Measurement of the Infinite Dilute Activity Coefficients and Diffusion Coefficients of Water and Straight Chain Alcohols in Cross-Linked Polyvinyl Alcohol by Inverse Gas Chromatography

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The infinite dilute activity coefficients and diffusion coefficients of water, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol in cross-linked polyvinyl alcohol (PVA) were measured in the temperature range of (363.15 to 413.15) K by inverse gas chromatography. The cross-linked PVA was obtained by dissolving PVA, cross-linking agent, and catalyst in water and characterized by FTIR spectra. The van Deemter equation was 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 the Arrhenius equation. Pre-exponential factor and activation energy are obtained from the Arrhenius equation.

Introduction

Molecular activity and diffusion coefficients of solvents are important and find applications in the analysis in many problems involving polymers, such as polymerization, separation, devolatilization, vacuum/gas stripping, and drying.[1−5] For a polymer + solvent system in the presence of very small amounts of solvent, it is difficult to measure the activity and diffusivity data by using conventional methods, such as bulk equilibration and gravimetric sorption/desorption experiments.[6] On the other hand, the inverse gas chromatography (IGC) technique has been developed as a fast and reliable technique to measure the activity and diffusion coefficients of polymer−solvent system at infinite dilution.

Polyvinyl alcohol (PVA) is a hydrophilic polymer membrane material that has been used extensively in the pervaporation process for dehydration.[7−9] Due to its strong hydrophilic characteristic, it often swells when water is passed through the PVA membrane. In order to prolong the life of the PVA membrane and enhance the separation factor of the membrane, cross-linking of PVA is necessary. Infinite dilute activity coefficients and diffusion coefficients of solvents in PVA have been reported previously.[10−13] However, there are no data on the infinite dilute activity and diffusion coefficients of solvents in a cross-linked PVA polymer.

A packed column IGC technique is used for determining the activity coefficients and diffusion coefficients of several solvents in the polymer. 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 water, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol in cross-linked PVA are reported. These data will be useful in a study of the mechanism of small molecules transferring in cross-linked PVA polymer and will assist in the prediction of separation results for various mixtures.

Experimental Section

Materials. PVA (average molecular weight 7.7×10^4 and saponification 98.06 %) was purchased from Kuraray Co. Ltd. Maleic anhydride (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, 1-butanol, and 1-pentanol (gas chromatography grade) were obtained as reagents from Beijing Beihua Fine Chemicals Company of China. Ultrapure deionized water (conductivity 1.20 $\mu S \cdot cm^{-1}$ to 1.25 $\mu S \cdot cm^{-1}$) was also 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 manufactor of China. The PVA polymer was dissolved in water that contained maleic anhydride as a cross-linking agent and a catalytic quantity of H_2SO_4 to prepare the coating solution. Then the coating solution with the theoretical cross-linking degree of 4 % denoted as cross-linked PVA was coated onto the Chromosorb-G supporter material by vibrating and slow evaporation of the solvent to get a uniform polymer coating.

The quality of the maleic anhydride was calculated as follows:

$$m_4 = \frac{m_3}{88} \times T_{cd} \times 98.06 \tag{1}$$

where m_4 and m_{PVA} are the mass of maleic acid and the monomer of PVA, respectively. T_{cd} is the theoretical cross-linking degree of cross-linked PVA.

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 with sodium bicarbonate of low concentration. The support material was then washed with water until the pH value of the washing 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

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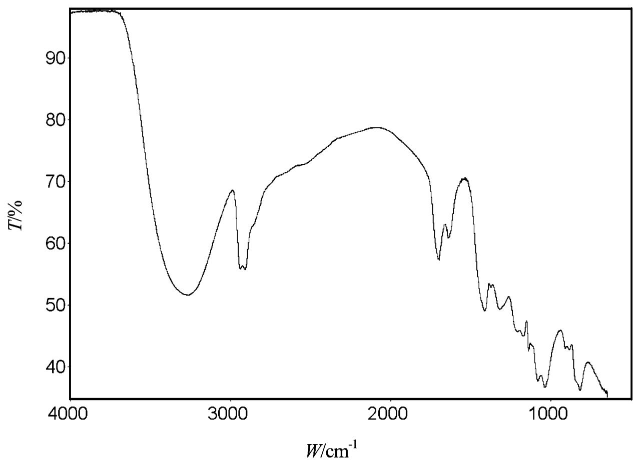


Figure 1. FTIR spectrum of the initial PVA.

