Infinite Dilute Activity and Diffusion Coefficients in Polymers by Inverse Gas Chromatography

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The infinite dilute activity and diffusion coefficients of solvents in poly(vinyl alcohol) and cross-linked poly(vinyl alcohol) are determined by using inverse gas chromatography technique with a packed column. Experimental results for water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 3-methyl-1-butanol in poly(vinyl alcohol); for water, methanol, and ethanol in cross-linked poly(vinyl alcohol) at different temperatures are presented. The van Deemter equation is used to obtain diffusion coefficients of solvents from the variation of chromatographic peak under the different flow rates of carrier gas. The interdependence on the infinite dilute diffusion coefficient and temperature follows Arrhenius equation well. Diffusion constant and activation energy are obtained from the Arrhenius equation.

Introduction

Knowledge of equilibrium and mass transfer properties is of considerable importance in a wide variety of manufacturing operations involving polymers, such as polymerization, devolatilization, vacuum/gas stripping and drying.[1−4] Accurate measurements of the activity and diffusion coefficients of solvents in polymer melts or solutions are requested. Conventional methods for measuring them have relied on bulk equilibration and gravimetric sorption/desorption experiments.[5] These techniques, however, become very difficult to apply to the polymer + solvent systems when the solvent is presented in vanishingly small amounts or at temperatures in the vicinity of or below the glass transition temperature. Moreover, the experimental time may become very long when the diffusion coefficient is small. On the other hand, in the last 20 years, inverse gas chromatography (IGC) had been developed as a fast and reliable technique for the measurement of the activity and diffusion coefficients, particularly in the highly polymer concentration region.[5] This region is critically interesting in the polymer industry, particularly in the manufacturing of polymer films and coating/drying operations. Furthermore, the increasingly more demanding environmental and health criteria regarding the volatile residuals in the polymer products have induced an increased interest in activity and diffusion coefficients at infinite dilution for volatile solvents in polymer melts. The data of activity and diffusion coefficients at infinite dilution provide the most valuable information in terms of molecule−molecule interactions as compared to those in the finite solvent concentration region. In the IGC method, the compositions of the stationary phase and the mobile phase are known. The interactions between the two phases are determined by analysis. In the case of polymer+solvent systems this can be done using a column packed with inert particles that had been coated with the polymer.

Poly(vinyl alcohol) (PVA) is a hydrophilic polymer membrane material, which is used extensively in the pervaporation process for dehydration.[6−8] However, there is little experimental data reported on the infinite dilute activity and diffusion coefficients of solvents in a PVA polymer.

In this work, a packed column IGC technique is adopted for determining the activity coefficients and diffusion coefficients of several solvents in polymers. The retention time and peak area of solvents are 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 infinite dilute activity and diffusion coefficients of solvents in PVA and cross-linked PVA are reported. Those data will be useful in a study of the mechanism of small molecules transferring in PVA polymer and will avail in the prediction of the separation results for various mixtures.

Experimental Section

Materials. Poly(vinyl alcohol) (PVA) was purchased from Kuraray Co. Ltd. The average molecular weight and saponification of the PVA were 77 000 and 98.06 %, respectively. Maleic acid (99 % content, gas chromatography grade), sodium bicarbonate (99 % content, gas chromatography grade), and concentrated sulfuric acid (98 % content, gas chromatography grade, called H_2SO_4 hereafter) were purchased from Beijing Second Chemistry Company of China. Methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1- pentanol, and 3-methyl-1-butanol were obtained as gas chromatography grade reagents from Beijing Beihua Fine Chemicals Company of China. Ultrapure deionized water was used. All chemicals were used without any further purification.

Preparation of Packed Column. Chromosorb-G, 60−80 mesh size, was purchased from Shanghai No. 1 reagent manufactory of China. For the systems of PVA, the PVA polymer was dissolved in water to prepare the coating solution, which was coated onto the Chromosorb-G support particles by agitation and slow evaporation of the solvent to obtain a uniform polymer

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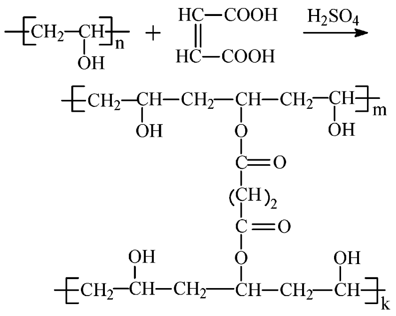
coating. The coated support particles were dried under vacuum to constant mass and then placed in a solvent-washed 200 cm long, 3 mm i.d. stainless steel tube, with the aid of a mechanical vibrator. The end of the tube was loosely plugged with steel wool.

