Diffusion of Gases in Polymer Blends Near the Lower Critical Solution Temperature

R. J. Li, T. K. Kwei, and A. S. Myerson
Dept. of Chemical Engineering, Polytechnic University, Brooklyn, NY 11201

Gas diffusion through miscible blends of polystyrene (PS) with poly(vinyl methyl ether) (PVME) and poly(styrene-stat-acrylonitrile) (PSAN) with poly(methyl methacrylate) (PMMA) is studied from temperatures below the corresponding lower critical solution temperature (LCST) to temperatures above. The Arrhenius equation describes the temperature dependence of diffusion coefficients of pure components. Diffusion coefficients of methane in the 20/80 PS/PVME blend also follow the Arrhenius equation in the temperature ranges above and below their corresponding LCST; however, discontinuity is observed in the LCST region. In contrast to the PS/PVME blend, discontinuity in the LCST region is not obvious for nitrogen and methane in the 50/50 PSAN/PMMA blend. These phenomena are discussed in terms of free volume and morphology changes in the LCST region.

Introduction

The behavior of diffusion coefficients near critical points and in metastable solutions is of interest as an important transport property of the system, because it reveals information related to concentration fluctuations which become large prior to phase transitions. In binary systems, diffusion coefficients decline to zero at the critical point (Claersson and Sundelof, 1957; Haase and Siry, 1968). Similar behavior was also noted in binary solid-solute/liquid-solvent systems in aqueous supersaturated solutions (Sorell and Myerson, 1982; Chang and Myerson, 1985; Chang, 1984). This behavior has been attributed to the fact that diffusion coefficients should equal zero at all points on the spinodal curve (locus of points when $d^2\Delta G/d\phi^2=0$, where ΔG is the Gibbs' free energy of mixing and ϕ is the volume fraction).

In ternary systems, the situation is more complex. In a ternary solution with a solvent and two solutes, four diffusion coefficients are of importance. The two main term diffusion coefficients relate the flux of each solute due to its own gradient and the two cross-term diffusion coefficients which give a measure of the flux of one solute due to the gradient of the second solute. In a ternary system at a critical point or at the spinodal curve, the determinant of D_{ij} ($D_{11}D_{22}-D_{12}D_{21}$) becomes zero. The increasing magnitude of the cross-term diffusion coefficients in a ternary supersaturated solution was experimentally shown by Lo and Myerson (1989) who demonstrated the rapid decline in the determinant of D_{ij} with increasing concentration in the supersaturated region.

This spinodal curve is the limit of the metastable region and can be approached in polymer-polymer blend systems. When the temperature of a compatible polymer blend approaches the lower critical solution temperature (LCST), the binary diffusion coefficient of each polymer in the blend approaches zero. When minute amounts of diffusant molecules are present in a polymer blend, the system becomes a ternary system. The spinodal curve and critical point, however, are still at essentially the same location.

An interesting question is whether the same fluctuations occurring near the spinodal curve and critical point affect significantly the diffusion of small molecules in polymer blends. Study on the diffusion of small molecules near the critical point might provide a means to probe the fluctuations which occur prior to phase separation. To our knowledge, no research has been done on the transport of small molecules in this critical range. This led us to work on gas diffusion near the LCST of a polymer blend (and on pure component polymers at the same temperature). This study was started with the objective of determining whether there was a drastic change in diffusion coefficient approaching the LCST. Our attention, however, was soon diverted to a second aspect of the diffusion phenomena, that is, the change in diffusion coefficient as the morphology and free volume change in the LCST region.

The polymer blends chosen in this study were polystyrene (PS) with poly(vinyl methyl ether) (PVME) and poly(methyl methacrylate) (PMMA) with poly(styrene-stat-acrylonitrile) (PSAN) which contains 30 wt. % of acrylonitrile. The blend systems were reported to be miscible and had relatively low

LCSTS (McMaster, 1975; Kwei et al., 1974). Methane and nitrogen were used as the diffusant molecules. The diffusion of methane through the PS/PVME system was studied using a dynamic sorption apparatus from 75°C to temperature above the LCST (=123°C) of the blend. A permeation apparatus was used to investigate the diffusion of nitrogen and methane through the PSAN/PMMA system at temperatures around its LCST (=173°C).

