Permeation of Binary–Liquid Mixtures through Elastomers

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SYNOPSIS

Permeation of binary liquid mixtures through two commercially available elastomers were examined. The four systems studied are benzene–cyclohexane/neoprene, toluene–n-hexane/neoprene, toluene–methanol/nitrile, and toluene–o-xylene/nitrile. Permeation rate–time curves for several mixture compositions were prepared for each system. In the first three systems, the difference in the plasticizing effect of the two liquids on the membrane was very large. The liquid with the smaller plasticizing effect showed a permeation enhancement and the liquid with the larger plasticizing effect experienced a permeation depression. Toluene–o-xylene/nitrile represented a system in which the two liquids plasticized the membrane at almost the same rate. This system showed a permeation depression for both liquids.

INTRODUCTION

Permeation of liquid mixtures through polymeric membranes has been studied extensively during the past several years. This growing interest is mainly due to its application in the separation of various organic liquid and organic aqueous mixtures. Another application of this process is in the protective clothing industry. Elastomers are usually used to protect workers against exposure to hazardous chemicals. Many of the chemicals to which workers may be exposed are multicomponent mixtures. However, only limited data are available on the permeation of liquid mixtures through elastomers. Nelson et al.[1] studied the permeation of chloroform–toluene mixture through neoprene and pentane–trichloroethylene mixture through polyethylene. They showed that liquid mixtures can exhibit large, positive, synergistic rates. Mickelsen et al.[2] studied the permeation of binary liquid mixtures through elastomeric materials. They measured the permeation rates and breakthrough times for methanol–n-butanol/nitrile, methylethylketone–n-hexane/viton and p-xylene–toluene/nitrile systems. They have

concluded that there could be an increase in employee risk resulting from a decrease in breakthrough time and an increase in the permeation rate over that of the pure components.

It is well known that the permeation of a liquid through a polymeric membrane can be enhanced if a second liquid which is more soluble is also present in the membrane. This has been illustrated clearly by the permeation of benzene–cyclohexane and methanol–water mixtures through poly(γ-methyl L-glutamate)[3,4]; toluene–methyl mixtures through poly(γ-methyl L-glutamate)[3,4]; toluene–methyl cyclohexane, toluene–heptane, and thiophene–benzene through polypropylene.[5] Huang and Lin[6] studied the permeation characteristics of 25 combinations of binary liquid mixtures through low-density polyethylene. They observed permeation enhancement effects for most systems. However, for the cyclohexane–2,2-dimethylbutane a permeation depression effect was noticed. They explained this phenomena on the basis that the hindrance caused by the bulky molecular volume of 2,2-dimethylbutane predominates over any plasticizing action that it may have on the polymer membrane.

Because of the lack of significant permeation data for liquid mixtures through elastomers, this project was undertaken to examine the performance of two polymeric materials against binary chemical mixtures.

Table I Liquid Mixture–Polymer Pairs Studied

Binary Liquid Mixture	Membrane	Steady-State Permeation Rate of Pure Liquid (μg/cm^2 min)		Solubility of Pure Liquids in Membrane (g/cm^3)	
		Component 1	Component 2	Component 1	Component 2
Benzene(1)–cyclohexane(2)	Neoprene	2100	4	3.76	0.86
Toluene(1)–n-hexane(2)	Neoprene	1150	12	2.95	0.24
Toluene(1)–methanol(2)	Nitrile	620	0	1.67	0.12
Toluene(1)–o-xylene(2)	Nitrile	375	130	1.67	1.22

EXPERIMENTAL

Two commercially available elastomers were used for the experiments; neoprene (from glove Model No. 29-870, Edmont Co.) with an average thickness of 0.53 mm, and nitrile (from glove Model No. 37-165, Edmont Co.) with an average thickness of 0.55 mm. Reagent grade chemicals, from Fisher Scientific (Norcross, GA), were used without additional purification.

The apparatus used for the permeation experiment was the same one described in previous paper.[7] A speed-adjustable mechanical stirrer was used in the feed chamber of the cell to reduce concentration gradient in the liquid mixture. The four binary liquid mixture/membrane systems studied are given in Table I.

RESULTS AND DISCUSSION

The steady-state permeation rates of the pure liquids through the two elastomers are given in Table I. For the benzene–cyclohexane/neoprene system, steady-state permeation rate of pure benzene through neoprene is more than 500 times that of pure cyclohexane. In the case of the second ternary system, toluene permeates through neoprene with a rate, which is 100 times that of pure hexane. For the third system chosen, one component (methanol) did not permeate through the elastomer (nitrile), whereas the other component (toluene) permeated with a modest rate. For the o-xylene–toluene/nitrile system, the permeation rate of both liquids are of the same order of magnitude.

The permeation rate–time curves for benzene–cyclohexane/neoprene system are given in Figures 1 and 2. Figure 1 shows that steady-state permeation rates of benzene decreased and the permeation curves move to longer time with an increase in the concentration of cyclohexane in the mixture. In the case of cyclohexane, the steady-state permeation rate goes through a maximum at approximately 40 wt % cyclohexane in mixture. The time required for cyclohexane to pass through the membrane (known as breakthrough time) goes through a minimum at 40 wt % cyclohexane. The steady-state permeation rates of benzene and cyclohexane, and the total permeation rates are plotted against the weight percent cyclohexane in Figure 3. The permeation rate of pure cyclohexane is extremely small (4 μg/cm^2 min), but the presence of benzene in the membrane has increased its rate tremendously. The permeation rate of cyclohexane from a liquid mixture containing 40 weight percent cyclohexane is about 600 μg/cm^2 min, which is 150 times that of pure liquid. The total permeation rate decreases with an increase in the concentration of cyclohexane.

