	2.36
Isooctane 25%	110	17.5	2.42
CCl ₄ 100%	98.5	14.1	2.01

toluene-cyclohexanone system. As noted for numerous examples of pure liquids,²⁻⁴ these plots are linear for the mixtures. Similar plots were observed for the other system but are not shown here. We may now assign a diffusion coefficient D_m for the mixture, treated as a single fluid, and the membrane pair. By analogy with previous results,²⁻⁴ this leads to the following relation between flux and concentration differential:

$$\text{total flux} = \frac{D_m}{l_d v_{r0}^{2/3}} (v_{12,0} - v_{12,i}) \quad (7)$$

With the aid of this equation, the slopes from Figure 4 and its analog for the other system were used to compute values of D_m for each mixture. The results are shown in Table I.

Previous work⁵ has shown that the diffusion coefficient for pure liquids in swollen networks depends on both the solvent viscosity and the swelling of the network. Thus, an extension of the pseudosingle fluid model would suggest that D_m should depend on the viscosity of the liquid mixture and v_{r0} . Table I shows D_m decreases regularly as the percentage of cyclohexanone increases. As the cyclohexanone content increases, both the viscosity and v_{r0} increase which act in the direction to lower the diffusion coefficient. For the isooctane-CCl₄ system, the D_m goes through a maximum with composition, and in fact the diffusion coefficients for the two pure components are about the same. These more complex results are apparently due to the opposition between η and v_{r0} produced in this system referred to earlier.

A more quantitative approach for examining the effects of η and v_{r0} on D_m is desirable. One route is to compare D_m to the self-diffusion coefficient of the liquid, D_0 , in the absence of the polymer. Li and Chang⁸ have shown that the following equation provides an excellent estimate of D_0 :

$$D_0 = \frac{kT}{2\pi\eta} \left(\frac{N}{V} \right)^{1/3} \quad (6)$$

where N is Avogadro's number and V is the molar volume of the liquid. Here, it is clear that self-diffusion is inversely related to the viscosity. Now we propose to look at the ratio of D_m/D_0 . Earlier we showed that, to a good approximation, hydrodynamics can be used to explain the frictional processes in concentrated polymer solutions^{9,10} and highly swollen gels,²⁻⁴ i.e., all other factors be-

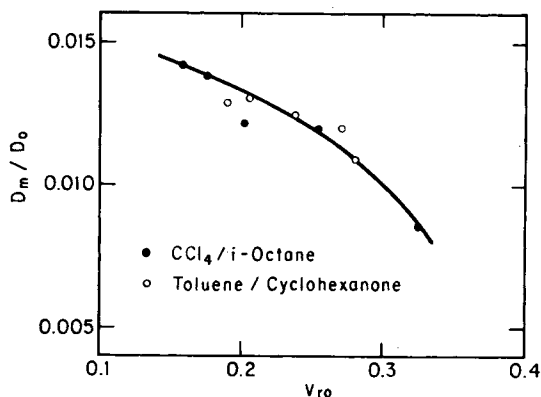


Fig. 5. Correlation of mixture diffusion coefficient results.

ing the same, the diffusion coefficient should be inversely proportional to η . Thus, if $D_m \propto 1/\eta$, the D_m/D_0 ratio cancels the viscosity dependency and also may account for small molar volume effects as well. Now, one may logically expect D_m/D_0 to depend on v_{r0} in some manner; however, it is important to point out that D_0 is a self-diffusion coefficient and D_m is a mutual diffusion coefficient, and the latter involves some terms of purely thermodynamic origin which endow this ratio with some unusual characteristics.

We have applied eq. (6) to the liquid mixtures to produce the D_0 entries in Table I, even though these values do not have a physical meaning for the mixture. These values were used to form the D_m/D_0 ratios plotted in Figure 5 versus v_{r0} . This approach seems to allow a way to separate the η and v_{r0} factors since, within the precision of the data, a single curve may be drawn through the points in Figure 5. More will be said later about this approach to correlating data when a wider variety of pure fluids are examined; however, for now, it is adequate to reinforce the idea that, in hydraulic permeation through swollen networks, mixtures do indeed appear to behave as if they were pure fluids having properties of the mixture. It should be recalled that in Figure 5, four of the ten points are for pure fluids and that the remaining mixture data form a common relation with them.