For the systems of cross-linked PVA, a coating solution was prepared by dissolving PVA prepolymer, maleic acid as cross-linking agent and a catalytic quantity of H_2SO_4 in water. Then the coating solution with the theoretical cross-linking degree of 2 % denoted as cross-linked PVA was coated onto the Chromosorb-G support material by vibrating and slow evaporation of the solvent to get a uniform polymer coating. The theoretical cross-linking degree (Tcd) of cross-linked PVA is calculated as follows:

$$Tcd = \frac{2M_3\cdot m_4}{0.9806m_2\cdot M_4} \qquad (1)$$

where M_4 and M_3 are the molecular weight of maleic acid and the monomer of PVA respectively; m_4 and m_2 are the mass of maleic acid and PVA used, respectively. PVA reacted with maleic acid under H_2SO_4 catalysis, as shown in eq 2, and the hydroxyl group could condense into an ester group with the elimination of water.



$$\left[CH_2-\underset{OH}{CH}\right]_n + \begin{matrix}HC-COOH\\ \|\\ HC-COOH\end{matrix} \xrightarrow{H_2SO_4}$$

$$\begin{matrix}\left[CH_2-\underset{OH}{CH}-CH_2-CH-CH_2-\underset{OH}{CH}\right]_m\\ |\\ O\\ |\\ C=O\\ |\\ (CH)_2\\ |\\ C=O\\ |\\ O\\ |\\ \left[CH_2-\overset{OH}{CH}-CH_2-CH-CH_2-\overset{OH}{CH}\right]_k\end{matrix} + H_2O \qquad (2)$$

The coated support particles were dried under vacuum to constant mass and were kept in a drying oven for the cross-linking reaction. After the cross-linking reaction, the H_2SO_4 and unreacted maleic acid were rinsed off with an aqueous solution dissolved 2 % mass fraction of sodium bicarbonate. The support material was then washed with water until the *p*H value of the runoff solution was close to 7. The support particles were dried under vacuum to constant mass and then placed in a solvent-washed 200 cm long, 3 mm i.d. stainless steel tube, with the aid of a mechanical vibrator. The end of the tube is loosely plugged with steel wool.

Apparatus and Procedure. The gas chromatograph SP-6800A (Shandong Lunan's Ruihong Chemical Co.) is equipped with a thermal conductivity detector (TCD). Pure hydrogen was used as the carrier gas in all experiments. 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.

Figure 1 is a schematic of an IGC unit.[10] The term inverse relates to the fact that chromatography is performed in an unusual way. Commonly, chromatography is applied for the separation and possible identification of the components of a given mixture. Generally, limited attention is paid to the chromatographic phase that fills the column as long as it operates properly. In IGC, the situation is exactly the "inverse" because one becomes interested in the chromatographic support and in order to characterize it one injects solutes of known properties.[11]

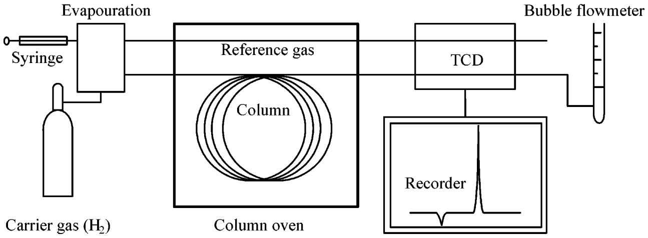


Figure 1. Schematic diagram of the IGC apparatus.

The carrier gas flowed directly to the reference side of the detector and to the column that was enclosed in the temperature controlled oven. A small pulse of the solvent was injected into the column. The solvent peak at the exit was measured with a thermal conductivity detector. From the difference between the retention time of the pulse and the retention time of a noninteracting gas, the equilibrium behavior could be determined. To obtain good data, one must be sure that there were no significant interactions between any exposed area of the solid support material and the solvent; the sizable pressure drop through the column must be measured and accounted for; and there should be no effects from varying the size of the injection pulse or the carrier gas flow rate.