The permeation curves for toluene and hexane in the toluene–hexane/neoprene system are shown in Figures 4 and 5, respectively. The steady state permeation rate of toluene through neoprene decreases from 1150 to 40 μg/cm^2 min as the concentration of hexane in the feed increases from 0 to 80 wt %. The highest permeation rate for hexane occurs for a feed mixture containing approximately 20 wt % hexane. It also corresponds to the shortest breakthrough time. The steady-state permeation rates of toluene and hexane and the total permeation rates are plotted against the weight percent of hexane in Figure 6. The permeation rate of hexane through neoprene from a liquid mixture containing 20 wt % hexane is 475 μg/cm^2 min, which is about 40 times higher than for pure hexane. The total permeation rate shows a maximum at approximately 20 wt % hexane.

The permeation rate–time curves for toluene methanol/nitrile system are given in Figures 7 and 8. Figure 7 shows that steady-state permeation rates of toluene decreases and the permeation curves move
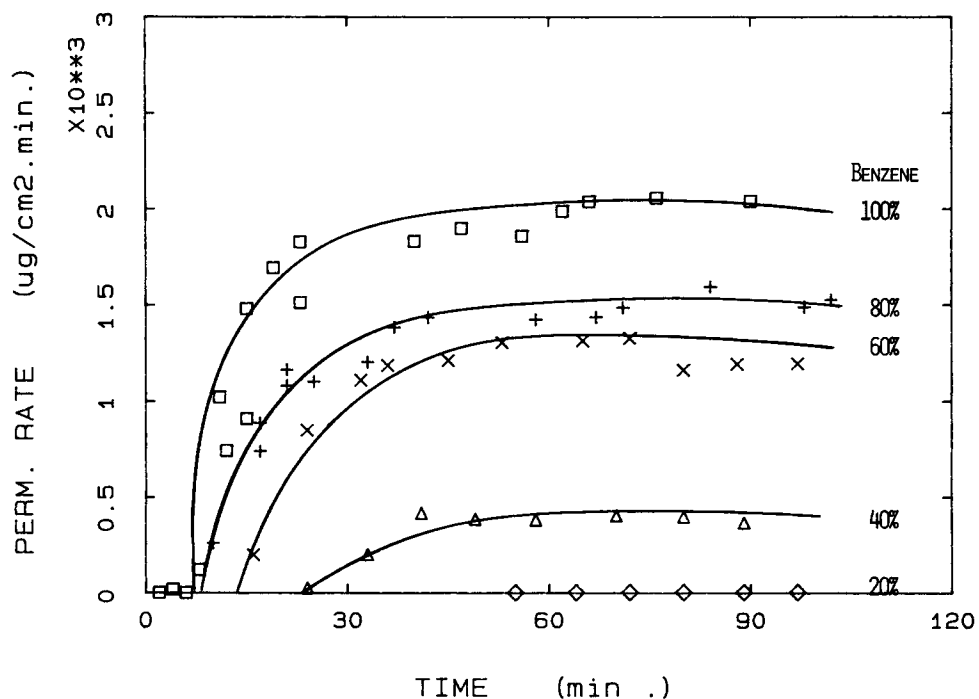
Figure 1   Permeation of benzene–cyclohexane mixtures through neoprene. Permeation curves for benzene.
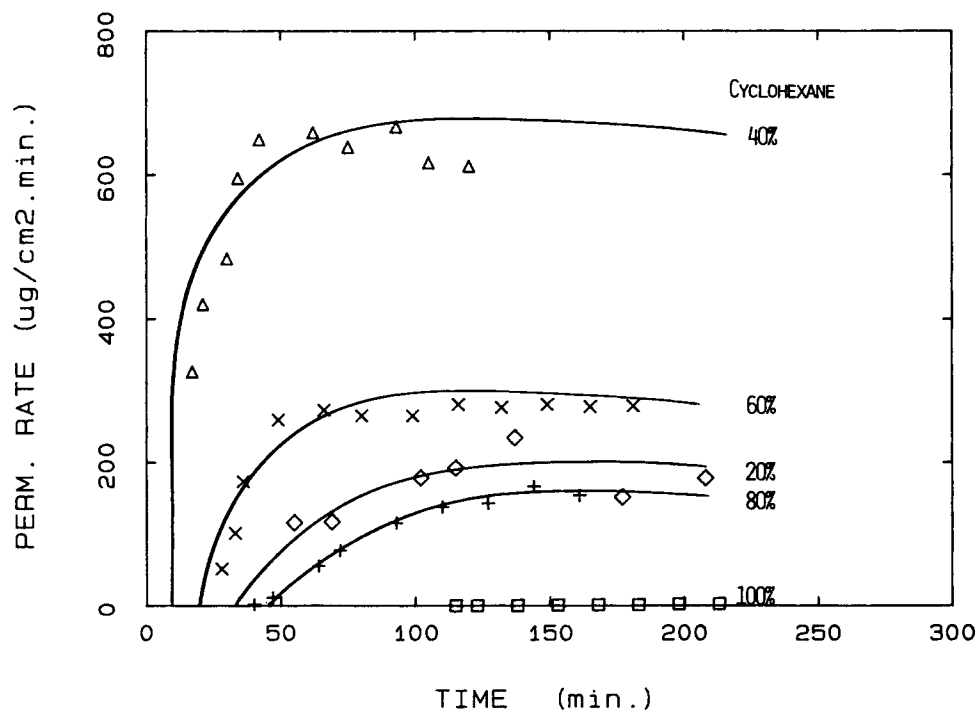