Experimental Studies

Materials

Polystyrene (PS) was obtained from Polyscience. The weight-average molecular weight was reported by the manufacturer to be 190,000. Poly(vinyl methyl ether) (PVME), with a reported weight-average molecular weight of 150,000, was purchased from Aldrich. It was supplied as the 50 wt. % solution in toluene. Prior to purification, the solution was transparent but yellowish in color. To obtain a clear solution, 50 g of PVME solution was diluted with 392 mL of toluene, and then 25 g of activated carbon was added and stirred for three days. The mixture was then filtered using a regular filter paper to remove the activated carbon solids. The solution was further filtered using fine filter paper (<3 μm in pore size). The resulting solution was clear and transparent. PVME was then precipitated in 4 L of hexane. The precipitate was collected and dried under vacuum at room temperature for four days. The purified PVME was stored in a vacuumed desiccator, which was placed in a refrigerator to prevent oxidation.

Poly(styrene-stat-acrylonitrile) (PSAN) containing 30 wt. % of acrylonitrile and poly(methyl methacrylate) (PMMA) were obtained from Scientific Polymer Products. The weight-averaged molecular weight of PSAN is 185,000; the weight-averaged molecular weight of PMMA is 93,000 and the number-averaged molecular weight 46,000.

The phase separation temperatures of the polymer blends were measured by the use of a light scattering apparatus. The heating rate was 1°C/min. The phase separation temperatures of PSAN/PMMA and PS/PVME blend at different compositions are shown in Figure 1. The LCST of PSAN/PMMA blends is 173°C, and the critical composition is 50 wt. % PSAN. The PS/PVME blend has an LCST at 123°C and a critical composition at 20 wt. % PS.

Preparation of films

To prepare films of PS or PS-rich blends, PS and PVME in the desired ratios were dissolved in HPLC-grade toluene to form solutions containing 10 wt. % of total polymer. Constant volumes of the polymer solution was cast on glass plates of 25 cm^2 to obtain films of the same thickness. The films were dried at room temperature under atmospheric pressure for 1 day. Then, the films were transferred to a vacuum oven, whose temperature was raised from room temperature to 120°C over a period of 4 days. The thickness of the film was measured with a Mitutoyo 227 low-force micrometer.

For PVME and PVME-rich blends, a thick film was prepared in a cylindrical stainless steel cup because the glass transition temperature of PVME is low ($T_g = -21$°C). The cup was filled with 10 wt. % polymer solution and then dried in a vacuum oven under room temperature overnight. As the solution level in the cup dropped, the cup was filled again. The above procedures were repeated until about 2.5 g of polymer sample remained in the cup. The sample was then dried in the vacuum oven by raising the temperature of the oven 5°C each day to 50°C. The weight of the sample was measured everyday until no weight change was detected.

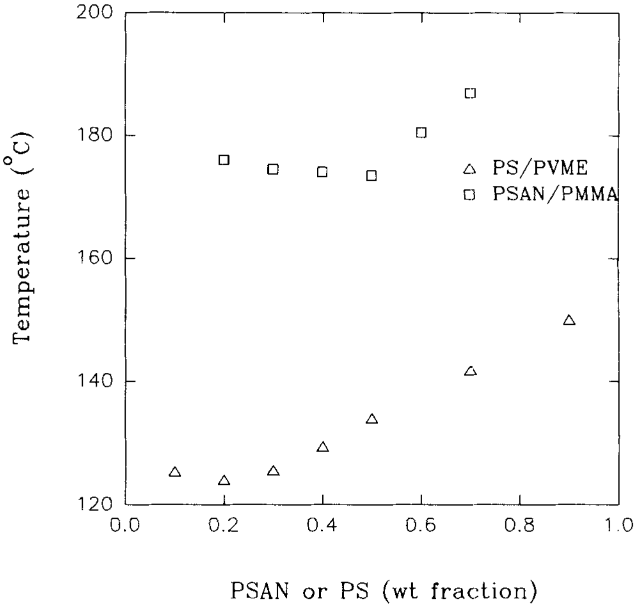

Figure 1. Phase diagram for PSAN/PMMA and PS/PVME blends.