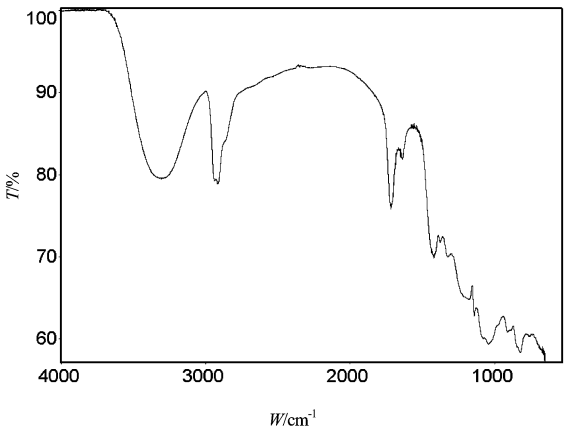


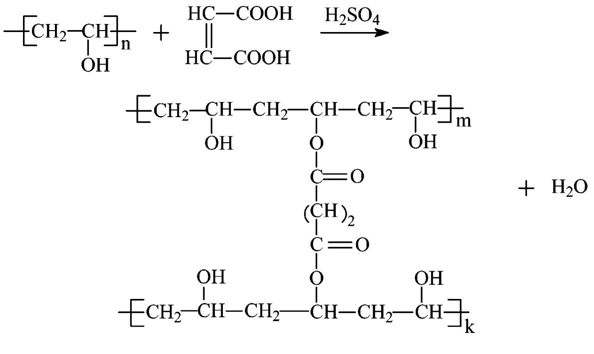
Figure 2. FTIR spectrum of the cross-linked PVA.

mechanical vibrator and a vacuum pump. The end of the tube is loosely plugged with steel wool.

The T_{cd} of cross-linked PVA was calculated as follows:

$$T_{cd} = \frac{2M_3 \cdot m_4}{0.9806 m_3 \cdot M_4} \tag{2}$$

where M_4 and M_3 are the molecular weight of maleic acid and the monomer of PVA, respectively; m_4 and m_3 are the mass of maleic acid and PVA used, respectively. PVA reacted with maleic acid under H_2SO_4 catalysis, as shown in eq 3, and the hydroxy group could condense into an ester group with the elimination of water:



(3)

Figures 1 and 2 show the FTIR spectra of initial PVA and the cross-linked PVA. It can be seen from figures that the character value cross-linked of hydroxy group in (3310 to 3300) cm^{-1} and (1630 to 1640) cm^{-1} peak regions are weaker than that of initial PVA, that is to say the cross-linked reaction has happened.

Apparatus and Procedure. The gas chromatograph SP-6800A (Shandong Lunan's Ruihong Chem. Co.) was equipped with a thermal conductivity detector (TCD). The specific procedure follows the methods used in the previous works.[10−13] Small amounts of solvent (0.4 μL) were injected in the column through a PVA septum using a 1 μL syringe, while about 40 μL of air was injected as an inlet component along with the liquid samples to determine the average velocity of carrier gas in the column. From the difference between the retention time of the pulse and the retention time of a non-interacting gas, the equilibrium behavior could be determined. Measurements were preformed over a wide range of flow rate at a constant temperature. In addition, replicated experiments were done six times at each flow rate to ensure that the results were reproducible at each fixed set of conditions.