Figure 2   Permeation of benzene–cyclohexane mixtures through neoprene. Permeation curves for cyclohexane.
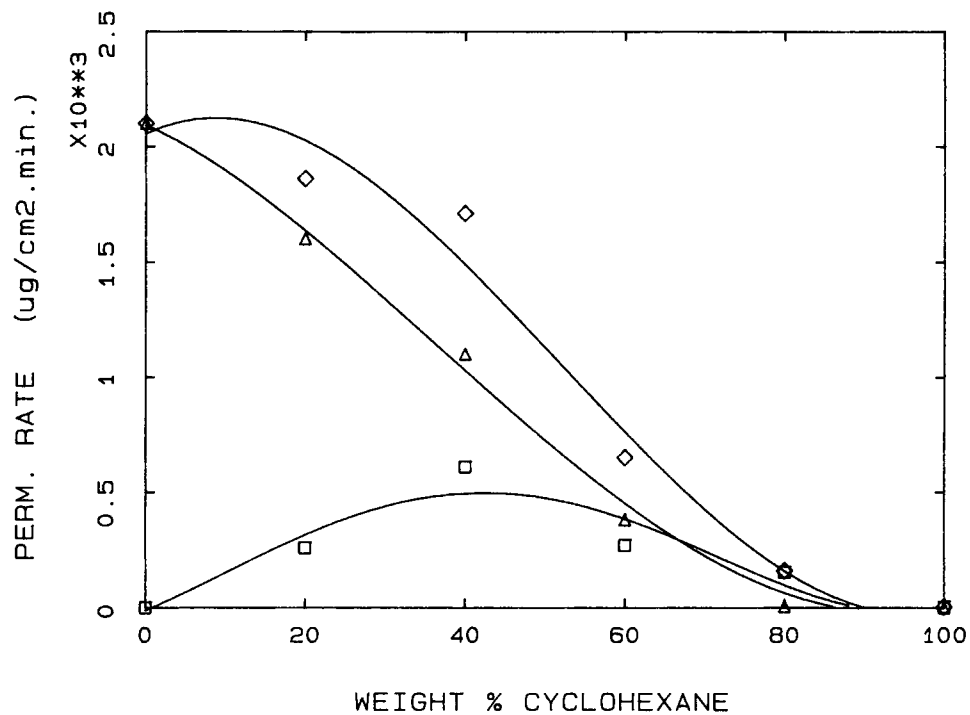
Figure 3 Steady-state permeation rates of benzene–cyclohexane mixtures through neoprene: (△) benzene; (□) cyclohexane; (◇) total.
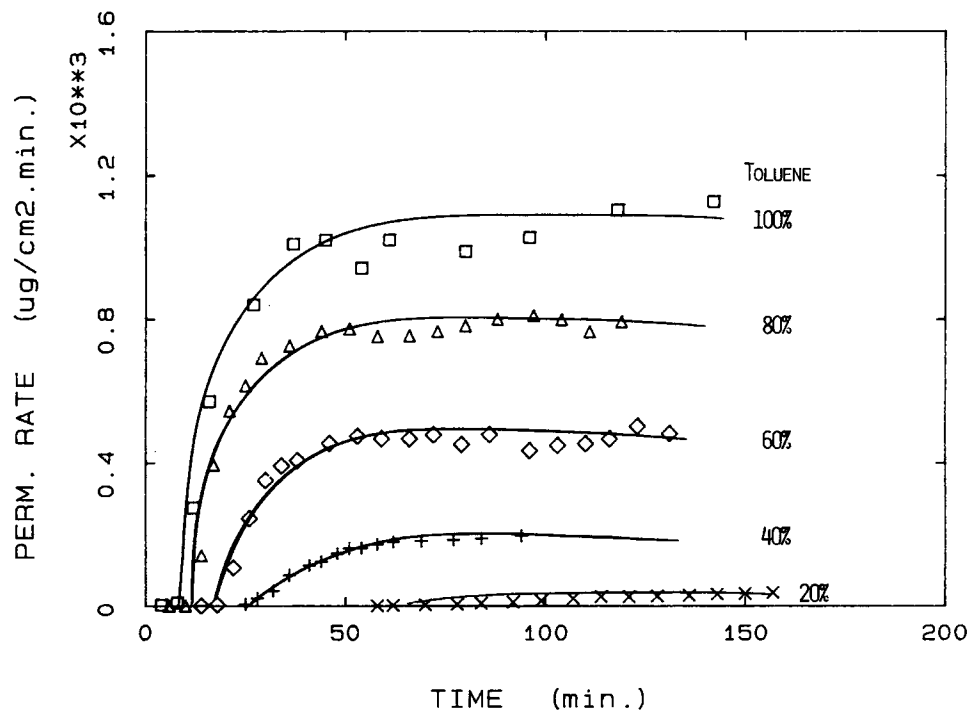