The flow rate of carrier gas was measured by means of a soap bubble flowmeter. Measurements were preformed over a wide range of flow rate at a constant temperature. In addition, replicated experiments were done at each flow rate to ensure that the results were reproducible at each fixed set of conditions. The pressure drop across the column was measured using a highly accurate manometer at each flow rate.

Theory

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

$$\Omega_1^{\infty} = \gamma_1^{\infty}\frac{M_2}{M_1} = \frac{273.15R}{v_g^{0}M_1}\frac{1}{\varphi_1^{s}P_1^{s}} \qquad (3)$$

where Ω_1^∞ is the activity coefficient of solvent in mass fraction scale, γ_1^∞ is the activity coefficient of solvent in mole fraction scale, R is the gas constant, M_1 the molar mass of solvent, P_1^s is the saturated vapor pressure of the pure solvent, φ_1^s is the saturated fugacity coefficients of the solvents. The saturated vapor pressures (P_1^s) of the solvents were calculated from the Antoine constants taken from the Dortmund Data Bank (DDB). The saturated fugacity coefficients of the solvents φ_1^s were calculated according to the Soave equation of state;[13] the necessary critical properties and acentric factors were also taken from DDB. In eq 3, v_g^0 is the retention volume per gram of polymer phase, measured at 273.15K, at infinite dilution of the probe and can be estimated from the retention time at temperature (T_{fm}) by using the following equation:

$$v_g^{0} = \frac{jF}{w_2}\frac{P_{fm} - P_w^{s}}{P_{fm}}\frac{273.15}{T_{fm}}(t_1 - t_a) \qquad (4)$$

where w_2 is the mass of polymer on the support material packed in the column, t_1 is the retention time of the solvent, t_a is the dead time required for an inert gas to pass through the column, F is the carrier gas volume flow measured by the soap bubble flowmeter at the pressure (P_{fm}) and temperature (T_{fm}), P_w^s is the saturated vapor pressure of water at T_{fm}. In eq 4, j is the compressibility factor determined from

$$j = \frac{3}{2}\frac{\left[\left(\frac{P_i}{P_o}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_o}\right)^3 - 1\right]} \tag{5}$$

where P_i and P_o are the inlet and outlet pressures of the column, respectively. Therefore, at each temperature and velocity of carrier gas, the compressibility factor can be determined directly from the measured data of P_o and P_i.

Diffusion Coefficient. According to the van Deemter's model,[9] infinite dilute diffusion coefficient can be obtained by the following equation:

$$D_{12}^{\infty} = \frac{8{d_2}^2}{\pi^2 C} \cdot \frac{k}{(1+k)^2} \tag{6}$$

where C is a parameter related to column characteristics, d_2 is the average thickness of the polymer on the support particles, and k is the so-called partition ratio. d_2 is determined from the equation as follows:

$$d_2 = \frac{w_2 \rho_5 d_5}{6 \rho_2 w_5} \tag{7}$$

where w_2 is the mass of the polymer coated on the support material; w_5 is the mass of support material; ρ_2 is the polymer density; ρ_5 is the density of support material; and d_5 is the average diameter of support particle.

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

$$k = \frac{t_1 - t_a}{t_a} \tag{8}$$

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

From Plate theory,[9] C in eq 6 is derived from the following equation:

$$H = A + B/u + Cu \tag{9}$$

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

H is calculated from the experimental eluted peak as follows:[14]

$$H = \left(\frac{l}{5.54}\right)\left(\frac{t_{1/2}}{t_1}\right)^2 \tag{10}$$

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:

$$u = \frac{jF}{\bar{a}}\frac{T_{col}}{T_{fm}} \tag{11}$$

where T_{col} and T_{fm} are the temperature of the column and flowmeter, 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.

