

Solvent Diffusion in a Modified Polyaniline

W. P. HSU,¹ K. S. HO²

¹ Department of Applied Chemistry, Chia-Nan College of Pharmacy and Science, #60, Section 1, Erh-Jen Road, Jen-Te Hsian, Tainan, Taiwan, Republic of China

² Department of Chemical Engineering, Kaohsiung Institute of Technology, Kaohsiung, Taiwan, Republic of China

Received 21 April 1997; accepted 7 July 1997

ABSTRACT: A dodecyl benzene sulfonic acid doped polyaniline was synthesized and cast into films. Water and ethanol were used as the main diffusional probes to study this polymer from 25°C to 45°C. Sorption of water in this polymer was found to be almost independent of temperature, but sorption of ethanol in the same polymer decreased mostly with increasing temperature. Water diffusion was non-Fickian, but ethanol diffusion was Fickian. Probably some rearrangement of polymer structure happened at temperatures between 40°C and 45°C as detected by two-stage sorption of water at 40°C and an abrupt increase in ethanol diffusivity from 40°C to 45°C. 1-Propanol diffusion at 32.5°C was also performed and also found to be Fickian, but the rate of diffusion was slower than that of ethanol. The sorbed amount of solvent in this polymer had the order (1-propanol > ethanol > water) owing to the most hydrophobic structure of this polymer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2095–2101, 1997

Key words: solvent diffusion; polyaniline

INTRODUCTION

Recently, aromatic conducting polymers such as polypyrrole, polythiophene, or polyaniline have received considerable attention owing to their good electrical, optical, and electrochemical properties.^{1–3} Among these polymers, a great deal of work was devoted to polyaniline, which can be readily used in applications such as light-weight batteries⁴ and electrochromic devices.⁵ However, due to the stiffness of their backbones, these conducting polymers are often insoluble in common organic solvents.⁶ One way of improving the solubility of the conducting polymers in organic solvents is through attaching alkyl side chains onto the backbones of polymers,⁷ since a polymer is often used in the environments with certain hu-

midity. A study of the effect of water diffusion in polymers becomes important.

In a previous investigation,³ no transition of unoriented poly(3-octyl thiophene) (POT) was detected by calorimetry at temperatures from 25°C to 50°C. However, diffusion and sorption of hexane vapor showed that POT went through structural rearrangement between 30°C and 35°C. In this article, a dodecyl benzene sulfonic acid doped polyaniline was synthesized and cast into films. Water and ethanol were used as the main diffusional probes to investigate any structural change in this polymer.

