Solution and Diffusion Properties of Cyclohexane, Cyclohexanol, and Cyclohexanone in Poly(ethylene glycol) by Inverse Gas Chromatography

Chuyi Zeng,[1,2] Min Huang,[1,3] Hong Zhao,[1,2] Jicheng Zhou,[1] Jiding Li[3]

[1]Department of Chemical Engineering, Xiangtan University, Hunan 411105, People's Republic of China
[2]Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 226-8503, Japan
[3]Membrane Technology and Engineering Research Center, Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

ABSTRACT: The solution and diffusion properties of cyclohexane, cyclohexanol, and cyclohexanone in poly(ethylene glycol) (PEG) and crosslinked PEG have been studied in the temperature range of 368.15 to 403.15 K using inverse gas chromatography (IGC) technique. The infinite dilute activity coefficient (Ω_{ip}^{∞}) and diffusion coefficient (D_{ip}^{∞}) have been determined for the above solvent/polymer systems. Accordingly, several thermodynamic functions, the diffusion pre-exponential factor, and activation energy have been attained. The results showed a decrease in Ω_{ip}^{∞} and an increase in D_{ip}^{∞} with rising temperature. The order of the relative magnitude of Ω_{ip}^{∞} and D_{ip}^{∞} of the solvents were explained by comparing their interactions with the polymer and their collision diameters, respectively. Moreover, Ω_{ip}^{∞} and D_{ip}^{∞} in crosslinked PEG were smaller than those in PEG at various temperatures. The analysis of Ω_{ip}^{∞}, the infinite dilute selectivity and capacity showed the possibility of using crosslinked PEG as an appropriate membrane material for the separation of cyclohexane, cyclohexanol, and cyclohexanone mixture. A thermodynamic study also implied that the solvent sorptions in the polymers were all enthalpically driven in the experimental range. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 124–134, 2012

Key words: activity coefficient; diffusion coefficient; poly(ethylene glycol); crosslinked; cyclohexanol; cyclohexanone

INTRODUCTION

Selective partial oxidation of alkanes by air or oxygen is a key challenge in the manufacture of organic building blocks and industrial intermediates.[1–4] Among them, the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone is very important reaction for commercial application.[5–7] Cyclohexanol and cyclohexanone are important organic intermediates in the petrochemical industry for the manufacture of caprolactam, nylon, and other products.[6] However, since cyclohexanol and cyclohexanone molecules are more reactive in oxidation than cyclohexane, their overoxidation prevents the selective synthesis at higher cyclohexane conversion.[3,4] In the present industrial technology, the conversion of this reaction is always controlled about 3–10% for keeping higher selectivity. Therefore, the reaction mixture contains a large amount of cyclohexane (about 95%),[4–7] and the industrial separation requires a three-step distillation.[4] Up to now, this technology suffers from low product efficiency, high investment, and energy consumption.[3,4] Otherwise, the separation technology based on polymeric membranes, compared to traditional separation technology, has many advantages: (1) high separation efficiency, (2) low energy consumption, (3) simple operation and so on.[8,9] The advantages of applying membrane separation technology to the selective oxidation of cyclohexane are not only to separate the products from the reaction system but also to avoid secondary reactions. Therefore, membrane separation integrated with the oxidation reaction can lead to quantum improvements in reaction efficiencies, yields, and process economics. However, at present, such research is still limited in this area.[10]

Knowledge of equilibrium and mass transfer properties is of considerable importance in a wide variety of membrane preparation, process design and manufacturing operations involving polymers.[11,12] However, fundamental investigation of the solution and diffusion properties of solvents in a polymeric membrane is still limited for the above

system.[10] Accurate measurements of the activity and diffusion coefficients of small molecules in polymer or its solution are requested for the aforementioned purposes. Conventional methods for measuring them have relied on bulk equilibration and gravimetric sorption/desorption experiments.[13] In the last 20 years, inverse gas chromatography (IGC) has been developed as a fast and reliable technique for measurement of the activity and diffusion coefficients at infinite dilution. The activity and diffusion coefficient data at infinite dilution provide the most valuable information in terms of molecule-molecule interactions as compared with those in the finite solvent concentration region.[14] In the IGC method, by knowing compositions of the stationary phase, and the mobile phase, the interactions between the two phases are determined by analysis. Predominantly IGC have been used to determine the activity coefficient and the diffusion coefficient of the mobile phase in the stationary phase at infinite dilution. In the case of solvent/polymer system this can be done using a column packed with inert particles that had been coated with the polymer.[14]

The poly(ethylene glycol) (PEG) is a hydrophilic polymer membrane material, which was used extensively in the pervaporation processes for dehydration, desulfuration, and aromatic/aliphatic mixture separation.[15–19] However, there is little experimental data reported on the activity and diffusion properties of cyclohexanol and cyclohexanone in a PEG polymer.

In this work, a packed column IGC technique has been adopted for determining the infinite dilute activity and diffusion coefficients in PEG polymers. The retention time and peak area of solvents have been determined over a variety of flow rates at a constant temperature as well as over a variety of temperatures at a fixed flow rate. The *van Deemter* equation[20] has been applied in the data analysis to obtain the diffusion coefficients. The infinite dilute activity and diffusion coefficients of cyclohexane, cyclohexanol, and cyclohexanone in PEG and in crosslinked PEG have been studied at various temperatures. The effects of temperature and crosslinking modification of PEG on the infinite dilute activity and diffusion coefficients of solvents have been investigated. Those data would be useful in a study of the mechanism of small molecules transferring in PEG polymers and in the prediction of the separation results for the cyclohexane, cyclohexanol, and cyclohexanone mixture.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG) was purchased from ALDRICH (Japan). The average molecular weight of the PEG was 200,000. Maleic anhydride (99% content, gas chromatography grade) and trimethylamine (>98% content, gas chromatography grade) were purchased from China Medicine Group (Shanghai Chemical Reagent Corp.). Sodium bicarbonate, cyclohexane, cyclohexanol, and cyclohexanone were purchased from Beijing Chemistry Corp. of China and in gas chromatography grade with the purity of 99.5%. The supporter of Chromosorb-G, whose size was of 60–80 mesh (average particle diameter 2.667 $\times$ 10^{-4}m), was purchased from Shanghai No. 1 reagent manufactory of China. Ultra pure deionized water was prepared by the ultrafiltration membrane equipment. All chemicals were used without any further purification.