Figure 4 Permeation of toluene–n-hexane mixtures through neoprene. Permeation curves for toluene.
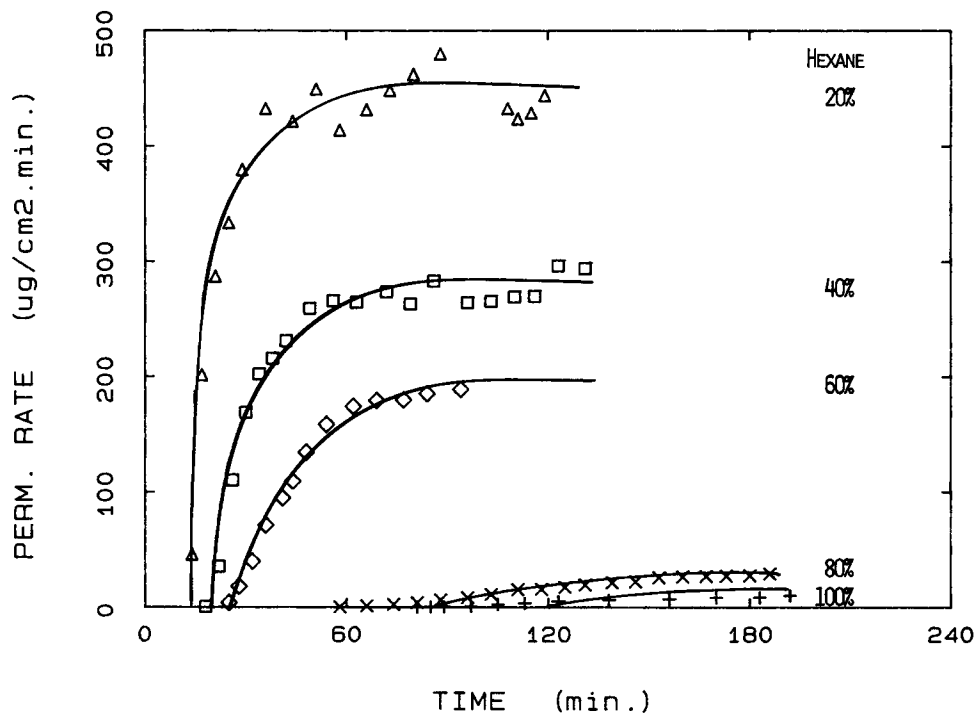
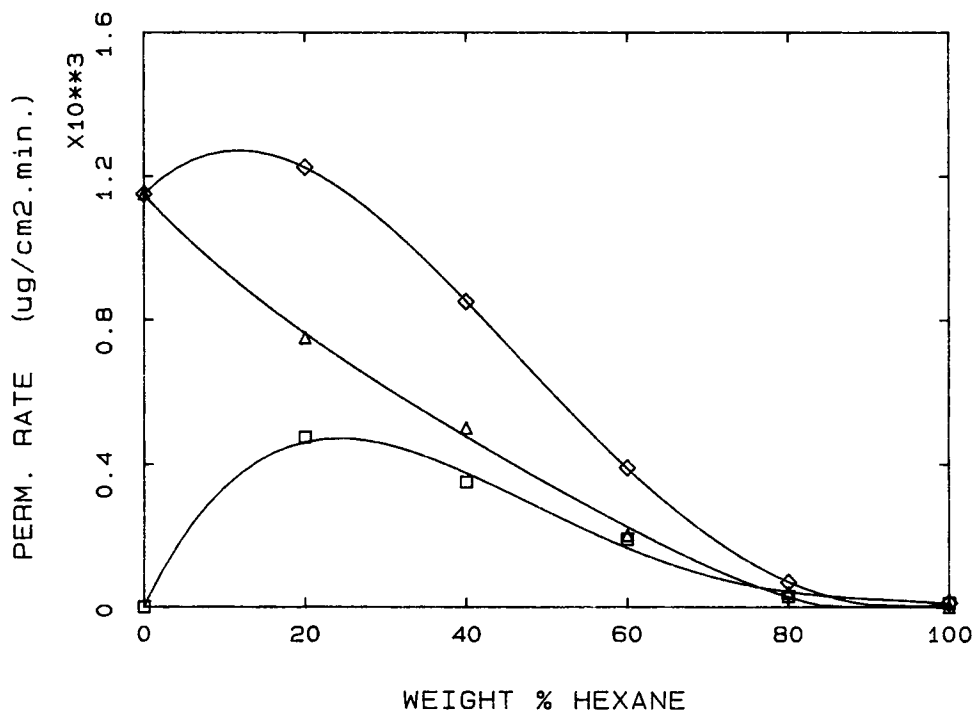**Figure 5** Permeation of toluene-n-hexane mixtures through neoprene. Permeation curves for n-hexane.