EXPERIMENTAL

Materials

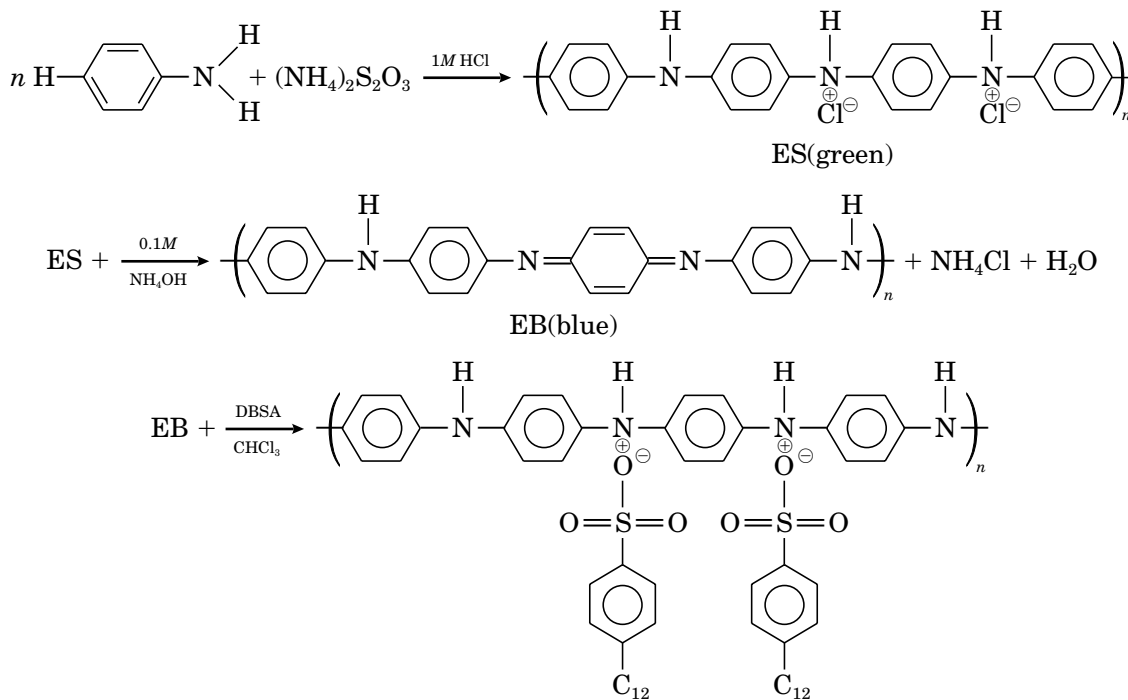
An emeraldine base (EB) form of polyaniline was synthesized by direct polymerization of aniline monomers in a 1M HCl aqueous solution with ammonium persulfate, then deprotonated with

Correspondence to: W. P. Hsu.
Contract grant sponsor: National Science Council, Republic of China; contract grant number: NSC-84-2216-E-041-002.

Journal of Applied Polymer Science, Vol. 66, 2095–2101 (1997)
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/112095-07

0.1M ammonium water. The EB form of polyaniline was protonated by dodecyl benzene sulfonic acid (DBSA) in a solution of chloroform and

m-cresol (3 to 1 volume ratio) for 24 h. The weight ratio between EB and DBSA is 1 to 2.5. The total synthesis scheme is shown as the following⁸:



After synthesis, this polymer was cast into films. All the films were placed under the hood overnight. For getting rid of the solvent and the residual DBSA, immersion of the films in water and vacuuming were performed several times until the weights of the films were constant. Then the films were kept for solvent diffusion studies.

Thermal Analysis and Infrared Spectroscopy

Thermal analysis of this polymer was performed by using a Perkin-Elmer differential scanning calorimeter. The heating rate was 10°C/min. The temperature range was from -10°C to 150°C. Fourier transform infrared (FTIR) measurements of

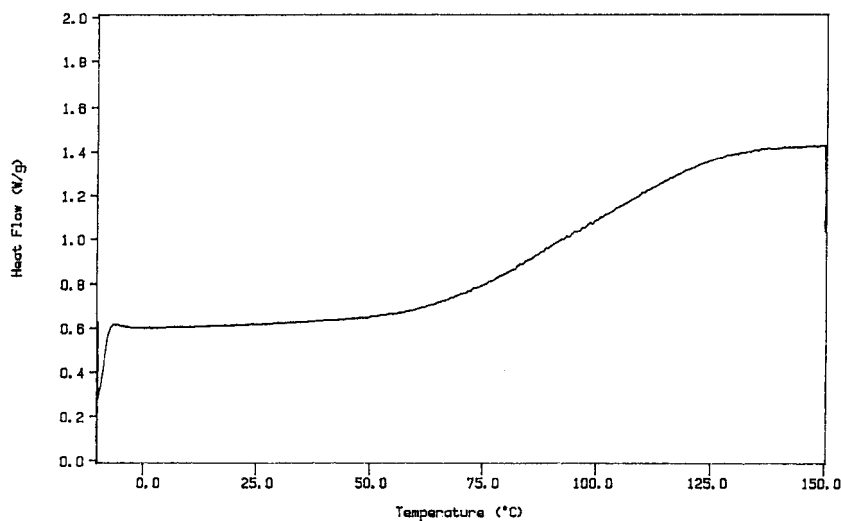


Figure 1 DSC thermogram.

