# Sorption and Diffusion of Volatile Organic Compounds in Polydimethylsiloxane Membranes

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**ABSTRACT:** Sorption and diffusion of ethanol, 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE) were investigated in polydimethylsiloxane (PDMS) membranes using a gravimetric technique. The thermodynamic equilibrium and kinetic properties were evaluated at temperatures of 25, 100, and 150°C. The sorption isotherms for TCA and TCE can be correlated well using the Flory–Huggins model. However, a three parameter Koningsveld–Kleinjtens variation to the Flory–Huggins equation is required for correlation of the ethanol isotherm. The solubility coefficients of TCA and TCE increase with activity, but it remains almost constant for ethanol. The calculated sorption energies reveal high positive heat of mixing for ethanol. TCA and TCE sorption in PDMS decreases strongly with temperature as opposed to ethanol. Clustering function analysis is used to explain the anomalous ethanol sorption and diffusion behavior in PDMS. TCA and TCE diffusivities do not exhibit large variations with volatile organic compound activity. However, ethanol demonstrates a maxima in its diffusivity at activities where it has minimum clustering tendencies. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 165–175, 1998

**Key words:** polydimethylsiloxane; volatile organic compounds; diffusion; membranes; permeation

## INTRODUCTION

Vapor permeation through membranes offers significant opportunities of energy savings and reuse of volatile organic compounds (VOCs), compared to conventional VOC control processes such as incineration, oxidation, or activated carbon.[1] Membranes showing high organic permeabilities and low air and water permeabilities are required in the membrane processes for VOC vapor permeation, as well as pervaporation from the aqueous phase. Several elastomeric materials, well known for their high permeabilities as well as organophilic behavior,

have already been proposed for this purpose.[2] These include natural and synthetic rubber, nitrile–butadiene rubber (NBR), and styrene–butadiene rubber (SBR), polydimethylsiloxane (PDMS), poly[1-(trimethylsilyl)-1-propyne] (PTMSP), polyethylene (PE), polybutadiene (PB), polyurethane (PU), polytetrafluoroethylene (PTFE), etc.[3] Dense PDMS membranes, also known as silicone rubber, offer a good compromise of high permeabilities and moderate selectivities in most cases and are widely used.

PDMS membranes have well-known vapor transport properties and good thermal stability. They have excellent processing ability for making ultrathin composite membranes. They exhibit selective transport for organic molecules with respect to polar molecules such as water and low molecular weight gases such as nitrogen, oxygen, and helium.[4] The membrane selectivities for or-

ganic vapors with respect to air or nitrogen are in the range of 10–1000.[5] The permeation of VOC vapors through a dense silicone rubber membrane involves three physical processes: sorption of VOC molecules at the feed side of the membrane, diffusion of the dissolved VOC through the membrane, and desorption of VOC molecules from the permeate side. Hence, measurement of sorption and diffusion data can elucidate the transport properties of permeants through these organics.[5] However, most relevant studies have involved organic permeation in silicone rubber membranes or dealt with sorption–desorption of organic vapors in other amorphous membranes.[4–6]

Favre et al.[7] investigated the diffusion of vapor organics in PDMS at 40°C. The clustering phenomenon of methanol and butanol vapors in PDMS was analyzed. The clustering tendency varied with the proton donating power. In another study by the same group, solvent clustering tendencies were investigated in PDMS, poly(vinyl alcohol), and poly(vinyl acetate) membranes using infrared spectroscopy, differential scanning calorimetry, X-ray scattering techniques, and visual observations.[8] Solvent diffusivities decreased with increasing activity due to a clustering tendency. Blume et al. compared the sorption and permeation behavior of PDMS and ethylene–propylene–diene rubber (EPDM) in the temperature range of −10 to 70°C.[9] The toluene solubility coefficient in PDMS was shown to drop with increasing crosslinking.

All the reported investigations of sorption and diffusion of organics in pure PDMS were limited to a temperature range of −10 to 70°C. Knowledge of membrane performance capabilities for VOC permeation in a larger temperature range will help in the development of high temperature vapor permeation modules for VOC separation. In the present study the sorption of three VOCs was investigated in PDMS membranes at temperatures of 25, 100, and 150°C. The three VOCs chosen were ethanol, 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE). The thermodynamic equilibrium and kinetic parameters were evaluated. Also, the clustering tendencies of the VOCs in PDMS were investigated to explain sorption anomalies. As part of our efforts to develop the zeolite filled PDMS membranes for VOC separation, this study will also provide useful information for interpretation and understanding of VOC permeation through the zeolite filled PDMS membranes.

## EXPERIMENTAL

### Membrane and VOCs

Two-part silicone rubber (Type 615) from General Electric was used to prepare PDMS membranes. Ten parts of rubber A (prepolymer with vinyl groups) and 1 part of crosslinker B (containing several SiH groups per polymer chain) were mixed thoroughly. The membranes were cast on a glass plate from a homogenous paste of silicone rubber. After curing at room temperature overnight, the membranes were placed in an oven at 80°C for 5–6 h to ensure complete crosslinking. The PDMS membranes synthesized were in the form of transparent clear films. The membranes (density of 0.98 g/cm$^3$) were of uniform thickness of about 150 $\mu$m as measured by an Olympus® SZH zoom stereo microscope system. The membranes were thermally stable up to 200°C.

The VOCs selected were TCA (Fisher, certified grade), TCE (Fisher, certified ACS grade), and ethanol (Aaper, absolute 200 proof). The VOCs were used without further treatment. The molar volumes of TCE, TCA, and ethanol were, respectively, 90.2, 100.7, and 58.4 cm$^3$/mol, and the vapor pressures were, respectively, about 9.6, 15.9, and 7.8 kPa at 25°C.

