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Permeation and sorption properties of benzene, cyclohexane, and *n*-hexane vapors in poly[bis(2,2,2-trifluoroethoxy)phosphazene] (PTFEP) membranes

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Abstract

The permeability and solubility of benzene, cyclohexane, and *n*-hexane (C-6 compounds) in poly[bis(2,2,2-trifluoroethoxy)phosphazene] (PTFEP) membranes were determined experimentally, and the corresponding diffusivity was obtained by analyzing the data with the solution-diffusion model. The permeability of benzene ranged from several hundreds to several thousands Barrers, and that of cyclohexane and *n*-hexane ranged from several decades to several hundreds Barrers. All the permeabilities increased exponentially with the vapor activity and increased with temperature. The sorption isotherms of those C-6 compounds were well described by the Henry's law relationship, and constant solubility at each temperature could be determined from the linear correlation. The solubility seems to be inversely proportion to the molecular size of the penetrant when there is not much strong polymer–penetrant interaction. The diffusivity of those C-6 compounds ranged from 10^{-7} to 10^{-9} cm^2/s, and the values of benzene were much larger than those of cyclohexane and *n*-hexane at the same temperature and vapor activity. The diffusivities of those C-6 compounds also increased exponentially with the vapor activity, and the relative magnitude of the diffusivity is determined by the molecular size (collision diameter) of them. The diffusivities of those C-6 compounds increased with temperature and their activation energies of diffusion were very similar possibly due to the same energy characteristic of polymer main chain movement.

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Keywords: Permeability; Solubility; Diffusivity

1. Introduction

Polyphosphazenes are inorganic backbone polymers containing alternate phosphorus–nitrogen single and double bonds with two organic side groups being attached to each phosphorus atom. Due to a large variety of side groups can be introduced into the polymers, they can be made with a wide range of chemical and physical properties and are versatile in many applications [1–4]. In recent years, polyphosphazenes have been used as membrane materials for a number of gases, organics/orgaincs and organic/water separations (pervaporation or vapor permeation) because they can be easily processed to make thin films with moderate high permeabilities, high temperature durability, and chemical stability [5–12]. The transport properties for a range of gases in these series of polymers have also received considerable attention [13–18] in order to support the development of the novel membrane materials and to understand the mechanism for gas transport within them. A molecular simulation approach has been adopted to study the diffusion of some permanent gases through semi-crystalline PTFEP [19]. However, the transport of volatile organic vapors in these phosphazene polymers has seldom been discussed [20].

Poly[bis(2,2,2-trifluoroethoxy)phosphazene] (PTFEP) is one of such phosphazene polymers, and it has been well characterized both chemically and physically [3,4]. Because the phosphorus–nitrogen bonds in the polymers are extremely flexible due to the low torsional energy, its glass transition temperature is relatively low (−56 °C). The polymer tends to be semicrystalline because of its regular structure in the side groups. The melting point of the crystalline polymer is about 226 °C. The polymer becomes a thermoplastic elastomer at room temperature. It can be easily dissolved in acetone and its membrane can be prepared by solution casting method [6–8]. Suzuki et al. have studied the separation for the systems of methanol–water, ethanol–water, and benzene–cyclohexane by pervaporation through this membrane. High selectivity between benzene and cyclohexane was reported [6].

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In this work, the sorption isotherms and the permeability for the vapors of a series of six-carbon organic vapors (benzene, cyclohexane, and *n*-hexane) in PTFEP have been determined from 25 to 55 °C. The solubility for these vapors in the polymers can be determined from the sorption isotherms, and the apparent diffusivity for them can be estimated according to the solution-diffusion model [20,21] once the permeability is determined. Benzene, cyclohexane, and *n*-hexane are either important raw materials or solvents in the chemical or other related industries, and they are highly volatile in the temperature range of working environment. The transport properties measured here can provide information for membrane selection or design in either vapor permeation or pervaporation [6,12] for their separation or recovery from waste air or water in a chemical process. They also represent the aromatic and aliphatic compounds of three different shapes of molecules. The vapors can also function as probes to examine the transport mechanism in these penetrant–polymer systems, which may lead to a hint of the structure-property relationship in the inorganic polyphosphazene polymers.

2. Experimental

2.1. Polymer synthesis and membrane preparation

PTFEP was prepared through the ring opening polymerization of hexachlorotriphosphazene ($(NPCl_2)_3$, Aldrich, USA) and then followed by substituting the chlorine in the linear chlorophosphazene polymer with a trifluoroethoxy group ($–OCH_2CF_3$) [2–4]. The chemical composition of the obtained PTFEP polymers was confirmed with FTIR and element analysis [22]. The averaged molecular weight of the PTFEP was determined by viscometry, and it was 94,000 ($\bar{M}_V$) [22]. The crystallinity of the polymer is about 38.6% measured by DSC according to the procedure suggested by Starannikova et al. [17]. Synthesized PTFEP was washed with methanol and water and dried before use.