Table 1. Infinite Dilute Activity Coefficient (Ω_1^{∞}) of Solvents in PVA at Different Temperatures[a]

	Ω_1^{∞}								
T/K	H_2O	C_1	C_2	1-C_3	2-C_3	1-C_4	2-C_4	1-C_5	iC_5
373.15	23.15	27.89							
378.15	23.85	26.65		81.26					
383.15	24.52	24.48							
388.15	24.52	23.32	38.61	53.22	137.69	52.26			
393.15	23.09	22.56	37.92		123.39		75.11	44.52	54.37
398.15		22.08	37.23	41.59	116.45	45.12	70.27	40.84	50.95
403.15			35.89	39.12	109.91	39.31	64.68	38.68	47.45
408.15			34.92	38.44	101.07	37.11	62.97	37.59	42.94
413.15				37.84	93.31	36.65	61.13	36.21	37.73
418.15				37.29	85.1	35.77	59.89	35.12	36.82
423.15				36.83	77.62	35.26	58.82	34.32	36.37
428.15				36.18	71.75	34.81	57.94	33.58	35.90

[a] H_2O, water; C_1, methanol; C_2, ethanol; 1-C_3, 1-propanol; 2-C_3, 2-propanol; 1-C_4, 1-butanol; 2-C_4, 2-butanol; 1-C_5, 1-pentanol; iC_5, 3-methyl-1-butanol.

These results may be used to determine diffusivity from experimental data as follows: solute 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 9 becomes 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_2) are determined, the infinite dilute diffusion coefficients of solvents in polymers (D_{12}^{∞}) can be obtained from C with eq 6.

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

$$D = D_0 e^{-\Delta E_D/RT} \tag{12}$$

where D_0 is the preexponential factor of the diffusion process independent from the temperature, and ΔE_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. R is the gas constant, and T is absolute temperature. In dilute solutions, where the diffusing species does not often encounter a polymer molecule, the diffusion rate is limited by the energy required for the diffusing species to escape its present surroundings and move into an adjacent environment.

Results and Discussion

The IGC was used to measure the infinite dilute activity and diffusion coefficients of water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 3-methyl-1-butanol in PVA and of water, methanol, and ethanol in cross-linked PVA at different temperatures. Measurements for each solvent−polymer pair were obtained at several carrier flow rates. Equations 3 and 4 were used to estimate the activity coefficients in polymer phase (Ω_1^{∞}), and the values of the appropriate activity coefficients were presented in Tables 1 and 2. The eq 6 was then used to estimate the diffusion coefficients in polymer phase (D_{12}^{∞}), and the values of the appropriate diffusion coefficients were presented in Tables 3 and 4.

As shown in Tables 1 and 2, to most of the systems in this work, the activity coefficient of solvent in polymer decrease with the system temperature rising. The correlations of the activity coefficient and the system temperature are shown in Figures 2 to 5 by Ω_1^{∞} versus T.

Table 2. Infinite Dilute Activity Coefficient (Ω_1^∞) of Solvents (Water, Methanol, and Ethanol) in PVA and in Cross-Linked PVA at Different Temperatures

	Ω_1^∞					
	water		methanol		ethanol	
T/K	PVA	cross-linked PVA	PVA	cross-linked PVA	PVA	cross-linked PVA
363.15		165.68		593.31		1007.00
368.15		170.54		589.80		958.70
373.15	23.15	176.60	0.41	581.29		870.68
378.15	23.8	186.00	0.50	577.31		805.35
383.15	24.35	196.16	0.69	568.80		744.25
388.15	24.91		1.00		38.61	
393.15	23.06		1.11		37.92	
398.15			2.05		37.23	
403.15					35.89	
408.15					34.92	

Table 3. Infinite Dilute Diffusion Coefficient (D_{12}^∞) of Solvents in PVA at Different Temperatures[a]

	$10^{10}\ D_{12}^\infty/(\mathrm{m^2 \cdot s^{-1}})$								
T/K	H_2O	C_1	C_2	1-C_3	2-C_3	1-C_4	2-C_4	1-C_5	iC_5
373.15	2.40	0.41							
378.15	4.76	0.50							
383.15	8.68	0.69							
388.15	17.64	1.00	0.780		0.255				
393.15	39.08	1.11	0.787		0.273				
398.15		2.05	0.793	0.578	0.301	0.563			
403.15			0.801	0.584	0.352	0.600		0.562	
408.15			0.805	0.608	0.383	0.669	0.490	0.639	0.636
413.15				0.638	0.437	0.706	0.535	0.717	0.663
418.15				0.668	0.458	0.765	0.566	0.771	0.704
423.15				1.058	0.506	0.873	0.621	0.901	0.749
428.15				1.400	0.657	0.965	0.672	0.990	0.815

[a] H_2O, water; C_1, methanol; C_2, ethanol; 1-C_3, 1-propanol; 2-C_3, 2-propanol; 1-C_4, 1-butanol; 2-C_4, 2-butanol; 1-C_5, 1-pentanol; iC_5, 3-methyl-1-butanol.