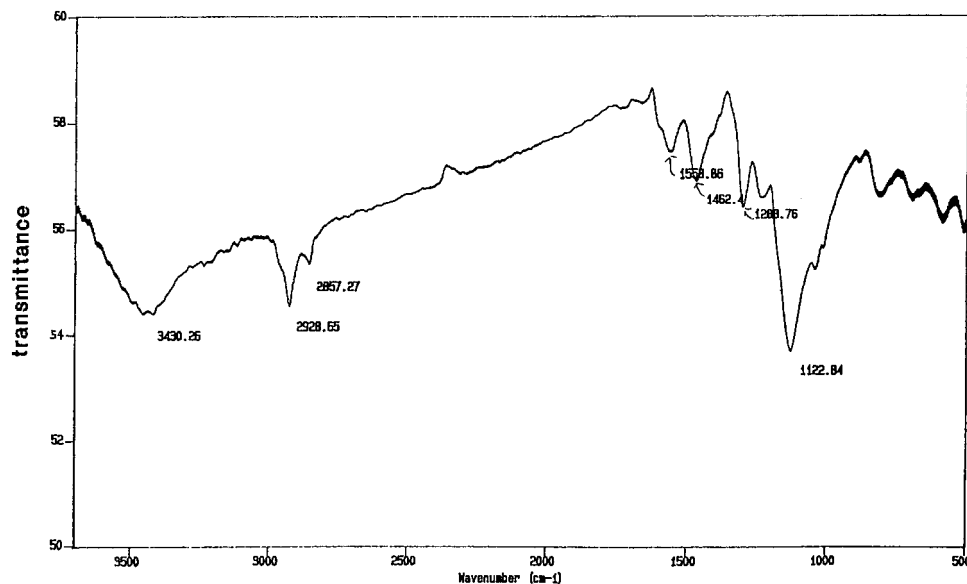


Figure 2 FTIR spectrum.

this polymer at room temperature were also performed. The number of scans and the resolution of measurements were 16 and 4 cm^{-1} , respectively.

Diffusion Studies

The thickness of the films was measured with a micrometer. The accuracy of measurements is 10^{-3} cm . The deionized water and ACS reagents of ethanol and 1-propanol were used as solvent in our studies. The film was immersed in the studied solvent inside a cylinder. The cylinder was placed in a constant temperature bath with 0.2°C accuracy. Then liquid water and ethanol diffusion were carried out from 25° to 45°C . For 1-propanol, the diffusion at only one temperature (32.5°C) was performed. The film was taken out from time to time and wiped off the surface liquid, then the weight of the film during sorption was measured by using a balance with 10^{-5} g accuracy. The measurements were performed at least two times and

the average values were reported. For Fickian diffusion, the diffusion coefficient D was calculated from the initial slope of a sorption curve, that is, the plot of M_t/M_∞ against $t^{1/2}/\ell$, where M_∞ is the equilibrium sorption, M_t is the amount sorbed at time t , and ℓ is the film thickness. The standard equation,

$$D = \pi/16 \times (\text{slope})^2 \quad (1)$$

was used to calculate the diffusion coefficients.⁹

RESULTS AND DISCUSSION

Characterization

DSC measurements were performed especially on a film with the residual DBSA still present. No observable transitions and solvent peaks were found in Figure 1. The DSC data show no significant heat change when temperature is lower than 50°C because DBSA is still in the acidic form. However, when temperature is higher than 75°C , the residual DBSA starts to form complexes with the undoped quinoid parts of polyaniline and causes the heat increase in the DSC curve. An FTIR spectrum performed before immersion of the films in water is shown in Figure 2, and the structural assignments are as follows: 1123 cm^{-1} (SO_3), 1289 cm^{-1} ($-\text{C}-\text{N}-$), 1462 cm^{-1} (quinoid), 1559 cm^{-1} (benzoid), 2857 cm^{-1} (CH_2), 2929 cm^{-1} (CH_3), the OH band (3430 cm^{-1}) exists be-

