

CONCENTRATION DEPENDENCE OF DIFFUSIVITY FOR THE STYRENE-POLYSTYRENE AND ETHYLBENZENE-POLYSTYRENE SYSTEMS

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In a previous paper,⁴⁾ a method of measuring the mutual diffusivity was proposed for the styrene-polystyrene (ST-PS) and ethylbenzene-polystyrene (EB-PS) systems in the temperature range from 425 to 525 K and the solvent concentration range up to 3 wt%. The diffusivities measured were correlated with an Arrhenius-type equation, assuming the diffusivity to be constant independently of solvent concentration. However, for many polymer-solvent systems it has been found experimentally that the diffusivity shows a strong dependence on solvent concentration, especially at concentrations close to zero.³⁾

In this paper the concentration dependence of the mutual diffusivity is evaluated, using the concentration distributions obtained in the previous paper⁴⁾ for both systems and comparing them with the free-volume theory of Vrentas and Duda.^{2,5)}

1. Numerical Analysis

The equations to be solved are fundamentally the same as in the previous paper.⁴⁾ The modifications are shown in the following.

(i) The concentration dependence of the logarithm of the mutual diffusivity ($\ln D$) is assumed to be a linear function of the mass fraction of the solvent ω in the narrow range up to 3 wt%:

$$\ln D = \ln \bar{D}_0 + b \cdot \omega \quad (1)$$

where \bar{D}_0 is the diffusivity at zero solvent concentration and b a constant defined by $(\partial \ln D / \partial \omega)$. Then \bar{D}_0 and b are considered to be functions of temperature alone.

(ii) The initial concentration distribution $C_0(z)$ for the ST-PS system is assumed to be the expression

$$\frac{C_0(z) - C_s}{C_\infty - C_s} = 1 - \exp(-a \cdot z^2) \quad (2)$$

where z is the distance from the evaporation surface, C_s the concentration at $z=0$, C_∞ the concentration at

$z=\infty$, and a a fitting parameter. This modification is introduced to determine the diffusivity accurately, because in a few experimental runs a concentration distribution of the solvent in the vicinity of the evaporation surface was observed in the zero-th time step, namely at the beginning of the diffusion.

The diffusion equation without reaction is given by

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + \left(\frac{\partial D}{\partial C} \right) \left(\frac{\partial C}{\partial z} \right)^2 \quad (3)$$

where C is the mass concentration and t the time. A conventional explicit method is not suitable for obtaining a stable solution of the non-linear differential equations, because the condition of the stable solution, $0 < D \Delta t / \Delta z^2 \leq 1/2$, could not always be satisfied at a fixed Δt and Δz during the convergence of D by the simplex optimization method, where D fluctuates greatly. To avoid this instability, we use the geometric mean for $(\partial C / \partial z)^2$ as

$$\left(\frac{\partial C}{\partial z} \right)^2 = \left(\frac{C_{i+1,j+1} - C_{i+1,j-1}}{2\Delta z} \right) \cdot \left(\frac{C_{i,j+1} - C_{i,j-1}}{2\Delta z} \right) \quad (4)$$

where subscripts i and j are the i -th time-step and the j -th distance-step, respectively. The Crank-Nicolson implicit method is applied for the term $\partial^2 C / \partial z^2$, thus making the differential equations solvable stably as far as the problem herein considered is concerned.

As $C_0(z)$ we can arbitrarily choose one of the measured concentration distributions at any time step. To solve the problem numerically, $C_0(z)$ must be expressed as a function of distance like Eq. (2), whose right-hand side becomes zero at $z=0$ and unity at $z=\infty$. For the ST-PS system Eq. (2) is the most preferable expression among the rational expressions studied. The parameters a and C_∞ in Eq. (2) can be determined to give the best fit for the observed distribution by the least squares method, assuming C_s to be zero.