Preparation of packed column

For the systems of PEG, the PEG polymer was dissolved in water to prepare 1.6 wt % coating solution, which was coated onto the Chromosorb-G support particles by agitation and slow evaporation of the solvent to obtain a uniform polymer coating. The coated support particles dried under vacuum to constant weight and placed in a solvent-washed stainless steel tube [201-cm long, 3 mm-internal diameter (i.d.)], with the aid of a mechanical vibrator. The end of the tube was loosely plugged with steel wool.

For the systems of crosslinked PEG, PEG as prepolymer, maleic anhydride as crosslinking agent, and trimethylamine as catalyst were dissolved in water to prepare a coating solution. The concentrations of PEG, maleic anhydride, and trimethylamine were 1.6, 1.6, and 0.3 wt %, respectively. Then the coating solution was coated onto the Chromosorb-G supporter by vibrating and slow evaporation of the solvent to get a uniform polymer coating. The coated supporter particles dried under vacuum to constant weight, and were kept in a drying oven for 10 h at 353.15 K. After that, the supporter covered with polymer was dealt with 2% sodium bicarbonate solution, and then deionized water until the pH of the washing became neutral. Similar to PEG system, the supporter particles coated with crosslinked PEG dried under vacuum to constant weight and placed in a solvent-washed stainless steel tube (201-cm long, 3 mm i.d.), with the aid of a mechanical vibrator. The end of the tube was loosely plugged with steel wool. The experimental column parameters were presented in Table I, where d_p is the average thickness of the polymer on the support particles; w_p is the mass of the polymer coated on the support material; w_s is the mass of support material; and d_s is the average diameter of support particle. The masses of the polymer and of the support material were weighed with a precision $\pm$ 0.0001 g.

Polymer	w_p (g)	w_s (g)	$d_p \times 10^6$ (m)	$d_s \times 10^4$ (m)	Length (m)	i.d. (mm)	Aging time (h)
PEG	0.2657	5.0192	4.925	2.667	2.01	3.00	20
Crosslinked PEG	0.2526	4.796	7.725	2.667	2.01	3.00	20

In addition, the according PEG and crosslinked PEG membranes were prepared following the same preparation conditions and using the similar coating solutions.

Infrared spectroscopy

Fourier transform infrared (FTIR) spectra of the PEG and crosslinked PEG membranes were recorded using a Nicolet IR 560 spectrometer with horizontal ATR accessory equipped with a ZnSe crystal. IR spectra were continuously collected at a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1} for at least 32 of sample scans.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) of the PEG and crosslinked PEG membranes were performed on SEIKO DSC 6200 Calorimeter. The polymer sample was placed in a sealed pan, which was heated from 273 to 423 K at a heating rate of 10 K min^{-1}.

IGC measurements

Gas chromatograph used in this work was GC-14C (Shimadzu, Japan), equipped with a flame ionization detector (FID). Figure 1 is a schematic of the IGC unit.[21] Nitrogen was used as the carrier gas and a small pulse of the solvent (0.1 μL) was injected into the column using a 0.5 μL syringe. The carrier gas flowed directly to the column which was enclosed in the temperature controlled oven. The output of the column was measured with FID. The temperatures of the injection block and the detector were set about 50 K above the column temperature to avoid condensation in the injector and detector. Experiments were carried out at various temperatures ranging from 368.15 to 403.15 K. And the temperature of the column was maintained constant to within ±1.0%. The flow rate of carrier gas was measured by means of a soap bubble flow meter. The flow rate was set for a series of runs at a constant temperature and was allowed to stabilize for at least 20 min before any injections were made. In addition, six replicate experiments were done at various flow rates to ensure that the results were reproducible. The pressure drop across the column was measured using a highly accurate manometer with an accuracy of ±0.1% in the full scale at a constant flow rate. The

equilibrium behavior could be determined from the difference between the retention time of the pulse and the retention time of noninteracting gas. At a given temperature, the data of the retention times was taken as the mean of six individual measures. To obtain good data, one must be sure that there are no significant interactions between any exposed area of the solid support material and the solvent; the sizeable pressure drop through the column must be measured and accounted for; and there could be no effects from varying the size of the injection pulse or the carrier gas flow rate.

THEORY

Solution properties

The generalized equations relating the measured data to activity coefficients of solvent in polymer are given as follows[12]:

$$\Omega_{ip}^{\infty} = \gamma_{ip}^{\infty} \frac{M_p}{M_i} = \frac{273.15R}{v_g M_i} \frac{1}{\varphi_i^s p_i^s} \tag{1}$$

where Ω_{ip}^{∞} is the activity coefficient of solvent i in mass fraction scale, γ_{ip}^{∞} is the activity coefficient of solvent i in mole fraction scale, M_i and M_p are the molar mass of solvent i and polymer p, respectively, p_i^s is the saturated vapor pressure of the pure solvent i, φ_i^5 is the saturated fugacity coefficient of solvent i. The saturated vapor pressures of the solvents were calculated from the Antoine equation.[22] The saturated fugacity coefficients of the solvents were calculated according to the Soave equation of state[23]; the necessary critical properties and acentric factors
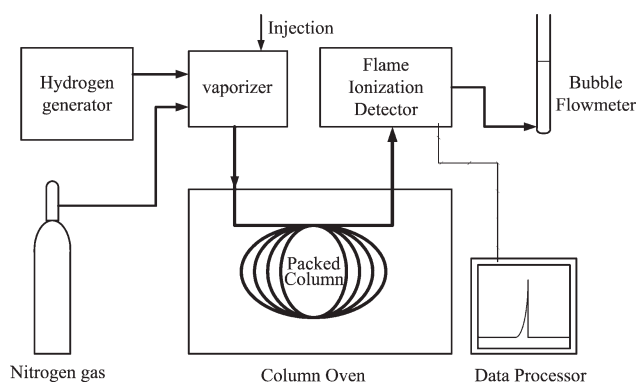