For the procedures of film preparation of PSAN/PMMA blends, see the previous article by Li et al. (1993).

Gas permeation experiments

A permeation apparatus (Koros et al., 1976) was used to measure permeation and diffusion coefficients of gases through PSAN/PMMA polymer films over the temperature range 120–180°C. Since the polymer becomes rubbery when the temperature is above its T_g, the film may deform under pressure during the permeation experiment. To avoid errors arising from film deformation, a procedure discussed previously by Li et al. (1993) was used.

Gas sorption experiments

A sorption apparatus similar to the one used by Koros and Paul (1976) was used to measure the solubility and diffusivity of gas in PS/PVME blends. For PS or PS-rich PS/PVME blends, films with the same thickness were loosely stacked inside the sorption cell. For PVME or PVME-rich blends, the cylindrical stainless steel cup filled with polymer sample was put inside the sorption cell. By monitoring the pressure change with time, the diffusion coefficients were calculated from (Crank, 1975):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{(1+\alpha+\alpha^2 q_n)} \exp(-Dq_n^2 t/\ell^2) \qquad (1)$$

where ℓ is the thickness of the film, D is the diffusion coefficient of gas, M_t is the amount of gas absorbed in the polymer at time t, M_∞ is the amount of gas absorbed at equilibrium, and t is the time elapsed. The q_ns are the nonzero positive roots of

$$\tan q_n = -\alpha q_n \qquad (2)$$

where α is the ratio of the volumes of the gas phase and the polymer sample divided by the solubility coefficient of the gas in the polymer. By comparing the pressure drop in the sorption cell observed experimentally with corresponding calculated values, the diffusion coefficient can be calculated. The temperature bath used was the same as that of the permeation apparatus. Two Setra 204 pressure transducers were used to measure the pressure. The pressure transducers were connected to an Omega WB-31 A/D converter which was connected to an IBM personal computer. Pressure readings on different channels were monitored and recorded on the computer for further analysis.

Results and Discussion

Diffusion of gases in PSAN/PMMA blends

The diffusion and permeation coefficients of nitrogen and methane through PSAN/PMMA blends were measured from 120 to 175°C. The compositions were two pure components and the 50/50 PSAN/PMMA blend which was the critical composition. The diffusion coefficients of methane and nitrogen for PSAN, PMMA, and 50/50 PSAN/PMMA are plotted vs. $1/T$ in Figures 2 and 3.

The Arrhenius equation was used to fit experimental results. The values of D_o and ΔE were tabulated by Li et al. (1993). There was no obvious discontinuity observed in the plot of log D vs. $1/T$ for the 50/50 PSAN/PMMA blend around the LCST.

Diffusion of methane in PS/PVME blends

The PS/PVME system was used for this study because the diffusion coefficients of gases are high in PVME but low in PS. Hopefully, large differences in D values may facilitate the detection of the discontinuity in the LCST region. In addition, the PS/PVME system has a LCST of 123°C which is experimentally more accessible (Figure 1). Methane was used since it had high solubility in the PS/PVME but would not plasticize or oxidize PS and PVME. Three polymer compositions used are PS, PVME, and the 20/80 PS/PVME blend. Again, the 20/80 blend was the critical composition of this system determined from the light scattering experiment.

