

# Solubility and Diffusion of Propane in Blends of Polystyrene and Poly(vinyl Methyl Ether) at $T > T_g$

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## Synopsis

The solubility and diffusion of propane in rubbery blends of polystyrene and poly(vinyl methyl ether) were investigated at low diffusant pressures. Solubility is characterized by Henry's law and diffusion by Fick's law with concentration-independent diffusion coefficients. The composition dependence of the solubility and diffusion parameters is presented. The diffusion coefficients for propane in the blends are related to those for the component polymers by using the glass transitions as reference temperatures.

## INTRODUCTION

The conditional miscibility, accessible glass transitions ( $T_g$ ), and other interesting properties have made blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) subjects of several experimental and theoretical investigations.<sup>1-12</sup> However, a systematic study of solubility and diffusion properties of this system has not been reported. The objectives of this investigation were to determine the solubility and diffusion parameters for propane in rubbery PS/PVME blends and evaluate the dependence of these parameters on composition, temperature, and miscibility.

## EXPERIMENTAL

The polymers investigated, polystyrene (PS) and poly(vinyl methyl ether) (PVME), were atactic and supplied by Polysciences, Inc., without using either polymerization or separation procedures to narrow the normal molecular weight distributions. Molecular weights were determined by viscosity measurements of benzene solutions using Mark-Houwink equations related to weight-average molecular weights. Reagent grade solvents distilled and stored over a drying agent were used.

Blends exhibiting a single  $T_g$  were prepared by casting thin films of PS/PVME mixtures on glass from 10% (w/w) solutions in toluene. It was necessary to use dried solvent to obtain clear blends. After allowing several days for initial solvent removal, the blends were placed in a vacuum oven at 30–40°C above  $T_g$  for about 85 h for further removal of solvent. Samples for the sorption experiments were prepared in shallow glass cups, 1.22 cm in diameter and 0.1–0.2 cm in depth, to maintain the sample geometry at  $T > T_g$ . Treatment in the vacuum oven at 40–50°C above  $T_g$  was required to form a sample of uniform thickness free from bubbles. Since some samples of high PS content cracked when cooled rapidly below  $T_g$ , rapid decreases in temperature were avoided when transferring the

TABLE I  
Properties of Component Polymers and Blends

$M_{20}$ :	0.00	0.25	0.50	0.75	1.00
$M_w$	34,000	—	—	—	23,000
Specific volume at 30°C (cm <sup>3</sup> /g)	0.962	—	0.951	0.943	0.940
$T_g$ (K)	247	253	275	303	334

samples to the sorption apparatus. Blend compositions are designated by mass fraction of the component polymers when no diffusant is present, i.e.,  $M_{20}$  = mass fraction of PS and  $M_{30}$  = mass fraction of PVME, with  $M_{20} + M_{30} = 1$ .

Sorption measurements using propane, 99.9% pure (Matheson), as diffusant and blends with  $M_{20} = 0.00, 0.25, 0.50, 0.75,$  and  $1.00$  were carried out at  $T > T_g$  in a low pressure, constant-volume cell previously described.<sup>13</sup> Only low pressures of propane could be used for the diffusion studies in these rubbery blends because desorption after equilibrium at high pressures often produced persistent bubbles.

Densities of the polymers were determined at 30°C using a density gradient column. The differential scanning calorimetry measurements were obtained with a DuPont Differential Scanning Calorimeter, Model 990, at a heating rate of 10K·min<sup>-1</sup>.<sup>12</sup> Successive scans from -60°C to 120°C provided reproducible  $T_g$ 's for these miscible samples.

Selected properties of the component polymers and their blends are provided in Table I.