Membranes of PTFEP were prepared by the solution-casting method. The casting solution was prepared by dissolving 10% PTFEP in acetone. The solution was thoroughly mixed, filtered, degassed, and then poured on a glass plate. The solvent was allowed to slowly evaporate at room temperature and a membrane film could be obtained in 1 day. The membrane was removed from the plate by floating with ethanol. A digital micrometer (Mitutoyo, IDF-112) was used to measure the thickness of the membranes. The thickness was determined in an average of 10 measurements at different points of the membranes. Only those with standard deviation less than 2% of the mean thickness were used for later permeation studies.

2.2. Permeation study

The classical membrane permeation method with a modified quasi-steady state analysis was adopted in this study. A two-compartment permeation cell was employed for the study, and the detailed design of the gas permeation apparatus can be found in our previous publication [23]. The cell and all the tubings and valves used in the permeation apparatus were made of stainless steel. The effective area of the membrane for permeation was 12.56 cm^2, and the membrane thickness was 5.4×10^{-3} cm. A MKS Baratron pressure transducer (121A, measuring range of 0–10 Torr) was used to monitor the down-stream pressure change with time. The upper-stream pressure was measured by using a MKS pressure transducer (122A) and it was kept almost constant during the experiment due to the relatively small amount permeated from the upper-stream, which has a large vapor reservoir, to the down-stream side.

For a volatile organic liquid compound, the upper-stream vapor pressure is limited by the saturated vapor pressure of the organic liquid so that it is not too larger than the down-stream pressure and the pressure difference across the membrane is changing during an experiment. By taking a mass balance over the down-stream volume, we have

$$J = \frac{22,400V}{ART}\frac{dp_2}{dt} = P\frac{(p_1 - p_2)}{l} \quad (1)$$

where J is the volumetric flux of the vapor through the membrane ($cm^3(STP)/cm^2$ s), p_1 and p_2 are the pressures of the upper stream and the down-stream (cmHg), respectively, P is the permeability ($cm^3(STP)$ cm/cm^2 s cmHg), A is the membrane area (cm^2), T is the testing temperature (K), R is the gas constant (6236.3 cm^3 cmHg/gmol K), 22,400 is the molar volume of an ideal gas at STP ($cm^3(STP)$/gmol), V is the down-stream volume, l is the membrane thickness (cm), and t is the time (s). By integrating Eq. (1), we can obtain the following relationship to calculate the permeability of the penetrant through the membrane.

$$\ln\frac{p_1}{p_1 - p_2} = P\frac{ART}{22,400Vl}t = kt \quad (2)$$

In each run, the vapor permeability can be obtained from the quasi-steady state slope (k) in a plot of $\ln(p_1/(p_1-p_2))$ versus t. A linear regression of the data gave the slope to calculate the permeability.

2.3. Solubility measurements

The equilibrium sorption amounts of vapors at various vapor pressures in a PTFEP membrane were determined gravimetrically. A continuous microbalance (Cahn, C-1000) was used to monitor the vapor gain in the sample during the sorption experiments. Detailed descriptions of the apparatus and experimental procedures were given elsewhere [24]. The solubility (S) was defined as the following relationship:

$$S = \frac{C}{p} = \frac{C}{ap^0} \quad (3)$$

where C is the concentration of the vapor in the polymer membrane in volume basis ($cm^3(STP)/cm^3$(polymer)), and p and p^0 are the vapor pressure and saturated vapor pressure (cmHg). Ideal gas behavior was assumed in the calculation of sorbed penetrant volume at STP. We can calculate the concentration of a particular vapor in the membrane by using the following equation

$$C = W \times \frac{22,400\rho_p}{M} \tag{4}$$

where M is the molecular weight of sorbed molecules, ρ_p is the density of polymer, and W is concentration based on weight (g/g polymer).

3. Results and discussions

3.1. Permeation properties

The permeabilities of benzene, cyclohexane, and *n*-hexane at various temperatures are shown in Figs. 1–3, respectively, as a function of the vapor activity on the upstream side. The permeability for all of the compounds increased with the vapor activity and the experimental temperature, and the values of the permeability ranged from several hundreds to several thousands Barrers (1 Barrer$=10^{-10}$(cm^3(STP) cm/cm^2 s cmHg)) for benzene and from several decades to several hundreds for cyclohexane and *n*-hexane. At the same temperature and vapor activity, the permeability for benzene is about one order of magnitude higher than that for cyclohexane or *n*-hexane, and the permeability for *n*-hexane is slightly higher than that of cyclohexane. Suzuki et al. [5] have applied the PTFEP membrane for separation of benzene and cyclohexane by pervaporation method. Good separation factor between benzene and cyclohexane was obtained in their study. Our results suggested that benzene/cyclohexane or benzene/*n*-hexane pairs could be separated by a vapor permeation apparatus as well.

