

Temperature Dependence of Sorption Parameters near T_g for Propane in a Miscible Blend of Polystyrene and Poly(vinyl Methyl Ether)

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Synopsis

The sorption of propane by 75:25% (w/w) miscible blends of polystyrene and poly(vinyl methyl ether) with different thermal histories was investigated near T_g . The dual-mode sorption model was used to analyze the results. The evidence indicates that the Henry's law constant for states below T_g cannot be smoothly extrapolated from the rubbery state.

INTRODUCTION

The dual-mode sorption model provides a useful equation for analyzing sorption isotherms of gases and vapors in glassy polymers.¹⁻⁹ The total equilibrium penetrant concentration C is described as two populations distinguishable by heats of sorption and diffusion coefficients. The model expressed as a three-parameter equation is

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

where b is the affinity factor, C_D the Henry's law term, C_H the Langmuir isotherm term, C'_H the Langmuir capacity, k_D the Henry's law constant, and p the equilibrium pressure of the penetrant. The Langmuir capacity is often associated with microvoids or low-density regions frozen into glassy amorphous polymers at temperatures below the glass transition T_g . At low pressure or small b , equation (1) reduces to

$$C = k^* p \quad (2)$$

with k^* the apparent Henry's law constant given by

$$k^* = k_D + C'_H b \quad (3)$$

The Langmuir isotherm term in equations (1) and (3) is eliminated upon passage from a glassy state to the rubbery state. Two phenomena explaining its elimination have been suggested; the disappearance of C'_H as T approaches T_g from lower temperatures⁶ and the condition that $k_D = C'_H b$ for $T > T_g$ to give by equation (3):⁷

$$k^* = 2k_D \quad (4)$$

for $T > T_g$; C'_H for $T < T_g$ is a constant, that is, $C'_H(T_g)$.

This paper describes the sorption of propane in a 75:25% (w/w) miscible blend of polystyrene (PS) and poly(vinyl methyl ether) (PVME) in the region of the T_g . Dual-mode sorption model parameters k_D , k^* , C'_H , and b are evaluated and discussed using results from sorption experiments with blend materials that had been subjected to three thermal histories.

EXPERIMENTAL

The atactic polymers polystyrene and poly(vinyl methyl ether) were obtained from Poly Sciences, Inc. Viscosity measurements of the polymers in benzene-solutions gave $M_w = 190,000$ for PS and $M_w = 34,000$ for PVME using the Mark-Houwink equation. Both values were within the ranges specified by the supplier. As expected, no crystallinity was evident when the polymers were examined by x-ray diffraction. Planar sheet samples were cast as previously described.¹⁰ Clear miscible blends of 75:25% (w/w) PS/PVME were obtained by casting dilute toluene solutions on clean mercury. The solvent was removed from the cast sheets by vacuum for several days at 85°C and exposed to extended periods under vacuum in the sorption apparatus before running sorption experiments. The T_g of the blend materials determined by dilatometry was 52°C. A single T_g was obtained by dilatometry and by DSC measurements. Reagent-grade solvents distilled and dried over molecular sieves were used.

Two 75:25% PS-PVME blends were prepared, and three thermal histories developed. Sample SC-1 was cooled slowly, an average rate of 0.75°C min⁻¹, from 85°C to room temperature; placed in the sorption apparatus; and sorption experimentation begun at 35°C. Sample Q was rapidly quenched from 85°C to below room temperature by exposure to the vapor above liquid nitrogen. Subsequent sorption experiments were initiated at 50°C. After investigating sample Q up to 85°C, it was very slowly cooled, an average rate of 0.05°C min⁻¹, to 50°C, where sorption experiments were initiated. This sample is designated SC-2.

A low-pressure apparatus similar to that previously described was used to pressures of 60 cm Hg.¹⁰ The sample chamber was the interior of a hollow vacuum stopcock with the pressure transducer attached directly to the bulb end of the stopcock. This modification of the apparatus provided a small sample chamber volume and reduced potential sources of leaks. The volume could be readily measured in the standard manner by expanding a gas into the chamber from a known volume. Blank sorption tests indicated no interference from the small amount of stopcock grease to which the outlet port of the chamber was exposed.

The vapor used in the sorption experiments was propane obtained from Matheson at a purity of 99.98%. It was subjected to bulb-to-bulb distillation before use. At the low pressures of these experiments, a simple equation of state using only the second virial coefficient was used.¹¹

TREATMENT OF DATA

For $T > T_g$, k^* in equation (2) was evaluated for each isotherm using a linear regression of the dependence of C on p . For $T < T_g$, the dual-mode sorption model parameters k_D , C_H , and b were determined for each is-

otherm iteratively by minimizing the mean deviation between the calculated and the experimental concentrations. The extent to which the sorption parameters could be altered within the limits of the mean deviation and still give a reasonable fit to the experimental isotherm was determined. These values are provided as average percentages for the sorption parameters by using $k_D \pm$ two standard deviations to calculate errors in b and C'_H .