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Table 1. Concentration dependence of diffusivity

Run no.	Temperature [K]	\bar{D}_0 [cm ² ·s ⁻¹]	b [—]
Styrene-Polystyrene System			
2-2	475	1.28×10^{-6}	23
2-3	500	2.72×10^{-6}	25
2-4	500	3.20×10^{-6}	14
2-5	450	6.26×10^{-7}	31
2-6	475	1.49×10^{-6}	18
2-7	526	6.58×10^{-6}	15
2-8	424	2.12×10^{-7}	52
Ethylbenzene-Polystyrene System			
3-1	475	1.50×10^{-6}	21
3-2	500	2.92×10^{-6}	13
3-3	450	4.42×10^{-7}	38
3-4	475	1.41×10^{-6}	19
3-5	425	1.75×10^{-7}	50
3-6	526	6.66×10^{-6}	3

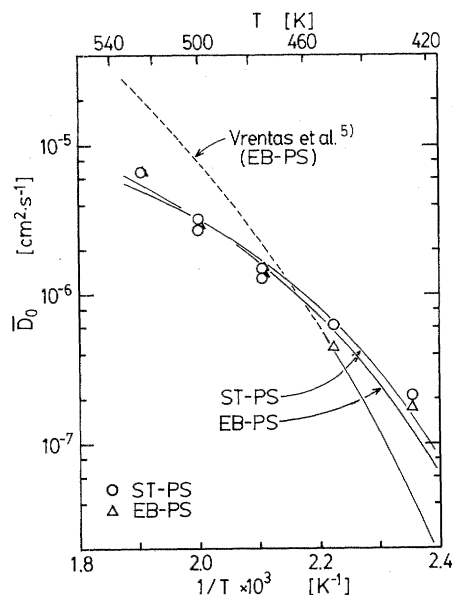
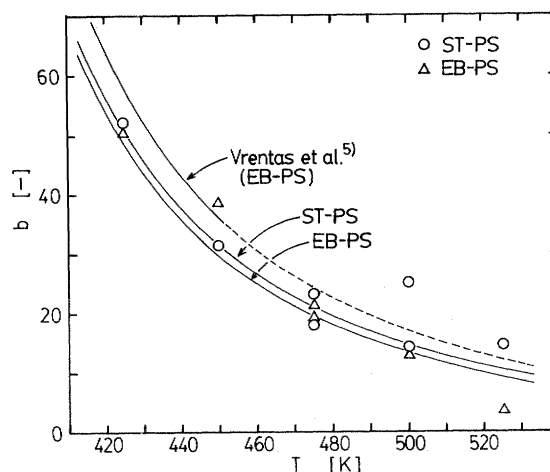
2. Results and Discussion

Table 1 shows the diffusivity at zero solvent concentration \bar{D}_0 and the constant b in Eq. (1) determined by the simplex optimization method. Figures 1 and 2 show the temperature dependences of \bar{D}_0 and b , respectively. The line labeled Vrentas *et al.*⁵⁾ indicates the predicted values at $\omega=0$ for the EB-PS system using their parameters, while the others indicate the correlated values at $\omega=0$ for both systems using the parameters determined from our experiments. It is observed that \bar{D}_0 and b for both ST and EB agree well with each other within the experimental error.

We originally intend to measure the diffusivity of the ST-PS system at an elevated temperature at which the actual devolatilization is carried out. The temperature range of our interest is far above the 115.5 to 178°C range of Duda *et al.*¹⁾ The solid and dotted lines of Vrentas *et al.* in Figs. 1 and 2 show the values in their experimental range of temperature and the values extrapolated over their range, respectively. \bar{D}_0 values predicted using the parameters of Vrentas *et al.* are larger than those obtained from our experiments at temperatures higher than about 470 K. This suggests that it is not appropriate to design a devolatilizer using the parameters determined from the diffusivity in the lower temperature range.