Table I Water Sorption and Diffusion

T ($^\circ\text{C}$)	Slope ($10^{-5}\text{ cm/s}^{1/2}$)	W.G. (%)
25.0	8.4 ± 2.6	34.6 ± 0.2
30.0	6.3 ± 0.1	33.2 ± 0.1
35.0	5.4	30.3 ± 2.6
40.0	—	32.1 ± 1.0
45.0	12.5 ± 1.5	31.3 ± 0.6

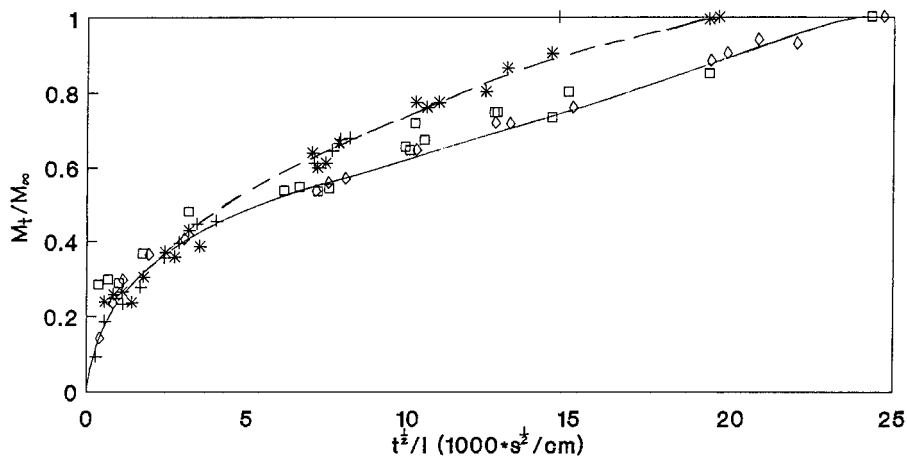


Figure 3 Water diffusion at 25°C and 30°C. (\square) 25°C (1), (\diamond) 25°C (2), ($*$) 30°C (1), ($+$) 30°C (2).

cause of nonvacuumed water or humidity. There are no features in the spectrum between 1800 and 2700 cm^{-1} because no functional groups of this polymer can demonstrate their vibration absorption peaks in this region.

All the lines from Figure 3 to Figure 8 in the following discussion were drawn just for viewing the data.

Water Diffusion

The sorption of water at temperatures from 25°C to 45°C is listed in Table I. Taking into consideration the inaccuracy of measurements, the sorbed amount of water in this polymer [expressed as W. G. (g water/100 g polymer)] was almost independent of temperature. The sorption curves at

25°C and 30°C are shown in Figure 3. In Figure 4, the sorption curves at 35°C and 40°C are plotted. The sorption curve at 45°C is shown in Figure 5. For each temperature two measurements (represented by two different data symbols) were reported. The only exception is 40°C, one with two measurements represented by one data symbol. All the sorption curves are non-Fickian, except the 40°C one can be classified as two-stage sorption, others are pseudo-Fickian¹⁰ sorption. For pseudo-Fickian sorption, the slope $[d(M_t/M_\infty)/d(t^{1/2}/l)(\text{cm/s}^{1/2})]$ of the sorption curves from 0.2 to 0.4 of M_t/M_∞ was calculated as an indication of the rate of diffusion. The calculated slopes are also shown in Table I. At temperatures from 25°C to 35°C, the calculated slopes are almost independent of temperature. At 45°C, the rate of diffusion