Theory

Activity Coefficient. The generalized equations relating the measured data to activity coefficients of solvent in polymer are given as[14]

$$\Omega_1^{\infty} = \gamma_1^{\infty} \frac{M_2}{M_1} = \frac{273.15R}{v_g^0 M_1} \frac{1}{\varphi_1^s P_1^s} \tag{4}$$

$$v_g^0 = \frac{jF}{w_2} \frac{P_{fm} - P_w^s}{P_{fm}} \frac{273.15}{T_{fm}} (t_1 - t_a) \tag{5}$$

$$j = \frac{3}{2} \frac{\left[\left(\frac{P_i}{P_0}\right)^2 - 1\right]}{\left[\left(\frac{P_i}{P_0}\right)^3 - 1\right]} \tag{6}$$

where γ_1^{∞} is the infinite dilute activity coefficient by mole fraction scale, Ω_1^{∞} is the infinite dilute activity coefficient by mass fraction scale, R is the gas constant, M_1 is the molar mass of solvent, 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}, P_i and P_o were the column inlet and outlet pressure, respectively, and P_1^s was the saturated vapor pressure of the pure solvent. 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.[15] The necessary critical properties and acentric factors were also taken from DDB.

Diffusion Coefficient. According to Van Deemter's model,[16] infinite dilute diffusion coefficient could be obtained by the following equation:

$$D_{12}^{\infty} = \frac{8d_2^2}{\pi^2 C} \cdot \frac{k}{(1+k)^2} \tag{7}$$

where D_{12}^{∞} is the infinite dilute diffusion coefficient, C is a parameter related to column characteristics, d_2 is the thickness of the stationary phase and k is the so-called partition ratio. d_2 and k were determined from the following equations:

$$d_2 = \frac{w_2 \rho_5 d_5}{6 \rho_2 w_5} \tag{8}$$

$$k = \frac{t_1 - t_a}{t_a} \tag{9}$$

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, d_5 is the average diameter of support particle, and t_1 and t_a are the retention times of solvent and unadsorbed material, such as air.

From plate theory,[16] C in eq 7 is related to column characteristics by the equation:

$$H = A + B/u + Cu \tag{10}$$

where H is the plate height equivalent to a theoretical plate (HEPT); u is the mean flow rate of the carrier gas; and A is a constant related to eddy diffusion. B depends on the axial diffusion in the gas phase and on the tortuosity or structural factors in the column, and C depends on, among other things, the probe diffusion in the liquid phase. At sufficiently high flow rates, the term B/u is small in relation to $A + Cu$, and the plot of H versus u should yield a straight line with a slope C.

H is calculated from the experimental eluted peak as follows:[17]

$$H = \left(\frac{l}{5.54}\right)\left(\frac{t_{1/2}}{t_1}\right)^2 \tag{11}$$

where l is the column height, $t_{1/2}$ 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, was calculated from the expression:

$$u = \frac{jV_0}{\bar{a}} \cdot \frac{T_{\text{col}}}{T_{\text{flow}}} \tag{12}$$

where T_{col} and T_{flow} 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; and V_0 is the corrected flow rate. In eq 12, j is the compressibility factor determined in eq 6.

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

$$D = D_o e^{-\Delta E_D/RT} \tag{13}$$

where D_o is the pre-exponential 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 the 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.

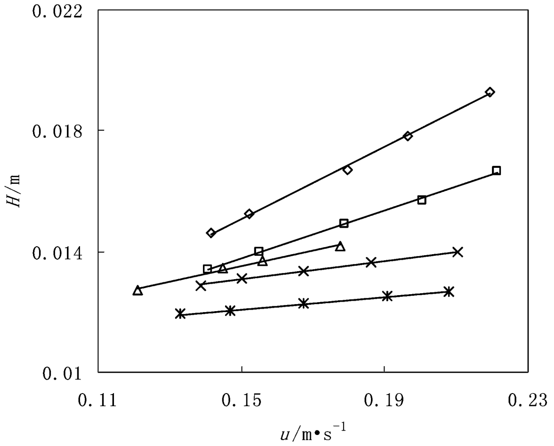


Figure 3. Relationship between the flow rate and the plate height of water in cross-linked PVA: ◇, 363.15 K; □, 368.15 K; △, 373.15 K; ×, 378.15 K; ∗, 383.15 K.