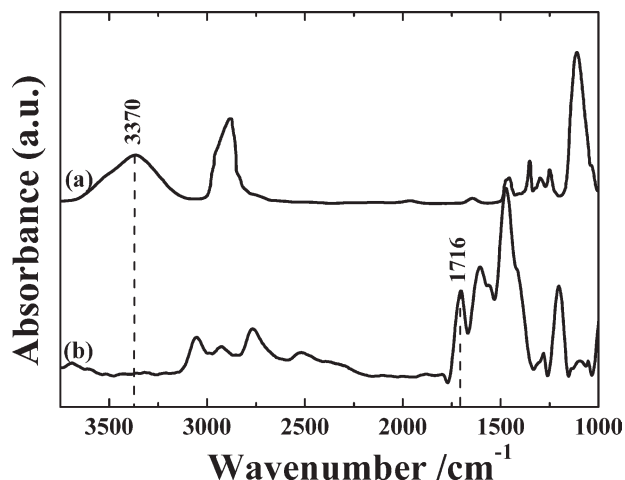**Figure 1** Schematic diagram of the IGC apparatus.

Figure 2 IR spectra of PEG (a) and crosslinked PEG (b) membranes.

were also taken from literature.[22] In Eq. (1), v_g is the specific retention volume measured at infinite dilution of the probe and can be estimated from the retention time at T_{fm} by using the following equation:

$$v_g = \frac{jF}{w_p} \frac{p_{fm} - p_w^s}{p_{fm}} \frac{273.15}{T_{fm}} (t_1 - t_a) \qquad (2)$$

where w_p is the mass of polymer on the support material packed in the column, t_1 the retention time of the solvent, t_a the dead time required for an inert gas to pass through the column, F the carrier gas volume flow measured by the soap bubble flowmeter at p_{fm} and T_{fm}, p_w^s the saturated vapor pressure of water at T_{fm}. In Eq. (2) j is the compressibility factor determined as follows,

$$j = \frac{3}{2} \cdot \frac{\left[\left(\frac{p_{in}}{p_{out}}\right)^2 - 1\right]}{\left[\left(\frac{p_{in}}{p_{out}}\right)^3 - 1\right]} \qquad (3)$$

where p_{in} and p_{out} are the inlet and outlet pressures of the column, respectively.

The partial molar enthalpy of sorption, $\Delta_s H$, is calculated from the following equation:

$$\Delta_s H = -R \frac{\partial \ln v_g}{\partial (1/T)} \qquad (4)$$

The infinite dilute molar excess enthalpy, $\Delta H_i^{E,\infty}$, is

$$\Delta H_i^{E,\infty} = R \frac{\partial \ln \Omega_{ip}^{\infty}}{\partial (1/T)} \qquad (5)$$

The molar enthalpy of vaporization to the ideal-gas state for the pure solvent, $\Delta_{vap}H^0$, is calculated as follows,

$$\Delta_{vap}H^0 = \Delta H_i^{E,\infty} - \Delta_s H \qquad (6)$$

The partial free energy of sorption, $\Delta_s G$, is calculated from the following equation:

$$\Delta_s G = -RT \ln\left[\frac{\rho_p j F(t_1 - t_a)}{w_p}\right] \qquad (7)$$

Here, ρ_p is the density of polymer. The entropy of sorption can be directly calculated by the thermodynamic relationship:

$$\Delta_s S = \frac{\Delta_s H - \Delta_s G}{T} \qquad (8)$$

Diffusion properties

According to the *van Deemter*'s model,[20] infinite dilute diffusion coefficient is obtained by the following equation:

$$D_{ip}^{\infty} = \frac{8d_p^2}{\pi^2 C} \cdot \frac{k}{(1+k)^2} \qquad (9)$$

where C is a parameter related to column characteristics, d_p is the average thickness of the polymer on the support particles and k is the so called partition ratio. d_p is determined from the equation as follows:

$$d_p = \frac{w_p \rho_s d_s}{6 \rho_p w_s} \qquad (10)$$

where w_p is the mass of the polymer coated on the support material; w_s is the mass of support material; ρ_p is the polymer density; ρ_s is the density of
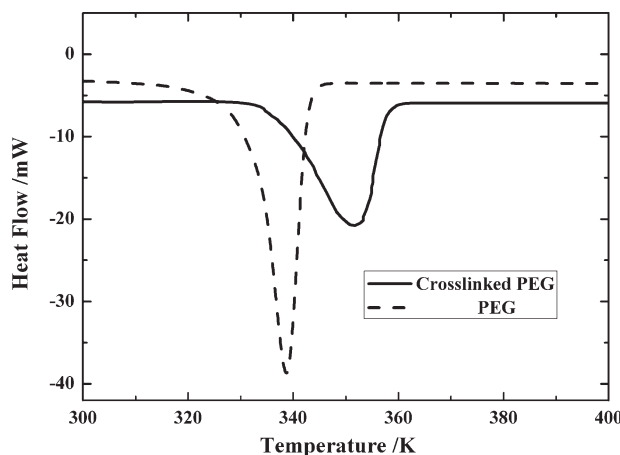

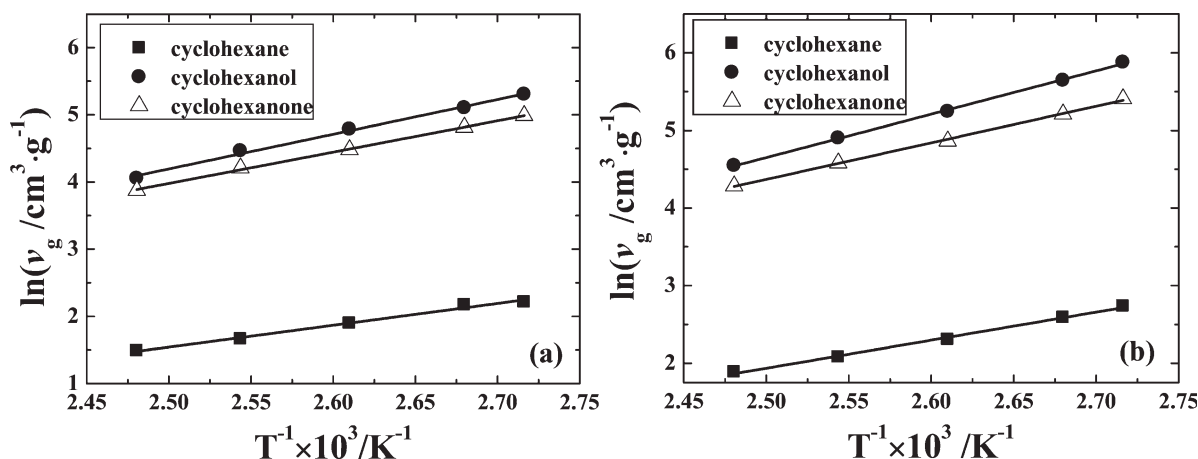**Figure 3** DSC thermograms of PEG and crosslinked PEG membranes.