The permeability for each compound at a particular temperature can be correlated with the following empirical equation:

$$P = P_0 \exp(\alpha a) \tag{5}$$

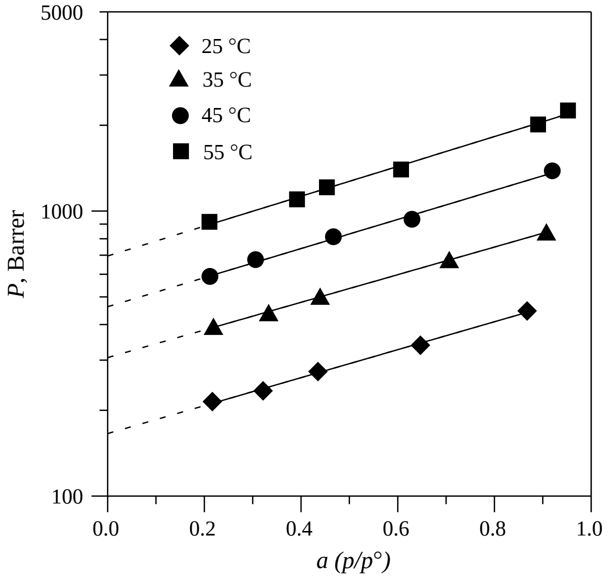

Fig. 1. Permeability as a function of activity for benzene in PTFEP membranes at various temperatures.

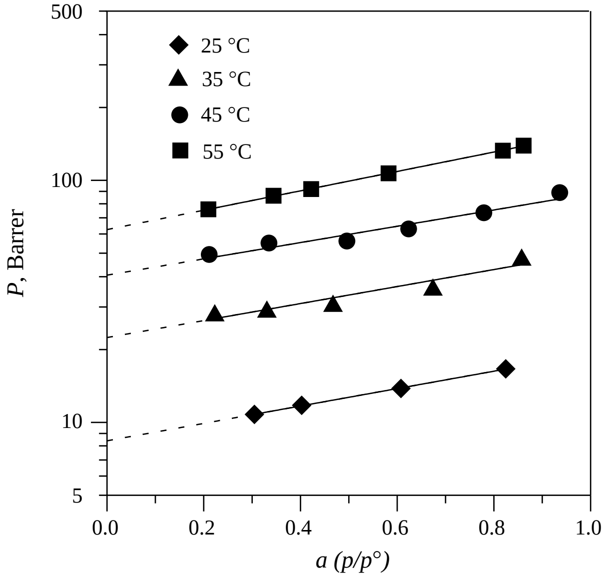

Fig. 2. Permeability as a function of activity for cyclohexane in PTFEP membranes at various temperatures.

where the pre-exponential factor P_0 is the permeability at zero activity and/or infinite dilute concentration for the penetrant in the membrane, and α is a correlation constant, which is related to the plasticization coefficient of the penetrant in the polymer. The regression results by Eq. (5) are listed in Table 1 for benzene, cyclohexane, and *n*-hexane, respectively. Not only the value of the pre-exponential factor P_0 for benzene is 10–20 times higher than cyclohexane and *n*-hexane, but also the vapor activity dependence of permeability (value of α) for benzene is stronger than that for cyclohexane and *n*-hexane at each experimental temperature. Both cyclohexane and *n*-hexane have the similar values in terms of P_0 and α. The results suggest that the separation of cyclohexane and *n*-hexane by this membrane is not favorable but the membrane possesses a good

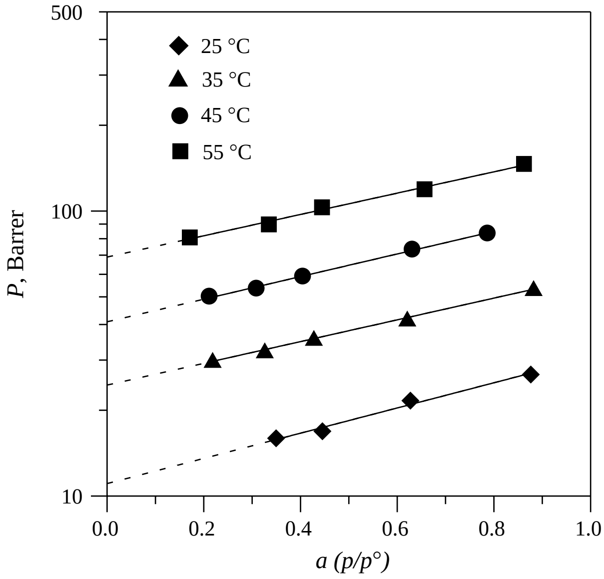

Fig. 3. Permeability as a function of activity for *n*-hexane in PTFEP membranes at various temperatures.