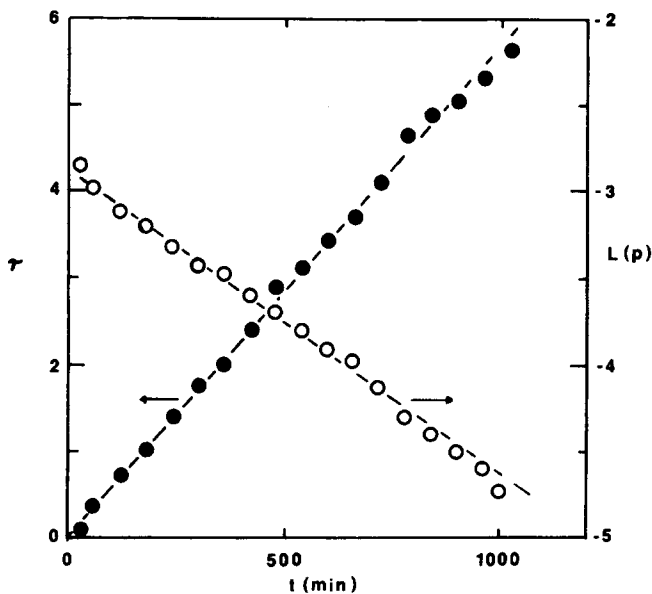


Fig. 1.  $\ln[(p - p_e)/(p_f - p_i)] \equiv L(p)$  and  $\tau$  vs.  $t$  for sorption of propane by a PS/PVME slab with  $M_{20} = 0.50$  at  $T = 80^\circ\text{C}$ .

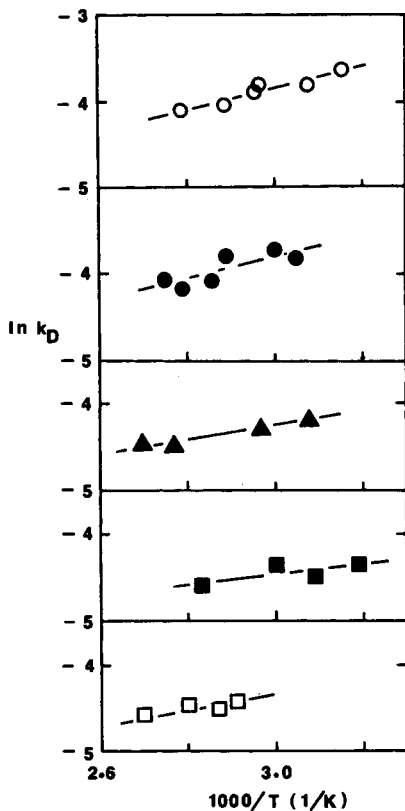


Fig. 2.  $\ln k_D$  vs.  $1/T$  for the solubility of propane in PS/PVME blends. Curves calculated by linear least squares regression.

### ANALYSIS OF SORPTION DATA

Sorption of diffusant from a finite bath by a polymer of plane-slab geometry was determined by measuring the diffusant pressure as a function of time. The transient sorption was analyzed using procedures provided by Lee<sup>14</sup> and by Carman and Haul<sup>15</sup> for Fickian diffusion with a constant diffusion coefficient  $D$  ( $\text{cm}^2/\text{s}$ ). Data graphed as prescribed by both procedures produced straight lines in the appropriate time ranges, and the values of  $D$  calculated by the two methods were in good agreement. This consistency of behavior and the apparent lack of dependence of  $D$  on diffusant concentration justify the use of these simple analyses for determining  $D$ . Figure 1 provides examples of the time dependence of the appropriate functions. Lee's equation of  $p(t)$  for sorption by a slab in a finite bath is

$$\tau = \frac{3\lambda^2}{4} \left[ \ln \left( \frac{p - p_i}{p_0 - p_i} \right) + \frac{1}{2} \left( \frac{p_0 - p_i}{p - p_i} \right)^2 - \frac{1}{2} \right] = \frac{Dt}{a^2} \quad (1)$$

where  $\lambda = (p_f - p_i)/(p_0 - p_f)$ ;  $p_i$  is the pressure of diffusant in equilibrium with the slab prior to the sorption;  $p_0$  is the initial pressure;  $p_f$  is the final pressure;  $D$  is the diffusion coefficient;  $t$  is the elapsed time, and  $a$  is the thickness of the

TABLE II  
Solubility Properties of Propane in PS, PVME, and Blends

Property	$M_{20}$				
	0.00	0.25	0.50	0.75	1.00
$\Delta\bar{H}_D$ (kJ/mol)	10	10	7	5	8
$\ln k_D^0$ <sup>a</sup>	-7.57	-7.49	-6.61	-6.15	-7.15
$\ln k_D$ (353K) <sup>a</sup>	-4.05	-3.99	-4.36	-4.54	-4.49