Figure 6 Steady-state permeation rates of toluene-n-hexane mixtures through neoprene: ($\triangle$) toluene; ($\square$) n-hexane; ($\diamond$) total.
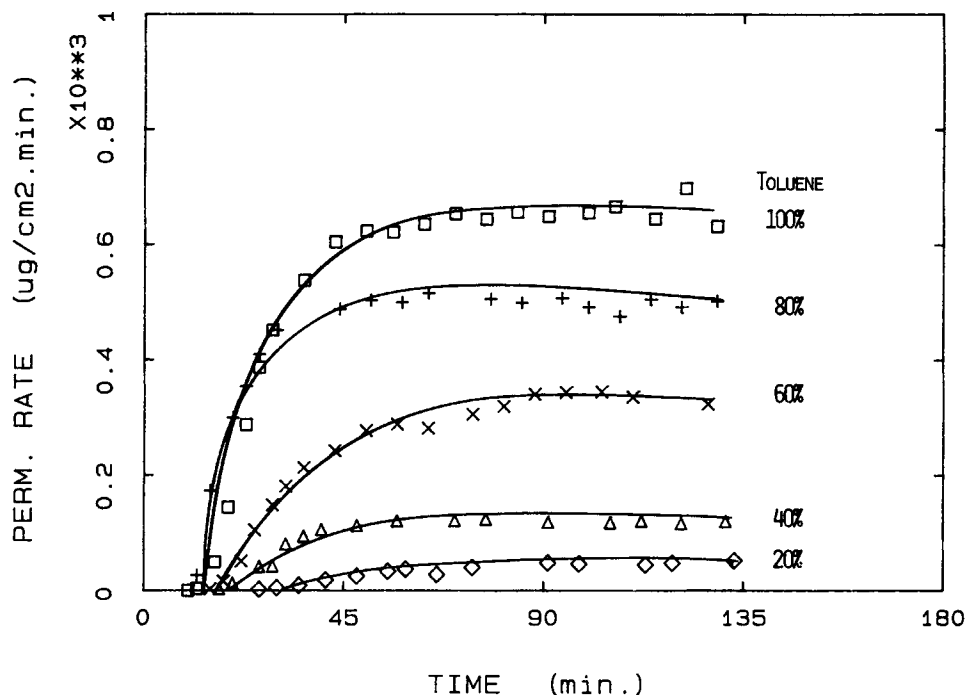
Figure 7   Permeation of toluene–methanol mixtures through nitrile. Permeation curves for toluene.
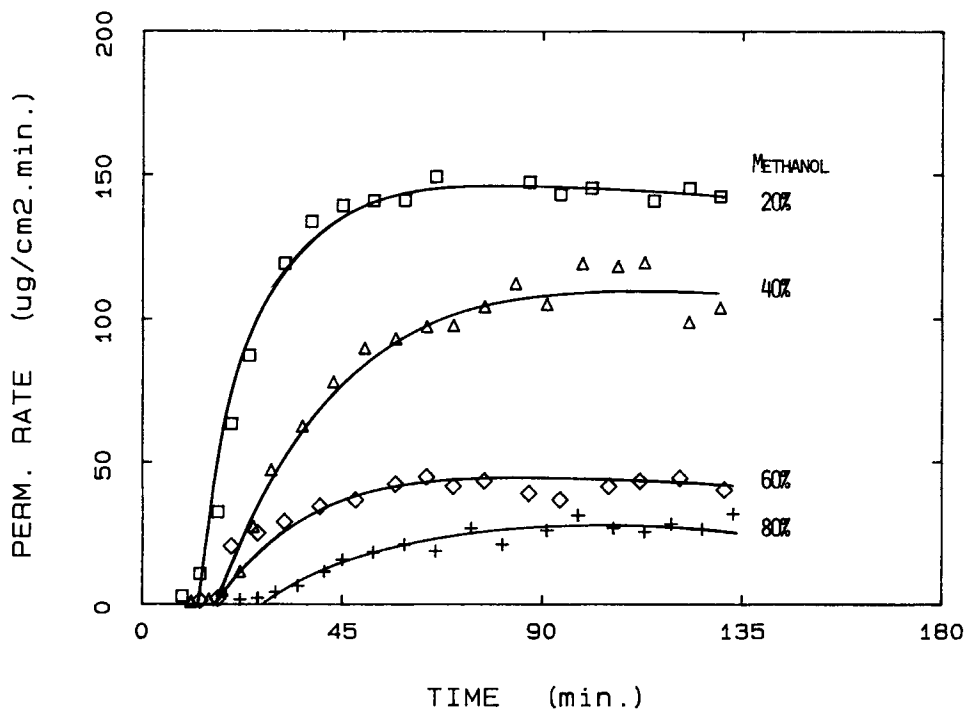

Figure 8   Permeation of toluene–methanol mixtures through nitrile. Permeation curves for methanol.

to longer times with an increase in the concentration of methanol in the liquid mixture. Pure methanol does not permeate through nitrile; however, the plasticizing effect of toluene causes methanol to go through the membrane. The maximum permeation rate of methanol occurs for a mixture containing approximately 20 wt % methanol. The steady-state permeation rates for toluene and methanol from Figures 7 and 8 are plotted versus the weight fraction of methanol in Figure 9, which shows that methanol can permeate through nitrile up to a rate of 140 μg/ cm^2 min, when mixed with toluene. This figure also indicates that the total permeation through nitrile shows a maximum for a mixture containing approximately 20 wt % methanol.

The permeation curves for toluene and o-xylene through nitrile are shown in Figures 10 and 11, respectively. The steady-state permeation rate of toluene decreases steadily from 375 to about 80 μg/ cm^2 min as the concentration of xylene increases from 0 to 60 wt %. There is a sudden decrease in the permeation rate of toluene for a mixture containing more than 70 wt % xylene. The steady-state permeation rate of xylene through nitrile is very small for mixtures containing less than 70 wt % xylene (the rates are less than 5 μg/cm^2 min). At 70 wt % o-xylene, there is a sudden jump in the steady-

state permeation rate (75 μg/cm^2 min), which increases steadily to 130 μg/cm^2 min as the concentration increases to 100% o-xylene. The steady-state permeation rates of the two components and the total permeation rates are plotted against wt % o-xylene in Figure 12. There is a minimum in the total permeation curve at about 60 wt % o-xylene.