Table 4. Infinite Dilute Diffusion Coefficient (D_{12}^∞) of Solvents (Water, Methanol, and Ethanol) in PVA and in Cross-Linked PVA at Different Temperatures

	$10^{10}\ D_{12}^\infty/(\mathrm{m^2 \cdot s^{-1}})$					
	water		methanol		ethanol	
T/K	PVA	cross-linked PVA	PVA	cross-linked PVA	PVA	cross-linked PVA
363.15		2.79		1.58		0.73
368.15		3.54		1.71		0.77
373.15	2.40	4.19	0.41	1.83		0.82
378.15	4.76	5.06	0.50	1.96		0.87
383.15	8.68	8.89	0.69	2.19		0.92
388.15	17.64		1.00		0.780	
393.15	39.08		1.11		0.787	

In the experimental results, most of the activity coefficient values of water are much lower than those of other solvents, probably due to the PVA and cross-linked PVA were hydrophilic polymer membrane materials. Most of the infinite dilute activity coefficients of solvents in PVA and in cross-linked PVA are in good agreement with the dependence of temperature, and the activity coefficients of solvents in polymers decrease with the system temperature rising in the covered range, except water. Furthermore, as shown in Figure 2, Figure 5, and Table 2, the difference of the activity coefficient between methanol and water is very small in PVA and distinct in cross-linked PVA. It is indicated that the cross-linked PVA is more suitable to be used in separation of the mixture of methanol + water.

The infinite dilute activity coefficients of alcohols with linear chain in PVA have almost the same value at a constant temperature as shown in Figure 3. Moreover, as shown in Figure 4, the infinite dilute activity coefficients of alcohols with branched chain in PVA at a constant temperature are distinguished clearly and decrease in the order: 2-propanol > 2-butanol > 3-methyl-1-butanol.

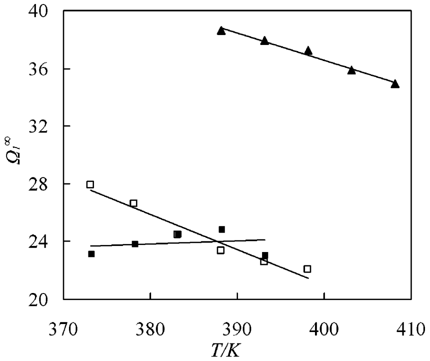


Figure 2. Temperature dependence of the infinite dilute activity coefficients Ω_1^∞ of solvents: ■, water; □, methanol; and ▲, ethanol in PVA.

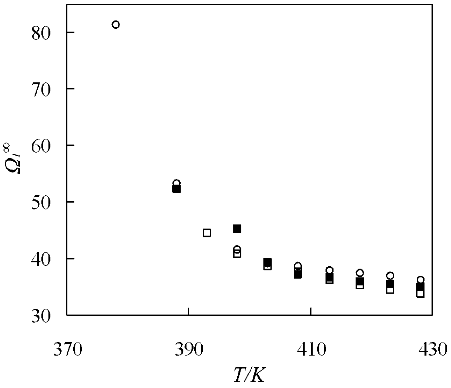


Figure 3. Temperature dependence of the infinite dilute activity coefficients Ω_1^∞ of solvents: ○, 1-propanol; ■, 1-butanol; and □, 1-pentanol in PVA.

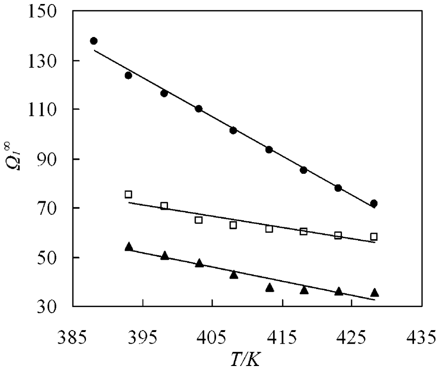


Figure 4. Temperature dependence of the infinite dilute activity coefficients Ω_1^∞ of solvents: ●, 2-propanol; □, 2-butanol; and ▲, 3-methyl-1-butanol in PVA.

