

## Transport and Equilibrium Phenomena of Gases in Styrene-Butadiene Block Copolymers

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The diffusion and solution behavior for a series of inert gases (helium, argon, nitrogen, krypton, and xenon) in films of styrene-butadiene block copolymers having different morphologies were studied by the static sorption method. The equilibrium solubility coefficients of gases in the copolymer films were described in terms of a model, in which additivity of volumes of both components was assumed. The temperature dependence of diffusion and solubility coefficients over the range from 25 to 75°C was represented by the Arrhenius-type equation with constant activation energy for diffusion and heat of solution, respectively. Thermodynamic parameters were evaluated, and mechanisms of gaseous diffusion and solution in the block copolymer films were discussed.

KEY WORDS: Diffusion coefficient / Solubility coefficient / Energy of activation for diffusion / Heat of solution /

### INTRODUCTION

In previous papers,<sup>1-3)</sup> we have described the permeation, diffusion, and solution behavior of inert gases in styrene-butadiene block copolymers. It was shown, as far as the kinetic nature at low temperatures is concerned, that diffusion and permeation processes of gases, except for small gas molecules like helium, are governed primarily by the behavior in a polybutadiene matrix. Results of solubility measurements at room temperature indicated that the transient (time-lag) method counts only the mobile penetrant in the polybutadiene matrix, while the equilibrium (desorption) method counts less diffusive ones in the polystyrene phase as well.

One of the most valuable source of information on the mechanism of diffusion is the variation of diffusion coefficients with temperature. For the system of inert gases and styrene-butadiene block copolymers, the temperature dependence of diffusion coefficient at temperatures between 25 and about 75°C was represented by the Arrhenius-type equation with constant activation energy for diffusion.<sup>1,3)</sup> The latter temperature is close to the glass transition temperatures of the polystyrene blocks in the copolymer samples. In this paper, the activation energy for diffusion is interpreted in light of the model proposed by Brandt<sup>4)</sup> and the transition state theory by Eyring and others.<sup>5)</sup>

The permeation and diffusion behavior of gases in the styrene-butadiene block copolymers at room temperature was explained well by a simple model in which additivity of volumes of both components was assumed.<sup>1-3)</sup> In the present study, we examine applicability of the model to the data of equilibrium solubility of gases.

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Further, the solubilities will be analyzed in terms of a theoretical treatment of solution of gases in polymers, which has been developed by Gee.<sup>6)</sup> We expect that the significance of the solubility data becomes much clear by relating them to the theory.

## EXPERIMENTAL

### Materials

The styrene-butadiene (S-B) block copolymers used in the present study were identical with those used previously.<sup>1,2)</sup> The morphologies of film specimens were observed by electron microscopy using the OsO<sub>4</sub> fixation technique. The domain structures of the specimens used in the measurements were (a) polystyrene (PS) rods embedded in a polybutadiene (PB) matrix (designated as sample R-1) and (b) a series of alternating lamellae of styrene and butadiene components (L-1). Electron micrographs of these specimens have revealed that the PS domains arrange randomly in the films.<sup>1)</sup> A commercial PB, Solprene 200, was employed as a reference material. Isomer contents of the PB chain in the PB and the block copolymer samples were almost comparable with one another.<sup>7)</sup> An anionically polymerized PS sample having molecular weight of  $1.06 \times 10^6$  was also employed as another reference material.

Inert gases of purity exceeding 99.995 % by volume were used as penetrant. These are helium, argon, nitrogen, krypton, and xenon.