RESULTS AND DISCUSSION

Values of the parameters obtained from the series of the sorption studies are presented in Table I.

Interpretation of the results from the extensive investigation of sample SC-1 requires consideration of the thermal history before the sorption experiments and the order of the sorption experiments. SC-1 was cooled slowly to 35°C and the sorption experiments performed in the order listed in Table I over a period of several weeks. The enhancement of k^* below T_g over projected values from $T > T_g$ is small, as indicated in Fig. 1, consistent with the slow cooling history and the absence of preconditioning at high propane pressure, as is the regimen for many sorption studies using glassy polymers. When the temperature was raised to 50°C, just a few degrees below the apparent T_g of 52°C, the initial isotherm obtained by increasing the pressure

TABLE I:
Sorption Parameters for the 75/25%(w/w) PS=PVME Blends

Series	Order	T (K)	$100 k_D$	C'_H	$100 b$	$100 k^*$
			cm ³ STP	cm ³ STP	cm Hg ⁻¹	cm ³ STP
			cm ³ ·cm Hg	cm ³		
SC-1	1	308	3.5 (± 11%)	2.1 (± 19%)	1.6 (± 40%)	6.79 (± 12%)
	2	293	4.0 (± 12%)	2.2 (± 22%)	1.8 (± 44%)	7.99 (± 13%)
	3	278	6.4 (± 11%)	3.2 (± 20%)	2.2 (± 50%)	13.3 (± 16%)
	4	323	2.4 (± 12%) ^a	1.4 (± 32%)	1.4 (± 55%)	4.33 (± 51%) ^b
	5	333				3.06 (± 4%)
	6	343				2.49 (± 4%)
	7	353				1.99 (± 4%)
	8	364				1.89 (± 4%)
	9	374				1.65 (± 4%)
Q	1	323				3.19 (± 8%)
	2	328				3.67 (± 4%)
	3	333				2.96 (± 4%)
	4	343				2.21 (± 4%)
	5	358				1.99 (± 4%)
SC-2	1	323				2.45 (± 4%) ^c
	2	327				3.14 (± 4%)
	3	338				2.71 (± 4%)
	4	356				2.00 (± 4%)

^a k^* , after extended annealing in vacuum at 323 K.

^b k^* , initial sorption isotherm.

^c k^* , after annealing.

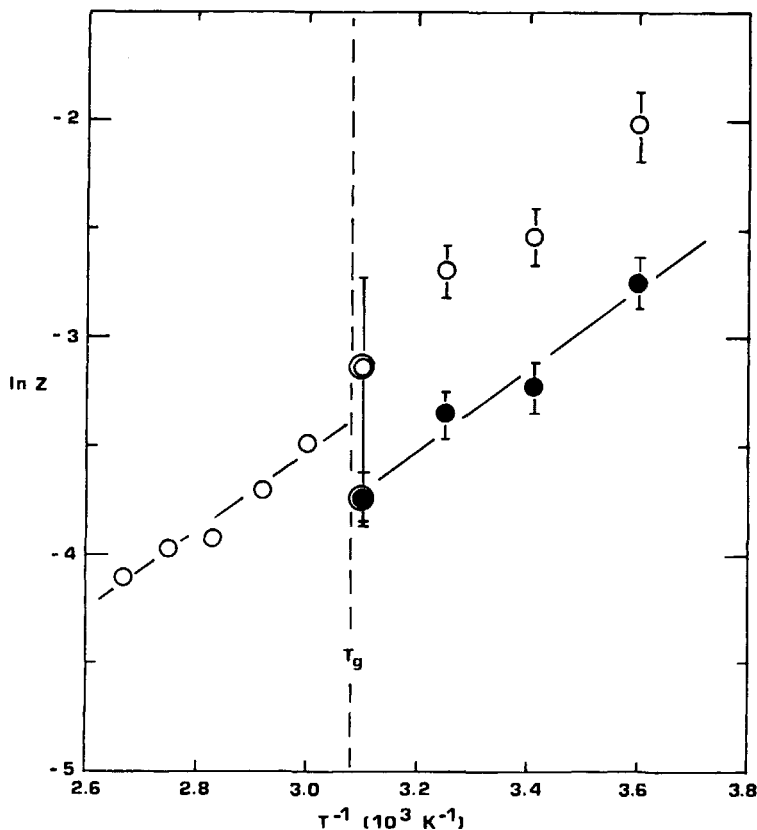


Fig. 1. $\ln Z$ versus T^{-1} for sample SC-1: $Z = k^*$, (○); $Z = k_D$, (●). See text for different method of calculating k^* and k_D for the points with concentric circles.