Figure 4 Temperature dependence on the specific retention volume v_g, for (a) solvent/PEG system and (b) solvent/cross-linked PEG system.

support material; and d_s is the average diameter of support particle.

The partition ratio, k, is calculated from the equation as follows:

$$k = \frac{t_1 - t_a}{t_a} \qquad (11)$$

where t_1 and t_a are the retention times of solvent and unabsorbed material, such as air.

From Plate theory,[20] C in Eq. (6) is derived from the following equation

$$H = A + B/u + Cu \qquad (12)$$

where H is the plate height equivalent to a theoretical plate (HEPT); u, is the linear velocity of the carrier gas; and A, is a constant related to eddy diffusion; B is depended on the axial diffusion in the gas phase and on the tortuosity or structural factors in the column, and C is depended on, among other things, the solvent diffusion in the polymer phase.

H is calculated from the experimental eluted peak as follows:

$$H = \left(\frac{l}{5.54}\right)\left(\frac{t_{1/2}}{t_1}\right)^2 \qquad (13)$$

where l is the column length, $t_{1/2}$ is the full peak width at half maximum and t_1 is the retention time of solvent obtained at the maximum of the peak.

The linear velocity of the carrier gas u, is calculated from the expression:

$$u = \frac{jF}{\bar{a}} \cdot \frac{T_{col}}{T_{fm}} \qquad (14)$$

where T_{col} and T_{fm} are the temperature of the column and flow meter, respectively; $\bar{a}$ is the volume of gas phase per unit length and determined by dividing the retention volume of air by the column length.

These results may be used to determine diffusivity from experimental data as follows: small molecule

TABLE II
Infinite Dilute Activity Coefficients Ω_{ip}^{∞} of Solvents (i) in PEG and in Crosslinked PEG at Various Temperatures

Temperature (K)	$\Omega_{ip}^{\infty \, a}$						
	Cyclohexane			Cyclohexanol		Cyclohexanone	
	PEG	PEG[b]	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG
368.15	19.25 ± 0.54	18.89	11.45 ± 0.42	13.89 ± 0.32	7.82 ± 0.27	3.26 ± 0.04	2.14 ± 0.03
373.15	17.55 ± 0.64	18.87	11.57 ± 0.28	13.28 ± 0.40	7.72 ± 0.25	3.22 ± 0.08	2.17 ± 0.06
383.15	17.89 ± 0.54	17.74	11.89 ± 0.20	11.52 ± 0.42	7.31 ± 0.28	3.17 ± 0.08	2.17 ± 0.08
393.15	17.71 ± 0.56	17.01	11.65 ± 0.41	10.47 ± 0.36	6.76 ± 0.22	3.01 ± 0.12	2.07 ± 0.06
403.15	16.77 ± 0.68	–	12.05 ± 0.32	10.74 ± 0.50	6.56 ± 0.14	3.09 ± 0.13	2.05 ± 0.10

[a] In this work, infinite dilute activity coefficients are taken as the mean of six individual measures with an estimated error taken as the standard deviation of this mean value..
[b] Data from the literature.[30]

TABLE III
Infinite Dilute Selectivities S_{ij}^{∞} and Capacities k_j^{∞} for PEG and Crosslinked PEG at Various Temperatures

| Temperature (K) | i—cyclohexane; j—cyclohexanol | | | | i—cyclohexane; j—cyclohexanone | | | |
| | S_{ij}^{∞} | | k_j^{∞} | | S_{ij}^{∞} | | k_j^{∞} | |
	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG
368.15	1.39	1.46	0.07	0.13	5.90	5.35	0.31	0.47
373.15	1.32	1.50	0.08	0.13	5.45	5.33	0.31	0.46
383.15	1.55	1.63	0.09	0.14	5.64	5.48	0.32	0.46
393.15	1.69	1.72	0.10	0.15	5.88	5.63	0.33	0.48
403.15	1.56	1.84	0.09	0.15	5.43	5.88	0.32	0.49

elution curves are obtained for a range of flow rates. From the measurements of peak width, a plot of H versus u is prepared. At sufficiently high flow rates, the term B/u is small in relation to $A+Cu$, and the second term on the right-hand side of Eq. (12) become negligible and the plot of H versus u will yield a straight line with a slope C. If the partition ratio k and the film thickness d_p are determined, the infinite dilute diffusion coefficients of solvents in polymers D_{ip}^{∞} can be obtained from C with Eq. (9)

In general, the temperature dependence of the diffusion coefficient is given by Arrhenius equation:

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (15)$$

where D_0 is the pre-exponential factor of the diffusion process independent from the temperature and E_D is the activation energy for a diffusing compound in a given polymer matrix to escape from its present surroundings and move into an adjacent different surrounding.

RESULTS AND DISCUSSION

FTIR spectra

As shown in Figure 2, compared to the PEG membrane, the spectra of crosslinked PEG membrane displayed a new absorbance signal at 1716 cm^{-1} (C=O stretching) and showed the decreasing intensity at about 3370 cm^{-1} (OH stretching). These changes were the evidences of crosslinking reaction of PEG.[24–27]

DSC thermogram

DSC thermograms of the PEG and crosslinked PEG membranes are illustrated in Figure 3. Glass transition in crosslinked PEG occurred at 351.7 K and in PEG at 338.6 K. Crosslinking reaction in PEG polymer reduced the mobility of polymer chains by hindering their rotations and increasing their stiffness, which induced higher glass transition temperature of crosslinked PEG than PEG. To characterizing the crosslink density, number average molecular weight of the polymer chains between the crosslink points, $\overline{M_c}$ can be calculated with the help of Nielsen equation as follows,[28]

$$\overline{M_c} = \frac{3.9 \times 10^4}{T_g - T_{g0}} \quad (16)$$

where T_g is the glass transition temperature of crosslinked PEG, T_{g0} is the glass transition temperature of PEG. Therefore, for crosslinked PEG, $\overline{M_c}$ is approximately equal to 3×10^3 g mol^{-1}.

