

Sorption/Desorption Properties of Ethanol, Toluene, and Xylene in Poly(Dimethylsiloxane) Membranes

YI-MING SUN* and JACK CHEN

Department of Chemical Engineering, Yuan-Ze Institute of Technology, Chung-Li, Taoyuan, Taiwan, R.O.C.

SYNOPSIS

Sorption/desorption kinetics and sorption equilibria have been determined for ethanol, toluene, and xylene vapors in a poly(dimethylsiloxane) membrane containing about 32 wt % silica resin at 25°C. Dependence of diffusion coefficient on vapor activity and sorption isotherms have been compared to identify the transport mechanisms of those penetrants in the PDMS membrane. The analysis of Zimm-Lundberg clustering functions showed that all three penetrants had a tendency to form clusters and ethanol molecules might be immobilized by the residual silanol groups within the silica resin in the membrane. The diffusion coefficient of toluene was roughly constant and that of xylene slightly decreased as increasing the vapor activity due to the competing effects of penetrant clustering and solvent swelling of polymer. The diffusion coefficient of ethanol versus activity exhibited a maximum due to the effects of ethanol immobilization and cluster formation. The free-volume effect by solvent swelling to diffusion was obscured by either penetrant clustering or immobilization for the three penetrant-polymer systems. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Recently, many investigations have been carried out to study the application of membrane processes to separate organic vapors from air.¹⁻¹⁰ Most of them suggested that poly(dimethylsiloxane) (PDMS) or silicone rubber was an excellent candidate for preparing the membranes required for such processes: the membrane selectivities of all kinds of organic vapors to air or nitrogen were reasonably good (range from several tens to several 1000) while high membrane permeabilities were maintained and the processability of PDMS to make ultra-thin composite membranes was comparably favorable.⁴

The permeation of organic vapor through a silicone rubber membrane is considered to involve three independent physical processes¹¹:

1. sorption of vapor molecules at feed side surface of the membrane;
2. diffusion of the dissolved vapor through the wall of the membrane; and

3. desorption of vapor molecules from the permeate side surface.

In order to obtain a more complete picture of these processes, sorption/desorption kinetic or diffusion data rather than permeation data alone are generally required. However, only a few articles have particularly addressed the information on PDMS membranes although many publications have been available for studying the permeation of organic vapors in silicone rubber membranes or the sorption/desorption of organic vapors in other amorphous rubbery polymers.¹¹⁻²⁰ It is of interest to study the sorption/desorption kinetics of organic vapors to depict the transport mechanisms of those penetrants in the PDMS membranes.

It is well known that the diffusion coefficient of penetrant increases approximately exponentially with penetrant concentration (or activity) for a large number of amorphous polymer-organic vapor or liquid systems when the penetrant is a good solvent or swelling agent for the polymer.^{12,13,21} The free-volume theory of diffusion is generally applicable to explain this relationship.^{22,23} However, it has been reported that while this relationship is observed for

* To whom correspondence should be addressed.

benzene in several carbon-carbon main-chain elastomeric polymers, the intrinsic diffusion coefficient of benzene in PDMS is independent of its concentration.¹⁶ In a more recent study, Blume et al.²⁰ reported that the diffusion coefficients, which were obtained from the kinetic sorption data alone, of methylene chloride, chloroform, and carbon tetrachloride in the PDMS membranes decreased as the vapor activities (or the concentrations of the sorbed vapors) increased. In this study, a number of anomalies that have also been observed in the sorption/desorption kinetics of ethanol, toluene, and xylene in PDMS membranes are reported. The free-volume approach does not account for the diffusion of these organic penetrants in the PDMS membranes. Penetrant immobilization and cluster formation played important roles in these systems.