### Adsorption and Diffusion Measurements

The experimental setup for adsorption and diffusion measurement primarily consisted of a modified Cahn vacuum microbalance system (CAHN C-1000) as shown in Figure 1. One arm of the balance had a quartz basket suspended at its end to hold the membrane sample. The temperature of the quartz basket was maintained at the desired temperature with an Omega® CN76000 temperature controller connected to a tubular furnace mounted on the outside of the 2-in. i.d. Pyrex balance tube. The furnace was so mounted that the quartz sample basket was exactly at its center. The temperature was measured by a thermocouple (K-type Omega® KMTSS-032G-12). The pressure inside the tube was measured by two thermocouple pressure gauges, an analog ATM Edwards 507 (P-1), and digital Omega® PX302 050AV (P-2), which covered the low (0–1 torr) and high (1–760 torr) pressure range, respectively. The VOC delivery system was designed to deliver pure VOC vapor or N$_2$ gas. The liquid VOC reservoir was placed in a constant temperature bath to prevent evaporative cooling. The difference between the
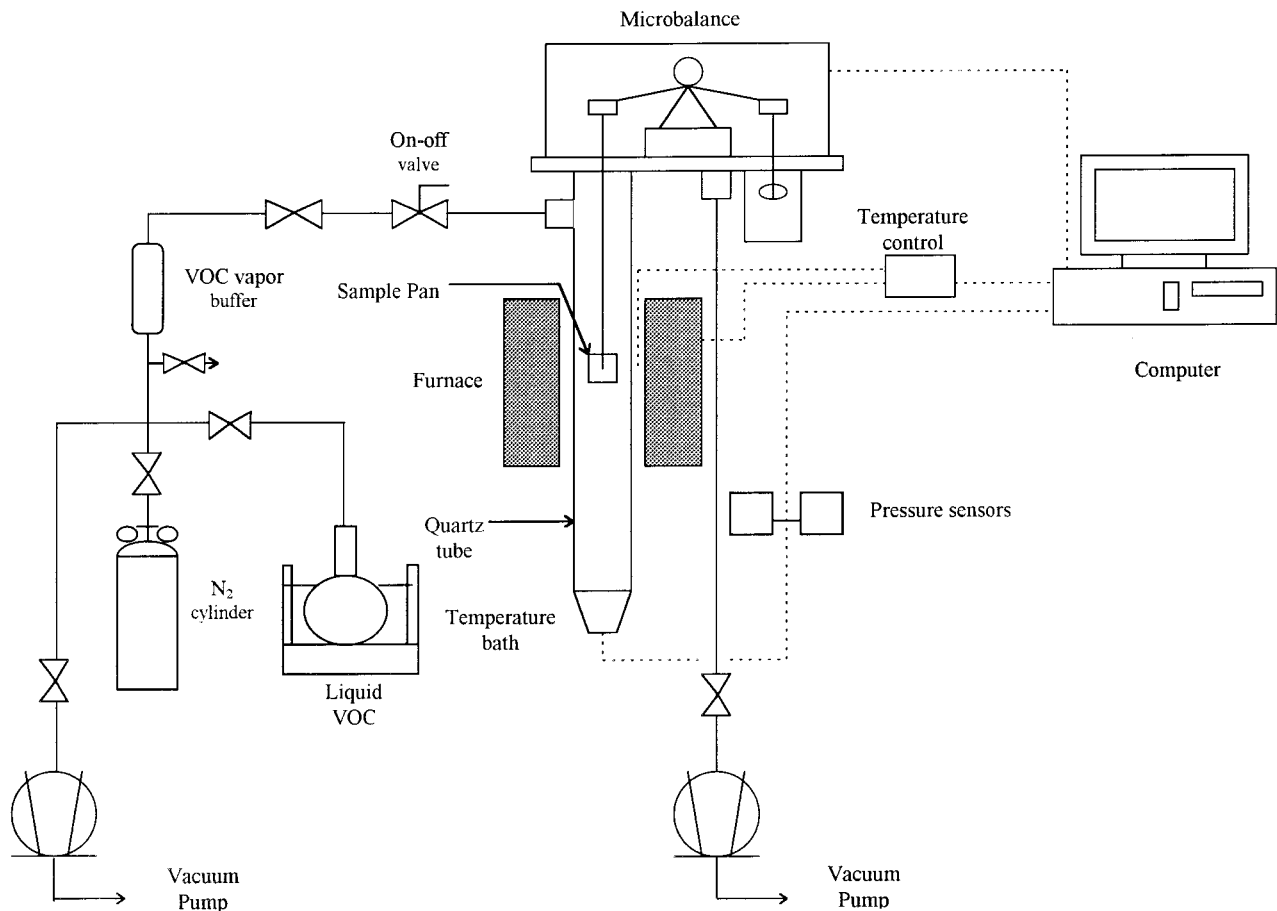
**Figure 1**    Schematic of Cahn C-1000 microbalance system apparatus for measurement of sorption–diffusion of VOCs in PDMS membranes.

VOC saturation vapor pressure and pressure in the balance tube provided the driving force for VOC flow. VOC vapors were first accumulated in a buffer chamber and then introduced in the balance to ensure a rapid, step function type pressure change in the system.

About 10–20 mg of membrane sample was held in the quartz basket. The membrane sample weight was verified by first weighing it in an accurate weighing pan and then in the microbalance. The samples were activated at 175°C under a vacuum of $10^{-2}$ torr for a minimum of 12 h prior to the experiment. The VOC delivery system was evacuated before each run. Starting from a full vacuum, the membrane sample was exposed to step changes in VOC partial pressures at constant temperature. At each VOC partial pressure, the membrane weight changed due to adsorption of VOC. The transient and equilibrium weight changes were logged. After equilibrium was reached, the pure VOC partial pressure was in- creased further by a small step. This step was repeated until VOC saturation pressure was reached. The VOC reservoir was maintained at a constant temperature of 25°C to avoid chilling due to evaporation. Isotherms were recorded at three temperatures of 25, 100, and 150°C. The adsorption isotherms for a VOC at the three temperatures were measured up to the same maximum VOC pressure determined by its saturated pressure at the reservoir temperature (25°C) ($p_{max}$ is, respectively, 9.6, 15.9, and 7.8 kPa for TCE, TCA, and ethanol).