Table 1
Permeability at infinite dilute concentration (P_0) and correlation constant (α) in Eq. (5) for benzene, cyclohexane and *n*-hexane in PTFEP membranes at various temperatures and corresponding activation energy of permeation (E_P)

Temp. (°C)	Benzene		Cyclohexane		*n*-Hexane	
	P_0	$\alpha(r^2)$	P_0	$\alpha(r^2)$	P_0	$\alpha(r^2)$
25	166	1.13 (0.9971)	8	0.83 (0.9995)	11	1.00 (0.9875)
35	306	1.12 (0.9996)	22	0.81 (0.9197)	25	0.88 (0.9986)
45	462	1.16 (0.9954)	41	0.77 (0.9473)	41	0.91 (0.9975)
55	695	1.21 (0.9956)	63	0.92 (0.9998)	69	0.86 (0.9931)
$E_P(r^2)$	38.4 (0.9936)		54.1 (0.9752)		48.9 (0.9924)	

Units: Barrers for P_0, dimensionless for α, and KJ/mol for E_P; r^2, linear correlation coefficient.

permselectivity toward benzene than the cyclohexane or *n*-hexane and the permselctivity between benzene and cyclohexane or *n*-hexane may increase with vapor activity.

The temperature dependence of the permeability at infinite dilute concentration for these compounds is shown in an Arrhenius plot (Fig. 4). The activation energies of permeation (E_p) at infinite dilute concentration for benzene, cyclohexane, and *n*-hexane were determined and they were also attached in Table 1. The E_p for benzene is smaller than that for *n*-hexane and then smaller than that of cyclohexane. The permeation rate of benzene is less sensitive to temperature than that of the other two compounds. The permselectivity between benzene and cyclohexane or *n*-hexane may decrease with increasing temperature.

It is well accepted that the solution-diffusion model [21] can generally describe the permeation of a penetrant through a dense membrane. The permeation through a membrane is considered as three steps: (1) the penetrant dissolves in the upstream-side surface of the membrane, (2) diffuses through the membrane, and (3) desorbs from the downstream-side surface of the membrane. The permeability of a penetrant through a membrane is determined by two independent factors: the solubility and the diffusivity for each compound in PTFEP membranes. The former is due to the thermodynamic equilibrium between the penetrant vapor and the membrane surface (steps 1 and 3), and the equilibrium is generally assumed to be true anytime during the permeation if the flux is not too large. The later is a kinetic process for the moving of the penetrant in the polymer membranes (step 2), and it can be related to the concentration gradient of the penetrant as described by Fick's first law:

$$J = -D\frac{\mathrm{d}C}{\mathrm{d}x} \tag{6}$$

where D is the diffusivity, C is the concentration in the membrane, and x is the distance in the membrane in the direction of transport. Depending on the degree of the interaction between the penetrant and the polymer membrane, diffusivity may vary with the concentration of the penetrant in the membrane. In order to differentiate the effects of sorption equilibrium and diffusion on the permeation process, independent sorption measurement for these vapors in the PTFEP membranes was carried out at the same temperature range.

3.2. Sorption isotherms and solubility

The sorption isotherms for benzene, cyclohexane, and *n*-hexane in PTFEP at various temperatures are shown in Figs.

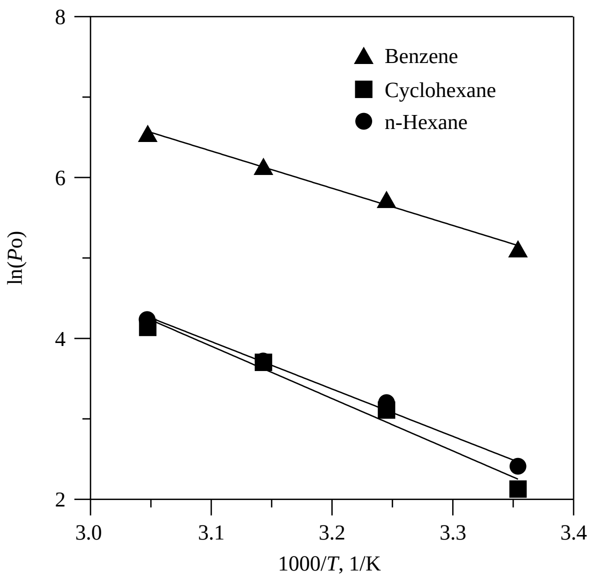

Fig. 4. Arrhenius plots for the permeabilities at infinite dilute concentration (P_0) of benzene, cyclohexane, *n*-hexane in PTFEP membranes.

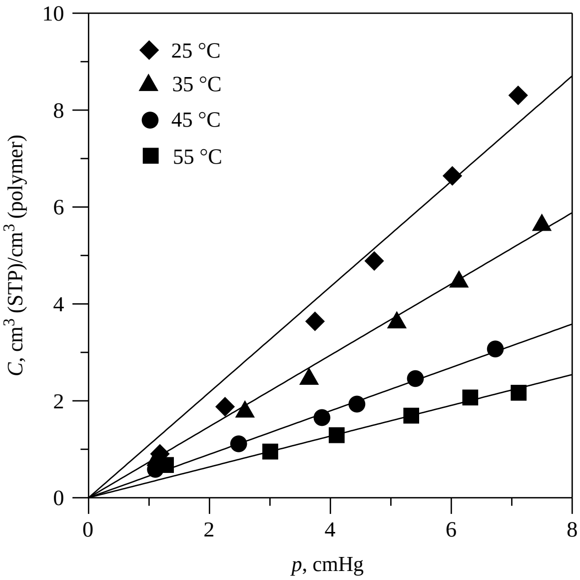

Fig. 5. Sorption isotherms for benzene in PTFEP membranes at various temperatures.