The permeation rate of a liquid through a membrane depends on the solubility and diffusion coefficient of the liquid in the membrane. The permeation process is usually described by Fick's law. If it is assumed that no bulk flow exits, the permeation flux of component i (with respect to stationary coordinates) is given by

$$J_i = D_i \frac{dC_i}{dZ} \qquad (1)$$

where J_i = permeation flux of component i; C_i = concentration of component i in membrane; Z = distance; and D_i = diffusion coefficient of component i. Diffusion coefficient depends on the concentration of the liquids in the membrane. An apparent diffusion coefficient D_i is usually defined such that
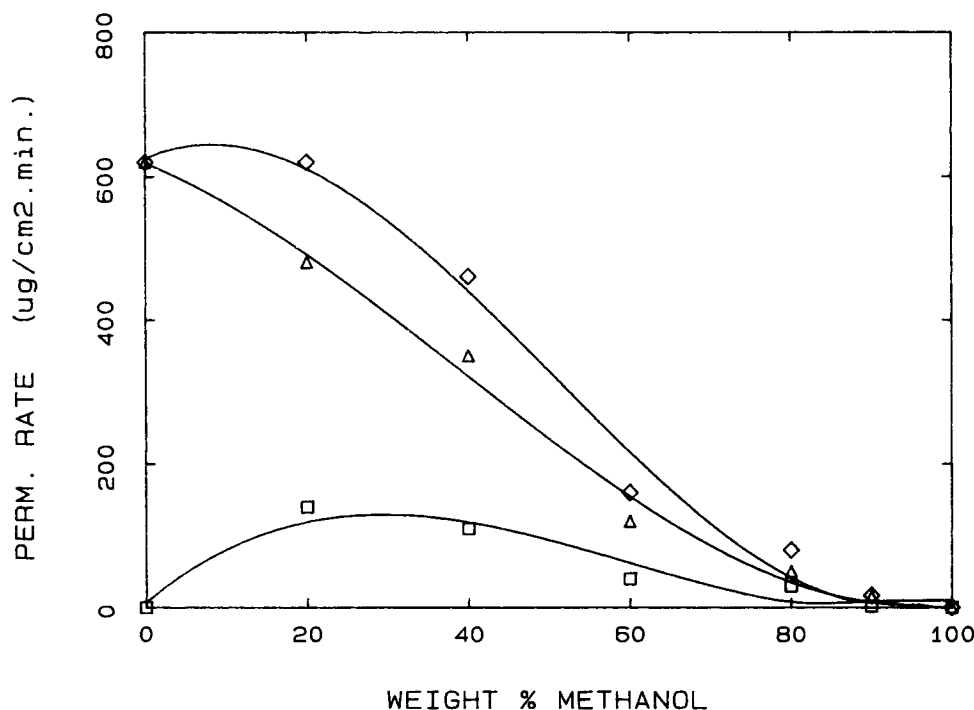
$$J_i = D_i C_i^s / L \qquad (2)$$

Figure 9   Steady-state permeation rates of toluene–methanol mixtures through nitrile: (△) toluene; (□) methanol; (◇) total.
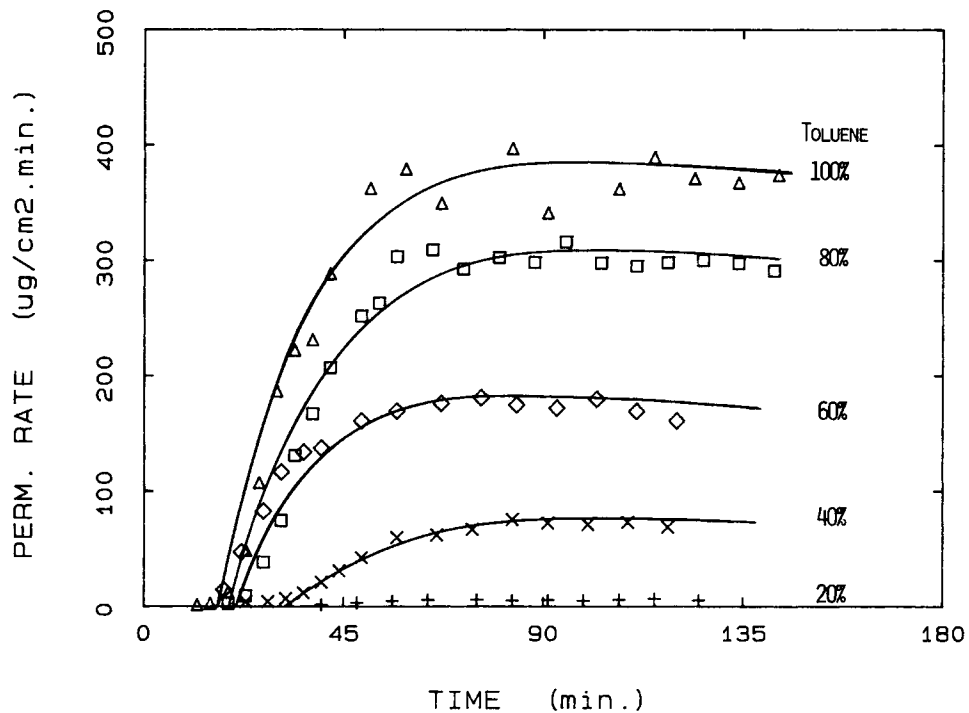
Figure 10   Permeation of toluene–o-xylene mixtures through nitrile. Permeation curves for toluene.
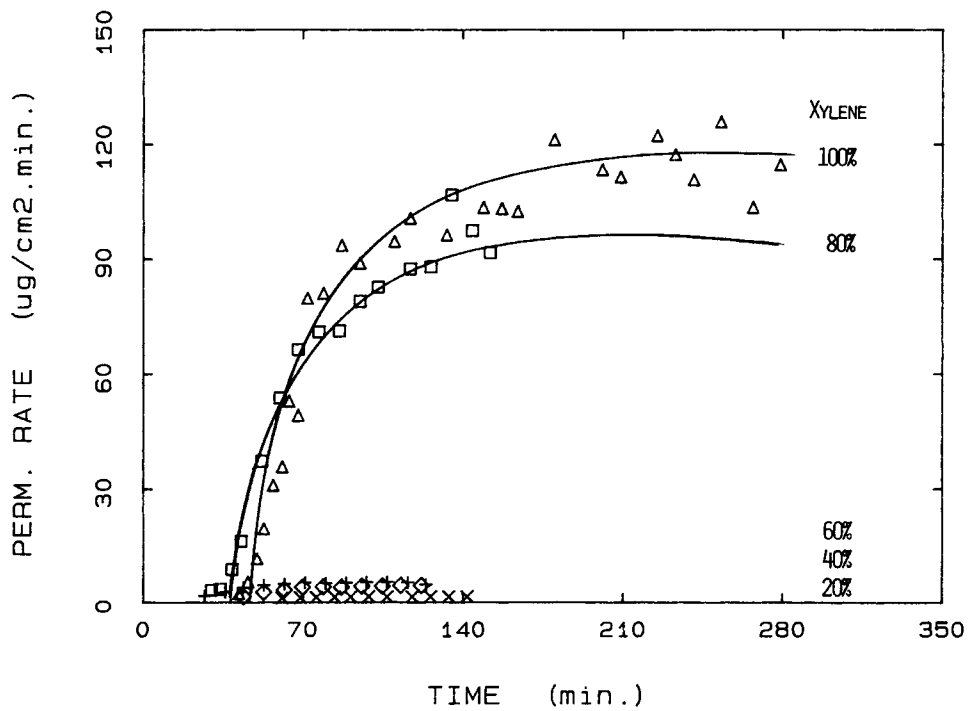