## RESULTS AND DISCUSSION

### Adsorption Isotherms

The equilibrium weight-change data were used to construct the adsorption isotherms. The VOC uptake by the membrane was expressed in units
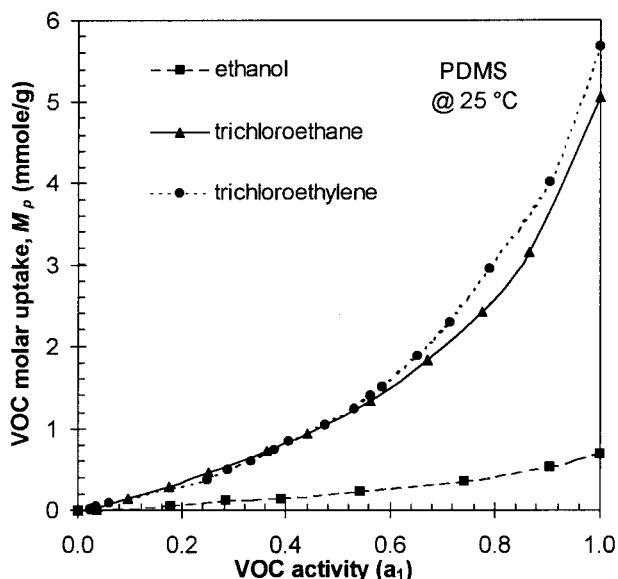
**Figure 2**  VOC isotherms on PDMS at 25°C.

of millimoles/gram and plotted against relative pressure $(p/p_{max})$ of the VOC. For the adsorption isotherms at 25°C, this relative pressure is the same as the activity of the VOC in the polymer, $a_1$, because for ideal gas (at low pressure) $a_1 = p/p_s$ and in this study $p_{max} = p_s$ at 25°C. The VOC adsorption isotherms on PDMS at 25°C are shown in Figure 2. The isotherms cover the entire range of VOC partial pressures at 25°C. For TCA and TCE, the isotherms show a continuous increase in the gradient with increasing VOC activity. Thus, TCA and TCE are good solvents for the PDMS polymer. The molar uptake values for TCA and TCE are much higher than that of ethanol, which is a poor solvent for PDMS.

The Flory–Huggins theory was used to describe the experimental sorption isotherms. This model is typically valid for sorption of hydrocarbon vapors in elastomeric polymers. For the binary system of membrane and VOC, the Flory–Huggins equation was written[10] as

$$\ln(a_1) = \ln(\phi_1) + \left(1 - \frac{V_1}{V_2}\right)(1 - \phi_1)$$
$$+ \chi_{12}(1 - \phi_1)^2 \quad (1)$$

where $\phi_1$ is the VOC volume fraction in the polymer (solubility), $V_1$ is the VOC molar volume, $V_2$ is the PDMS molar volume, and $\chi_{12}$ is the VOC–polymer interaction parameter.

Equation (1) relates the vapor phase activity

of the VOC $(a_1)$ to the volume fraction in the polymer phase $(\phi_1)$. Typically, $V_1 \ll V_2$, so $1 - V_1/V_2$ was taken as 1. The polymer–permeant interaction parameter $(\chi_{12})$ is the only adjustable parameter in eq. (1). The molar uptake $(M_P)$ shown in Figure 2 was converted to VOC volume fraction $(\phi_1)$ by the following equation,

$$\phi = \frac{M_p V_1}{M_p V_1 + 1/\rho_P} \quad (2)$$

where $\rho_P$ is polymer density. The sorption isotherms for TCE and TCA at 25°C are shown in Figure 3 and Figure 4 in which the VOC volume fraction $(\phi_1)$ is plotted against the VOC activity $(a_1)$. TCE and TCA are good solvents for PDMS and exhibit high solubility in the polymer phase $(\phi_{1,max} = 0.34$ for TCE). This results in considerable swelling of the PDMS polymer. The dotted lines in Figure 3 and Figure 4 represent the fitting of the adsorption data by the Flory–Huggins equation, eq. (1). As can be seen, the equilibrium isotherm is modeled very well by the conventional Flory–Huggins equation. The polymer–VOC interaction parameter, $\chi_{12}$, calculated from the experimental data, is also plotted on the right axis. It is basically constant over the entire range of VOC partial pressures as assumed by the Flory–Huggins equation.

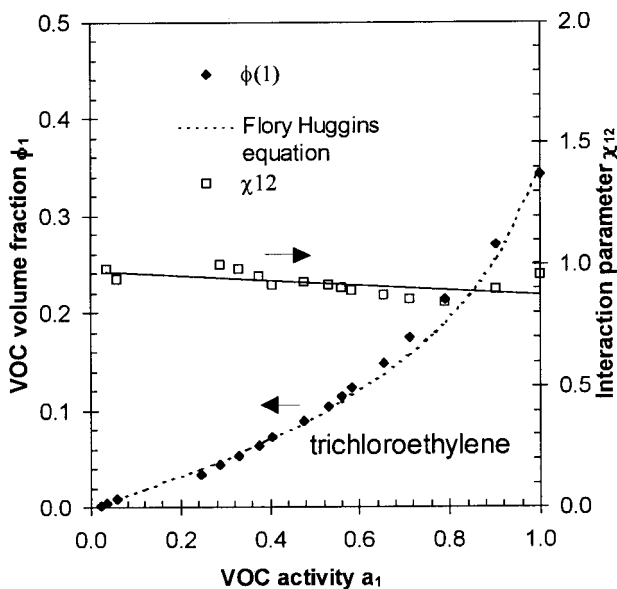Figure 5 shows the isotherm for ethanol on PDMS at 25°C. As can be seen, the maximum eth-



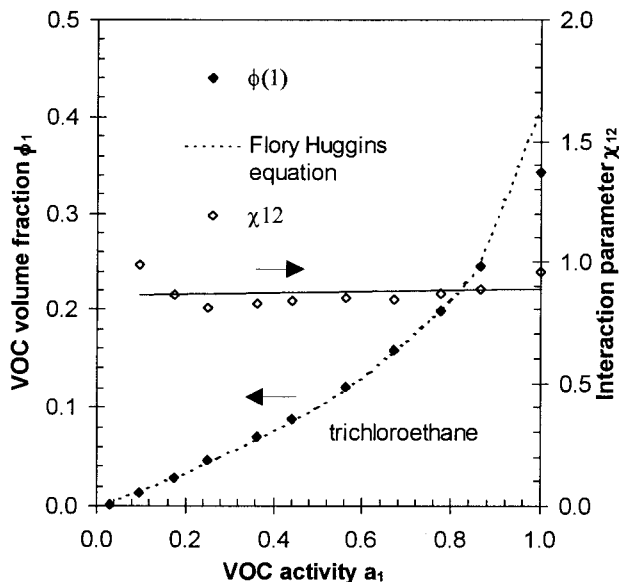**Figure 3**  Trichloroethylene isotherm on PDMS and Flory–Huggins model.