Diffusion coefficients vs. $1/T$ for PS, PVME, and 20/80 PS/PVME are given in Figure 4. The diffusion coefficient of PVME increased with temperature in the entire temperature range from 75 to 130°C. In contrast, the diffusion coefficients of PS increased from 75 to 100°C, but there was an apparent decrease after raising the temperature to above the T_g of PS ($T_g = 101$°C). The anomalous decrease is caused by an experimental artifact. As discussed earlier, the PS films of the same thickness were stacked inside the sorption cell. When the temperature was raised to above the T_g of PS, the PS film became rubbery and adhered to each other. This decreased the contact area between the gas and the films. As a result of the area reduction, the pressure decay was slowed and this decreased the diffusion coefficient calculated from this experiment. For this reason, the measurement was not included in Figure 4.

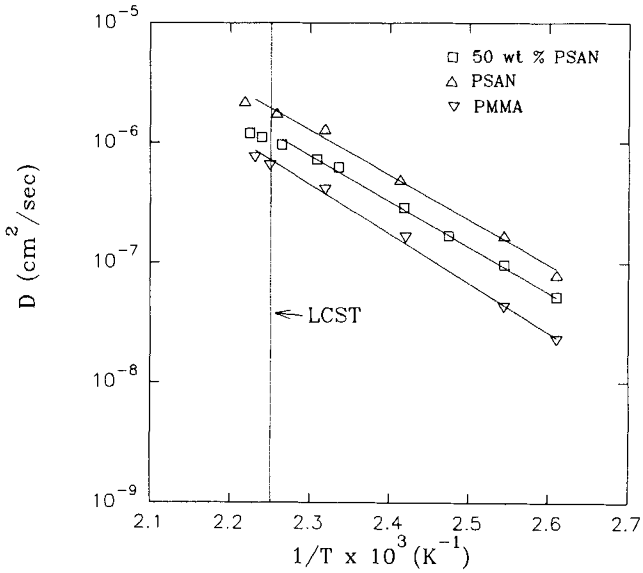

Figure 2. Diffusion coefficients of nitrogen in PSAN/PMMA blend system.

Regressions following the Arrhenius equation were taken for temperatures ranging from 75 to 100°C for PS and from 75 to 130°C for PVME to calculate preexponential factors and activation energies of diffusion coefficient. ΔE and D_o for PVME are 7.3 cal/mol and 0.26 cm_2/s, respectively; ΔE and D_o for PS below its glass transition temperature are 11.7 kcal/mol and 2.04 cm^2/s.

Dynamic sorption experiments for the 20/80 PS/PVME blend were carried out with temperatures increasing from 75 to 136°C. Small temperature increments were used around

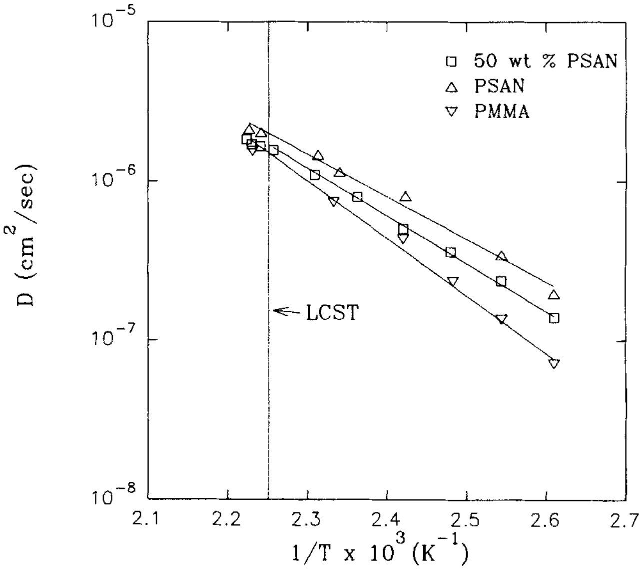

Figure 3. Diffusion coefficients of methane in PSAN/PMMA blend systems.