As shown in Tables 3 and 4, the temperature plays a very important role on the diffusion process, and the diffusion coefficients of solvents in polymers increase as the temperature increase in all the systems. The temperature dependence can be presented by Arrhenius equation as eq 12. The correlations of ln D_{12}^∞ versus $1/T$ are shown in Figures 6 to 9.

Figures 6 to 9 show that the plot of ln D_{12}^∞ versus $1/T$ is linear, which confirmed that ΔE_D is independent of temperature in the covered range. The activation energies for all the three solvents were calculated from the fitted straight lines and shown in Tables5 and 6.

In the Figures 6 to 9, the infinite dilute diffusion coefficients of solvents in PVA and in cross-linked PVA are in agreement

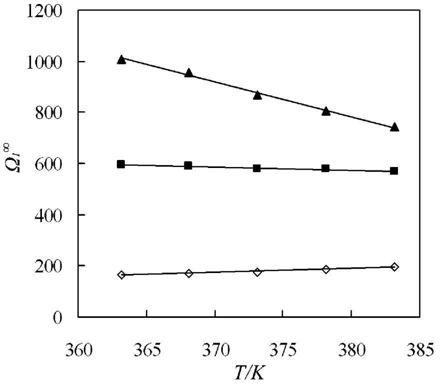


Figure 5. Temperature dependence of the infinite dilute activity coefficients Ω_1^∞ of solvents: ◇, water; ■, methanol; and ▲, ethanol in cross-linked PVA.

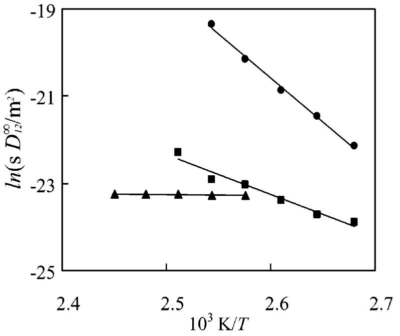


Figure 6. Temperature dependence of the infinite dilute diffusion coefficients D_{12}^∞ of solvents: ●, water; ■, methanol; and ▲, ethanol in PVA.

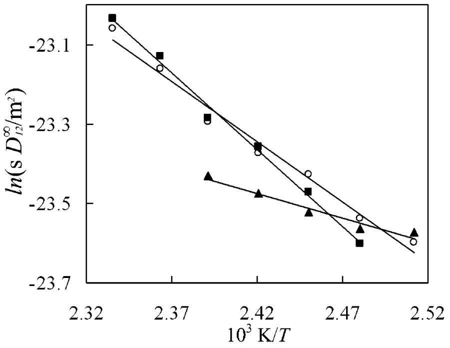


Figure 7. Temperature dependence of the infinite dilute diffusion coefficients D_{12}^∞ of solvents: ▲, 1-propanol; ○, 1-butanol; and ■, 1-pentanol in PVA.

with dependence of temperature, and the diffusion coefficients of solvents in polymers increase with the system temperature rising in the covered range. Among the curves, the ones related to ethanol in PVA and in cross-linked PVA change slightly under the influence of temperature. As shown in Figure 6, Figure 9, and Table 4, the difference of the diffusion coefficients between methanol and ethanol is very small in PVA and distinct in cross-linked PVA. And it is indicated that the cross-linked PVA is more suitable to be used in separation of the mixture of methanol and ethanol. Furthermore, the infinite dilute activity coefficients of solvents in PVA at a constant temperature decrease in the order: water > methanol > ethanol. It is possibly because that the length and the size of the path the molecule should follow the free volume available to the polymer segment to exchange positions with the solvent molecules during solvent diffusion in polymer, and the bigger solvent molecule is disadvantageous to diffuse in polymer.

Moreover, the difference of diffusion coefficients to the different systems may be also related to a number of other factors such as the shape of the solvent molecule, the polarity of the solvent molecules, and the size of the hole required accommodating the molecule, and it makes the phenomena become complicated. The infinite dilute diffusion coefficients of alcohols with linear chain in PVA are almost the same value at a constant temperature in Figure 7. Otherwise, as shown in Figure 8, the infinite dilute diffusion coefficients of alcohols with branched chains in PVA at a constant temperature are distinguished and increase in the order: 2-propanol < 2-butanol < 3-methyl-1-butanol. From Table 3, it is observed that the infinite dilute diffusion coefficients of the alcohols with linear chain are always larger that the ones with branched chains with the same carbon number at a constant temperature in PVA.