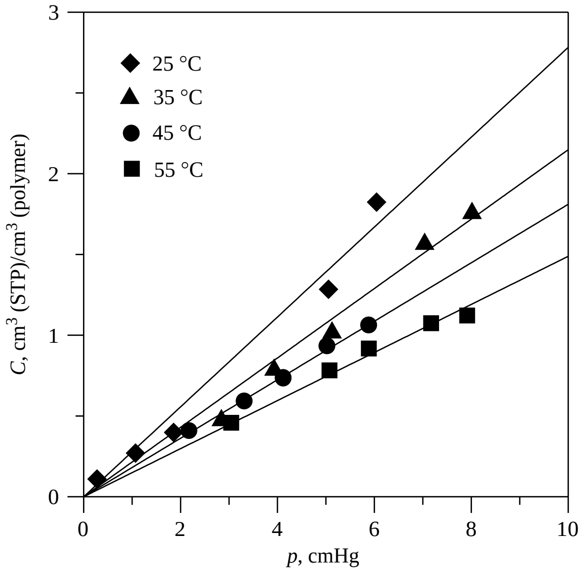

Fig. 6. Sorption isotherms for cyclohexane in PTFEP membrane at various temperatures.

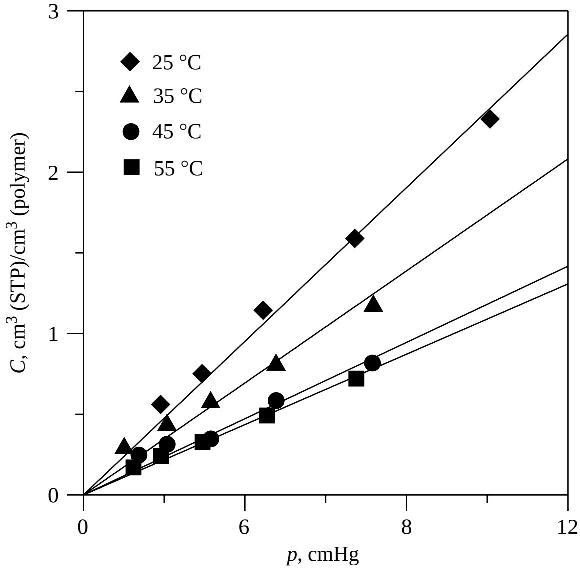

Fig. 7. Sorption isotherms for n-hexane in PTFEP membrane at various temperatures.

Table 2
Solubility (S) for benzene, cyclohexane, and n-hexane in PTFEP membranes at various temperatures and corresponding heat of sorption (ΔH_S)

Temp. (°C)	$S(r^2)$		
	Benzene	Cyclohexane	n-Hexane
25	1.09 (0.9931)	0.28 (0.9903)	0.24 (0.9975)
35	0.74 (0.9991)	0.22 (0.9962)	0.17 (0.9889)
45	0.45 (0.9991)	0.18 (0.9997)	0.12 (0.9898)
55	0.32 (0.9943)	0.15 (0.9986)	0.11 (0.9974)
$\Delta H_S(r^2)$	−33.8 (0.9996)	−16.9 (0.9949)	−21.4 (0.9599)

Unit: (cm^3(STP)/cm^3(polymer)(cmHg)) for S and KJ/mol for ΔH_S; r^2, linear correlation coefficient.

5–7, respectively. The equilibrium sorption amount increases with vapor pressure for those compounds at various temperatures, and the relationship can be closely described by a linear correlation; that is, Henry's law sorption isotherm. Although some of the data deviated from the linear regression, Henry's law correlation seemed adequate for most of the data. It has been proposed that the phosphorus–nitrogen bonds in the main chain are highly flexible so that the free volume or interstitial space between polymer chains is large enough to accommodate the sorbed molecules without altering the relative positions of main structure [20]. The symmetry of the side groups attached to the main chain make the polymer nonpolar and the side groups themselves are inactive so that the penetrant–polymer interaction is weak to cause significant plasticization or swelling effect on the phosphazene polymers. Ideal solution behavior is resulted, and Henry's law can well correlate the sorption isotherm for these organic vapors.

The solubilities of benzene, cyclohexane, and n-hexane in PTFEP could be calculated from the slopes of these regressions according to Eq. (3), and they are given in Table 2. It is found that the solubility of benzene is much higher than that of cyclohexane and n-hexane. Due to the ideal sorption behavior, it is assumed that the free volume within the PTFEP polymer is not significantly altered upon sorption and most sorbed molecules only fill the existing free volume. Benzene molecules are smaller than cyclohexane and n-hexane molecules. Their van der Waals volumes are 0.1193, 0.1413, and 0.1753 l/mol for benzene, cyclohexane, and n-hexane, respectively [25]. In addition, benzene molecules are flat in shape and they contain aromatic resonance electron structure. A higher packing density for benzene is allowed in such an unperturbed polymer interstitial space and the electron lone pairs in the main chain of PTFEP may favor benzene sorption. In contrast, cyclohexane and n-hexane are larger in size and they are saturated hydrocarbons; therefore, the existing free volume in the polymer can accommodate fewer amounts of the molecules of cyclohexane or n-hexane and not much specific interaction between the penetrant and the polymer exists to dilate the polymer chain spacing and increase the sorption capability of PTFEP polymer.