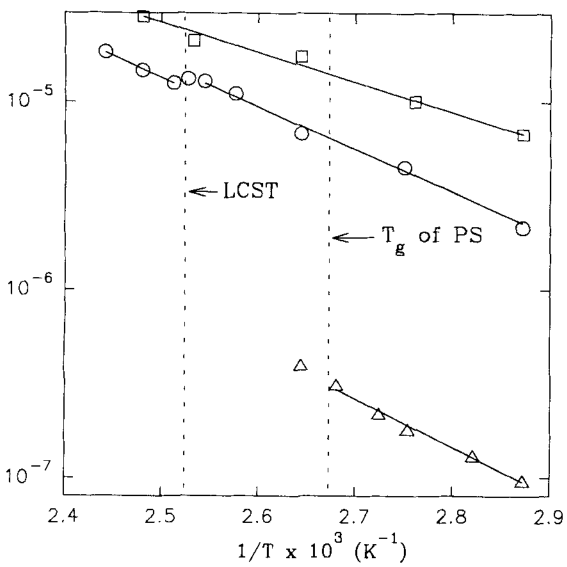

Figure 4. Diffusion coefficients of methane in PS/PVME blends vs. temperature.

(□) PVME; (○) 20/80 PS/PVME; (△) PS>

123°C (120, 122.5, 125 and 130°C) to study the gas transport behavior in the LCST region. In contrast to the PSAN/PMMA system, a discontinuity in the Arrhenius plot was observed between 120 and 125°C. The regression analysis provided two nearly parallel lines for temperatures ranging from 75 to 120°C and from 125 to 136°C, respectively. The values of ΔE and D_o of 20.80 PS/PVME blend are 10.4 cal/mol and 7.89 cm^2/s for temperatures below LCST and 10.9 kcal/mol and 11.6 cm^2/s for temperatures above LCST.

The discontinuity in D around the LCST of PS/PVME blend is most likely caused by the phase separation of the polymer blend. Experimental results for the PSAN/PMMA blend, however, do not show an obvious discontinuity. The reason is believed to be the small difference between the diffusion coefficients of PSAN and PMMA near the LCST [D(PSAN)/D(PMMA) = 2.7 for methane]; therefore, even if there is a change in diffusion coefficient due to phase separation, it is difficult to detect the change experimentally. To illustrate this point, we applied the effective medium theory (Sax and Ottino, 1984) to model the transport of small molecules in dispersed polymers blends. Calculations based on the model were compared with the predictions of the linear logarithmic mixing rule (Hopfenberg and Paul, 1978) for the prediction of the transport behavior of small molecules in a homogeneous blend. The coordination number and the solubility ratio, S_a/S_b, were assumed to be 6 and 0.5, respectively. The results indicate that the diffusion coefficient of a 50/50 blend predicted from effective medium theory differs by only 5% from the linear logarithmic mixing rule when $D_a/D_b = 2.7$. The difference increases with the ratio D_a/D_b and reaches 17% when D_a/D_b is 20. Since the PS/PVME system has a much larger diffusion coefficient difference between the two components, the discontinuity can be observed experimentally.

It was interesting to note that the diffusion coefficients of methane essentially did not change in the PS/PVME blend in the temperature range from 120 to 125°C. The values of D are smaller than what one would expect by extrapolating the low-temperature data. The experimental results seem to imply that there is no or only small free volume change of the blend in the LCST region.

While the free volume of a homogeneous system always increases with temperature, Wendorff et al. (1987) reported a volume shrinkage when the temperature of a poly(vinylidene fluoride)-poly(methyl methacrylate) blend is raised beyond the LCST phase boundary. On the other hand, Tsujita et al. (1992) found an increase in the specific volume of a 25/75 PS/PVME blend upon raising the temperature beyond the LCST boundary. Thus, the apparent discontinuity of the diffusion coefficient in the vicinity of LCST cannot be explained by free volume consideration alone.