EXPERIMENTAL

Materials

The PDMS membrane was prepared from a two-component rubber, SYLGARD™ 184 silicone elastomer base and curing agent, which were kindly supplied by Dow Corning Taiwan, Inc. The particular PDMS elastomer was chosen because it was a good coating material for making composite membranes and it had been used in at least two membrane preparation studies.^{24,25} According to the information provided by Dow Corning, the elastomer contains about 62% dimethylvinyl-terminated PDMS, 32.3% dimethylvinylated and trimethylated silica resin, 5.7% dimethyl methylhydrogen siloxane cross-linker, and a trace of organo-platinum catalyst.²⁶ Certified 99.8 vol % pure ethanol was purchased from Riedel-de Haën, Germany, and reagent grade toluene and xylene were supplied by OSAKA, Japan. The solvents were used without further purification.

Membrane Preparation

The solution of silicone elastomer base and curing agent in toluene was cast on a Plexiglas plate and cross-linked at 25°C for 72 h to yield an almost clear and transparent membrane, which was cut into a circular disc of 4.46-cm diameter. The thickness of the membrane was measured by a digital thickness gage (Mitutoyo IDF-112) equipped with a 1.0-cm diameter stylus, and it was given as 0.380 mm in an average of 10 measures in different points of the

membrane. The density of the film was determined as 0.9998 g/cm³.

Apparatus and Procedures

The integral sorption/desorption experiments described by Crank and Park²⁷ were applied in this investigation to study the transient sorption/desorption kinetics of vapors in PDMS membranes. In a sorption experiment, a uniform flat membrane initially placed in a vacuum system at a pressure P_i ($P_i < 10^{-3}$ torr) was suddenly exposed to an organic vapor with pressure P_f being maintained constant. The gain in weight of the membrane sheet was measured as a function of time (t). In a desorption experiment, the fully equilibrated membrane in the sorption experiment was suddenly brought to vacuum. The loss in weight was recorded versus time.

The sorption/desorption system, as shown in Figure 1, includes three main parts: a continuous gravimetric unit (Cahn-1000 electronic balance) in a constant temperature chamber, an organic vapor supply unit maintained at a selected temperature to supply a fixed vapor pressure of organic solvent, and a vacuum line. The penetrant mass uptakes or losses in the polymer membrane were continuously recorded by a computerized data acquisition system. The pressures of the organic vapors were monitored by a Baratron-type pressure transducer (MKS, 128A).

The sorption/desorption kinetics and equilibrium amounts of PDMS membrane for different solvents

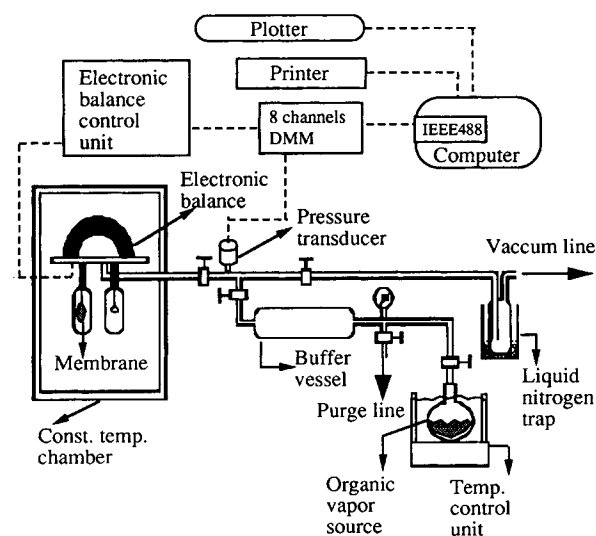


Figure 1 Sorption/desorption apparatus.

have been made at different vapor pressures and a constant temperature of 25°C.