Comparison with Pervaporation

Pervaporation experiments were performed with the system isooctane- CCl_4 using a downstream vapor phase pressure of essentially zero. The flux obtained at zero pressure is the maximum obtainable^{2-4,11,12} and will be called the ceiling flux here. The solid dots in the upper part of Figure 6 show the fluxes for various feed mixtures obtained in this manner. For pure liquids, the ceiling flux can be estimated from hydraulic permeation data using an extrapolation procedure.^{2-4,11} The open squares in Figure 6 show the ceiling fluxes estimated in this way for the mixtures, and the agreement with the pervaporation values is excellent. The ceiling flux for CCl_4 is more than twice as large as for isooctane, which is approximately the situation at low pressures in hydraulic permeation, even though it is the more viscous of the two. This apparently is due to the higher swelling with CCl_4 . The mixture results are very interesting in that a slight maximum in flux is observed near the 25% isooctane region. The hy-

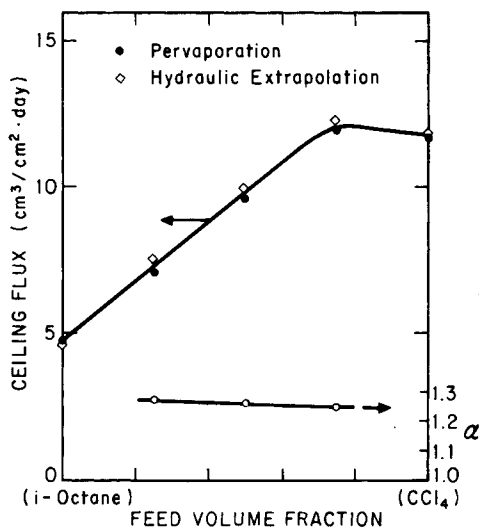


Fig. 6. Upper curve shows ceiling fluxes measured in pervaporation and estimated by extrapolation of hydraulic permeation data to infinite pressure. Lower curve gives separation factor for CCl_4 relative to iso-octane.

draulic permeation behavior was similar. Again, the competition between the η and v_{r0} factors is in evidence.

Samples of the vapor phase permeate were collected and analyzed, and a very definite enrichment of CCl_4 was observed in all cases. These results are shown in the lower part of Figure 6 in terms of a separation factor α , defined as follows:

$$\alpha \equiv \frac{\left(\frac{\Phi}{1-\Phi}\right)_{\text{permeate}}}{\left(\frac{\Phi}{1-\Phi}\right)_{\text{feed}}} \quad (8)$$

where Φ is the volume fraction of CCl_4 in the feed or permeate. Separation factors of the order of 1.26 were observed, which is interesting, since no separation was detected in the hydraulic mode. The fact that some separation occurred in the pervaporation mode is significant, and several factors may be responsible. First of all, the restriction of eq. (3) is no longer applicable, since in this mode the right side of this equation is to be replaced by $RT \ln[a_{10}^s/(p_1/p_1^*)]$, where p_1 is the partial pressure of species 1 in the downstream vapor, and p_1^* is the equilibrium vapor pressure species of 1. By reducing the total pressure of the downstream vapor, p_1 can be made as small as one wishes and, as a result, $\mu_{10} - \mu_{11}$ can be made as large as one wishes. However, another important factor is that near the downstream surface, in this mode the concentration of penetrants is very small and the mechanism of molecular diffusion is dramatically altered.^{9,11} At high swelling, hydrodynamics as described earlier dominate, while at low penetrant concentrations, where these molecules are far apart and separated by polymer chains, the mechanism shifts to one where the structural features of the diffusing molecules and the mobility of the chains dominate.^{2,9} In this structural regime, the two penetrants can move rather independently of each other and the smaller one would be expected to diffuse more rapidly. It is significant

to note that the molar volume of CCl_4 is 98.5 cc/mole compared to the 167 for isooctane. Recent results¹¹ have shown that pervaporation into high vacuum is dominated by the very low diffusion coefficients that exist in the downstream layers of the membrane caused by the very low content of penetrant there. It is evidently this region which is responsible for the separation exhibited here.

It has been noted earlier that for separation processes, pervaporation may generally be expected to provide higher productivity than reverse osmosis simply because larger driving forces can be imposed. For this same reason, pervaporation may also give greater selectivity. Further gains in selectivity are also likely in pervaporation since, on the vapor side of the membrane, the state of plasticization of the polymer may be greatly reduced, and this will enhance the selectivity of the transport process as proposed above.

SUMMARY

The experiments reported here show that hydraulic permeation of liquid mixtures through a highly swollen membrane does not produce any separation of the mixture. In fact, the mixture may be regarded as a pseudosingle fluid with properties of the mixture, and then the permeation data may be analyzed by solution-diffusion model equations intended for pure liquids. The diffusion coefficients deduced for mixtures in this way appear to be governed by frictional forces that are hydrodynamic in origin.

Pervaporation through this same membrane does produce some selectivity for the one system examined. It is proposed that this separation occurs because pervaporation into a high vacuum produces a region in the membrane on the downstream side with very low penetrant content, and thus the state of plasticization of the polymer is low. The two species move independently of each other in this zone compared to the highly swollen state, and transport under these circumstances is more selective. Molecular size controls diffusion here rather than viscosity of the fluid. For separation of liquid mixtures, the pervaporation mode has numerous advantages over the hydraulic mode even though some impressive separations have been reported for the latter.¹³

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