Once the phase boundary was crossed, the diffusion coefficients of methane in the 20/80 PS/PVME blend increased with temperature, again in accordance with the Arrhenius equation. In the experiments performed, the PS/PVME blend was kept at the experimental temperature for 2 days before the gas sorption experiments were started. Based on the NMR study of Chu and coworkers (1990), we assumed that the blend has separated into two phases having compositions close to the equilibrium values. Although the compositions in the two coexisting phases must change with temperature, it is possible that the changes are small or have little effect on gas diffusion through the blend system. Therefore, a linear relation between diffusion coefficient and reciprocal temperature is still observed.

Literature Cited

Chang, Y. C., and A. S. Myerson, "The Diffusivity of Potassium Chloride and Sodium Chloride in Concentrated, Saturated and Supersaturated Aqueous Solutions," *AIChE J.*, **31**, 890 (1985).

Chang, Y. C., "Concentration Dependent Diffusion of Solid-Solute, Liquid Solvent Systems in the Supersaturated Region," PhD Thesis, Georgia Inst. of Technol., Atlanta (1984).

Claersson, S., and L. O. Sundelof, "Free Diffusion Near the Critical Miscibility Temperature," *J. Chem. Phys.*, **54**, 914 (1957).

Crank, J., *The Mathematics of Diffusion*, Oxford University Press, London (1975).

Chu, C. W., L. C. Dickinson, and J. C. W. Chien, "Study of Critical Phenomena of PS/PVME Blends by Solid State NMR," *J. Appl. Polym. Sci.*, **41**, 2311 (1990).

Haase, R., and M. Siry, "Diffusion in Kritischen Entmischungsgebiet Binarer Flussiger Systeme," *Z. Phys. Chem.* (*neue Foge*), **57**, 56 (1968).

Hopfenberg, H. B., and D. R. Paul, "Polymer Blends," D. R. Paul and S. Newman, eds., Vol. I, Academic Press, New York (1978).

Koros, W. J., D. R. Paul, and A.A. Rocha, "Carbon Dioxide Sorption and Transport in Polycarbonate," *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 687 (1976).

Koros, W. J., D. R. Paul, and A. A. Rocha, "Design Considerations for Measurement of Gas Sorption in Polymers by Pressure Decay," *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1903 (1976).

Kwei, T. K., T. Nishi, and R. F. Roberts, "A Study of Compatible Polymer Mixtures," *Macromol.*, **7**, 667 (1974).

Li,, R. J., W. P. Hsu, T. K. Kwei, and A. S. Myerson, "Diffusion and Permeation of Gases in Miscible Poly(Methyl Methacrylate) and Poly(Styrene-Stat-Acrylonitrile): Above and Below the Glass Transition Region," *AIChE J.*, **39**, 1509 (1933).

Lo, P. Y., and A. S. Myerson, "Ternary Diffusion Coefficients in Metastable Solutions of Glycine-Valine-H$_2$O," *AIChE J.*, **35**, 676 (1989).

MacMaster, L. P., "Aspects of Liquid-Liquid Phase Transition Phenomena in Multicomponent Polymer Systems," *Adv. Chem. Serv.*, No. 142, ACS, Washington, DC (1975).

Sax, J., and J. M. Ottino, "Modeling of Transport of Small Molecules in Polymer Blends: Application of Effective Medium Theory," *Polym. Eng. Sci.*, **23**, 165 (1983).

Sorell, L. S., and A. S. Myerson, "Diffusivity of Urea in Concentrated Saturated and Supersaturated Solutions," *AIChE J.*, **28**, 772 (1982).

Tsujita, Y., M. Kato, T. Kinoshita, and A. Takizawa, "Miscibility Estimated by the Volume Change due to Mixing of a Polystyrene/Poly(Vinyl Methyl Ether) Blend System," *Polymer*, **33**, 773 (1992).

Wendorff, J. H., Y. Li, and M. Wold, "Investigations of Volume Changes Attending Mixing of Poly(Methyl Methacrylate) and Poly(Ethyl Acrylate) with Poly(Vinylidene Fluoride)," *Polymer Commun.*, **28**, 265 (1987).

Manuscript received Sept. 13, 1993, and revision received Feb. 9, 1994.