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Temperature Dependence of Partition Coefficients for Polymer−Solvent Systems

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Introduction

An important and interesting aspect of penetrant sorption in polymers is the temperature dependence of K, the partition coefficient for the penetrant between the gas and polymer phases. Of particular interest is the possible difference in the temperature dependence above and below T_{g2}, the glass transition temperature of the pure polymer. The inverse gas chromatography (IGC) experiment provides a useful and convenient method of measuring the temperature dependence of the solubility for polymer−penetrant systems at low penetrant mass fractions. The objective of this paper is to compare IGC data for the temperature dependence of K with the predictions of a theory[1] which has been proposed for the sorption of penetrants in glassy and rubbery polymers.

Theory

At low pressures, where the gas phase is ideal, the proposed theory states that the sorption process can be described by the following set of equations:

$$\frac{p_1}{p_1^0} = \phi_1 \exp[\phi_2 + \chi{\phi_2}^2]\, e^F \tag{1}$$

$$F = \frac{M_1{\omega_2}^2(\hat{C}_p - \hat{C}_{pg})A}{RT}\left(\frac{T}{T_{gm}} - 1\right) \qquad T < T_{gm} \tag{2}$$

$$F = 0 \quad T \geq T_{gm} \tag{3}$$

Here, p_1 is the pressure of the penetrant (component 1) in the gas phase, T is the temperature of the sorption process, p_1^0 is the vapor pressure of the liquid penetrant at T, M_1 is the molecular weight of the penetrant, and ω_2 is the mass fraction of the polymer (component 2). Also, $\hat{C}_p$ is the specific heat capacity at constant pressure for the equilibrium liquid polymer, $\hat{C}_{pg}$ is the specific heat capacity at constant pressure for the glassy polymer, ϕ_1 and ϕ_2 are volume fractions of penetrant and polymer, respectively, and χ is the interaction parameter of the Flory−Huggins theory.[2] The parameter χ may be a function of temperature but not of concentration. Finally, it has been assumed that the concentration dependence of T_{gm} (the glass transition temperature of the polymer−penetrant mixture at a particular penetrant mass fraction) can be represented by the following linear approximation:

$$T_{gm} = T_{g2} - A\omega_1 \tag{4}$$

Here, ω_1 is the mass fraction of the penetrant in the liquid phase, and A is a constant that depends on the nature of the penetrant used to depress the glass transition temperature of a particular polymer.

The partition coefficient K provides a linear relationship between ρ_1, the solvent mass density in the polymer phase, and ρ_g, the penetrant mass density in the gas phase:

$$\rho_1 = K\rho_g \tag{5}$$

Also, in IGC experiments, a parameter α, defined by the following equation, is usually determined:

$$\alpha = \frac{\bar{R}}{K\tau} \tag{6}$$

Here, $\bar{R}$ is the radius of the polymer−gas interface in the experiment, and τ is the thickness of the polymer film. Utilization of eqs 1−6 and the perfect gas law produce the following expressions for the temperature dependence of α (and, hence, of K) at low penetrant mass fractions:

$$\ln\left[\frac{\alpha\tau T}{\bar{R}}\right] = \ln\left(\frac{M_1\hat{V}_1}{R}\right) + \ln p_1^0 + (1 + \chi) \qquad T \geq T_{g2} \tag{7}$$

$$\ln\left[\frac{\alpha\tau T}{\bar{R}}\right] = \ln\left(\frac{M_1\hat{V}_1}{R}\right) + \ln p_1^0 + (1 + \chi) + \frac{M_1(\hat{C}_p - \hat{C}_{pg})A}{R}\left(\frac{1}{T_{g2}} - \frac{1}{T}\right) \qquad T < T_{g2} \tag{8}$$