Solution property results

The IGC was used to measure the infinite dilute activity of cyclohexane, cyclohexanol, and cyclohexanone in PEG and crosslinked PEG at various temperatures. Measurements for each solvent/polymer system were obtained at several carrier flow rates.

TABLE IV
Partial Molar Enthalpy of Sorption ($\Delta_s H$), Partial Molar Excess Enthalpy at Infinite Dilution ($\Delta H_i^{E,\infty}$), and Molar Enthalpy of Vaporization ($\Delta_{vap}H^0$) of Solvents in PEG and Crosslinked PEG

| Solvent | $\Delta_s H$ (kJ mol^{-1}) | | $\Delta H_i^{E,\infty}$ (kJ mol^{-1}) | | $\Delta_{vap}H^0$ (kJ mol^{-1}) | |
	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG
Cyclohexane	−27.0	−30.1	3.43	−1.47	30.5	28.6
Cyclohexane[a]	−26.2[30]; −21.9[33]	–	3.38[28]	–	30.5[30]; 29.4[33]	–
Cyclohexanol	−43.0	−46.5	10.2	6.68	53.2	53.2
Cyclohexanone	−38.8	−39.2	2.38	1.91	41.2	41.1

[a] Data from the literature.

TABLE V
Partial Molar Free Energy of Sorption ($\Delta_s G$), and Partial Molar Entropy of Sorption ($\Delta_s S$) at Various Temperatures in PEG and Crosslinked PEG

Temperature (K)	$\Delta_s G$ (kJ mol^{-1})						$\Delta_s S \times 10^2$ (kJ mol^{-1} K^{-1})					
	Cyclohexane		Cyclohexanol		Cyclohexanone		Cyclohexane		Cyclohexanol		Cyclohexanone	
	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG
368.15	−8.27	−9.21	−17.3	−18.9	−16.3	−17.5	−5.09	−5.68	−6.99	−7.49	−6.11	−5.90
373.15	−7.64	−9.13	−16.9	−18.6	−16.0	−17.2	−5.19	−5.62	−6.99	−7.48	−6.10	−5.89
383.15	−7.21	−7.98	−16.4	−17.7	−15.4	−16.4	−5.16	−5.77	−6.95	−7.53	−6.10	−5.94
393.15	−6.33	−7.55	−15.7	−16.8	−14.9	−15.8	−5.26	−5.74	−6.95	−7.55	−6.08	−5.95
403.15	−5.39	−7.21	−14.6	−16.2	−14.2	−15.3	−5.36	−5.68	−7.04	−7.51	−6.10	−5.94

Equation (2) was used to estimate the specific retention volume v_g. The relationship between v_g and temperature is shown in Figure 4. It is indicated that there were linear correlations between $\ln v_g$ and $1/T$ for all the above solvent/polymer systems. Such linear correlations implied that no phase transition occurred in the covered temperature range. As was expected, the v_g values decreased with an increase of temperature as was observed for other polymers.[29]

As shown in Table II, Ω_{ip}^∞ of cyclohexane, cyclohexanol and cyclohexanone in PEG and in crosslinked PEG decreased with the rising temperature. Moreover, Ω_{ip}^∞ of solvents in the same polymer at a constant temperature clearly decreased in the order: cyclohexane, cyclohexanol, and cyclohexanone. Generally, the smallest values of Ω_{ip}^∞ indicate the stronger interactions between polymer and solvent. The hydroxyl group in cyclohexanol and the ketone group in cyclohexanone can interact more strongly with the polar parts of the polymer. Cyclohexanone and cyclohexnanol revealed smaller values of Ω_{ip}^∞ than cyclohexane. The results also show that ketone interacts with polymer more strongly than hydroxyl. The infinite dilute activity coefficients of solvents in crosslinked PEG were smaller than that in PEG, which was attributed to enhanced polar interactions due to the additional polar groups of crosslinking reagent in the crosslinked PEG. The infinite dilute activity coefficients of cyclohexane in PEG were compared with the data reported in the literature. As shown in Table II, it was manifested that the data obtained in this work were of agreement with that in the literature.[30–33]

The infinite dilute selectivity $S_{ij}^\infty = \Omega_{ip}^\infty / \Omega_{jp}^\infty$ and the infinite dilute capacity $k_j^\infty = 1/\Omega_{jp}^\infty$ can be calculated from the experimental values of Ω_{ip}^∞ for different separation problems. From the analysis of selectivity and capacity at various temperatures presented in Table III, we can conclude that selectivities S_{ij}^∞ for separating cyclohexane/cyclohexanol by crosslinked PEG were quite higher than that of PEG, and the capacities of cyclohexanol in crosslinked PEG were higher than that in PEG at various temperatures. The selectivities S_{ij}^∞ for separating cyclohexane/cyclohexanone by crosslinked PEG and PEG were similar; however, the capacities of cyclohexanone in crosslinked PEG were higher than PEG at various temperatures. Those comparisons showed the possibility of using crosslinked PEG as an
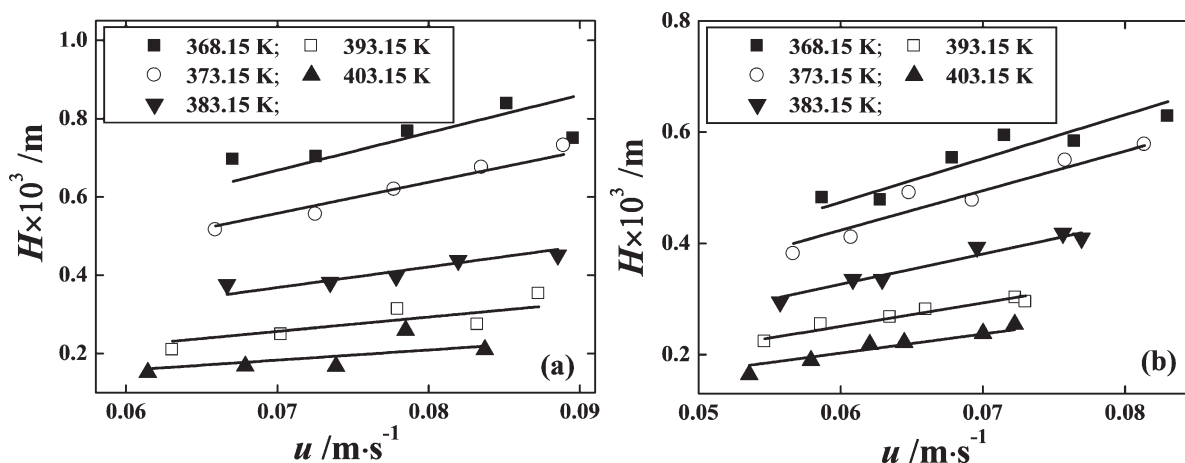