Figure 11   Permeation of toluene–o-xylene mixtures through nitrile. Permeation curves for o-xylene.
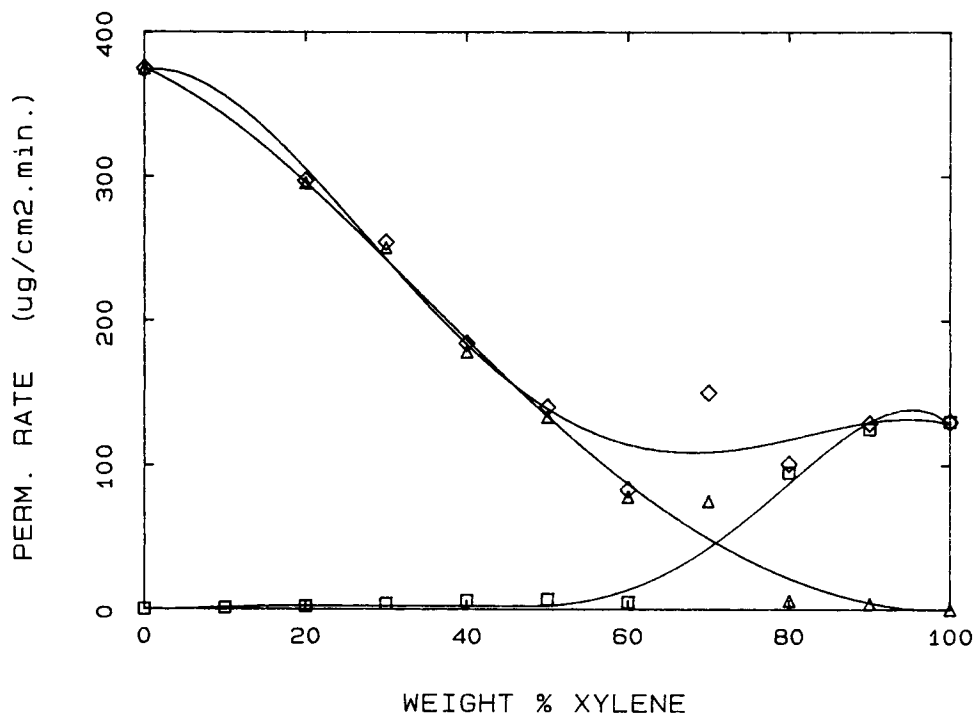
Figure 12 Steady-state permeation rates of toluene–o-xylene mixtures through nitrile:
($\triangle$) toluene; ($\triangle$) o-xylene; ($\Diamond$) total.

and

$$D_i = D_i^0 \exp(K_{ii}C_i^s + K_{ij}C_j^s) \qquad (3)$$

where C_i^s = solubility of liquid i in polymer; K_{ij} = plasticizing coefficient representing effect of j; D_i^0 = diffusion coefficient at zero concentration; and L = membrane thickness. Substitution of eq. (3) into (2) yields

$$J_i = \frac{D_i^0 C_i^s}{L} \exp(K_{ii}C_i^s + K_{ij}C_j^s) \qquad (4)$$

If each liquid is permeated through the membrane independent of the other liquids, a permeation flux J_i^* can be defined as

$$J_i^* = \frac{D_i^0 C_i^s}{L} \exp(K_{ii}C_i) \qquad (5)$$

The ratio of actual permeation flux J_i to this idealized flux J_i^* for the two components 1 and 2 are

$$J_1/J_1^* = \exp(K_{12}C_2^s)$$

$$J_2/J_2^* = \exp(K_{21}C_1^s) \qquad (6)$$

These ratios represent the effect of one liquid on the permeation rate of the other liquid in the polymer.