Data Analysis

A typical sorption/desorption conjugate pair is shown in Figure 2. The data are mostly described by Fickian diffusion except that a slight fluctuation (generally within few seconds) in the early stage of the experiment occurs due to the sudden change of vapor pressure at the beginning of an experiment. However, the data collected during this stage were truncated in the analysis. Dashed lines are used in Figure 2 to indicate this truncation. Both initial slope method and half-time method^{12,28} were used to analyze the sorption/desorption data in order to determine the diffusion coefficients (D_s for sorption and D_d for desorption). Because the data were mostly Fickian, agreeable results were generally obtained from both methods. If the diffusion coefficient is concentration-dependent, the average diffusion coefficient is $\bar{D} = 1/C_0 \int_0^{C_0} D dC$, where 0 to C_0 is the concentration range existing in the sheet during that experiment. We can use the average of the D_s and D_d to obtain $D = D_{ave} = (D_s + D_d)/2$ as a better approximation to $\bar{D} = 1/C_0 \int_0^{C_0} D dC$ than either D_s or D_d separately. The diffusion coefficients calculated here are based on the unswollen penetrant-free polymer frame of reference and are expressed in cm^2/s .²⁸

For a solvent-polymer system, the sorption equilibrium data can be used to calculate the

interaction parameter (χ_{12}) in the Flory-Huggins equation^{19,29,30}:

$$\begin{aligned} \ln a_1 &= \ln(p/p^0) \\ &= \ln \nu_1 + (1 - \nu_1) + \chi_{12}(1 - \nu_1)^2 \quad (1) \end{aligned}$$

where 1 denotes solvent and 2 denotes polymer, a_1 is the solvent activity, ν_1 is the volume fraction of solvent sorbed, p is the organic solvent vapor pressure in mmHg, and p^0 is the saturated solvent vapor pressure in mmHg.

RESULTS AND DISCUSSION

A sorption isotherm illustrates the equilibrium amount of penetrant sorbed by a polymer versus external penetrant vapor activity (or pressure) at a given temperature, and it is principally governed by the thermodynamics of the system. The relative strengths of the interactions between the penetrant molecules and the polymer or between the penetrant molecules themselves within the polymer determine the isotherm.

Five types of sorption isotherms have been identified in polymer systems and they are: (I) Henry's law sorption, (II) Langmuir-type sorption, (III) Flory-Huggins sorption, (IV) BET sorption, and (V) Dual-mode sorption.³¹ The classification of types I-IV was first proposed by Rogers³² and later adopted by deV. Naylor in his monograph.³¹ We will use their classification in our later discussion.

The isotherms of equilibrium solvent uptakes at 25°C are shown in Figure 3. The thermodynamic activity of solvent was determined by the ratio of actual vapor pressure to the solvent's saturated vapor pressure. The amounts of sorbed solvents at equilibrium increase as the corresponding solvent activities increase. Toluene and xylene show a type III isotherm, and ethanol shows a type IV isotherm. The sorption of toluene and xylene with a type III isotherm are believed to follow the classical Flory-Huggins theory, and that of ethanol with type IV is a combination of Langmuir-type sorption and Flory-Huggins sorption.³²

For many organic solvents, type III isotherms commonly result in most polymer materials.^{19,30-32} The equilibrium sorptions are generally described by the Flory-Huggins equation [eq. (1)]. According to the equation, the interaction parameter χ_{12} between penetrant and polymer can be determined. The corresponding χ_{12} values of toluene and xylene

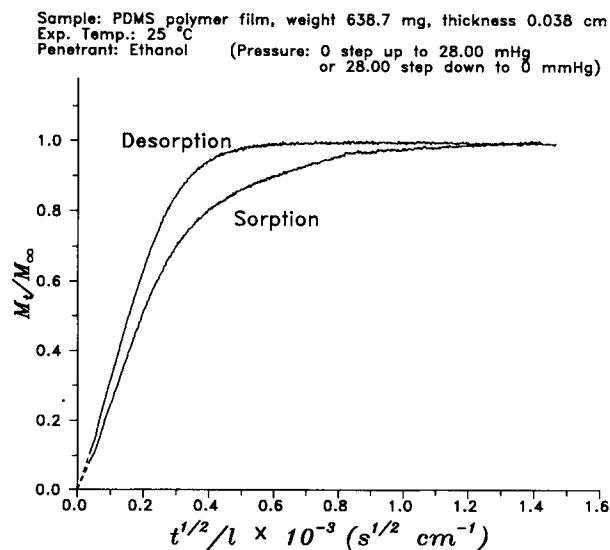


Figure 2 Typical sorption/desorption conjugate pair.