<sup>a</sup>  $k_D$  and  $k_D^0$  cm<sup>3</sup>(stp)/cm<sup>3</sup>-cm Hg.

slab with an impenetrable backing. A modified form of Carman and Haul's equation for  $p(t)$  is<sup>16</sup>

$$\frac{p - p_f}{p_f - p_i} = \sum_{n=1}^{\infty} \frac{Z_n}{\lambda} \exp\left(\frac{-DQ_n^2 t}{a^2}\right) \quad (2)$$

which for large  $t$  reduces to the simple-exponential form

$$\ln\left(\frac{p - p_f}{p_f - p_i}\right) = \ln \frac{Z_1}{\lambda} - \frac{DQ_1^2 t}{a^2} \quad (3)$$

A graph of  $\ln[(p - p_f)/(p_f - p_i)]$  vs.  $t$  gives an intercept at  $t = 0$  with the value  $\ln(Z_1/\lambda)$  which permits the evaluation of  $Q_1$  by

$$\frac{Z_1}{\lambda} = \frac{4Q_1 \cos^2 Q_1 - 2 \sin 2Q_1}{2Q_1 - \sin 2Q_1} \quad (4)$$

and, hence,  $D$  from the slope. The values of  $D$  calculated from the data in Figure 1 are  $2.0 \times 10^{-7}$  cm<sup>2</sup>/s and  $2.4 \times 10^{-7}$  cm<sup>2</sup>/s using Lee's and Carman and Haul's procedures, respectively.

The difficulty in determining  $p_0$  in a finite-volume sorption experiment has been documented.<sup>17,18</sup> The modified Carman and Haul procedure does not require  $p_0$  to evaluate  $D$ .<sup>16</sup> The Lee procedure is sensitive to the accuracy of determining  $p_0$ . In our calculations an estimate of  $p_0$  was determined by extrapolation of a plot of  $p$  vs.  $t^{1/2}$  to  $t = 0$ . This procedure normally gave values of  $D$  determined by the two methods that were in agreement and the plots of  $\tau$  vs.  $t$  extrapolated to the origin. However, for a few experiments at high temperatures when Apiezon T stopcock grease was used, sorption by excess grease apparently caused the observed curvature in the  $\tau$  vs.  $t$  plot and extrapolation that did not pass through the origin. In these cases eq. (1) was used to determine  $p_0$  as a parameter. This method provided a refinement of  $p_0$  necessary to obtain consistent equilibrium sorption values.

## RESULTS AND DISCUSSION

The sorption experiments were carried out on the polymers and their blends over a temperature range of about 30°C and at equilibrium pressures less than 30 cm Hg. The solubility was determined at two pressures for most temperatures to determine the dependence of solubility on pressure. The solubilities were described by Henry's law