**Figure 4** Trichloroethane isotherm on PDMS and Flory–Huggins model.

anol volume fraction in PDMS is very small ($\phi_{1,max}$ = 0.04) compared to TCA and TCE. Thus, ethanol is not a good solvent for PDMS. The dotted line plotted on the left axis represents the sorption data predicted by the one parameter Flory–Huggins equation, eq. (1). As seen from Figure 5, it is not sufficient to accurately predict the adsorption of ethanol on PDMS due to the curvature of the data.

The interaction parameter ($\chi_{12}$) is also continuously decreasing as seen in Figure 5. This variation in $\chi_{12}$ with activity requires more sophisticated approaches for describing the isotherms as the conventional Flory–Huggins equation assumes constant $\chi_{12}$. The Koningsveld and Kleinjtens variation law[11] was applied that assumes that the enthalpy of mixing is related to VOC interacting surface fraction, rather than the volume fraction as assumed in the Flory–Huggins equation. It states the following variation law,

$$\chi_{12} = \alpha + \frac{\beta(1 - \omega)}{(1 - \omega(1 - \phi_1))^2} \quad (3)$$

where $\alpha$ is an empirical constant, $\beta$ is linked to mixing enthalpy, and $\omega$ is a function of the coordination number of the network. This variation given by eq. (3), when combined with the Flory–Huggins equation, eq. (1), gave rise to a three parameter expression. The parameters were determined by a nonlinear curve fit of the experi-

mental data. The calculated values for ethanol are $\alpha$ = 1.55, $\beta$ = 0.12, and $\omega$ = 0.93. The model adequately describes the ethanol isotherm (solid line plotted on the left axis in Fig. 5) and the variation in experimental $\chi_{12}$ (solid line plotted on the right axis in Fig. 5). Thus, while the Flory–Huggins theory performs very well for good solvents, more sophisticated approaches such as the variation law given in eq. (3) are required for polar solvents. This is consistent with similar observations on sorption of methanol and $n$-butanol in PDMS.[7] The calculated values of all the model parameters for ethanol are given in Table I along with reported parameters for other alcohols for comparison.

The value of $\chi_{12}$ for ethanol ( = 2.46) is much higher than that for TCA and TCE ($\chi_{12}$ for TCA = 0.87 and $\chi_{12}$ for TCE = 0.94). This results in less convexity of the ethanol isotherm. The maximum volume fraction for ethanol in PDMS ($\phi_{1,max}$ = 0.04) compares well and falls within similar values reported for $n$-butanol ($\phi_{1,max}$ = 0.19) and methanol ($\phi_{1,max}$ = 0.02).[7] The calculated value of the Flory–Huggins interaction parameter for ethanol, $\chi_{12}$ = 2.46, also lies within the values reported for $n$-butanol ($\chi_{12}$ = 1.28) and methanol ($\chi_{12}$ = 3.21).[7] This trend in maximum volume fraction and interaction parameter is consistent with the variation in the polar character and size of the permeants. As the size of the molecule increases, the polar character decreases, thus, increasing the solubility of these alcohols in PDMS.
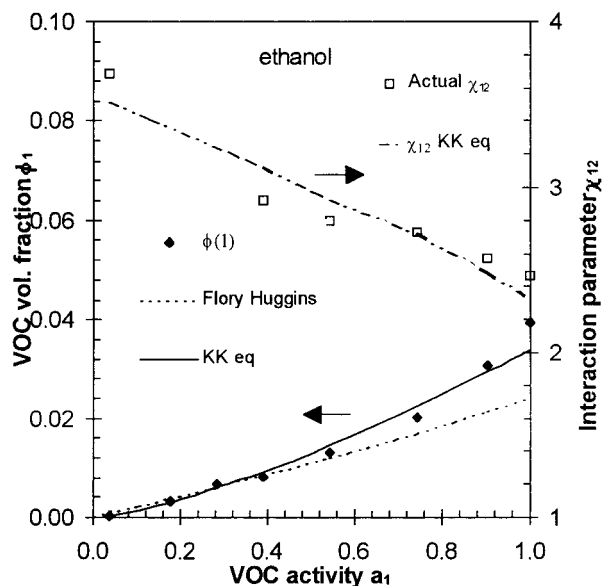


**Figure 5** Ethanol isotherm on PDMS and Flory–Huggins model.

**Table I   Isotherm Parameters for TCA, TCE, and Alcohols in PDMS at 25°C**

| VOC | $\phi_{1,max}$ | $\chi_{12}$[a] | $\alpha$ | $\beta$ | $\omega$ | Source |
|---|---|---|---|---|---|---|
| TCA | 0.35 | 0.87 | — | — | — | This work |
| TCE | 0.34 | 0.94 | — | — | — | This work |
| 1-Butanol | 0.19 | 1.28 | 0.94 | 0.25 | 0.88 | Favre et al.[7] |
| Ethanol | 0.04 | 2.46 | 1.55 | 0.12 | 0.93 | This work |
| Methanol | 0.02 | 3.21 | 1.56 | 0.15 | 0.94 | Favre et al.[7] |

[a] From $\phi_{1,max}$.

## Solubility

The solubility coefficient $(S)$ is an important parameter in determining the overall permeability of the membrane. The solubility coefficients were calculated from the VOC adsorption isotherms according to the following equation[10]:

$$S = \frac{c}{P} \tag{4}$$

where $c$ is the VOC concentration in the polymer phase $[cm^3 \ (STP)/cm^3]$, and $P$ is the VOC pressure in the vapor phase $(cmHg)$. The concentration of the VOCs in PDMS $(c)$ was calculated from the molar uptake $(M_P)$ by assuming ideal gas behavior. The solubility coefficients for the three VOCs in PDMS as a function of activity at 25°C are plotted in Figure 6.