The examination of theory and experimental data[8] reveals that the solubility of binary liquid mixtures in polymers varies with the composition of the liquid mixture as shown in Figure 13. Two extreme cases are shown in this figure. Case I represents a system in which one liquid (component 1) has a large solubility in the polymer, and the other liquid dissolves only slightly in it. Case II represents a system in which the solubility of both liquids in the polymer are almost the same. For a ternary system that follows Case I, $K_{21}C_1^s$ is much larger than $K_{12}C_2^s$. According to eq. (7), the permeation rate of component 2 is enhanced tremendously. On the other hand, permeation rate of component 1 can be depressed. This can be explained as follows: The total amount of the liquids that can enter a polymer is limited. This is due to the fact that the polymer network cannot be swollen beyond the limit of elasticity of the membrane. The permeation enhancement of component 2 can therefore reduce the permeation rate of component 1 (permeation depression). This means that K_{12} can be negative. For the binary liquid–polymer systems that follow Case II in Figure 13, permeation enhancement or depression
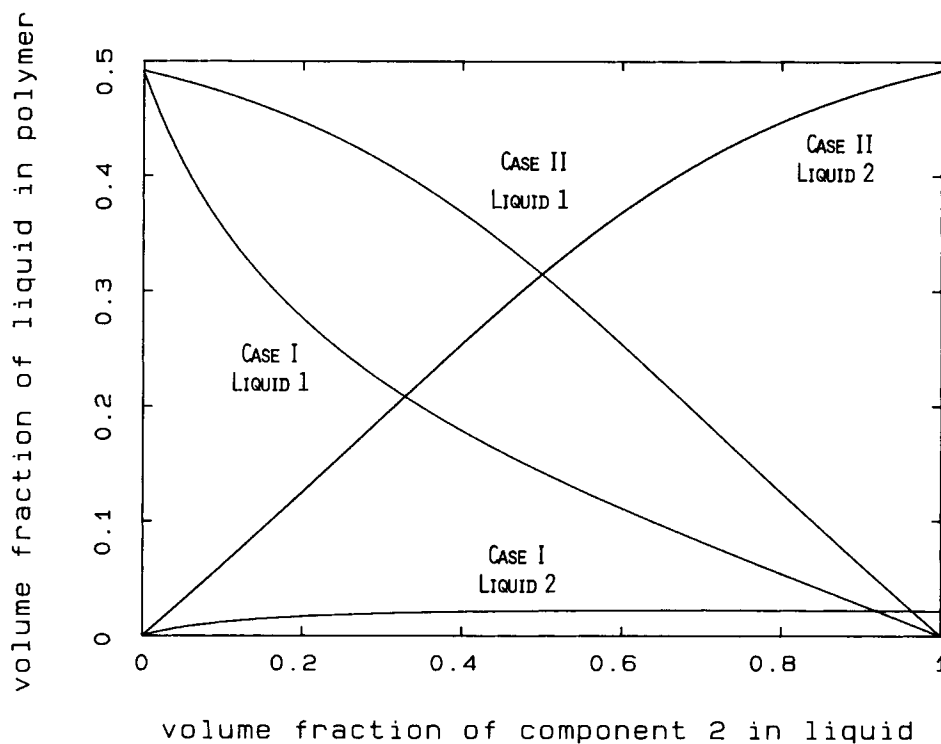
Figure 13 Solubility of binary liquid mixtures in polymers.

may be experienced for both liquids. If the solubility of the liquids in the polymers are large, the presence of one component will actually reduce the amount of the second liquid in the membrane. This is due to the elasticity limit of the polymer, which was explained before. Therefore, the solubility of one liquid is increased at the expense of the other. For this situation, K_{12} and K_{21} are negative, and permeation depression is experienced. If the solubility of both liquids are small, the presence of one liquid has a positive effect on the other and both liquids experience permeation enhancement (K_{12} and K_{21} are positive).

The solubilities of the pure liquids in the membranes studied in this work are given in Table I. The first three systems follow Case I in Figure 13. As expected the permeation of component 2 (the liquid with low solubility in polymer) is enhanced and the other component showed permeation depression. In the case of toluene–o-xylene/nitrile systems, both components have large solubilities in the nitrile, and permeation depression is experienced for the liquids.

CONCLUSION

Permeation of binary–liquid mixtures through elastomers were studied. The systems in which the

membrane is plasticized strongly by one of the components and weakly by the other, one component was affected synergetically by the other. The liquid with the smaller permeation rate experiences a permeation enhancement, and the other liquid shows a permeation depression.

The systems in which the solubilities of pure liquids in the membrane are of the same order of magnitude, the liquids can show permeation enhancement or depression. If the solubilities are large, the presence of one component will reduce the amount of the other liquid in the membrane and permeation depression is experienced for both liquids. If the solubilities are small, each liquid is affected synergetically by the other, which results in permeation enhancement for both liquids.

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