The ratio of the solubility between cyclohexane and n-hexane (1.2–1.5) approximates the inverse of their van der Waals volume ratio (1.2). It seems that solubility is inversely proportional to the molecular size of the penetrant of a similar kind in such a system. The intrinsic free volume within the polymer may determine the amount of sorbed molecules. The postulation would be true if the interaction between the sorbed molecules and the polymer is about the same and the free volume within the polymer is not significantly altered due to sorption. Similar case was also obtained for the solubility of water and ethanol in PTFEP membrane. The inverse of their van der Waals volume ratio is about 2.8, while their solubility ratio is about 2.1 between water and ethanol [23].

The solubility for the vapors in the phosphazene polymers is relatively independent of the sorbed concentration, while that of many organic vapors in a rubbery polymer of carbon backbone would increase with increasing vapor activity or sorbed concentration in the polymer. It seems that the main chains of phosphazene polymer are very flexible and a large fraction of free volume already exists so that the sorption of vapor does not cause significant increase in solubility due to swelling [18]. In addition, the crystalline region within the polymer functions as physical crosslinks and it also keeps the polymer from large swelling. Furthermore, PTFEP is a highly fluorinated polymer, and it has been known that the fluorinated polymers exhibit low solubility towards hydrocarbon gases and vapors [26]. Poorer interaction between fluorocarbons and hydrocarbons could be another potential reason for the lack of dependence of solubility of the C-6 compound vapors on pressure in PTFEP.

The solubilities of benzene, cyclohexane, and *n*-hexane at various temperatures were plotted in Fig. 8, and were analyzed by the van't Hoff equation

$$S = S_0 \exp\left(\frac{\Delta H_S}{RT}\right) \tag{7}$$

The heats of sorption could be determined, and they are also shown in Table 2. Because the solubility decreases as temperature increases, the heat of sorption is negative (exothermic) for all of these three compounds. The heat release of benzene sorption is higher than that of *n*-hexane sorption and then higher than that for cyclohexane sorption. From the point of view of energy consideration, sorption of benzene is the most favored one and sorption of cyclohexane is the least favored. However, the molecular size effect may reverse the order of solubility for cyclohexane and *n*-hexane.

3.3. Diffusivities

According to the solution-diffusion model, the apparent diffusivity through the membrane could be determined from the following equation [20,21]:

$$D = \frac{P}{S} \tag{8}$$

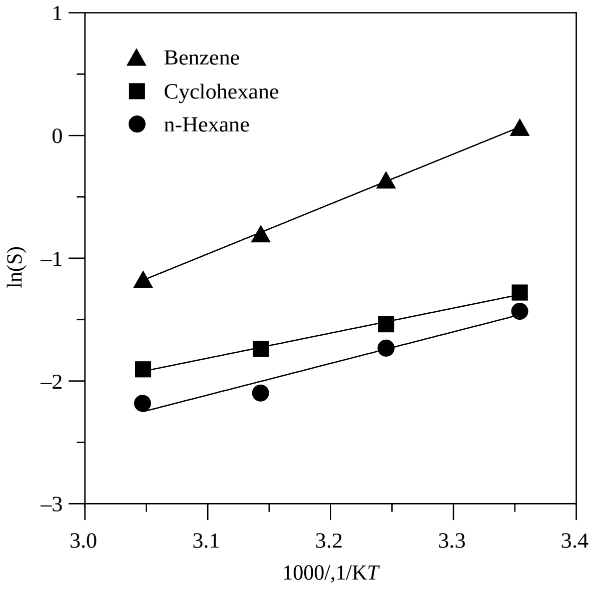

Fig. 8. Van't Hoff plots for the solubilities of benzene, cyclohexane, *n*-hexane in PTFEP membranes.

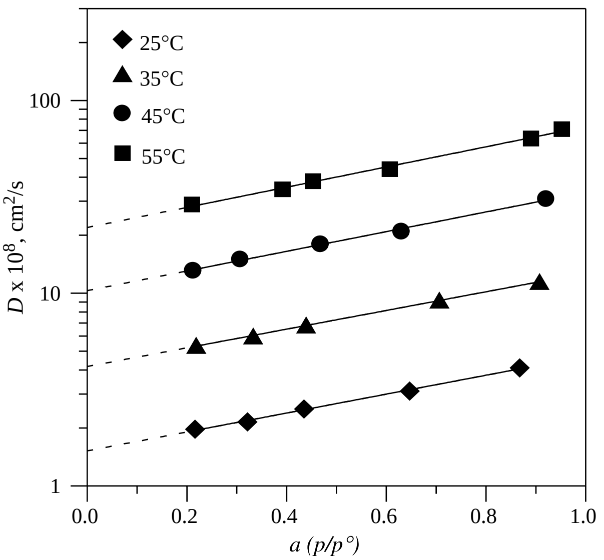

Fig. 9. Diffusivity as a function of activity for benzene in PTFEP membranes at various temperatures.