As shown in Tables 5 and 6, diffusion activation energy is positive, that is to say, the process of solvent molecule diffusion

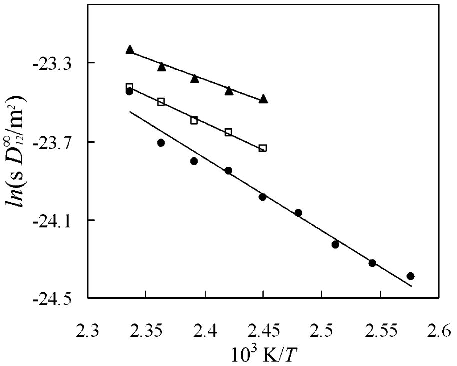


Figure 8. Temperature dependence of the infinite dilute diffusion coefficients D_{12}^∞ of solvents: ●, 2-propanol; □, 2-butanol; and ▲, 3-methyl-1-butanol in PVA.

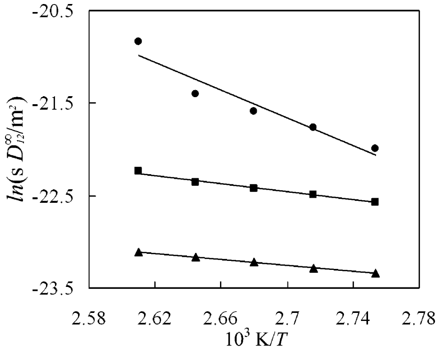


Figure 9. Temperature dependence of the infinite dilute diffusion coefficients D_{12}^∞ of solvents: ●, water; ■, methanol; and ▲, ethanol in cross-linked PVA.

Table 5. Activation Energy (ΔE_D) for Diffusion and Diffusion Constant (D_0) of Solvents in PVA

solvent	D_0/(m^2·s^{-1})	ΔE_D/(kJ·mol^{-1})
water	7.50×10^{13}	167.97
methanol	1.60	75.90
ethanol	1.51×10^{-10}	2.13
1-propanol	1.04×10^{-9}	9.58
2-propanol	3.33×10^{-7}	30.73
1-butanol	1.14×10^{-7}	25.28
2-butanol	3.92×10^{-8}	22.69
1-pentanol	8.49×10^{-7}	32.25
3-methyl-1-butanol	1.23×10^{-8}	17.92

Table 6. Activation Energy (ΔE_D) for Diffusion and Diffusion Constant (D_0) of Solvents in Cross-Linked PVA

solvent	D_0/(m^2·s^{-1})	ΔE_D/(kJ·mol^{-1})
water	0.21	61.90
methanol	6.71×10^{-8}	18.29
ethanol	6.45×10^{-9}	13.54

in polymer is endothermic. The chains of solvent molecule cause a small increase of activation energy. The same consideration can explain the deviation for the diffusion constant.

Conclusion

The infinite dilute activities, the infinite dilute diffusion coefficients, the diffusion constants, and the activation energies of water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, and 3-methyl-1-butanol in PVA and of water, methanol, and ethanol in cross-linked PVA were determined at several different temperatures by inverse gas chromatography. The experimental results showed that (1) the activity coefficient values of water were much lower than those of other solvents dealt with this work in both PVA and cross-linked PVA, (2) the infinite dilute activity coefficients of alcohols with linear chain in this work had almost the same value at a constant temperature, and (3) the infinite dilute activity coefficients of alcohols with branched chain were distinguished and decreased in the order: 2-propanol > 2-butanol > 3-methyl-1-butanol at a constant temperature. The experimental results also showed that (1) the infinite dilute diffusion coefficients of alcohols with linear chain in PVA were almost the same value at a constant temperature, (2) the infinite dilute diffusion coefficients for a solvent studied in this work in both PVA and cross-linked PVA increased with the rising of temperature, and (3) the infinite dilute diffusion coefficients of the alcohols with linear chain were always larger that the ones with branched chains with the same carbon number at a constant temperature in PVA.

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