### Method

Measurements of the diffusion coefficient  $D$  and the equilibrium solubility coefficient  $S$  were made by the modified static sorption method. The apparatus and procedure have been described in detail elsewhere.<sup>2)</sup>

## RESULTS AND DISCUSSION

### Diffusivity

In the temperature region between 25 and 75°C, the diffusion coefficient have the exponential temperature dependence of an activated process,<sup>1,3)</sup> *i.e.*

$$D = D_0 \exp(-E_D/RT) \quad (1),$$

where the frequency factor  $D_0$  and the activation energy for diffusion  $E_D$  are inde-

Table I. Energies of Activation for Diffusion

Gas	$E_D/\text{kJ mol}^{-1}$				$d_{T=298\text{K}}/\text{\AA}$
	S-B block copolymer		PB	PS	
	R-1	L-1			
He	17.6	16.3	17.2	—	2.17
Ar	23.0	24.7	25.4	32.9	3.61
N <sub>2</sub>	27.2	30.6	22.5	31.6	3.75
Kr	30.4	31.6	30.5	36.6	4.11
Xe	28.5	35.2	28.8	50.2	4.80

Table II. Values of the Frequency Factor  $D_0$  for Diffusion

Gas	$D_0/10^{-6}\text{cm}^2\text{s}^{-1}$			
	S-B block copolymer		PB	PS
	R-1	L-1		
He	15.4	13.2	16.1	—
Ar	1.96	1.31	2.24	0.048
N <sub>2</sub>	1.54	0.88	1.98	0.035
Kr	1.12	0.56	1.65	0.0080
Xe	0.56	0.26	0.80	0.0006

pendent of temperature. Table I lists values of  $E_D$  in this region of temperature. Diameters of the inert gases at 25°C, which have been estimated from gas viscosities,<sup>8)</sup> are also given in the table. It is noted that the values of  $E_D$  for the block copolymers are close to those for PB. These values are fairly smaller than those for PS. The frequency factors are shown in Table II.

Brandt has presented a model for the diffusion of small molecules in polymers and derived an expression for the activation energy for diffusion.<sup>4)</sup> In this treatment, the activation energy is assumed to consist of two contributions: (a) an intermolecular energy term and (b) an intramolecular energy term. The intermolecular term is due to the repulsion which the polymer chains experience from their neighbors on making room for the penetrant molecule, and is a function of the cohesive energy density of the polymer. The diffusion process of small molecules in rubbery polymers is considered to be governed mostly by this effect. According to Brandt's expression the intermolecular term depends on the diameter of the penetrant molecule. The intramolecular term is considered to arise from the bending of the two neighboring chains and is expressed as a function of the flexibility of the chain segments. For the diffusion in glassy polymers this term dominates, and the activation energy is expressed as to be proportional to the square of the diameter of the penetrant molecule.

In Fig. 1 the measured activation energies for diffusion  $E_D$  are plotted against the diameter of the gas molecule  $d$  and  $d^2$ . As expected  $E_D$  for PS is proportional to  $d^2$ ,

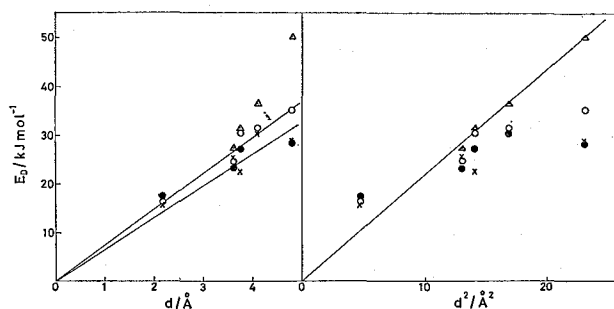


Fig. 1. Activation energy for diffusion versus gas diameter and square of gas diameter.  
S-B block copolymer, ●: R-1, ○: L-1; ×: PB, △: PS.

while values of  $E_D$  for two copolymers and PB depend on  $d$ . The linear dependence on  $d$  of  $E_D$  for the copolymer samples indicates that the diffusion processes of gases in the copolymer films are governed primarily by the mobility of polymer chains in the rubbery PB matrix. This is consistent with the conclusion derived previously.<sup>1,3)</sup> The values of  $E_D$  for sample L-1 have somewhat stronger dependence on  $d$  than that for samples R-1 and PB.