The calculated diffusivity data were plotted with vapor activity for benzene, cyclohexane, and *n*-hexane as shown in Figs. 9–11, respectively. The diffusivities for those C-6 hydrocarbons in PTFEP ranged from 10^{-9} to 10^{-7} cm^2/s. The diffusivity of benzene was roughly 4–5 times larger than that of cyclohexane and 3–3.5 times larger than that for *n*-hexane at the same temperature or vapor activity. The order of the relative magnitude for the diffusivity of those compounds could be qualitatively correlated with their collision diameters. Lennard-Jones collision diameters are 5.349, 6.182, and 5.949 Å for benzene, cyclohexane, and

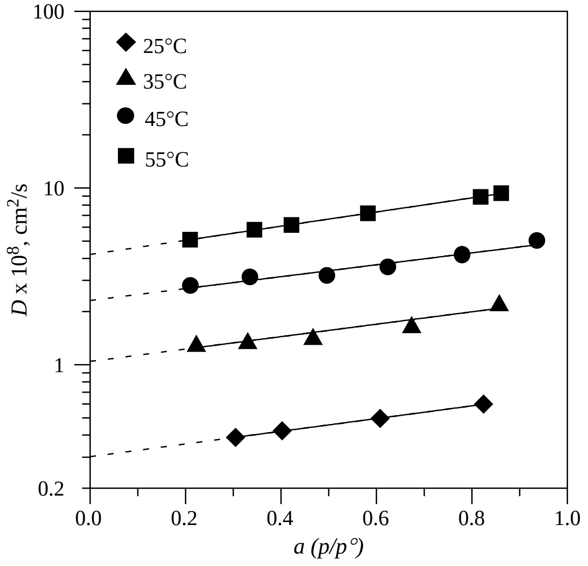

Fig. 10. Diffusivity as a function of activity for cyclohexane in PTFEP membranes at various temperatures.

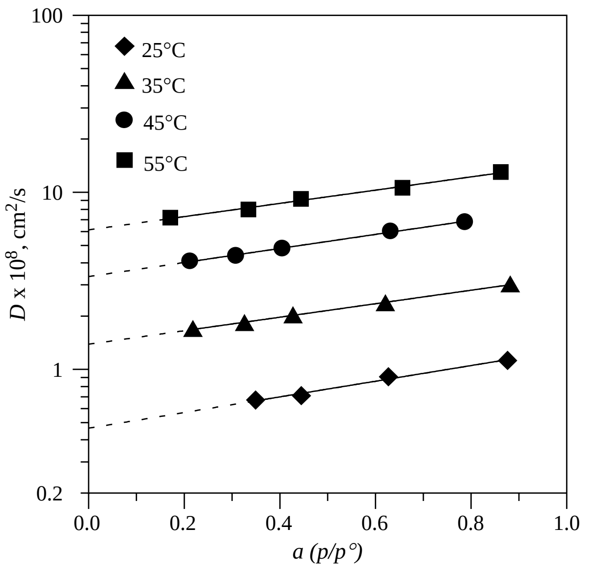

Fig. 11. Diffusivity as a function of activity for *n*-hexane in PTFEP membranes at various temperatures.

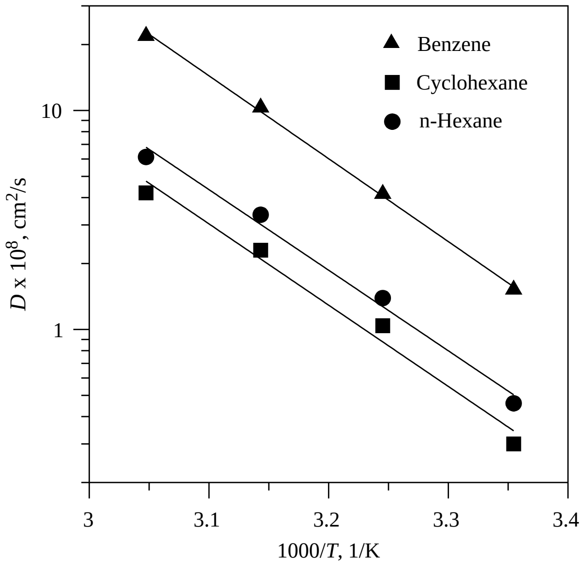

Fig. 12. Arrhenius plots for the diffusivities at infinite dilute concentration (D_0) of benzene, cyclohexane, *n*-hexane in PTFEP membranes.

n-hexane, respectively [27]. Benzene has the smallest collision diameter and is the highest in diffusivity, and the reverse is true for cyclohexane. Due to the compact shape of its molecule structure, benzene is the fastest moving compound within the polymer among the triad. In addition, the much larger diffusivity for benzene may be caused by its ability to access much more interstitial free volume than the other two compounds, as indicated in their relatively values of solubility data. Although *n*-hexane carries two more hydrogen atoms and its molecular size (van der Waals volume) is larger than cyclohexane, the shape of *n*-hexane molecule is linear and it has the advantage of small cross-section area in its longitudinal direction for moving like a reptile so that *n*-hexane can diffuse faster than cyclohexane.