Figure 5 Relationship between the flow rate u and the plate height H of cyclohexane in PEG (a) and crosslinked PEG (b) at various temperatures.
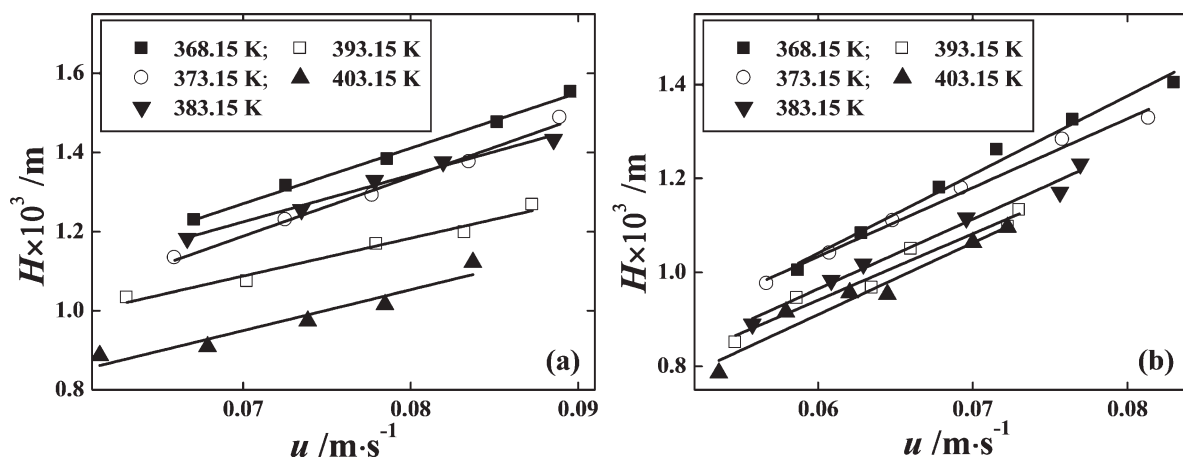
Figure 6 Relationship between the flow rate u and the plate height H of cyclohexanol in PEG (a) and crosslinked PEG (b) at various temperatures.

appropriate membrane material for the pervaporation separation of cyclohexane/cyclohexanol/cyclohexanone mixture.

The partial molar enthalpy of sorption, $\Delta_s H$, the molar excess enthalpy, $\Delta H_i^{E,\infty}$, and the molar enthalpy of vaporization to the ideal-gas state for the pure solutes, $\Delta_{vap} H^0$, were calculated following eqs. (4)–(6) and listed in Table IV. As summarized in Table IV, $\Delta_s H$, and $\Delta H_i^{E,\infty}$ of cyclohexane, cyclohexanol and cyclohexanone in crosslinked PEG were smaller than that in PEG. $\Delta_{vap} H^0$ of cyclohexane, cyclohexanol and cyclohexanone in PEG were almost the same as that in crosslinked PEG. Actually, $\Delta_{vap} H^0$ presented in this work were very similar to the molar enthalpy of vaporization to the ideal-gas state, measured traditionally by the calorimetric method or by the vapor pressure.[30–34]

The IGC method obtains another way to determine the driving force of solvent molecule sorption in the polymer. The results of the partial molar enthalpy of sorption, $\Delta_s H$, the partial molar free energy

of sorption, $\Delta_s G$, and partial molar entropy of sorption, $\Delta_s S$, calculated following eqs. (4), (7), and (8) respectively, were listed in Tables IV and V. As presented in Tables IV and V, the values of $\Delta_s H$, $\Delta_s G$, and $\Delta_s S$ are all negative in this work. It implies that cyclohexane, cyclohexanol, and cyclohexanone sorption in PEG and crosslinked PEG are all enthalpically driven in the whole experimental range. In addition, as shown in Table V, $\Delta_s S$ values do not change much with temperature that agrees with the general thinking in thermodynamics.

Diffusion property results

The plots of plate height, H, versus linear velocity, u, were constructed for each solvent in PEG and crosslinked PEG at different temperatures. Figures 5–7 illustrates the linear relationships of H with u for cyclohexane, cyclohexanol, and cyclohexanone in PEG and crosslinked PEG in the temperature range of 368.15–403.15 K. The parameters C at various
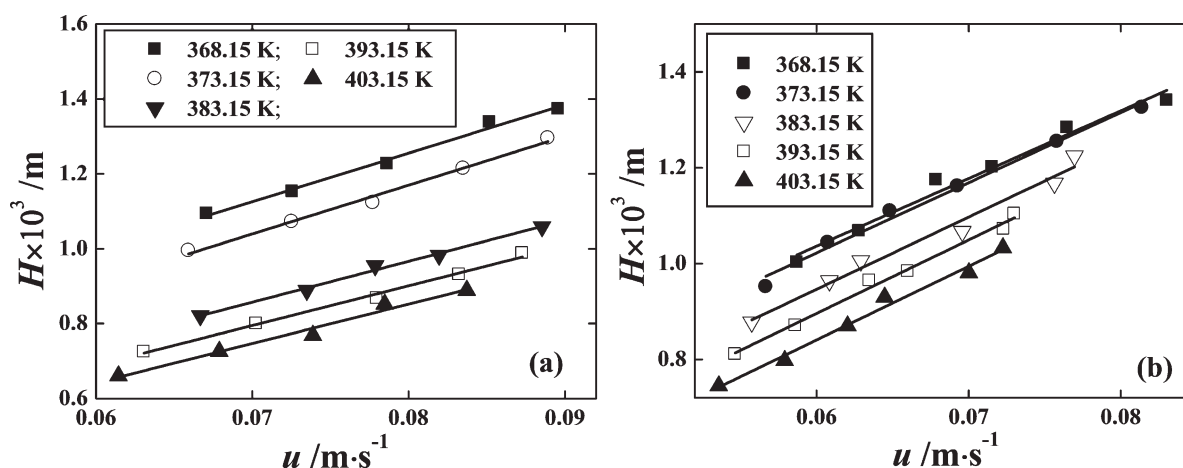