Here, $\hat{V}_1$ is the partial specific volume of the solvent at infinite solvent dilution. Since the temperature dependence of $\hat{V}_1$ is generally small (generally less than a 5% contribution), the following equations can be derived for the temperature variations of αT at temperatures above and below T_{g2}:

$$\left[\frac{\partial(\ln(\alpha T))}{\partial\left(\frac{1}{T}\right)}\right] = \frac{\partial(\ln p_1^0)}{\partial\left(\frac{1}{T}\right)} + \frac{\partial\chi}{\partial\left(\frac{1}{T}\right)} \qquad T \geq T_{g2} \tag{9}$$

$$\left[\frac{\partial(\ln(\alpha T))}{\partial\left(\frac{1}{T}\right)}\right] = \frac{\partial(\ln p_1^0)}{\partial\left(\frac{1}{T}\right)} + \frac{\partial\chi}{\partial\left(\frac{1}{T}\right)} - \frac{M_1A(\hat{C}_p - \hat{C}_{pg})}{R} \qquad T < T_{g2} \tag{10}$$

Also,

$$\left[\frac{\partial(\ln(\alpha T))}{\partial\left(\frac{1}{T}\right)}\right]_{T=T_{g2}^+} - \left[\frac{\partial(\ln(\alpha T))}{\partial\left(\frac{1}{T}\right)}\right]_{T=T_{g2}^-} = \frac{M_1A(\hat{C}_p - \hat{C}_{pg})}{R} \tag{11}$$

In general, $\ln p_1^0$ can be represented[3] by a linear function of $(1/T)$, and Flory[2] has proposed that χ should be a linear function of $(1/T)$. Also,

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$$\frac{\partial(\ln p_1^0)}{\partial\left(\frac{1}{T}\right)} < 0 \tag{12}$$

$$\frac{\partial\chi}{\partial\left(\frac{1}{T}\right)} > 0 \tag{13}$$

Since the magnitude of the first term of eq 9 is generally greater than that of the second term

$$\frac{\partial(\ln(\alpha T))}{\partial\left(\frac{1}{T}\right)} < 0 \quad T \geq T_{g2} \tag{14}$$

Also, for temperatures below T_{g2}, it is evident from eq 10 that there is an additional negative term in the expression for the temperature derivative so that the absolute values of the temperature derivatives are described by the following inequality:

$$\left|\frac{\partial(\ln(\alpha T))}{\partial\left(\frac{1}{T}\right)}\right|_{T=T_{g2}^-} > \left|\frac{\partial(\ln(\alpha T))}{\partial\left(\frac{1}{T}\right)}\right|_{T=T_{g2}^+} \tag{15}$$

The predictions of the proposed theory for sorption in glassy and rubbery polymers can be summarized as follows:

(1) The quantity ln(αT) should be a linear function of (1/T) at temperatures both above and below T_{g2}. This follows from eqs 9 and 10.

(2) The magnitude of the slope of the ln(αT) vs (1/T) curve should be greater below T_{g2} (eq 15).

(3) The difference in slopes should follow the prediction of eq 11.

These predictions will now be compared to IGC solubility data.

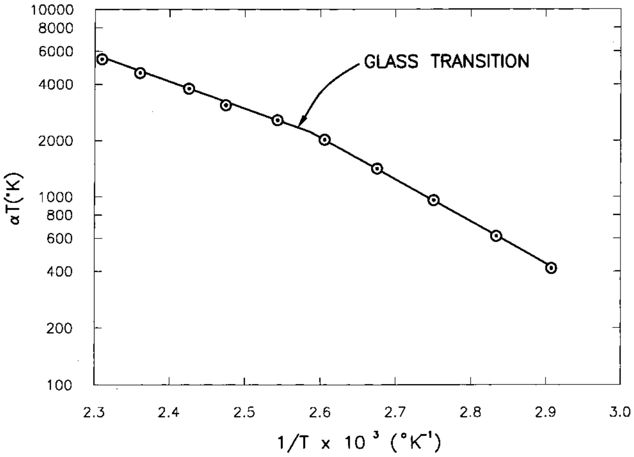

Figure 1. Temperature dependence of αT for the methanol–PMMA system.