in steps exhibited the usual curvature characteristic of glass polymers, but with a small curvature. There was no reduction in the amount of vapor sorbed over a period of 2–3 days after an equilibrium sorption was established. However, subsequent desorption for approximately twice the time required for a sorption experiment resulted in a sorption isotherm that collapsed toward a linear, or Henry's law, dependence of C on p . This sequence of desorption and interval sorption isotherm determinations was carried out four times. No further change was observed after about 100 h total annealing in vacuum at 50°C. The first and fourth isotherms are shown in Fig. 2. Assuming the slope of the fourth isotherm corresponds to k_D in equation (1), with $C'_H = 0$ as a result of the extensive annealing in vacuum just below T_g , parameters C'_H and b could be calculated for the initial isotherm despite the small number of points, although the resulting relative errors are necessarily larger than for the other determinations. This difference in calculation method is noted in Table I and Fig. 1. The value of k_D is consistent with the values obtained by the standard calculation at the lower temperature.

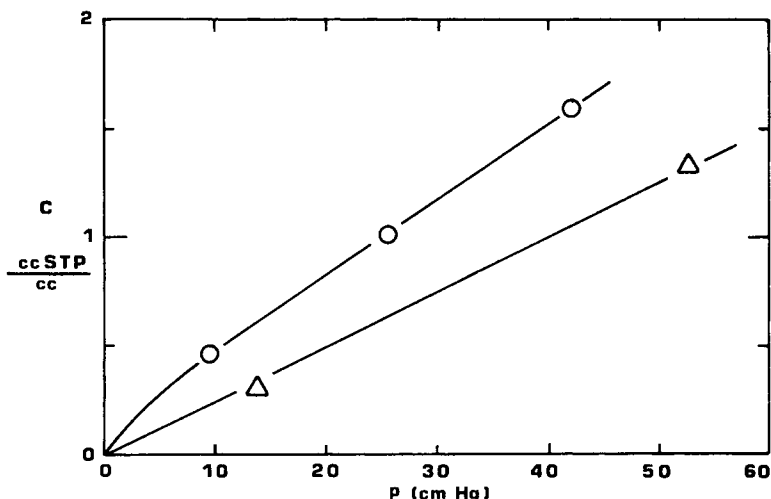


Fig. 2. C versus p for sample SC-1 at 323 K: first isotherm, (O); fourth isotherm, (Δ).

The reduction of C'_H during sub- T_g annealing under vacuum and an apparent lack of this reduction during annealing at even a low activity of propane are consistent with findings for other systems. The volumetric increase response to high vapor pressure at $T < T_g$,¹² the volume densification by sub- T_g annealing under vacuum,^{9,12,13} and the lack of densification when annealed at low vapor activity^{14,15} have been demonstrated in other systems.

The values of the sorption parameters for samples Q and SC-2 are combined with results for SC-1 in Table I and Fig. 3. The values of k^* are consistent for the three series of experiments at $T > T_g$. The interesting result is that the quenched material exhibited a value of k^* at 50°C that appears to be an extrapolation of the values above T_g . Extended annealing of sample Q in vacuum at 50°C did not reduce k^* . However, the very slowly cooled SC-2, effectively annealed in vacuum at this very slow rate, gave a value of k^* at 50°C consistent with the k_D obtained for SC-1 after annealing at 50°C. This value and the linear dependence of C on p indicate that C'_H approaches zero in sample SC-2 at 50°C after extended annealing in vacuum. This implies that the regimen excluding this annealing leaves $C'_H > 0$. All samples exhibited an increase in k_D upon increasing the temperature through T_g , particularly SC-2, for which the solubility constant increased almost 30% within an extremely small temperature range about T_g .

The evidence indicated that k_D in equation (1) for $T < T_g$ is not a smooth extrapolation of k^* evaluated at $T > T_g$, at least for this polymer blend with propane as a penetrant. At T_g , $k^* = 1.4 k_D$. This ratio of k^*/k_D is less than the value of 2 predicted for a system with a constant C'_H in equation (4).¹⁷ The values of C'_H obtained for SC-1 are presented in Figure 4. Although the accuracy is low, C'_H appears to decrease as $T \rightarrow T_g$ approaching a value of approximately 1 at T_g . This could reflect the effects of annealing in vacuum.