A fundamental relationship between the energy and the entropy of activation was demonstrated by Meares.<sup>9)</sup> The application of the theory of absolute reaction rates to diffusion<sup>9)</sup> gives

$$D = e\lambda^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{E_D}{RT}\right) \quad (2),$$

where  $\Delta S^*$  is the entropy of activation associated with a mole of unit diffusion acts,  $\lambda$  the unit distance travelled, and  $e$ ,  $k$ , and  $h$  have their usual meanings. Comparison with Eq. (1) shows that

$$D_0 = e\lambda^2 \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \quad (3).$$

Using the values of  $\lambda$  assumed by Meares, *i.e.* 9Å for PS and 27Å for PB, R-1, and L-1,<sup>9)</sup> we calculated  $\Delta S^*$  from  $D_0$  using Eq.(3). Figure 2 shows relation between the entropy and the energy of activation for diffusion. A linear relationship, except for the data of helium as diffusant, is obtained for PB, R-1, and L-1. The relation for PS is also represented by a straight line. It is noted that the entropy of activation for PS is much smaller than that for PB and two copolymer samples if comparison is made at a certain activation energy.

A theoretical justification of the linear relationship between the entropy and the activation energy for diffusion has been given by Lawson based upon a continuum theory.<sup>10)</sup> Lawson has shown that the ratio,  $\Delta S^*/E_D$ , is independent of the nature

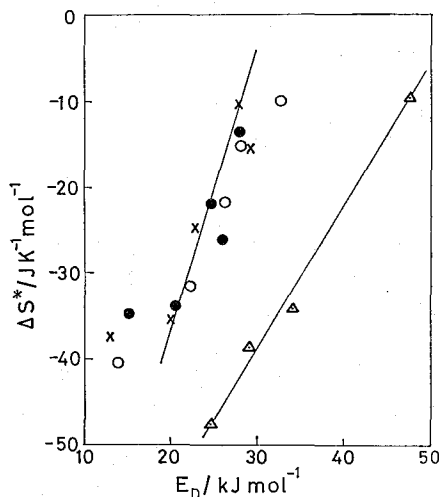


Fig. 2. Relation between entropy and energy of activation for diffusion. The symbols have the same meaning as in Fig. 1.

of penetrants and is approximately equal to  $4\alpha$ , where  $\alpha$  is the volume thermal expansion coefficient of the polymer. From the slopes of the straight lines drawn in Fig. 2, values of  $\alpha$  were determined as  $7.2 \times 10^{-4}$  and  $4.1 \times 10^{-4} \text{K}^{-1}$  for PB and PS, respectively. These values are compared well with those estimated from dilatometry, *i.e.*  $7.8 \times 10^{-4}$  and  $2.5 \times 10^{-4} \text{K}^{-1}$  for PB and PS, respectively.<sup>11)</sup> For the block copolymer values of  $\alpha$  were obtained from our dilatometric measurements as  $5.5 \times 10^{-4}$  and  $5.4 \times 10^{-4} \text{K}^{-1}$  for samples R-1 and L-1, respectively.<sup>12)</sup> Plots for the copolymer samples shown in Fig. 2 harmonize well with the results of dilatometry. Hence it may be concluded that the ratios  $\Delta S^*/E_D$  for the systems of inert gas and S-B block copolymer are independent of penetrant and are determined only by the thermal expansion coefficient of the copolymer as in the case of penetrant and amorphous homopolymer systems.

### Solubility

The transport behavior of gases in the S-B block copolymers at 25°C was explained well by a simple model in which additivity of volumes of both components was assumed.<sup>1,3)</sup> If we assume that the model describes also equilibrium solubility data of gases in the copolymer samples, the equilibrium solubility  $S$  is written as

$$S = v_B S_B + v_S S_S \quad (4)$$

Here,  $v_B$  and  $v_S$  are respectively the volume fractions of PB and PS components, and  $S_B$  and  $S_S$  denote the solubility coefficients of the penetrant in PB and PS, respectively.