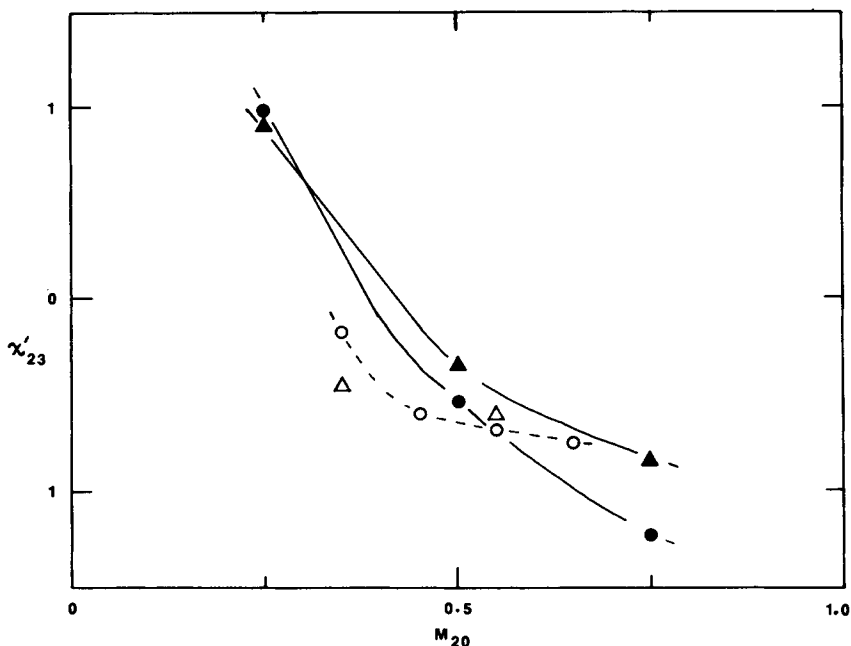


Fig. 3.  $\chi'_{23}$  vs.  $M_{20}$  for the solubility of propane in PS/PVME blends: (●) 60°C; (▲) 80°C.  $\chi'_{23}$  was calculated using eq. (9). The points represented by ○ and △ are from Ref. 5 for solubility of benzene in PS/PVME blends at 30°C and 50°C, respectively.

$$C_f = k_D p_f \quad (5)$$

where  $C_f$  is the propane solubility [ $\text{cm}^3(\text{stp})/\text{cm}^3$ ],  $p_f$  the equilibrium pressure (cm Hg), and  $k_D$  the Henry's law constant [ $\text{cm}^3(\text{stp})/\text{cm}^3 \cdot \text{cm Hg}$ ]. The temperature dependence of  $k_D$  is given by

$$k_D = k_D^0 \exp(-\Delta\bar{H}_D/RT) \quad (6)$$

where  $\Delta\bar{H}_D$  is the molar heat of sorption (kJ/mol). Figure 2 presents the dependence of  $k_D$  on temperature, and Table II provides values of  $\ln k_D^0$ ,  $\Delta\bar{H}_D$ , and  $\ln k_D$  at 353 K for the polymers and their blends. Barrie et al.<sup>19</sup> report data for sorption of propane in a high molecular weight PS ( $T_g = 373$  K). The  $k_D$ 's determined using the dual sorption analysis at  $T < T_g$  are greater than those obtained in this system for PS, e.g.,  $k_D = 0.023 \text{ cm}^3(\text{stp})/\text{cm}^3 \cdot \text{cm Hg}$  compared with  $0.013 \text{ cm}^3(\text{stp})/\text{cm}^3 \cdot \text{cm Hg}$  in this work. The value of  $E_D$  was also somewhat greater, about 13 kJ/mol.

The Flory-Huggins mixing rule used effectively to describe solubility in miscible blends is<sup>5,20-22</sup>

$$\ln k_D = \ln k_{1b} = \phi_{20} \ln k_{12} + \phi_{30} \ln k_{13} + \chi'_{23} \phi_{20} \phi_{30} \quad (7)$$

where propane, PS, PVME, and blends are designated 1, 2, 3, and b,  $\phi_{20}$  and  $\phi_{30}$  are the volume fractions of the blends without propane,  $k_{12}$  and  $k_{13}$  are the Henry's law constants for propane in the component polymers, and  $\chi'_{23}$  is the binary interaction parameter defined by

$$\chi'_{23} = (\bar{v}_1/\bar{v}_2)\chi_{23} = (\bar{v}_1/\bar{v}_3)\chi_{32} \quad (8)$$