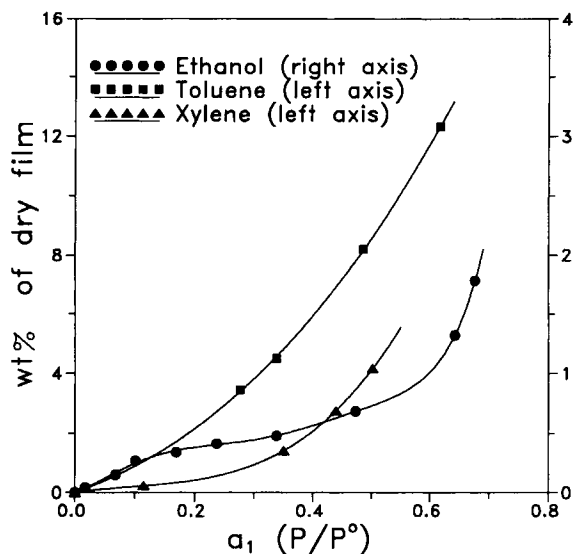


Figure 3 Sorption isotherms for ethanol, toluene, and xylene in PDMS at 25°C.

to PDMS used in this study are shown in Figure 4. Both of them decrease linearly with increasing penetrant activities. These results suggest that the sorbed compound becomes more soluble as its concentration in the polymer increases.

These behaviors are explained by either the effect of solvent swelling (plasticizing) or the effect of inherently stronger penetrant-penetrant interactions than corresponding polymer-penetrant interactions. The former interpretation implies that sorbed molecules may loosen (plasticize) the polymer structure and make it easier for subsequent molecules to enter the polymer. The latter one implies that the formation of penetrant-penetrant pairs is much easier than the formation of penetrant-polymer pairs; therefore, once the penetrants get into the polymers they will bring in more penetrants.³²

Both mechanisms also have great influences on the dependence of diffusion coefficient on penetrant concentration. The solvent swelling effect can result in increase of total free volume in the polymer matrix; therefore, the mobility and diffusion coefficient of the sorbed molecules will increase. The so-called free-volume theory of diffusion is generally applied to describe the diffusion processes.^{13,22,23} However, the formation of penetrant-penetrant pairs shows negative effect to the diffusion of penetrants. In some cases penetrant clustering may result so that the mobility and the diffusion coefficient of the sorbed molecules will decrease. A clustering function has been proposed by Zimm and Lundberg^{33,34} to give

an indication of the overall tendency for the formation of penetrant-penetrant pairs.

$$G_{11}/V_1 = -(1 - \nu_1) [\partial(a_1/\nu_1)/\partial a_1]_{P,T} - 1 \quad (2)$$

where V_1 , ν_1 , and a_1 are the partial molecular volume, volume fraction, and thermodynamic activity of penetrant, respectively. For an ideal system, the activity coefficient does not vary with concentration, $[\partial(a_1/\nu_1)/\partial a_1]_{P,T} = 0$, which implies that $G_{11}/V_1 = -1$, and no clustering occurs. For other nonideal systems, $[\partial(a_1/\nu_1)/\partial a_1]_{P,T}$ can be determined from sorption isotherm data. When $G_{11}/V_1 > -1$, clustering may arise, and when $G_{11}/V_1 < -1$, localized sorption of penetrant on specific polymer sites may occur.

The solvent swelling of polymer and clustering of penetrants are two competitive mechanisms with opposite effects for concentration dependence of diffusion coefficient. For a lot of organic solvents in polymer, swelling will generally be predominant and render the diffusion coefficient increases as solvent concentration increasing.^{12,13,16,21,30} Clustering of penetrant is relatively rare in most penetrant-polymer systems, but is not uncommon in many water-polymer systems where the hydrogen bonding between water molecules becomes important and thus the diffusion coefficient of penetrant decreases with concentration, such as water in a number of poly(alkyl methacrylate),³⁵ ethyl cellulose,³⁶ and