Estimation of Uncertainties. In this work, infinite dilute activity coefficients and infinite dilute diffusion coefficients are calculated from these measured data below: P_i, the estimated uncertainty in this quantity, is ± 0.002MPa; P_0, the estimated uncertainty in this quantity, is ± 0.002KPa; F, which is taken as the mean of 4 individual volume flows with an estimated error taken as the standard deviation of this mean value; t_1, which is taken as the mean of 6 individual measures with an estimated error taken as the standard deviation of this mean value; t_a, which is taken as the mean of six individual measures with an estimated error taken as the standard deviation of this mean value; $t_{1/2}$, which is taken as the mean of six individual measures with an estimated error taken as the standard deviation of this mean value. The contribution from all of the estimated uncertainties as notes above are computed in the computer program used to process the raw data using the formulas listed in the previous section, and this total error is used to set uncertainty estimates on the final infinite dilute activity coefficients and infinite dilute diffusion coefficients.

Results and Discussion

The IGC was previously used to measure the infinite dilute activity and diffusion coefficients of water, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol in PVA.[13] At this time, the activity and diffusion coefficients of these small molecule solvents were measured in cross-linked PVA (4 % T_{cd}) at different temperatures. Measurements for each solvent−polymer pair were obtained at several carrier flow rates.

Infinite Dilute Activity Coefficient. Equations 4 and 5 were used to estimate the activity coefficient in polymer phase, Ω_1^∞,

Table 1. Infinite Dilute Activity Coefficient Ω_1^∞ of Solvents in Cross-Linked Polyvinyl Alcohol at Different Temperatures

T	Ω_1^∞					
K	water	methanol	ethanol	1-propanol	1-butanol	1-pentanol
363.15	353 ± 8	720 ± 20	1240 ± 50			
368.15	344 ± 8	680 ± 20	1030 ± 40			
373.15	390 ± 10	670 ± 20	960 ± 40	2220 ± 60	920 ± 30	1040 ± 40
378.15	380 ± 10	660 ± 10	840 ± 40			
383.15	370 ± 10	650 ± 10	670 ± 30	2250 ± 60	900 ± 30	950 ± 40
393.15				1890 ± 60	900 ± 30	910 ± 40
403.15				1430 ± 50	860 ± 30	890 ± 30
408.15				1280 ± 50	780 ± 30	880 ± 30
413.15				1120 ± 40	720 ± 20	740 ± 30

Table 2. Infinite Dilute Activity Coefficient Ω_1^∞ of Solvents in Polyvinyl Alcohol at Different Temperatures[13]

T	Ω_1^∞					
K	water	methanol	ethanol	1-propanol	1-butanol	1-pentanol
373.15	23.15	27.89	93.70			
378.15	23.85	26.65	82.64			
383.15	24.35	24.48	45.43			
388.15	24.91	23.32	38.61			
393.15	23.06	22.56	37.92			
403.15		22.08	37.23	39.12	39.31	38.68
408.15			35.89	38.44	37.11	37.59
413.15			34.92	37.84	36.65	36.21
418.15				37.29	35.77	35.12
423.15				36.43	35.26	34.32
428.15				36.18	34.81	33.58

the values of the appropriate activity coefficients under the cross-linked and uncross-linked conditions are presented in Tables 1 and 2, respectively.

From an examination of the data listed in Table 1, it is clear that in the cross-linked PVA the values of the infinite dilute activity coefficients of water, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol in the same temperature have the order below:

1-propanol > 1-pentanol > 1-butanol > ethanol > methanol > water

Compared with these alcohols, the values of the infinite dilute activity coefficients of water is smaller. It is indicated that, in cross-linked PVA, water is more easily dissolved than other alcohols.