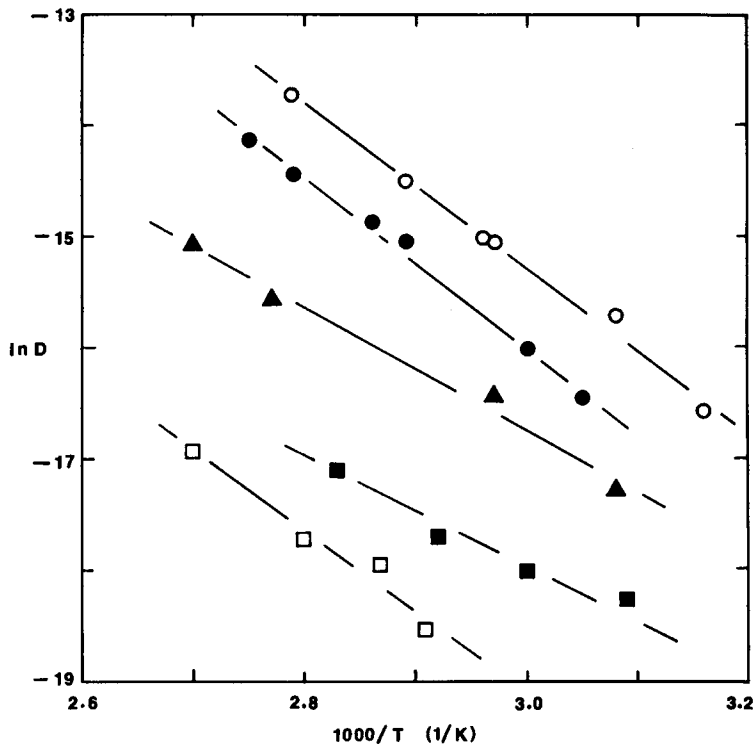


Fig. 4.  $\ln D$  vs.  $1/T$  for diffusion of propane in PS/PVME blends.  $M_{20}$ : (○) 0.00; (●) 0.25; (▲) 0.50; (■) 0.75; (□) 1.00. Curves calculated by linear least squares regression.

where  $\bar{v}_i$  is the molar volume of component  $i$  and  $\chi_{23}$  and  $\chi_{32}$  are the Flory interaction parameters. Since the densities of the two component polymers are nearly identical, the volume fractions in eq. (7) can be replaced by component polymer mass fractions. The compositional variation of  $k_D$  for the system cannot be described by a single  $\chi'_{23}$  at a given temperature. Using experimental values of  $k_{12}$ ,  $k_{13}$ , and  $k_{1b}$ ,  $\chi'_{23}$  can be evaluated point by point for the blends using

$$\chi'_{23} = \frac{\ln k_{1b} - M_{20} \ln k_{12} - M_{30} \ln k_{13}}{M_{20}M_{30}} \quad (9)$$

The values of  $\chi'_{23}$  at 60°C and 80°C are presented in Figure 3, with values obtained by Kwei et al.<sup>5</sup> at 30°C and 50°C using toluene as the probe. The shapes of the curves representing the dependence of  $\chi'_{23}$  on  $M_{20}$  are similar, with a temperature reversal occurring in each determination. However, the slopes obtained in this work are much greater than those obtained by Kwei et al.<sup>5</sup> The values near  $M_{20} \approx 0.5$  are also consistent with results reported by Stein<sup>23</sup> based on an analysis of the temperature dependence of the radius of gyration of PS in PS/PVME blends. The cloud-point studies<sup>5</sup> and observations of single glass transitions<sup>5,12</sup> indicate the blends are miscible to all compositions, at least in the 50–90°C temperature range. However, Kwei et al.<sup>5</sup> conclude from NMR  $T_2$  results that imperfect mixing, perhaps in the form of microclusters differing in

TABLE III  
Diffusion Parameters; Propane in PS, PVME, and Blends

$M_{20}$	$\ln D_0$ (cm <sup>2</sup> /s)	$E_d$ (kJ/mol)	$D$ (80°C) (cm <sup>2</sup> /s)	$D(T_g)$ (cm <sup>2</sup> /s)
0.00	7.00	62	$8.1 \times 10^{-7}$	$1.0 \times 10^{-10}$
0.25	7.46	65	$4.1 \times 10^{-7}$	$1.0 \times 10^{-10}$
0.50	-0.11	46	$1.4 \times 10^{-7}$	$1.6 \times 10^{-9}$
0.75	-5.38	35	$3.3 \times 10^{-8}$	$5.4 \times 10^{-9}$
1.00	2.79	61	$1.7 \times 10^{-8}$	$5.4 \times 10^{-9}$

composition, occurs in PS/PVME blends at  $M_{20} \approx 0.5$ . This imperfect mixing could influence the values of  $\chi_{23}$  obtained by eq. (9) at  $M_{20} \lesssim 0.5$  and perhaps make the use of this equation at low values of  $M_{20}$  questionable. It is evident, and consistent with the results obtained by Kwei et al.,<sup>5</sup> that  $\chi_{23}$  is negative for  $M_{20} \lesssim 0.4$ .