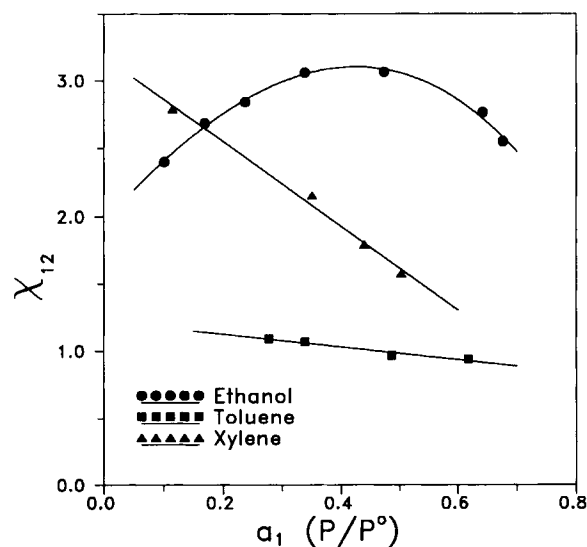


Figure 4 Flory-Huggins interaction parameters as a function of vapor activity for ethanol, toluene, and xylene in PDMS at 25°C.

PDMS.^{37,38} Competition between those two mechanisms may result in canceling the concentration dependence of the diffusion coefficient. It was probably the case for benzene in PDMS,¹⁶ where the intrinsic diffusion coefficient was found constant along the concentration range studied, and for ethanol in rubbery polyurethane,³⁹ where a sigmoidal increase of the diffusion coefficient with increasing concentration was identified.

Diffusion coefficient decreases with increasing penetrant concentration other than the water-polymer system were seldom reported. Data of diffusion coefficients decreased with vapor activities for methylene chloride, chloroform, and carbon tetrachloride in the PDMS membranes were quite exceptional in the literature.²⁰ In the present study, the diffusion coefficients of toluene and xylene deduced from sorption-kinetics showed clear decreases with vapor activities (Fig. 5), and those from desorption-kinetics showed an increase with toluene activity and constant with xylene activity (Fig. 6). The average diffusion coefficient of toluene is roughly constant and that of xylene decreases slightly with their vapor activities as shown in Figure 7. Furthermore, the rate of desorption was faster than the corresponding rate of sorption, as indicated by the fact that $D_d > D_s$ for all the sorption-desorption pairs. According to Crank's analysis of sorption-desorption kinetics for Fickian diffusion, this behavior is, qualitatively speaking, an indication

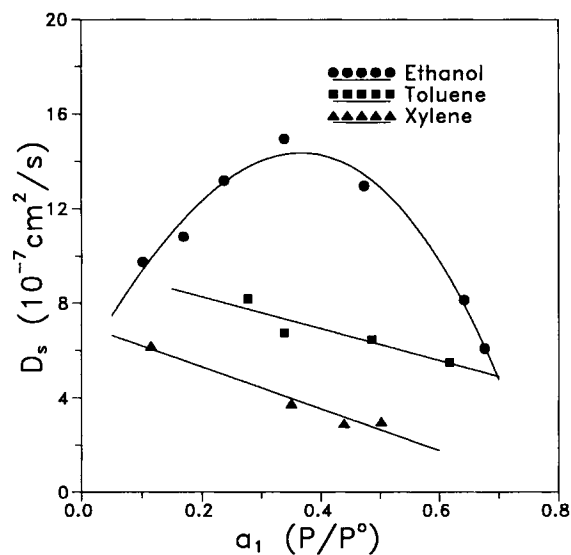


Figure 5 Integral diffusion coefficients of sorption (D_s) as a function of vapor activity for ethanol, toluene, and xylene in PDMS at 25°C.