The equilibrium solubility coefficients at 25°C were calculated using Eq.(4) and compared with measured values in Table III. The measured solubility coefficients for PB and PS are also given in the table. For all the combinations of gases and block copolymers tested the calculated values agree well with the measured ones.

Table III. Equilibrium Solubility Coefficients  $S_{25}$  at 25°C

Gas	$S_{25}/10^{-3} \text{ cm}^3 \text{ (STP)} (\text{cm}^3 \cdot \text{cmHg})^{-1}$					
	S-B block copolymer				PB	PS
	R-1		L-1		Measured	Measured
	Measured	Calculated	Measured	Calculated	Measured	Measured
He	0.25	0.24	0.23	0.23	0.26	0.17
Ar	3.2	3.7	3.3	3.9	3.26	5.03
N <sub>2</sub>	1.33	1.6	1.37	1.7	1.42	2.29
Kr	9.8	12	9.9	13	10.1	17.8
Xe	49	57	51	62	47.0	89.0

In the temperature region between 25 and 75°C, the temperature dependence of  $S$  is expressed in terms of an Arrhenius-type equation,<sup>2,3)</sup> *i.e.*

$$S = S_0 \exp(-\Delta H_s/RT) \quad (5)$$

where  $\Delta H_s$  is the apparent heat of solution. Again assuming the additivity of volumes of styrene and butadiene components we calculated the apparent heat of solution

for the block copolymer samples by the relation

$$\Delta H_s = v_B \Delta H_{sB} + v_S \Delta H_{sS} \quad (6)$$

Here  $\Delta H_{sB}$  and  $\Delta H_{sS}$  are the apparent heats of solution for PB and PS, respectively. The results are shown in Table IV together with measured values for the copolymer samples and the homopolymers. Agreement between the calculated and the measured values is fairly good. Thus we can draw a conclusion that the simple model, in which the volume additivity of components has been assumed, describes satisfactorily not only the observed transport properties but also the measured equilibrium solubilities of gases in the copolymer in the region between 25 and 75°C.

Table IV. Heats of Solution

Gas	$\Delta H_s / \text{kJ mol}^{-1}$					
	S-B block copolymer				PB	PS
	R-1		L-1			
	Measured	Calculated	Measured	Calculated	Measured	Measured
He	5.0	—	4.6	—	9.2	—
Ar	-2.1	-4.4	-5.0	-6.0	-1.6	-13.6
N <sub>2</sub>	1.7	-2.3	0.0	-4.3	1.6	-13.8
Kr	-5.6	-8.0	-6.5	-9.7	-5.1	-17.5
Xe	-14.2	-13.3	-14.2	-15.0	-10.2	-23.2

Gee considered that the free energy of solution of gases in polymers is represented by the sum of free energies of gas condensation and liquid-polymer mixing.<sup>6)</sup> According to his theory the logarithm of  $S$  of a gas in a polymer is correlated with the normal boiling point  $T_b$  of the gas through the formula

$$-\ln 76S = \left( \frac{\Delta S_v}{R} \right) \left( 1 - \frac{T_b}{T} \right) - \ln \left( \frac{22400}{V_{dg}} \right) + 1 + \mu \quad (7)$$

where  $\Delta S_v$  is the entropy of vaporization of the gas,  $V_{dg}$  is the molar volume of the dissolved gas, and  $\mu$  is the Flory-Huggins interaction parameter.<sup>13)</sup>

In Fig. 3 the logarithm of equilibrium solubility  $S_{25}$  at 25°C is plotted against  $T_b$ . With exceptions for helium solution in the copolymer samples and PB, the plots are well represented by straight lines having the same slope. Presumably a smaller value of  $\Delta S_v$  for helium than those for other gases is responsible for the deviation. It is considered, however, that the solution mechanism for small gas molecules like helium in the copolymer would be different from that for other gas molecules having larger volume. Plots for PS are higher than those for the copolymer and PB. This indicates that the interaction parameter for PS differs from those for PB and the copolymer.