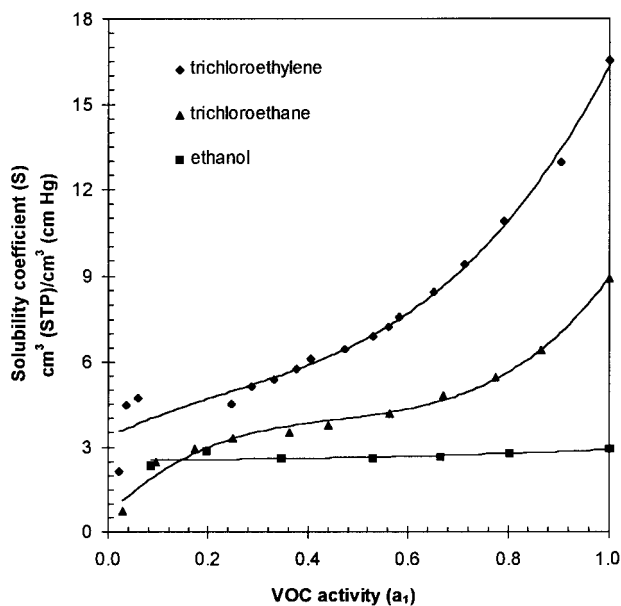For TCA and TCE, the good solvents for PDMS, the solubility coefficient continuously increases with activity; for ethanol it remains constant with activity. The solubility coefficient is a measure of the slope of the adsorption isotherm. For TCA and TCE, as their concentration in PDMS increases, the solubility increases due to considerable swelling of the polymer and creation of more and more free volume in the polymer to hold additional VOCs. On the other hand, ethanol does not cause high swelling of the polymer (low $\phi_{1,max}$). Furthermore, it tends to associate more with other ethanol molecules due to hydrogen bonding as discussed later. Hence, ethanol solubility is a weak function of activity. This results in nonsatisfactory fitting of the sorption data by the Flory–Huggins model for ethanol as seen in Figure 5.

Figure 7 and Figure 8 show the variation of the solubility coefficient with temperature for TCA and ethanol, respectively, at different relative pressures. The three lines represent isotherms
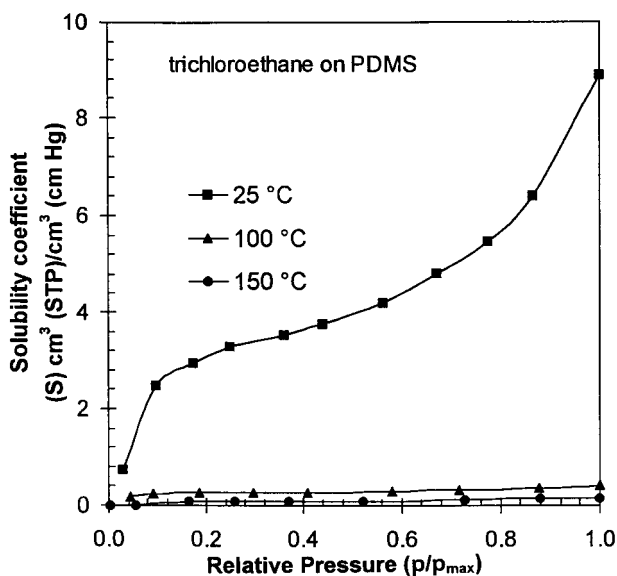


**Figure 6**   VOC solubility as a function of activity in PDMS at 25°C.



**Figure 7**   Effect of temperature on the TCA solubility coefficient in PDMS.
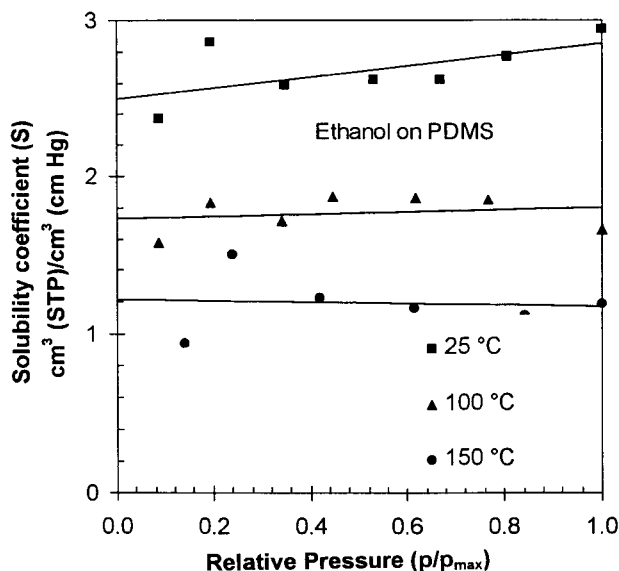
**Figure 8** Effect of temperature on the ethanol solubility coefficient in PDMS.

measured at temperatures of 25, 100, and 150°C. As can be seen in Figure 7, temperature has a strong effect on the TCA solubility coefficient. Similar trends were observed in the TCE and are not shown for the sake of avoiding repetition.

For ethanol, on the other hand, the effect of temperature on the solubility coefficient is not pronounced as seen in Figure 8. Ethanol molecules tend to form hydrogen bonds between them because of their polar character. This bonding phenomenon plays an important role in determining ethanol solubility in PDMS and is a weak function of temperature. Hence, ethanol solubility does not decrease much with temperature. From the solubility data at the three temperatures the heat of adsorption ($\Delta H_s$) was calculated using the following equation[10]:

$$S = S_0 \exp\left(\frac{-\Delta H_s}{RT}\right) \qquad (5)$$

As seen in Figure 6 and Figure 7, the solubility coefficient ($S$) is a strong function of pressure for TCA and TCE. Hence, in the calculation of the heat of adsorption, the solubility coefficients were calculated at relative pressures of VOC of 0.2, 0.4, 0.6, 0.8, and 1 and at three temperatures. $\Delta H_s$ values were calculated using eq. (5) at these five pressures. The average of these five values are

reported in Table II along with the average solubility coefficients.