The parameters D_0 , E and ξ in the free-volume theory of Vrentas and Duda determined from our experiments are listed in Table 2 with the other parameters used and those determined by Vrentas *et al.*⁵⁾ for comparison. Since the constant b derived from the free-volume theory is a function only of ξ at $\omega=0$, the parameter ξ is at first determined by assuming that the value of b obtained is that at $\omega=0$. Then D_0 and E are determined by the simplex method.

Since E is defined as the critical energy that a

**Fig. 1.** Diffusivities at zero solvent concentration \bar{D}_0 for the ST-PS and EB-PS systems**Fig. 2.** Concentration dependence of diffusivity ($b = \partial \ln D / \partial \omega$) for the ST-PS and EB-PS systems**Table 2.** Free-volume parameters for solvent(1)-polymer(2) system

Parameter*		ST-PS	EB-PS	EB-PS by Vrentas <i>et al.</i> ⁵⁾
\bar{V}_1^*	[cm ³ /g]	0.912	0.946	0.946
\bar{V}_2^*	[cm ³ /g]	0.850	0.850	0.850
K_{11}/γ	[cm ³ /gK]	1.47×10^{-3}	1.49×10^{-3}	1.49×10^{-3}
K_{12}/γ	[cm ³ /gK]	5.82×10^{-4}	5.82×10^{-4}	5.82×10^{-4}
$K_{21} - T_{g1}$	[K]	-92.4	-84.4	-84.4
$K_{22} - T_{g2}$	[K]	-327	-327	-327
ξ	[—]	0.55	0.52	0.59
χ	[—]	0.42	0.45	0.45
D_0	[cm ² /s]	1.61×10^{-5}	1.41×10^{-4}	1.95
E	[kJ/mol]	-12.5	-2.53	31.1

* Definition of the symbols is the same as in Ref. 2.

molecule needs to overcome attractive forces, it is expected to have a positive value. The values of E which give the best fit for our experimental results, however, become negative for both ST and EB. Vrentas *et al.*⁵⁾ also obtained a negative value of E for the toluene-polystyrene system. We conclude at least that the free-volume theory of Vrentas and Duda is a correlative rather than a predictive method at a temperature extremely far above the glass transition temperature of the polymer.

Nomenclature

a	= parameter defined in Eq. (2)	[cm ⁻²]
b	= parameter defined in Eq. (1)	[—]
C	= mass concentration	[g·cm ⁻³]
C_s	= surface concentration	[g·cm ⁻³]
$C_0(z)$	= initial concentration distribution	[g·cm ⁻³]
C_∞	= concentration at $z = \infty$	[g·cm ⁻³]
D	= mutual diffusivity	[cm ² ·s ⁻¹]
D_0	= pre-exponential factor	[cm ² ·s ⁻¹]
\bar{D}_0	= diffusivity at zero solvent concentration	[cm ² ·s ⁻¹]
E	= critical energy per mole needed to	

	overcome attractive forces	[kJ·mol ⁻¹]
t	= time	[s]
Δt	= step of time	[s]
z	= distance from evaporation surface	[cm]
Δz	= step of distance	[cm]
ξ	= ratio of critical molar volume of solvent jumping unit to that of polymer	[—]
ω	= mass fraction of solvent	[—]
<Subscripts>		
i	= time-step	
j	= distance-step	

Literature Cited

- 1) Duda, J. L., Y. C. Ni and J. S. Vrentas: *J. Appl. Polym. Sci.*, **22**, 689 (1978).
- 2) Duda, J. L., J. S. Vrentas, S. T. Ju and H. T. Liu: *AIChE J.*, **28**, 279 (1982).
- 3) Fujita, H.: *Fortschr. Hochpolym.-Forsch.*, **3**, 1 (1961).
- 4) Sakakibara, Y., H. Takatori, I. Yamada and S. Hiraoka: *J. Chem. Eng. Japan*, **23**, 170 (1990).
- 5) Vrentas, J. S., J. L. Duda, H.-C. Ling and A.-C. Hou: *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 289 (1985).