As shown in Tables 1 and 2, all of the infinite dilute activity coefficients of solvents increase after cross-linking. It is probably due to the polarity of PVA decrease after cross-linking; the dissolution ability of these small solvents that have polarity also decrease. And in these solvents, the dissolution ability of the alcohols decreases more distinctly than that of the water. It is indicated that in one hand after cross-linking, due to the distinct difference between water and the alcohols, it is more easy to separate the mixture of alcohols + water. On the other hand, cross-linking reduces the solubility of water in PVA, so it reduces the degree of the swelling of the PVA membranes and prolongs the using life of the PVA membranes.

Infinite Dilute Diffusion Coefficient. Figure 3 illustrates the linear relationships of plate height *H* with mean flow rate of the carrier gas *u* for water in cross-linked PVA in different temperatures. The values *C* in eq 10 were determined from the slope of the lines. These values were then used in eq 7 to estimate the diffusion coefficient in polymer phase, D_{12}^∞. The values of the appropriate diffusion coefficients under the cross-linked and uncross-linked conditions are presented in Tables 3 and 4, respectively.

From an examination of the data in Table 3, it is clear that the value of the infinite dilute diffusion coefficients of water, methanol, and ethanol at the same temperature in the cross-linked PVA have the order below:

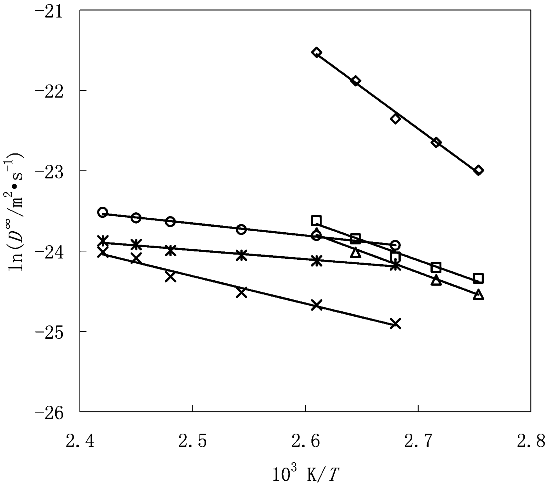


Figure 4. Arrhenius plots for the infinite dilute diffusion coefficients vs temperature in cross-linked PVA: ◇, water; □, methanol; △, ethanol; ×, 1-propanol; ∗, 1-butanol; ○, 1-pentanol.

water > methanol > ethanol

This difference may be related to a number of factors such as size and shape of the solvent molecule or the size of the hole required to accommodate the molecule. The effect of the size of the molecules of these solvents may be investigated through knowledge of the molar volumes, which have the following order:

ethanol > methanol > water

The length and the size of the path the molecule must follow during its diffusion, and the free volume is available to the polymer segment to exchange positions with the solvent molecules. The bigger solvent molecule is disadvantageous to diffuse in polymer.

The values of the infinite dilute diffusion coefficients of 1-propanol, 1-butanol, and 1-pentanol at the same temperature in the cross-linked PVA have this order:

1-pentanol >1-butanol >1-propanol

This difference may be due to the factors such as the polarities of the solvent molecules and the size and shape of the molecules. Because both of PVA and cross-linked PVA have hydrogen bonds, so they both have polarities. When the small solvents that possess polarities cross the polymers, the factors such as the acting force between them and the size and shape of the solvents all could affect the diffusion coefficients.

As shown in Tables 3 and 4, the infinite dilute diffusion coefficients of the small solvents decrease after the cross-linking

Table 3. Infinite Dilute Diffusion Coefficient D_{12}^∞ of Solvents in Cross-Linked Polyvinyl Alcohol at Different Temperatures