At each temperature, the diffusivity of those compounds increased with their vapor activity. Since the solubility is constant at each temperature, the diffusivity for those compounds carries the same form of the relationship with vapor activity as that in Eq. (5) and can be correlated with the sorbed vapor concentration in the polymer [28,29]:

$$D = D_0\exp(\alpha a) = D_0\exp(AC) \tag{9}$$

where D_0 is the diffusivity at zero activity or concentration, and A is the plasticization coefficient and $A = \alpha/Sp^0$. The plasticization coefficient may be related to the free-volume parameters as suggested by Fujita [25]. Nevertheless, Eq. (9) is purely an empirical form for the diffusivity of small molecule in polymer and it has the merits of being simple for practical use.

The diffusivity of those compounds increases with temperature. The mobility of the penetrants increases and the polymer chains themselves are more flexible at higher temperatures. Therefore, the penetrants can have better ability to diffuse through the polymer matrix when the temperature is higher. The activation energies of diffusion (E_D) for those penetrants could be determined by the Arrhenius plot of the D_0 data (Fig. 12) as well as by the following equation:

$$E_P = \Delta H_S + E_D \tag{10}$$

which was derived from the solution-diffusion model (Eq. (8)), the van't Hoff equation for the heat of sorption, and the Arrhenius equations for permeability and diffusivity. The activation energies of diffusion for all of the penetrants were

Table 3
Diffusivity at infinite dilute concentration (D_0) and plasticization coefficient (A) for benzene, cyclohexane, and *n*-hexane in PTFEP membranes at various temperatures and corresponding activation energy of diffusion (E_D)

Temp. (°C)	Benzene		Cyclohexane		*n*-hex*ane*	
	D_0	A	D_0	A	D_0	A
25	1.52	0.109	0.30	0.305	0.46	0.279
35	4.16	0.103	1.04	0.247	1.39	0.228
45	10.31	0.116	2.30	0.191	3.34	0.227
55	21.90	0.116	4.20	0.188	6.13	0.162
E_D (r^2)	72.2 (0.9988)		70.9 (0.9903)		70.3 (0.9815)	

Unit: 10^{-8} cm^2/s for D_0, cm^3(polymer)/cm^3 (STP) for A, and KJ/mol for E_D; r^2, linear correlation coefficient.

roughly the same in their numerical values as shown in Table 3. It suggested that benzene, *n*-hexane, and cyclohexane might have the same energy barrier of diffusion when they permeated through the membranes. The size of the penetrants seems not a deterministic factor to the energy barrier of diffusion. The perturbation of the polymer main chains may account for the energy barrier of diffusion due to the same energy characteristic of polymer main chain movement. The argument will be true if there is not much interaction between the penetrant and PTFEP. The activation energy of diffusion of benzene is slightly higher than that of cyclohexane and *n*-hexane. It may be caused by the stronger interaction of the resonance electron in benzene and the lone pair electrons in PTFEP. Another possible reason of the slight difference in the activation energy may come from the errors or uncertainty in the experiments or the data fitting procedure.

4. Conclusions

The permeability and solubility for benzene, cyclohexane, and *n*-hexane in PTFEP membranes were experimentally obtained from 25 to 55 °C. The solution-diffusion model was applied to calculate the diffusivity through the membrane. The permeability and the diffusivity increase and the solubility decreases with temperature for those C-6 compounds in PTFEP.

Henry's law can closely describe the sorption isotherms for them and constant solubility is obtained for each penetrant at various temperatures. The magnitude of the solubility is related to the molecule size of the penetrants. When the interaction between the polymer and the penetrant is similar and not too strong, the existing free volume determines the amount of sorbed molecules under the same vapor activity. Smaller molecules may have higher solubility in the polymer. The ratio of solubilities between cyclohexane and *n*-hexane is not much different from the inverse of the ratio of their van der Waals volumes. Both cyclohexane and *n*-hexane are saturated alkane compounds with similar interaction with the PTFEP polymer; therefore, only the size and shape of the molecules may affect the solubility.

The permeability and diffusivity of each compound increased with vapor activity or sorbed concentration and an exponential relationship can correlate the dependence. The activation energies of diffusion are very similar possibly due to the same energy barrier of diffusion for those C-6 compounds in PTFEP. It is the perturbation of polymer main chains determines the energy barrier of diffusion and the relative size (collision diameter) of the penetrant determines the relative magnitude of the diffusion coefficient of those penetrants.

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