The diffusion coefficients are shown as a function of temperature in Figure 4. An Arrhenius equation

$$D = D_0 \exp(-E_d/RT) \quad (10)$$

describes the results, and selected diffusion parameters are listed in Table III. The value of  $E_d$  at  $M_{20} = 0.25$  is near that predicted by the linear dependence on  $M_{20}$ , while  $E_d$  is well below a linear dependence for  $M_{20} \gtrsim 0.4$ . A maximum is the more expected result.<sup>24</sup> The dependence of  $\ln D$  on  $M_{20}$  is shown at several temperatures in Figure 5. Only small positive and negative deviations are ob-

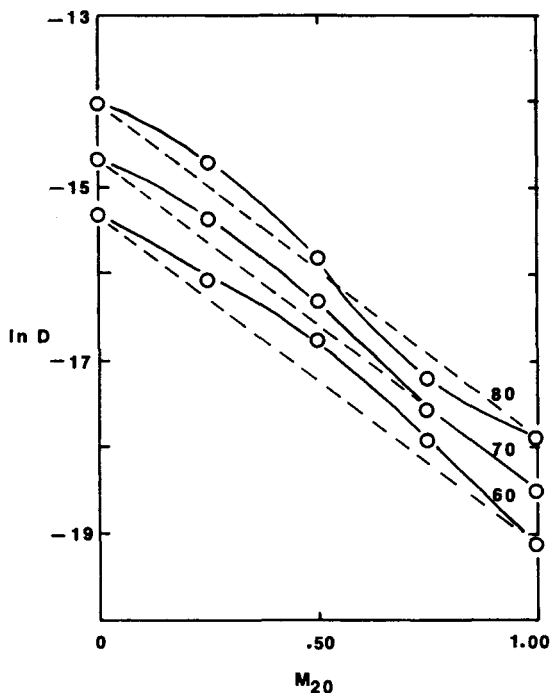


Fig. 5.  $\ln D$  vs.  $M_{20}$  for diffusion of propane in PS/PVME blends:  $T$  indicated on curves.

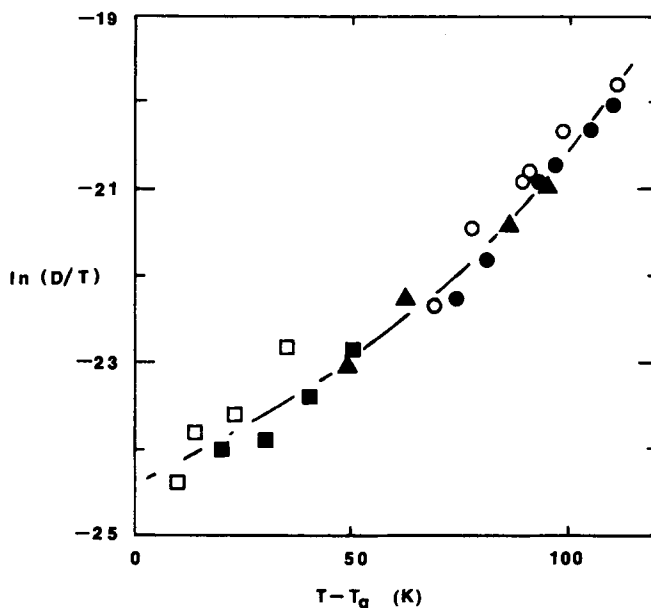


Fig. 6.  $\ln(D/T)$  vs.  $T - T_g$  for diffusion of propane in PS/PVME blends.  $M_{20}$ : (○) 0.00; (●) 0.25; (▲) 0.50; (■) 0.75; (□) 1.00. Curve drawn for visual fit.

served. The values of  $D$  are greater than those reported by Barrie et al.<sup>19</sup> for a high molecular weight PS obtained by dual sorption analysis, e.g.,  $D = 2.5 \times 10^{-9}$  cm<sup>2</sup>/s compared with  $D_D = 1.8 \times 10^{-10}$  cm<sup>2</sup>/s.

As suggested by segmental motion considerations,<sup>25</sup>  $\ln(D/T)$  vs.  $T - T_g$  plots as a single curve in Figure 6 for all compositions, similar to that observed by Semancik and Rogers<sup>26</sup> for random copolymers of isoprene and methyl methacrylate. This procedure provides a means of relating  $D$  for the component polymers to  $D$  for the blends provided that  $D$  for the component polymers is determined over a suitable temperature range and  $T_g$  is known for each blend.