According to Gee's relationship,  $\Delta H_s$  is given by

$$\Delta H_s = \mu RT + \Delta S_v T_b \quad (8)$$

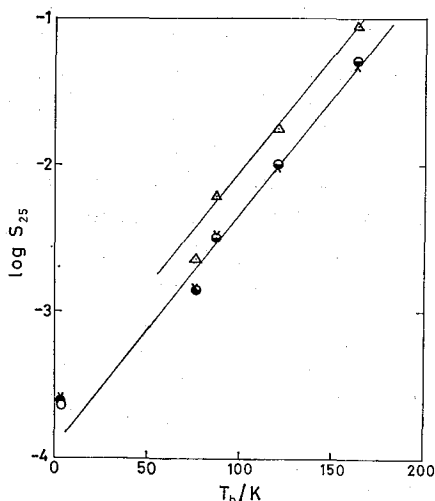


Fig. 3. Logarithm of equilibrium solubility coefficient at 25°C versus normal boiling point of penetrant. The symbols have the same meaning as in Fig. 1.

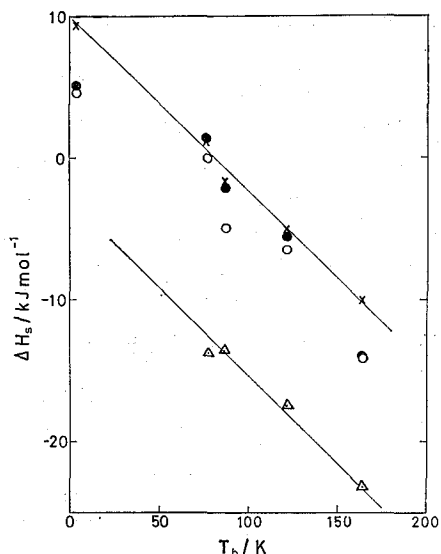


Fig. 4. Heat of solution versus normal boiling point of penetrant. The symbols have the same meaning as in Fig. 1.

Figure 4 shows the relation between  $\Delta H_s$  and  $T_b$ . The data are well represented by straight lines, except for those of helium solution. Again it is seen that the value of  $\mu$  for PS is different from those for PB and the copolymer. It is noted that the values of  $\mu$  for two copolymer samples and PB are somewhat different from one another, which was not discernible in plots shown in Fig. 3.

The equivalent molecular diameters  $d_g$  of the dissolved penetrants were calculated from  $(6V_{dg}/\pi)^{1/3}$  using the values of  $V_{dg}$ , which were estimated according to Gee's relationship, Eq.(7). Table V lists the values of  $d_g$ . As mentioned before, rather large values for helium suggest that a different molecular mechanism is operating in solution processes of the gas in PB and the copolymer samples. The values for the gases, except for those for helium, are of the same order of magnitude as van der Waals molecular diameters. The values of  $d_g$  in the S-B block copolymers are almost

Table V. Equivalent Molecular Diameters of Dissolved Penetrants

Gas	$d_g/\text{\AA}$			
	S-B block copolymer		PB	PS
	R-1	L-1		
He	43.0	44.2	42.5	—
Ar	5.6	5.6	5.6	4.8
N <sub>2</sub>	7.6	7.5	7.4	6.3
Kr	5.4	5.4	5.4	4.4
Xe	4.8	4.7	4.8	3.9

the same as those in PB, and are larger than those in PS. This indicates that the nature of microstructure of the PS domains in the copolymer samples is modified to a certain extent from that in solids of homoPS by virtue of the presence of PB domains. There seems to be no substantial difference in characteristic volumes, in which the dissolved gas molecules reside, between PB and PS domains in the copolymer. Since the characteristic volume is determined by the molecular constraints imposed by the polymer matrix, this suggests that molecular motions in the PS phase affected by those of connected PB block chain segments. Observation of rather high values of mechanical loss tangent for these copolymer samples in the temperature region between two dispersion peaks of both components,<sup>12)</sup> may be considered as a fact to support this view.

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