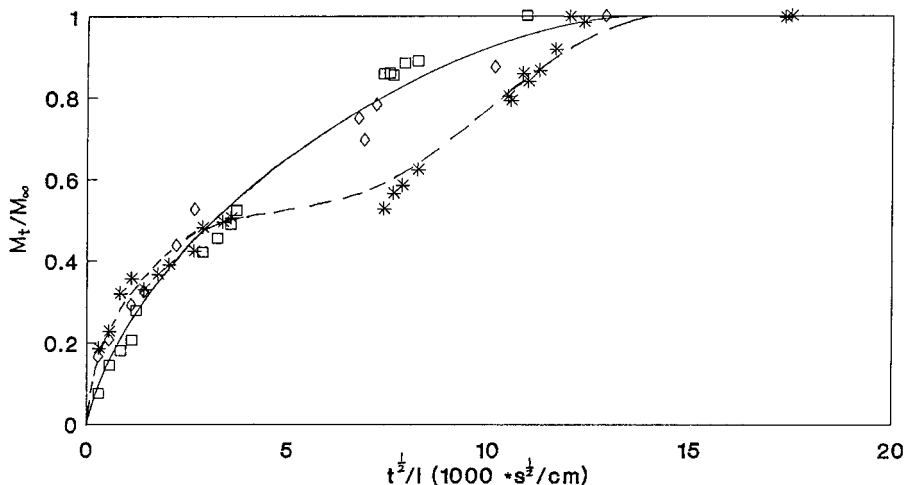


Figure 4 Water diffusion at 35°C and 40°C. (\square) 35°C (1), (\diamond) 35°C (2), ($*$) 40°C.

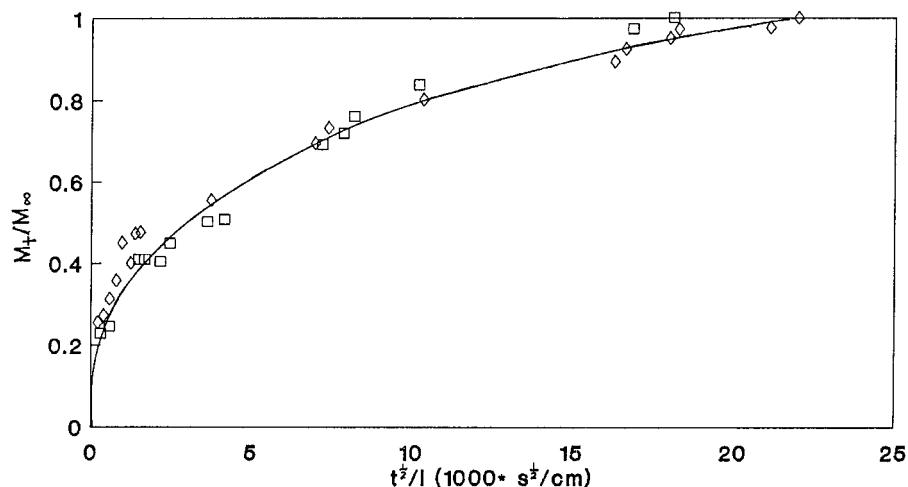


Figure 5 Water diffusion at 45°C. (□) 45°C (1), (◇) 45°C (2).

is faster than those of low temperature ones. The 40°C one was not calculated because of two-stage sorption. The interpretation for two-stage sorption proposed by Bagley and Long¹¹ is as follows. A quasi-equilibrium is reached rapidly first at the polymer surface and then by simple diffusion throughout the polymer sheet. The second stage of sorption is associated with an increase in surface concentration which occurs slowly compared with the diffusion process and is the rate-determining factor for sorption. The concentration is virtually uniform throughout the sheet and increases at a rate independent of the thickness. We do not have other experimental data or techniques aside from water diffusion studies to support this interpretation.

