Measurement of the infinite dilute activity coefficients and diffusion coefficients of small molecule solvents in cross-linked polyvinyl alcohol by inverse gas chromatography

Ding Wang, Jiding Li[*] *, Chuyi Zeng, Jian Chen and Cuixian Chen*
Department of Chemical Engineering, Tsinghua University. Beijing, China

Introduction

Molecular activity and diffusion coefficients of solvents are important and find wide range of applications to analyze in many problems including polymers, such as polymerization, separation, devolatilization, vacuum/gas stripping and drying.[1-5] The polyvinyl alcohol (PVA) is a hydrophilic polymer membrane material, which was used extensively in the pervaporation process for dehydration. But due to its strong hydrophilic characteristic, it often occurs swelling when the water through the PVA membrane. In order to prolong the life of the PVA membrane and enhance the separation factor of the membrane, the process of cross-linking of PVA is necessary. 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 is 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 diffusion coefficients of water, methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol in cross-linked PVA are reported. Those data will be useful in a study of the mechanism of small molecules transferring in cross-linked PVA polymer and will avail in the prediction of the separation results for various mixtures.

Experimental

The gas chromatograph SP-6800A (Shandong Lunan's Ruihong Chem. Co.) was

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. Because the experiment was processed under the infinite dilute conditions, the carrier gas could flow directly to the reference side of the detector and to the column which was enclosed in the temperature controlled oven. Small amounts of solvent (0.4ul) were injected in the column through a PVA septum using a 1ul syringe, while about 40ul of air were injected as an inlet component along with the liquid samples to determine the average velocity of carrier gas in 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 non-interacting 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;

_____
*Corresponding author. Tel: +86-10-62782432, Fax: +86-10-62770304.
E-mail address: lijiding@mail.tsinghua.edu.cn

the sizeable 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.
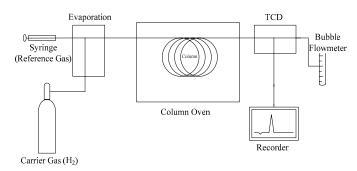

Figure 1. a schematic diagram of the IGC apparatus used for measurement of the diffusion coefficient

Results and discussion

Infinite dilute activity coefficient

The values of the appropriate activity coefficients were presented in Tables 1

Table 1. the infinite dilute activity coefficient Ω_1^∞ of solvents in cross-linked PVA at different temperatures

T/K	Ω_1^∞					
	water	methanol	ethanol	1-propanol	1-butanol	1-pentanol
363.15	352.61	721.57	1235.46			
368.15	343.52	675.78	1031.87			
373.15	384.82	668.45	957.96	2218.214	922.86	1043.30
378.15	383.15	663.34	843.88			
383.15	371.54	646.79	667.68	2248.615	905.85	945.28
393.15				1886.672	904.08	911.79

T/K					
403.15			1433.453	856.03	887.38
408.15			1274.469	779.44	881.31
413.15			1115.603	722.23	739.90

Infinite dilute diffusion coefficient

The values of the appropriate diffusion coefficients were presented in Tables 2

Table 2. the infinite dilute diffusion coefficient D_{12}^{∞} of solvents in cross-linked PVA at

different temperatures

T/K	$D_{12}^{\infty}\times10^{10}/(m^2\cdot s^{-1})$					
	water	methanol	ethanol	1-propanol	1-butanol	1-pentanol
363.15	1.03	0.268	0.220			
368.15	1.46	0.307	0.265			
373.15	1.96	0.351	0.324	0.153	0.318	0.405
378.15	3.16	0.439	0.371			
383.15	4.47	0.550	0.473	0.194	0.334	0.458
393.15				0.226	0.359	0.493
403.15				0.275	0.380	0.543
408.15				0.345	0.409	0.570
413.15				0.373	0.428	0.611

Discussion

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 (the theoretical cross-linking degree 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 and (2) the infinite dilute activity coefficients of alcohols increased with the increasing temperature in cross-linked PVA. 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 and (3) the infinite dilute diffusion coefficients of solvents increased with the rising of temperature in cross-linked PVA.

Acknowledgements

References

[1]. Caruthers, J. M.; Chao, K. C.; Venkatasubramanian, V.; Kioa, R. S. S.; Novenario, C. R.; Sundaram, A. Handbook of Diffusion and Thermal Properties of Polymers and Polymer Solutions; DIPPR/AIChE: New York, 1998.

[2]. Vrentas, J. S.; Duda, J. L. Molecular diffusion in polymer solutions. AIChE J. **1979**, 25, 1-24.

[3]. Romdhane, I. H.; Danner, R. P. Polymer-solvent diffusion and equilibrium parameters by inverse gas-liquid chromatography. AIChE J. **1993**, 39, 625-635.

[4]. Davis, P. K.; Danner, R. P.; Duda, J. L.; Romdhane, I. H. Use of Inverse Gas Chromatography To Study Binary Polymer-Solvent Systems near the Glass Transition Temperature. *Macromolecules* **2004**, 37, 9201-9210.

[5]. Zhao, C.; Li, J.; Jiang, Z.; Chen, C. Measurement of the infinite dilution coefficients of small molecule solvents in silicone rubber by inverse gas chromatography. European Polymer Journal **2006**, 42, 615-624.