The heat of mixing was calculated from the heat of adsorption ($\Delta H_s$) and the latent heat of VOC ($\Delta H_v$) by the following equation[10]:

$$\Delta H_{\text{mixing}} = \Delta H_s - \Delta H_v \qquad (6)$$

The low and approximately zero heat of mixing for TCA and TCE signifies their affinity for the PDMS. The $\Delta H_s$ value for TCE ($-35.37$ kJ/mol) is consistent with that reported in the literature ($-35.23$ kJ/mol).[9] The calculated value of $\Delta H_s$ and the observed molar uptake at 25°C were used to interpolate the maximum TCE sorption in PDMS to 60°C. This calculated value of 1.49 mmol/g compares very well with the experimental value of 1.40 mmol/g reported for TCE adsorption in PDMS at 60°C.[12] This verifies the data for sorption at 25°C and also the heat of adsorption. Ethanol has a very low heat of adsorption as compared to TCA and TCE. The very high positive heat of mixing of ethanol demonstrates its "incompatibility" with the PDMS polymer matrix. The high value of $\Delta H_m$ is consistent with the higher interaction parameter ($\chi_{12} = 2.56$) for ethanol, as derived earlier.

## Cluster Function

Ethanol has anomalous solubility behavior in PDMS compared to TCA and TCE. It exhibits much lower solubility in PDMS. Its isotherm could not be correlated as well by the one parameter Flory–Huggins equation. Its solubility coefficient did not increase with activity, as is observed for TCA and TCE shown in Figure 6. Furthermore, the variation in solubility coefficient with temperature for ethanol was lower. Ethanol also exhibits a lower heat of adsorption and a high positive heat of mixing. These effects are consistent with the observations that ethanol is not a good solvent for PDMS. However, a more detailed quantitative analysis is required to explain these deviations. Hence, the clustering phenomenon was examined for the three VOCs. The clustering theory gives little information regarding the mechanism of sorption and cannot be used to predict the sorption isotherms. However, it provides an important tool to analyze the sorption isotherms by quantifying the mean molecular clustering tendencies.

The cluster integral function is defined in terms

**Table II   VOC Solubility Coefficients, Heat of Adsorption, and Mixing in PDMS**

| VOC | Average Solubility Coefficient (S) [cm$^3$ (STP)/cm$^3$ (cmHg)] | | | $-\Delta H_s$ (kJ/mol) | $-\Delta H_v$ (kJ/mol) | $\Delta H_{(mixing)}$ (kJ/mol) |
|---|---|---|---|---|---|---|
| | 25°C | 100°C | 150°C | | | |
| Ethanol | 2.95 | 1.67 | 1.19 | $-6.62$ | $-38.56$ | 31.94 |
| Trichloroethane | 7.98 | 0.43 | 0.15 | $-32.58$ | $-29.86$ | $-2.72$ |
| Trichloroethylene | 16.54 | 1.38 | 0.61 | $-35.37$ | $-31.40$ | $-3.97$ |

of the partial volume fraction and the thermodynamic activity of the permeant. It determines the tendency of clustering for a particular permeant and is given by[13]

$$G = -(1 - \phi_1)\left(\frac{\partial(a_1/\phi_1)}{\partial a_1}\right)_T - 1 \qquad (7)$$

where $G$ is the cluster function integral. For an ideal system,

$$\left(\frac{\partial(a_1/\phi_1)}{\partial a_1}\right)_T = 0 \qquad (8)$$

and $G = 0$, $G > -1$, and $G < -1$ indicate, respectively, no clustering, a clustering tendency, and localized sorption of permeant on specific polymer sites.

The differential function in eq. (7) was determined numerically from the experimental data of $(a_1/\phi_1)$ versus $a_1$ (curve fitting followed by numerical differentiation). The cluster integral function $G$ is plotted in Figure 9 against VOC activity (at
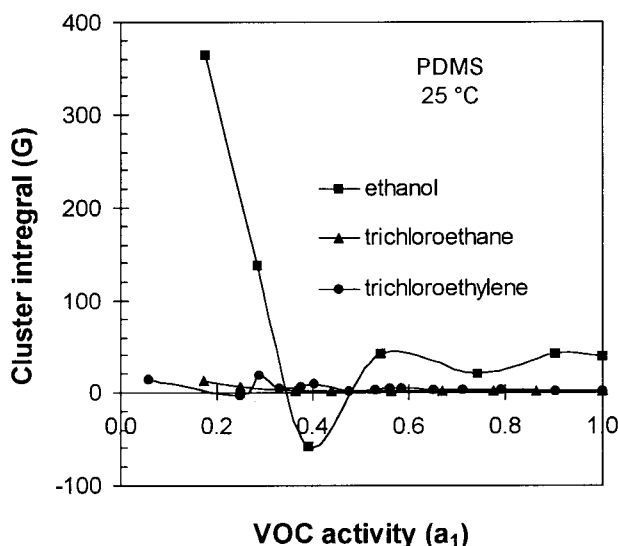


**Figure 9**   Zimm plots for ethanol, TCA, and TCE in PDMS at 25°C.

25°C). The value of the cluster integral is well over 1 for ethanol almost over the entire range of ethanol activity. However, it shows a minima near $a_1 = 0.4$. This implies that ethanol has a tendency to form clusters almost over the entire range of its partial pressures at 25°C. As seen later, the ethanol diffusivity shows a maxima in the activity range close to 0.4. The clustering tendency has been examined for ethanol in 30 wt % silica resin filled PDMS membranes.[5] In that case, the values of the cluster function were $G \ll -1$ for low ethanol activities and $G \gg 1$ for higher activities. The low value of $G \ll -1$ in their case signified immobilization by the silica resin that was effective at lower activities. Even in that case inversion in the cluster function plot was observed at $a_1 = 0.4$, which is consistent with the minima in our results.