Ethanol and 1-Propanol Diffusion

The sorption curves at 30.5°C and 32.5°C are shown in Figure 6. In Figure 7(a), the sorption curves at 35°C and 40°C are plotted, and the sorption curves at 40°C and 45°C are shown in Figure 7(b). The 40°C curve was plotted twice for the sake of data comparison. The extended linear region of the uptake curves indicates that the sorption-diffusion process is likely to be concentration-dependent. However, we only reported liquid ethanol diffusion in this article. Ethanol vapor diffusion experiments are needed to substantiate this assumption. All the sorption curves in Figures 6, 7(a), and 7(b) are Fickian. The diffusion coefficients were calculated using the equation

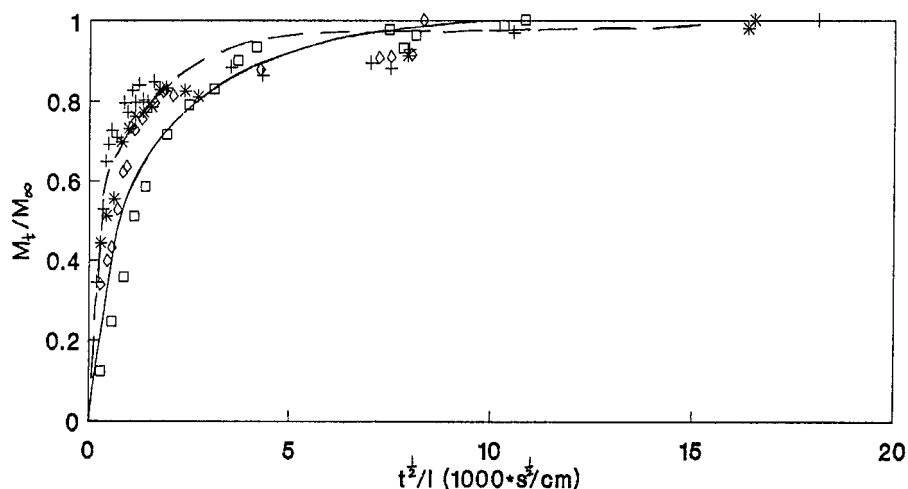


Figure 6 Ethanol diffusion at 30.5 and 32.5°C. (□) 30.5°C (1), (◇) 30.5°C (2), (*) 32.5°C (1), (+) 32.5°C (2).