T	$D_{12}^\infty \times 10^{10}/(\mathrm{m}^2 \cdot \mathrm{s}^{-1})$					
K	water	methanol	ethanol	1-propanol	1-butanol	1-pentanol
363.15	1.03 ± 0.07	0.27 ± 0.02	0.22 ± 0.01			
368.15	1.4 ± 0.1	0.31 ± 0.02	0.27 ± 0.02			
373.15	2.0 ± 0.1	0.35 ± 0.02	0.32 ± 0.02	0.15 ± 0.01	0.32 ± 0.01	0.41 ± 0.01
378.15	3.2 ± 0.2	0.44 ± 0.03	0.37 ± 0.02			
383.15	4.5 ± 0.3	0.55 ± 0.03	0.47 ± 0.03	0.19 ± 0.01	0.33 ± 0.02	0.46 ± 0.01
393.15				0.23 ± 0.02	0.36 ± 0.02	0.50 ± 0.02
403.15				0.28 ± 0.02	0.38 ± 0.02	0.54 ± 0.03
408.15				0.35 ± 0.03	0.41 ± 0.03	0.57 ± 0.03
413.15				0.37 ± 0.03	0.43 ± 0.03	0.61 ± 0.03

Table 4. Infinite Dilute Diffusion Coefficient D_{12}^{∞} of Solvents in Polyvinyl Alcohol at Different Temperatures[13]

T	$D_{12}^{\infty} \times 10^{10}/(\mathrm{m^2 \cdot s^{-1}})$					
K	water	methanol	ethanol	1-propanol	1-butanol	1-pentanol
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			
393.15	39.08	1.11	0.787			
403.15		2.05	0.793	0.584	0.600	0.562
408.15			0.801	0.608	0.669	0.639
413.15			0.805	0.638	0.706	0.717
418.15				0.668	0.765	0.771
423.15				1.058	0.873	0.901
428.15				1.400	0.965	0.990

Table 5. Activation Energy for Diffusion and Diffusion Constant of Solvents in Cross-Linked Polyvinyl Alcohol

solvent	$D_0/(\mathrm{m^2 \cdot s^{-1}})$	$\Delta E_D/(\mathrm{kJ \cdot mol^{-1}})$
water	1.98×10^{2}	85.49
methanol	2.43×10^{-5}	41.54
ethanol	3.49×10^{-5}	43.13
1-propanol	1.37×10^{-7}	28.31
1-butanol	6.50×10^{-10}	9.42
1-pentanol	2.34×10^{-9}	12.58

occurred. The reason may be that the cross-linking agent concentration increase could result in the decrease of the free volume of the PVA network. It can also be seen from Table 3 that the infinite diffusion coefficients of the solvents in cross-linked PVA increase with the rising of temperature, it is because that the higher the temperature is, the faster the diffusion of small molecules in cross-linked PVA.

From Table 3, it can be seen that temperature plays a very important role on the diffusion process. The relationship between the temperature and the infinite dilute diffusion coefficient is given by Arrhenius equation in eq 13. Figure 4 indicates that the plot of ln D^{∞} versus $1/T$ is linear, which confirmed that ΔE_D is independent of temperature in the covered range. The activation energies for all six solvents were calculated from the fitted straight lines and are shown in Table 5.

Conclusion

In the present investigation, the infinite dilute activity and diffusion coefficients of water, methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol in cross-linked PVA (T_{cd} of 4 %) were determined at several different temperatures by inverse gas chromatography. The Van Deemter model of chromatographic process was used to calculate the diffusion coefficient using the information from the chromatography peak and the retention time. The experimental results showed that (1) the infinite dilute activity coefficient values of water were much lower than those of other solvents dealt with this work in cross-linked PVA, (2) the infinite dilute activity coefficients of alcohols decreased with the increasing temperature in cross-linked PVA, and (3) the infinite dilute activity coefficients of all these solvents increased distinctly after cross-linking. The experimental results also showed that (1) for water, methanol, and ethanol, the infinite dilute diffusion coefficients of solvents decrease with the increasing length and size of the molecules at the same temperature in cross-linked PVA; (2) for 1-propanol, 1-butanol, and 1-pentanol, the infinite dilute diffusion coefficients of solvents decrease with the increasing polarities of the molecules at the same temperature in cross-linked PVA; (3) the infinite dilute diffusion coefficients of solvents increased with the rising of temperature in cross-linked PVA; and (4) the infinite dilute diffusion coefficients of all these solvents decreased after cross-linking.

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