Figure 7 Relationship between the flow rate u and the plate height H of cyclohexanone in PEG (a) and crosslinked PEG (b) at various temperatures.

<div align="center">

TABLE VI
Infinite Dilute Diffusion Coefficients D_{ip}^{∞} of Solvents in PEG and Crosslinked PEG at Various Temperatures

</div>

	$D_{ip}^{\infty} \times 10^{10}$ (m^2 s^{-1})					
	Cyclohexane		Cyclohexanol		Cyclohexanone	
Temperature (K)	PEG	Crosslinked PEG	PEG	Crosslinked PEG	PEG	Crosslinked PEG
368.15	2.93 ± 0.16	2.72 ± 0.10	2.10 ± 0.08	0.789 ± 0.019	2.72 ± 0.14	1.30 ± 0.04
373.15	3.15 ± 0.16	2.82 ± 0.12	2.28 ± 0.06	1.03 ± 0.04	2.94 ± 0.16	1.37 ± 0.04
383.15	3.94 ± 0.17	3.17 ± 0.10	3.27 ± 0.08	1.30 ± 0.04	4.00 ± 0.11	1.56 ± 0.04
393.15	4.93 ± 0.26	3.55 ± 0.14	4.16 ± 0.22	1.64 ± 0.08	4.42 ± 0.12	1.73 ± 0.05
403.15	5.75 ± 0.14	3.73 ± 0.10	5.08 ± 0.22	1.73 ± 0.06	5.39 ± 0.22	1.85 ± 0.10

[a] Infinite dilute diffusion coefficients are taken as the mean of six individual measures with an estimated error taken as the standard deviation of this mean value.

temperatures were determined from the slope of the lines. These values were then used in Eq. (9) for estimating the diffusion coefficients in polymer phase. The infinite dilute diffusion coefficients D_{ip}^{∞} of solvents in polymers were listed in Table VI.

As presented in Table VI, it is seen that the diffusion coefficients of solvents in polymers increased with the increasing temperature in all the systems. Generally, the temperature plays a very important role on the diffusion process. The mobility of the solvents increases and the polymer chains themselves are more flexible at higher temperatures. Therefore, the solvents can have better ability to diffuse through the polymer matrix when the temperature is higher. Moreover, D_{ip}^{∞} of solvents in polymers at a constant temperature clearly decreased in the order: cyclohexane, cyclohexanone, and cyclohexanol. The order of the relative magnitude for D_{ip}^{∞} of those solvents could be correlated with their collision diameters.[35,36] The collision diameter of solvent molecule can be estimated from the corresponding critical volume using the following equation[35]:

$$\sigma = 0.561(V_c^{1/3})^{5/4} \tag{16}$$

The critical volume V_c of cyclohexane, cyclohexanol, and cyclohexanone is 308, 322, and 311 cm^3 mol^{-1}, respectively,.[22] According to Eq. (16), the collision diameter of cyclohexane, cyclohexanol, and cyclohexanone is 0.611, 0.622, and 0.613 nm, respectively. Cyclohexane has the smallest collision diameter and is the highest in D_{ip}^{∞}, and the reverse is true for cyclohexanol. Because of the compact shape of its molecule structure, cyclohexane was the fastest moving solvent within the polymer among the triad. Furthermore, as presented in Table VI, it is indicated that the diffusion coefficients of solvents in crosslinked PEG were smaller than that in PEG at various temperatures. Crosslinking reaction influences the structure of PEG, since the chemical connections occur between polymer molecules and the reticular spatial structure forms, which weakens the mobility of polymer molecule and chain segments, and so lessens free volume. The above reason counted for the smaller D_{ip}^{∞} in crosslinked PEG.

The temperature dependence of D^{∞} was presented by Arrhenius equation as Eq. (15). The plots of lnD^{∞} versus $1/T$ are shown in Figures 8 and 9. It is indicated that the correlations of lnD^{∞} versus $1/T$
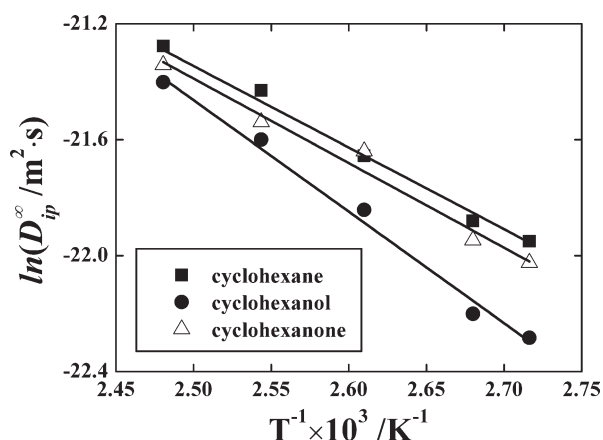

Figure 8 Relationship between the infinite dilute diffusion coefficient of solvents (cyclohexane, cyclohexanol, and cyclohexanone) and temperatures in PEG.
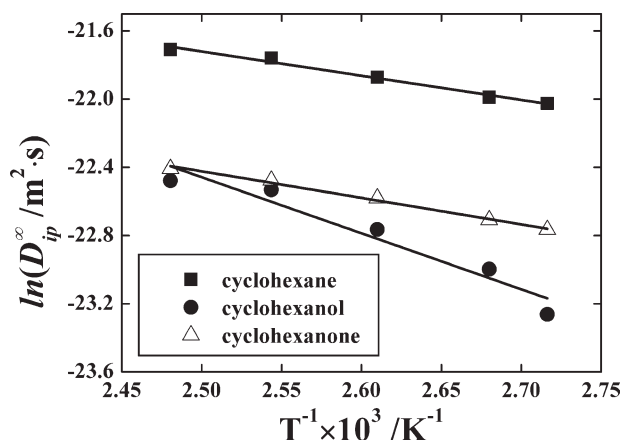

Figure 9 Relationship between the infinite dilute diffusion coefficient of solvents (cyclohexane, cyclohexanol, and cyclohexanone) and temperatures in crosslinked PEG.