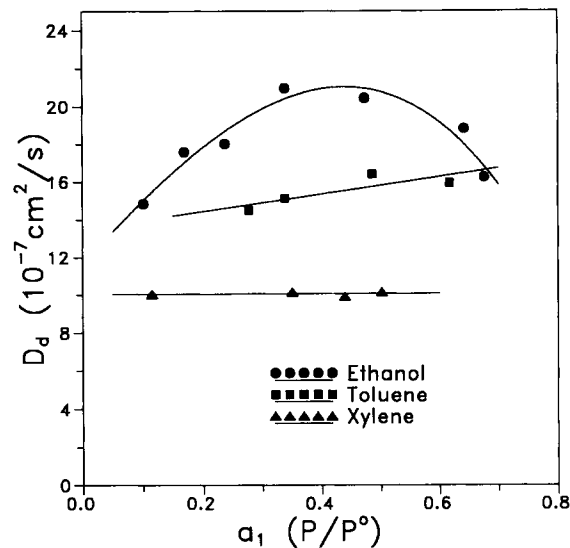


Figure 6 Integral diffusion coefficients of desorption (D_d) as a function of vapor activity for ethanol, toluene, and xylene in PDMS at 25°C.

of D decreasing as the concentration (activity) is increased.²⁸ However, it is not clear, at this point, that the diffusion coefficient of desorption is an increasing function of activity and the diffusion coefficient of sorption is a decreasing function of activity for toluene in the PDMS membrane.

The clustering functions for toluene and xylene in PDMS at 25°C are calculated from the corre-

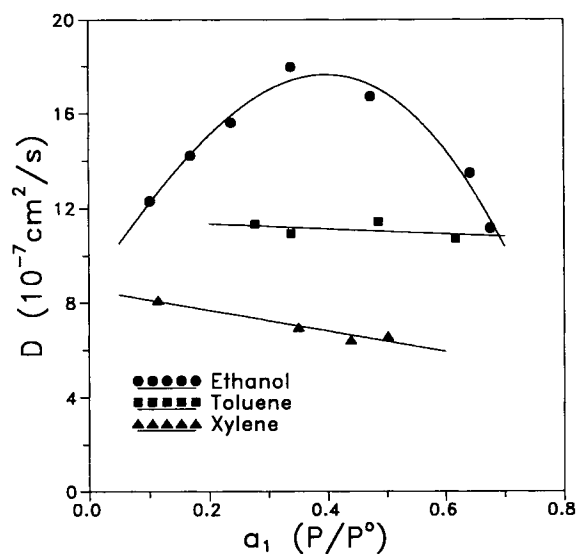


Figure 7 Averaged integral diffusion coefficients ($D = D_{ave} = (D_s + D_d)/2$) as a function of vapor activity for ethanol, toluene, and xylene in PDMS at 25°C.

sponding isotherm data and are shown in Table I. It is evident that their clustering functions are > -1 so that toluene and xylene tend to cluster in PDMS. The mobility of each toluene or xylene molecule is reduced due to the tendency of clustering, and consequently the diffusion coefficient of each solvent in PDMS decreases with vapor activity or sorbed concentration. Similar analysis were also carried out by the present authors for the data obtained by Blume et al.²⁰ Clustering functions for methylene chloride, chloroform, and carbon tetrachloride in PDMS at 40°C are also > -1 over the activity range studied. All the facts indicate that those organic vapors have a tendency to cluster in the PDMS membranes.

The PDMS polymer is well known for its highly flexible —Si—O— backbone chains. As a result, the polymer inherently contains a large portion of free volume in comparison with other carbon backbone polymers. The percentage of the free volume increased due to solvent swelling (plasticizing) is minimal. Besides, the interaction between those easily condensable penetrant molecules is possibly stronger than that between the penetrant molecules and the polymer segments of PDMS. Cluster formation becomes important in the transport processes of those penetrants in the PDMS membranes. Therefore, the diffusion coefficients of toluene and xylene are either kept constant or reduced as the sorbed concentration is increased.