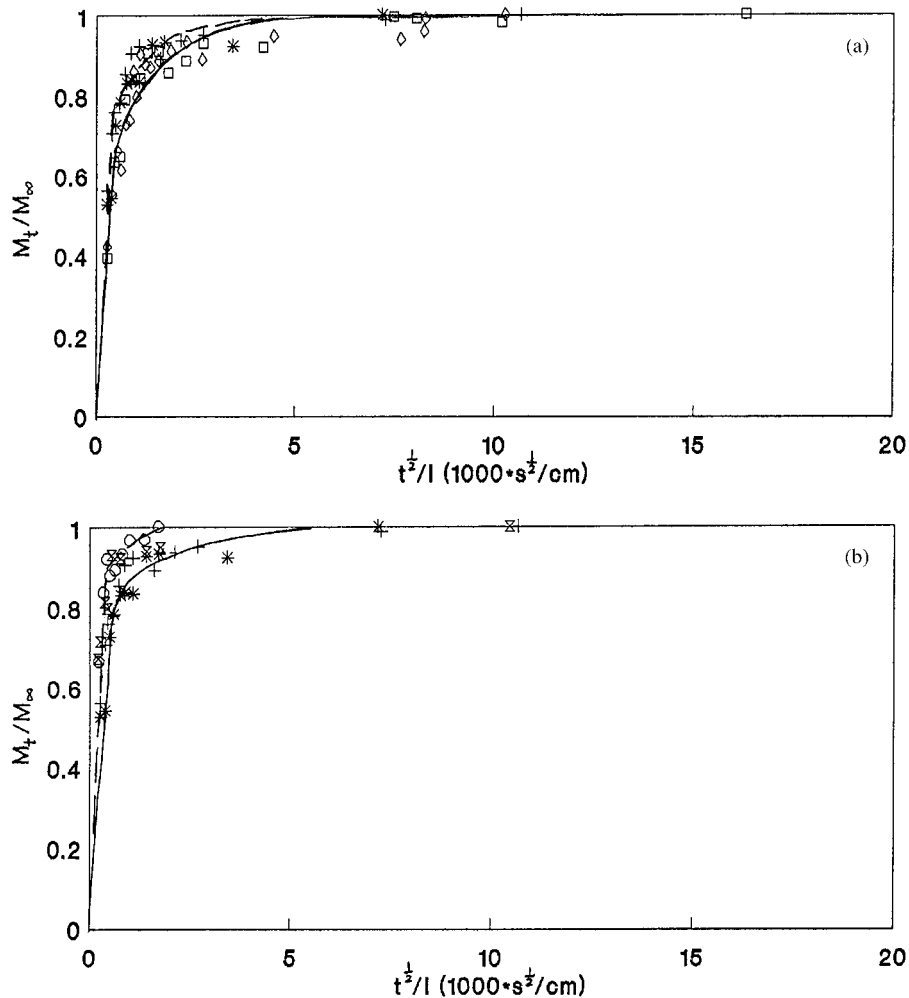


Figure 7 (a) Ethanol diffusion at 35°C and 40°C. (\square) 35°C (1), (\diamond) 35°C (2), ($*$) 40°C (1), ($+$) 40°C (2), (b) Ethanol diffusion at 40°C and 45°C. ($*$) 40°C (1), ($+$) 40°C (2), (\circ) 45°C (1), (\otimes) 45°C (2).

(1). Owing to insufficient data points at 45°C, the diffusion coefficient at this temperature was estimated. The diffusion coefficients and the sorption of ethanol are listed in Table II. The diffusion coefficients were found to increase slightly with increasing temperature from 30.5°C to 40°C, but the estimated diffusion coefficient at 45°C is much

higher than the low temperature ones. We have no explanation for the low value of diffusivity at 30.5°C, likely due to experimental error. The sorption of ethanol (expressed as W. G. in Table II) decreases with increasing temperature from 30.5°C to 40°C, but the sorbed amount of ethanol in this polymer at 45°C is about the same as that at 40°C. To summarize the result, $\ln D$ and $\ln S$ were plotted versus $1/T$ and shown in Figure 8. Activation energy of either one (D or S) cannot be calculated because of the nonlinearity of data.

To test how the hydrophobicity of solvents affects diffusion, 1-propanol diffusion at 32.5°C was also measured. The diffusion was Fickian, like ethanol. The diffusion coefficient and the sorbed amount were found to be 5.37×10^{-8} (cm^2/s) and 43.6%, respectively. Obviously, the diffusion coefficient of 1-propanol is slightly lower than the

Table II Ethanol Sorption and Diffusion

T (°C)	D ($10^{-8} \text{ cm}^2 \text{ s}^{-1}$)	W.G. (%)
30.5	4.3 ± 0.7	41 ± 1
32.5	8.4 ± 3.8	38 ± 1
35.0	8.5 ± 2.8	36 ± 1
40.0	9.3 ± 0.2	32 ± 2
45.0	53.0 ± 13.0	32 ± 1