TABLE VII
Preexponential Factor and Activation Energy for Solvent Diffusion at Infinite Dilution in PEG and in Crosslinked PEG

	PEG			Crosslinked PEG		
	Cyclohexane	Cyclohexanol	Cyclohexanone	Cyclohexane	Cyclohexanol	Cyclohexanone
D_0 (m^2 s^{-1})	6.10×10^{-7}	7.16×10^{-6}	7.55×10^{-7}	1.29×10^{-8}	6.52×10^{-7}	8.95×10^{-9}
E_D (kJ mol^{-1})	23.40	31.98	24.25	11.82	27.32	12.94

were linear. The activation energies and pre-exponential factors were calculated from the slopes and intercepts of fitted lines and shown in Table VII. It is seen from Table VII that the diffusion activation energy was positive, that was to say, the process of solvent molecule diffusion in polymer was endothermic.

The activation energy of diffusion is the most dominant parameter in the diffusion process; it is the energy needed to enable the dissolved molecule to jump into another "hole." It is clear that larger holes are necessary for the diffusion of larger solvent molecules; hence, the activation energy will be larger for the diffusion of bigger molecules and the diffusion coefficient will be smaller. Accordingly, smaller collision diameter of solvent molecule caused smaller activation energy. Cyclohexane has the smallest collision diameter and is the smallest in E_D, and the reverse is true for cyclohexanol. Apparent activation energies of solvent diffusion in crosslinked PEG measured in the present work were lower than that in PEG, supporting the published results for other polymers.[37,38]

CONCLUSIONS

The selective oxidation of cyclohexane to cyclohexanol, and cyclohexanone is a very important reaction for commercial application. Membrane separation integrated with the oxidation reaction can lead to quantum improvements in reaction efficiencies, yields, and process economics. Experimental study of solution and diffusion properties is of considerable importance, but limited in this area. The solution and diffusion properties of cyclohexane, cyclohexanol and cyclohexanone at infinite dilution in PEG and in crosslinked PEG were investigated at the temperature ranging from 368.15 to 403.15 K by IGC technique. The infinite dilute activity coefficient (Ω_{ip}^{∞}) and diffusion coefficient (D_{ip}^{∞}) were determined for the above solvent/polymer systems at various temperatures. Ω_{ip}^{∞} of cyclohexane, cyclohexanol, and cyclohexanone in PEG and in crosslinked PEG decreased with the rising temperature. Moreover, Ω_{ip}^{∞} of solvents in polymers at a constant temperature clearly decreased in the order: cyclohexane, cyclohexanol, and cyclohexanone; and Ω_{ip}^{∞} of sol-

vents in crosslinked PEG were smaller than that in PEG. The results of the infinite dilute selectivity and capacity suggested that crosslinked PEG would be a promising membrane material for the separation of cyclohexane, cyclohexanol, and cyclohexanone mixture. Based on IGC measurement data, the thermodynamic functions were achieved. The thermodynamic study implied that the solvent sorptions in the polymers are all enthalpically driven in the experimental range. These data are very important to better understand the nature of the polymers and are helpful in expanding the thermodynamic models. The experimental data shows the following relationships of D_{ip}^{∞} with temperature: for the certain solvent and polymer, D_{ip}^{∞} increased with the rising of temperature. Cyclohexane has the smallest collision diameter and was the highest in D_{ip}^{∞} and the reverse was true for cyclohexanol. D_{ip}^{∞} of solvents in crosslinked PEG was smaller than that in PEG at various temperatures. Meanwhile, the observed solvent diffusivity data for six solvent/polymer systems were also correlated using Arrhenius equation, and the pre-exponential factors and activation energies were obtained. It should be expected that the data in this work could be useful to the polymeric membrane material selection, to the polymeric membrane preparation and to the separation for cyclohexane, cyclohexanol, and cyclohexanone mixture.

NOMENCLATURE

$\bar{a}$	volume of gas phase per unit length
C	parameter related to column characteristics
d	thickness or diameter, as mentioned, m
E_D	activation energy, kJ mol^{-1}
D	diffusion coefficient, m^2 s^{-1}
D_0	pre-exponential factor, m^2 s^{-1}
F	carrier gas volume flow, cm^3 min^{-1}
G	free energy, kJ mol^{-1}
H	enthalpy, kJ mol^{-1}; or plate height, m as mentioned
j	compressibility factor
k	capacity or partition ratio as mentioned
l	column length
M	molar mass, g mol^{-1}
p	pressure, Pa

R	gas constant, equal to 8.3145 J mol^{-1} K^{-1}
S	selectivitiy, or entropy, kJ·mol^{-1}·K^{-1}, as mentioned
T	temperature, K
t	time, s
$t_{1/2}$	full peak width at half maximum, s
t_1	retention time of the solvent, s
t_a	dead time, s
u	linear velocity of the carrier gas, m s^{-1}
v_g	specific retention volume, cm^3 g^{-1}
V	volume, cm^3
w	mass fraction

Greek letters

γ	activity coefficient based on molar fraction
ρ	density, g m^{-3}
σ	collision diameter, nm
ϕ	fugacity coefficient
Ω	activity coefficient based on mass fraction

Superscripts

0	ideal-gas state
E	Excess
∞	infinite dilute
s	saturated

Subscripts

c	critical state
col	column
fm	Flowmeter
i	solvent i
in	inlet
j	solvent j
p	Polymer
out	Outlet
s	supporter or sorption
vap	Vaporization
w	Water

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