For TCA and TCE, the value of the cluster integral at 25°C is close to zero over the entire partial pressure range, signifying a very low clustering tendency. This difference in the cluster function integral values explains the vastly different adsorption behavior of ethanol, and TCA and TCE in PDMS. Ethanol shows an appreciable clustering tendency in PDMS. This clustering tendency arises because of the affinity of ethanol molecules for each other due to hydrogen bonding. This reduces the swelling of the PDMS polymer due to ethanol, which results in low ethanol solubility.

The classic Flory–Huggins theory assumes random distribution of permeant in the polymer. This assumption does not hold due to the clustering tendency of ethanol, and hence, a more complex three parameter model is required to correlate the ethanol isotherm. Ethanol molecules fail to create more free volume in the PDMS polymer for additional molecules, which results in almost constant values of solubility coefficient ($S$) over the entire partial pressure range. The tendency of ethanol molecules to form hydrogen bonding among themselves plays an important role in its adsorption. This is a weak function of tempera-
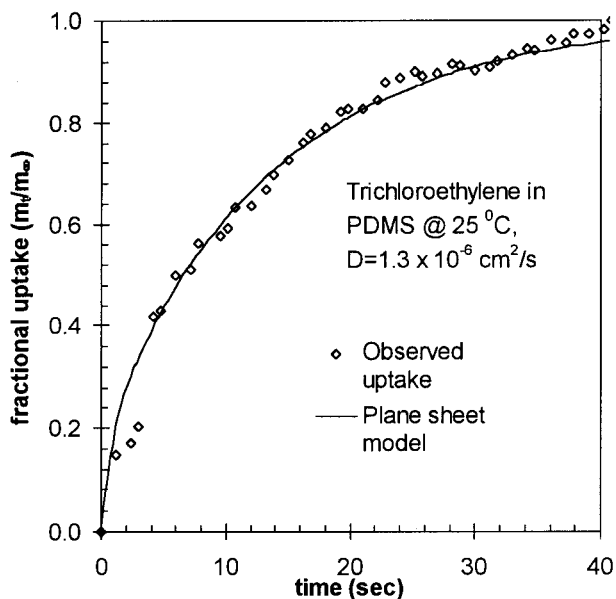
**Figure 10** Diffusivity in PDMS. Calculation by plane sheet model.

ture. Thus, the adsorption capacity of PDMS for ethanol is a weak function of temperature. This reduced dependence of the solubility on temperature results in a low heat of adsorption. The weak affinity for PDMS reflects in the high value of the polymer–permeant interaction parameter $\chi_{12}$ and high heat of mixing $\Delta H_m$.

## Diffusivity

The transient weight change data were utilized to investigate kinetic parameters including the diffusivity. The membranes were in the form of thin films of $\sim 150\ \mu$m thickness. Hence, the diffusion of VOCs in PDMS was considered as 1-dimensional bounded by the two surfaces of the membrane. The following solution is available to the partial differential equation describing 1-dimensional diffusion in a plane sheet[14]:

$$\frac{m_t}{m_\infty} = \frac{q_t - q_0}{q_\infty - q_0} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2}$$

$$\times \exp\left\{\frac{-D(2n+1)^2\pi^2 t}{4l^2}\right\} \quad (9)$$

The experimentally observed uptake curve, $m_t/m_\infty$ versus $t$, for TCE sorption in PDMS at 25°C is given in Figure 10. The diffusivity $D$ was obtained by regression of the experimental data

with eq. (9) using a FORTRAN nonlinear 1-dimensional optimization subroutine. The uptake curve calculated from eq. (9) is also plotted in Figure 10. As shown, the model agrees well with the experimental data.

The diffusivities of TCE and ethanol in PDMS at 25°C are plotted versus activity in Figure 11. Diffusivity versus activity data for TCA are similar to those for TCE. A very low concentration dependence on diffusivity was observed for TCE, which has a low clustering tendency. According to the free volume theory, the diffusivity of these organics should increase with concentration. However, in the polymers with low glass transition temperatures ($T_g$), this dependence of diffusivity on concentration is reduced. PDMS has a very low glass transition temperature ($T_g = 151$ K). Hence, almost constant diffusivities were observed for TCA and TCE in PDMS. The dependence of diffusivity on concentration is stronger in glassy polymers than in rubbery polymers. The constant VOC diffusivities observed in PDMS are consistent with similar observations on benzene in natural rubber ($T_g = 200$ K) and PDMS.[15]

Ethanol diffusivity did not remain constant, but a maxima was seen in diffusivity at $a_1 \sim 0.4$. This corresponds to a minima in its cluster integral plot as seen in Figure 9. Hence, the tendency to form clusters is minimum for ethanol at $a_1 = 0.4$, which is symbolized by a maxima in its mobility at that activity. Thus, the equilibrium and kinetic data collected in this work authenticate each other. The VOC diffusivities at three temperatures were used to calculate the diffusion activation energy ($E_D$) by the following Arrhenius equation[10]:

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (10)$$

The results are summarized in Table III. The diffusivities were calculated at the same relative pressure at various temperatures to nullify the effect of activity on diffusivity, if any. The diffusional activation energies for the three VOCs are of the same order of magnitude, although the value for ethanol ($E_D = 6.15$ kJ/mol) is lower than that for the other VOCs. The ethanol diffusivity at 25°C is of the same order of magnitude as those reported for $n$-butanol and methanol at 40°C (3.11 $\times 10^{-6}$ and $18.70 \times 10^{-6}$ cm$^2$/s, respectively).[7] The value is slightly higher than $1.2 \times 10^{-6}$ cm$^2$/s reported in 30 wt % silica filled PDMS at 25°C.
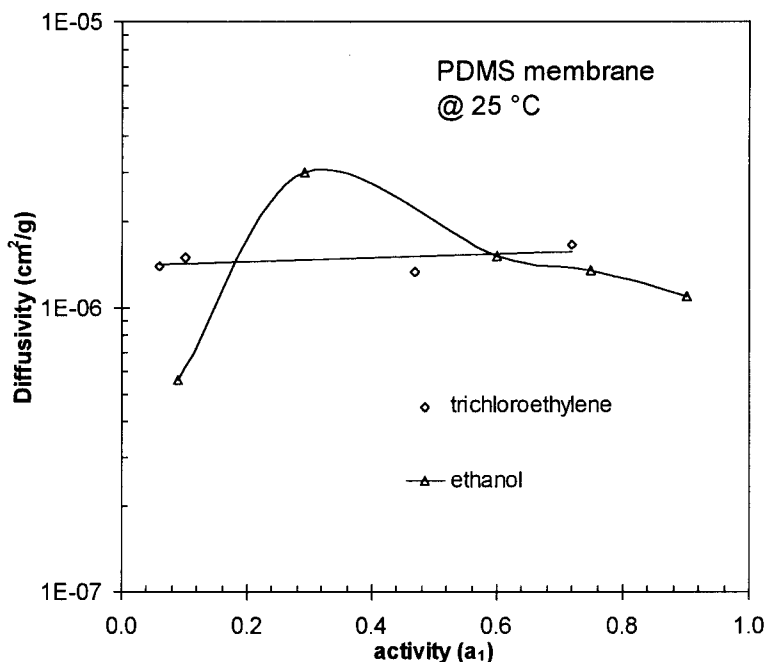
**Figure 11** VOC diffusivities in PDMS at 25°C as a function of activity.

This is due to the silica filler that tends to lower the ethanol diffusivity due to penetrant immobilization.

The diffusivity values for TCA and TCE are only slightly higher than the $1.2 \times 10^{-6}$ cm$^2$/s reported for higher molecular weight organics like toluene in PDMS.[5] This is expected, because the effect of molecular size on diffusivity in polymers is much less pronounced for rubbery polymers. The TCE diffusivity interpolated to 60°C is 2.8 $\times$ $10^{-6}$ cm$^2$/s, which is on the same order of magnitude as reported in the literature ($1.5 \times 10^{-6}$ cm$^2$/s).[12] The calculated diffusional activation energy for TCE ($E_D = 14.21$ kJ/mol) compared very

**Table III   VOC Diffusivities and Diffusional Activation Energies in PDMS and Zeolite**

| VOC | $T$ (K) | $D$ ($\times 10^{-6}$ cm$^2$/s) | $E_D$ (kJ/mol) |
|---|---|---|---|
| Ethanol | 298 | 1.52 | 6.15 |
| | 373 | 1.57 | |
| | 423 | 3.59 | |
| Trichloroethane | 298 | 3.23 | 11.60 |
| | 373 | 7.49 | |
| | 423 | 12.90 | |
| Trichloroethylene | 298 | 1.44 | 14.21 |
| | 373 | 6.11 | |
| | 423 | 7.25 | |

well with the 12.08 kJ/mol reported earlier by Blume et al.[9] However their $E_D$ value was indirectly determined from permeation and sorption measurements, whereas in this study $E_D$ was determined from the measurement of transient uptake data at various temperatures.

## CONCLUSIONS

The sorption and diffusion of three VOCs (ethanol, TCA, and TCE) were investigated in PDMS membranes at temperatures of 25, 100, and 150°C. The thermodynamic equilibrium and kinetic parameters were evaluated. TCA and TCE exhibited high sorption in PDMS, because these are good solvents for PDMS ($\phi_{1,\max} = 0.34$ for TCE). The sorption isotherms could be correlated very well using the one parameter Flory–Huggins model. However, ethanol exhibited very low sorption in PDMS ($\phi_{1,\max} = 0.04$). A three parameter modification to the Flory–Huggins equation was required for satisfactory correlation of the sorption data.

The solubility coefficients for TCA and TCE increased with activity; for ethanol it was almost constant. TCA and TCE solubility coefficients exhibited strong dependence on temperature as opposed to ethanol. Ethanol had a high positive heat of mixing, signifying its incompatibility with the

polymer matrix. Hence, the clustering phenomenon of the VOCs in PDMS was investigated to explain these anomalies. Ethanol had strong clustering tendencies, due to its polar character, and susceptibility for hydrogen bonding.

The kinetic analysis indicates diffusivities of the order of $10^{-6}$ cm$^2$/s for the three VOCs. TCA and TCE diffusivities increase slightly with activity. However, ethanol diffusivity shows maxima at $a_1 \sim 0.4$, corresponding to the minima in its cluster function plot.

## NOMENCLATURE

$a_1$     VOC activity ($=p/p_s$)
$D$     diffusivity (cm$^2$/s)
$D_0$     preexponential factor (cm$^2$/s)
$E_D$     diffusional activation energy (kJ/mol)
$G$     cluster integral function
$\Delta H_m$     heat of mixing (kJ/mol)
$\Delta H_s$     heat of adsorption (kJ/mol)
$\Delta H_v$     latent heat of vaporization of VOC (kJ/mol)
$l$     half-thickness of membrane (m)
$m_\infty$     VOC uptake at saturation (g/g)
$m_t$     VOC uptake at any time $t$ (g/g)
$M_p$     molar uptake of VOC by polymer (mmol/g)
$P$     permeability [Barrer $= 10^{-10}$ cm$^3$(STP)/ cm cmHg s]
$p$     VOC partial pressure (torr) (cmHg)
$p_s$     VOC saturation pressure (torr)
$p_{\max}$     maximum VOC pressure in the isotherm, same as $p_s$ at 25°C
$q_\infty$     final VOC concentration in the membrane (mmol/g)
$q_0$     initial VOC concentration in the membrane (mmol/g)
$q_t$     concentration of VOC in the polymer phase at any time $t$ (mmol/g)
$R$     universal gas constant (8.314 J/mol K)
$S$     solubility coefficient [cm$^3$(STP)/cm$^3$ cmHg]
$S_0$     preexponential factor [cm$^3$(STP)/cm$^3$ cmHg]
$T$     temperature (K)
$T_g$     glass transition temperature (K)
$V_1$     VOC molar volume (cm$^3$/mol)
$V_2$     polymer molar volume (cm$^3$/mol)

### Greek Letters

$\chi_{12}$     VOC–polymer interaction parameter
$\phi_1$     VOC volume fraction in the membrane

### Subscripts

1     for VOC
2     for polymer

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