The sorption and diffusion of ethanol in PDMS membrane are more complicated. The Langmuir-type curvature to the isotherm at low activities in-

dicates a competitive sorption on a fixed number of sites. Silica resin presented in the PDMS membranes is suspected to provide such sites.^{26,40} Hydrogen bonding may form between the hydroxyl group of ethanol and the residual silanol groups in the resin. However, the competitive sorption does not guarantee a large equilibrium sorbed amount (owing to limited number of silanol groups). The Langmuir sites only contribute to the ethanol sorption less than 0.5% by weight of dry polymer (Fig. 3). At higher activities, the isotherm gradually increases after the Langmuir curvature and increases sharply above $a_1 = 0.6$. The later portion is dominated by Flory-Huggins type sorption. The interaction parameter χ_{12} calculated shows an increase up to $a_1 = 0.4$ and a decrease afterward. As a result, the solubility of ethanol in the PDMS membrane has a minimum in the vicinity of $a_1 = 0.4$.

The diffusion coefficients (D_s , D_d , and D) versus activity (a_1) curves for ethanol in the PDMS membranes also exhibit maxima at the same activity (Figs. 5, 6, 7). The Langmuir sites may immobilize the penetrant molecules so that the diffusion coefficient of ethanol is small at low activities. As the activity or sorbed amount increases, there are more free molecules available for diffusion and consequently the diffusion coefficient also increases. When the activity is larger than 0.4, the diffusion coefficient of ethanol decreases with increasing activity. Clustering of ethanol probably accounts for such behavior. The clustering function of ethanol clearly demonstrates the tendency of penetrant immobilization at low activities and clustering formation at high activities (Table I). It should be noted that the D_d is larger than D_s throughout the activity range studied no matter whether the diffusion coefficient is an increasing function (as $a_1 < 0.4$) or a decreasing function (as $a_1 > 0.4$) of activity. This result is contradictory with that obtained by Barrie and Machin.⁴⁰ Further investigations are probably needed to explain this discrepancy.

CONCLUSIONS

The present work suggests that the diffusion mechanisms of organic vapors in the PDMS membrane studied are rather complicated because cluster formation and Langmuir-type penetrant immobilization may occur in addition to the swelling induced free-volume effect. Because the polymer already

Table I Clustering Functions in PDMS at 25°C

	a_1	ν_1	G_{11}/V_1
Ethanol	0.101	0.003	-142
	0.169	0.004	-126
	0.237	0.005	-103
	0.338	0.006	-55.1
	0.473	0.009	33.2
	0.642	0.016	182
	0.676	0.022	216
Toluene	0.277	0.038	5.67
	0.338	0.049	5.59
	0.486	0.086	5.33
	0.617	0.124	5.07
Xylene	0.115	0.003	85.3
	0.350	0.016	84.2
	0.439	0.031	81.6

contains a large portion of inherent free volume at the experimental temperature, the percentage of the free volume increased due to solvent swelling becomes minimal. Therefore, penetrant clustering and immobilization on specific sites are more important effects in the systems studied.

Toluene and xylene have Flory-Huggins type isotherms, and their interaction parameters are characterized by a decreasing function of activity. The solubilities of toluene and xylene monotonically increase as their activities increase. The Zimm-Lundberg analysis indicates clustering may arise in these two systems. The diffusion coefficient of toluene is roughly kept constant and that of xylene slightly decreases as the vapor activity is increased due to the competing effects of penetrant clustering and swelling of polymer.

The sorption isotherm of ethanol is similar to BET-type sorption, and its interaction parameter function increases then decreases as the vapor activity increases and exhibits a maximum at activity of about 0.4. The Zimm-Lundberg analysis indicates the tendency of penetrant immobilization at low activities and cluster formation at high activities. The diffusion coefficient of ethanol also increases then decreases as activity and exhibits a maximum at activity of about 0.4. The ethanol immobilization at low activities in terms of a specific Langmuir-type sorption is probably due to the existence of the residual silanol groups in the silica resin.

Sorption/desorption kinetics as well as sorption equilibria provide essential information about the transport mechanisms of penetrants in the membranes. The approach can be applied to interpret the behavior of vapor permeability data such as the work done by Blume et al.²⁰ Membrane material selections for recovery of organic vapors from air can also benefit from such studies.

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