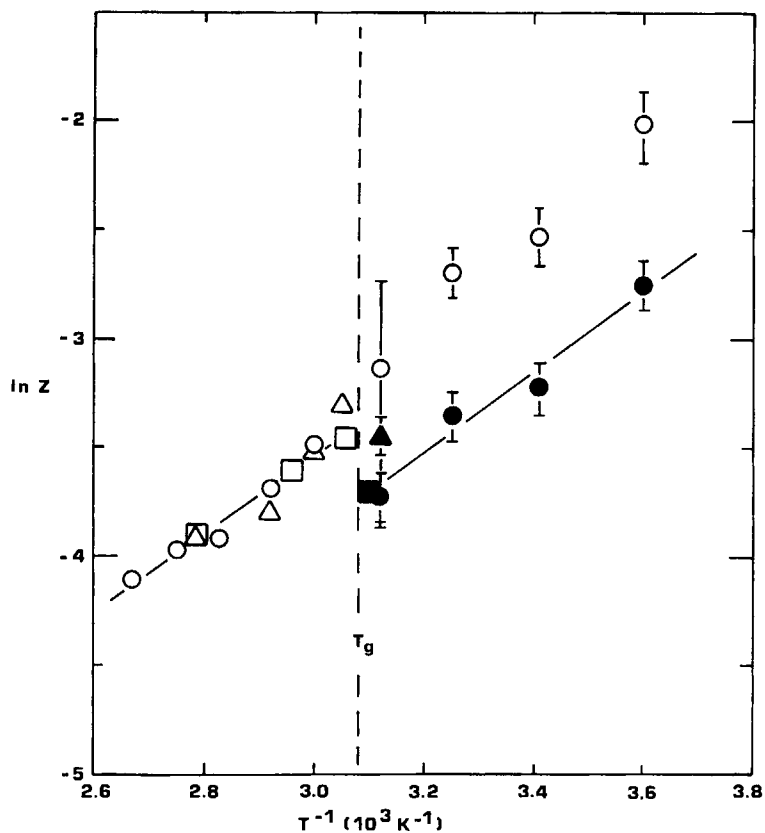


Fig. 3. $\ln Z$ versus T^{-1} : SC-1, $Z = k^*$ (\circ), $Z = k_D$ (\bullet); Q, $Z = k^*$ (\triangle), $Z = k_D$ (\blacktriangle); and SC-2, $Z = k^*$ (\square), $Z = k_D$ (\blacksquare).

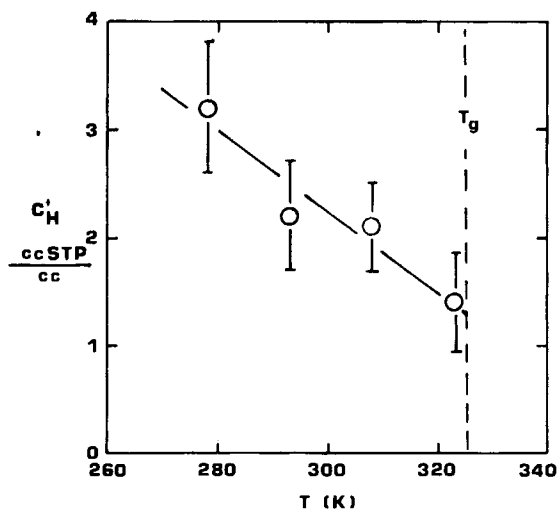


Fig. 4. C'_H versus T for SC-1. Line represents least-squares linear regression.

These results appear to be more consistent with the method of elimination of the Langmuir isotherm term by $k_D = C'_H b$ at $T = T_g$, than by $C'_H = 0$.

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References

1. R. J. Pace and A. Datyner, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1103 (1980).
2. W. R. Vieth, J. M. Howell, and J. H. Hsieh, *J. Membr. Sci.*, **1**, 177 (1976).
3. P. Masi, D. R. Paul, and J. H. Barlow, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 15 (1982).
4. A. S. Michaels, W. R. Vieth, and J. A. Barrie, *J. Appl. Phys.*, **34**, 1 (1963).
5. J. A. Barrie, M. J. L. Williams, and K. Munday, *Polym. Eng. Sci.*, **20**, 20 (1980).
6. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1655 (1981).
7. R. J. Pace and A. Datyner, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1657 (1981).
8. W. J. Koros and D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1947 (1978).
9. J. A. Yavorsky and H. G. Spencer, *J. Appl. Polym. Sci.*, **25**, 2109 (1980).
10. H. G. Spencer and J. A. Yavorsky, *J. Appl. Polym. Sci.*, **28**, 2937 (1983).
11. J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon, Oxford, 1969, p. 81.
12. A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5**, 63 (1979).
13. A. H. Chan and D. R. Paul, *Polym. Eng. Sci.*, **20**, 87 (1980).
14. A. R. Barends and H. B. Hopfenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1757 (1979).
15. H. B. Hopfenberg, *Proc. IUPAC, I.U.P.A.C., Macromol. Symp.*, **28th**, 736 (1982).

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