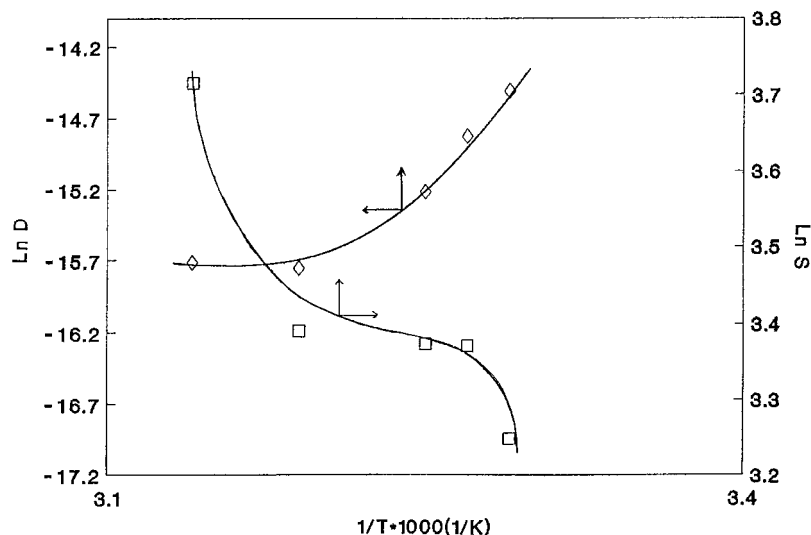


Figure 8 $\ln D$ and $\ln S$ vs. $1/T$ (ethanol).

ethanol one (8.41×10^{-8} cm²/s) because of its bigger molecular structure. 1-Propanol is more hydrophobic than ethanol, so the sorbed amount of 1-propanol is larger than that of ethanol (38.3%) because the polymer structure is mostly hydrophobic. The same reason can be used to explain the difference of sorption between ethanol and water because ethanol is more hydrophobic than water.

There is little difference between the sorption at 40°C and at 45°C for both water and ethanol, but the much larger value of the diffusion coefficient of ethanol at 45°C than the diffusivity at 40°C may be related to the structural change of polymer. The observation of the two-stage diffusion of water at 40°C lends further support to possible structural rearrangement of this polymer between 40°C and 45°C.

CONCLUSION

The diffusion of water in a dodecyl benzene sulfonic acid doped polyaniline is quite different from the ethanol and 1-propanol ones. Water diffusion is non-Fickian, but ethanol and 1-propanol diffusion are Fickian. Owing to the mostly hydrophobic polymer structure, the sorbed amount of solvent has the following order: 1-propanol > ethanol > water. The sorption of water in this polymer is almost independent of temperature, but the sorption of ethanol decreases mostly with increasing

temperature. The doped polyaniline probably goes through structural rearrangement between 40°C and 45°C as detected by the diffusion of water and ethanol.

The financial support by the National Science Council, Republic of China, under Grant NSC-84-2216-E-041-002, is greatly appreciated.

REFERENCES

1. T. A. Skotheim, Ed. *Handbook of Conducting Polymers*, Vol. 1, Marcel Dekker, New York, 1987.
2. M. Aldissi, *Proceedings of the International Conference on the Science and Technology of Synthetic Metals, Synth. Met.* 1988–1989, p. 27.
3. W. P. Hsu, K. Levon, K. S. Ho, A. S. Myerson, and T. K. Kwei, *Macromolecules*, **26**, 1318 (1993).
4. T. Nakajima and T. Kawagoe, *Synth. Met.*, **28**, 629 (1989).
5. M. T. Nguyen and L. H. Dao, *Electrochem. Soc.*, **136**, 2131 (1989).
6. J. H. Lai, Ed. *Polymers of Electronic Applications*, CRC Press, Boca Raton, Florida, 1989, Chap. 4.
7. M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Comm.*, 873 (1986).
8. Y. Cao, P. Smith, and A. J. Heeger, *Synth. Met.*, **48**, 91 (1992).
9. J. Crank, *Mathematics of Diffusion*, Oxford Univ. Press, London, 1975, Chap. 4.
10. J. Crank, *Mathematics of Diffusion*, Oxford Univ. Press, London, 1975, p. 255.
11. E. Bagley and F. A. Long, *J. Am. Chem. Soc.*, **77**, 2172 (1955).