A mixing rule with a reliable basis involves the dependence of  $\ln P$  on composition, where  $P$  is the permeability.<sup>21</sup> The dependence of  $\ln P$  on  $M_{20}$  is ex-

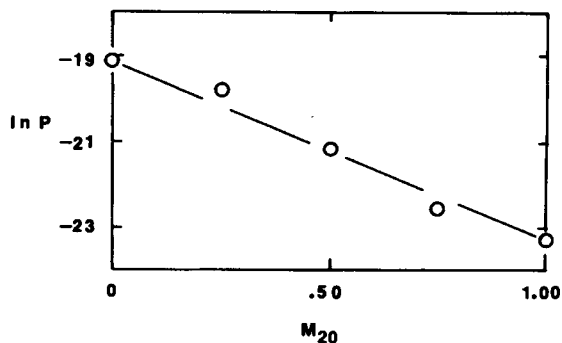


Fig. 7.  $\ln P$  vs.  $M_{20}$  for sorption of propane in PS/PVME blends at  $T = 80^\circ\text{C}$ . Permeability calculated by  $P = k_D D$ .



pected to be monotonic for miscible blends and sigmoid for blends containing a microdispersed phase indicative of a reversal of the continuous phase at some composition.  $P$  was evaluated for these systems by  $P = k_D D$  [ $\text{cm}^2\text{-cm}^3(\text{stp})/\text{s-cm}^3\text{-cm Hg}$ ] and a graph of  $\ln P$  vs.  $M_{20}$  at  $80^\circ\text{C}$  is presented in Figure 7. No large deviation from linearity is observed.

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## APPENDIX: NOMENCLATURE

$a$	thickness of absorbing slab with one impenetrable surface (cm)
$C_f$	diffusant solubility [ $\text{cm}^3(\text{stp})/\text{cm}^3$ ]
$D$	diffusion coefficient ( $\text{cm}^2/\text{s}$ )
$D_0$	preexponential term in Arrhenius equation for $D$ , eq. (10) ( $\text{cm}^2/\text{s}$ )
$E_d$	activation energy for diffusion (kJ/mol)
$\Delta\bar{H}_d$	molar enthalpy of sorption (kJ/mol)
$k_D$	Henry's law constant for diffusant in blends [ $\text{cm}^3(\text{stp})/\text{cm}^3\text{-cm Hg}$ ]
$k_D^0$	defined by eq. (6) [ $\text{cm}^3(\text{stp})/\text{cm}^3\text{-cm Hg}$ ]
$k_{12}$	Henry's law constant for diffusant in PS ( $\text{cm}^3(\text{stp})/\text{cm}^3\text{-cm Hg}$ )
$k_{13}$	Henry's law constant for diffusant in PVME ( $\text{cm}^3(\text{stp})/\text{cm}^3\text{-cm Hg}$ )
$\bar{M}_w$	mass average molecular mass
$M_{20}$	mass fraction of PS in the polymer blends; in the absence of diffusant
$M_{30}$	mass fraction of PVME in the polymer blends; in the absence of diffusant
PS	polystyrene; indexed as component 2
PVME	poly(vinyl methyl ether); indexed as component 3
$p_i$	diffusant pressure in equilibrium with the slab prior to initiating the sorption (cm Hg)
$p_0$	diffusant pressure in equilibrium with the slab surface at initiation of sorption (cm Hg)
$p$	diffusant pressure at elapsed time $t$ (cm Hg)
$p_f$	final diffusant pressure in equilibrium with the slab (cm Hg)
$P$	permeability coefficient; $P = k_D D$ ( $\text{cm}^2\text{-cm}^3(\text{stp})/\text{s-cm}^3\text{-cm Hg}$ )
$Q_n$	roots of the auxiliary equation for the Laplace transform solution to obtain eq. (2)
$T_g$	glass transition (K or $^\circ\text{C}$ )
$t$	elapsed time (s)
$\bar{v}_i$	molar volume of component $i$ in the blends
$Z_i/\lambda$	defined by eq. (4)
$Z_n\lambda$	defined by eq. (2)
$\phi_{20}$	volume fraction of PS in the blends, in the absence of diffusant
$\phi_{30}$	volume fraction of PVME in the blends, in the absence of diffusant
$\tau$	defined by eq. (1)
$\chi_{23}$	binary interaction parameter, related to Flory interaction parameters $\chi_{23}$ and $\chi_{32}$ by eq. (8)

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