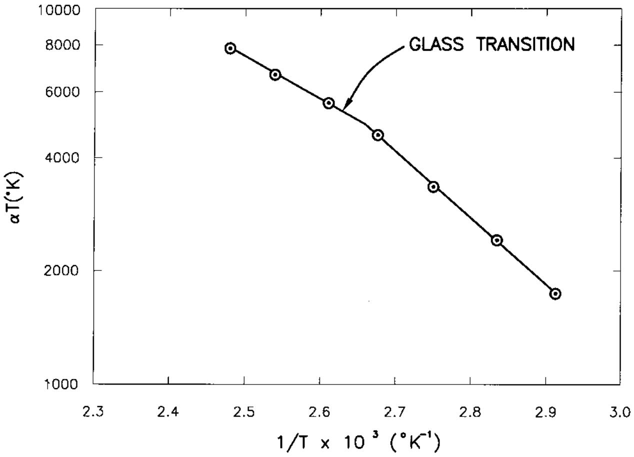

Figure 2. Temperature dependence of αT for the methanol–PPMS system.

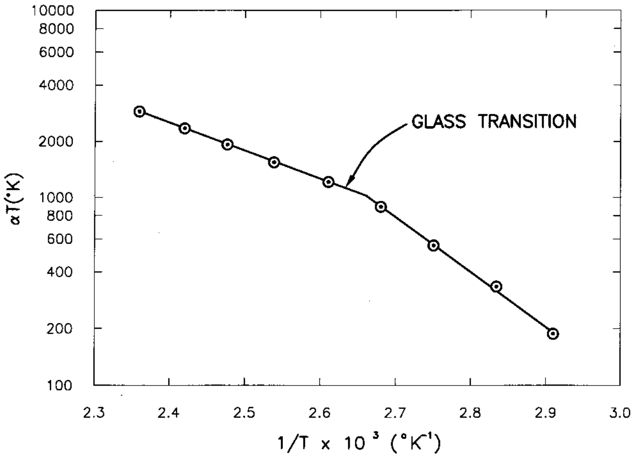

Figure 3. Temperature dependence of αT for the ethyl acetate–PPMS system.

Results and Discussion

Plots of ln(αT) vs (1/T) are presented in Figures 1–3 for the methanol–PMMA, methanol–PPMS, and ethyl acetate–PPMS systems. Here, PMMA represents poly(methyl methacrylate) and PPMS represents poly(p-methyl styrene). The data in these figures were reported by Arnould.[4] In all three cases, the data both above and below T_{g2} are satisfactorily represented by straight lines, and, in all three cases, the magnitude of the slope below T_{g2} is greater than that above T_{g2}. Hence, the first two predictions of the theory listed above are consistent with experimental IGC data. The third prediction (eq 11) is more difficult to evaluate because T_{gm} vs ω_1 data (and, hence, the value of A) are often not available. An estimate for A can however be produced for the methanol–PMMA system. A glass transition temperature for the methanol–PMMA system has been reported,[5] but the solvent volume fraction is 0.24, and hence, these data are not of much use in estimating A near $\omega_1 = 0$. Data for the glass transition temperature for the water–PMMA system have been reported[6] near $\omega_1 = 0$. The dependence of T_{gm} on ω_1 for this system near $\omega_1 = 0$ is well represented by the Fox equation with a slope which is 45% higher than the expected slope. If we assume that the T_{gm} vs ω_1 data for the methanol–PMMA system are also represented by the Fox equation with a slope which is 45% higher than the expected slope, then a value of $A = 1500K$ can be estimated. Although there is of course no direct justification for this calculation, a value of $A = 1500K$ is reasonable when compared to the value for the water–PMMA system. The experimental value of the slope difference (the left-hand side of eq 11) is 1750K. The theoretical value calculated from eq 11 (with $A = 1500\ K$ and $\hat{C}_p - \hat{C}_{pg} = 0.0760$ cal/g K) is 1800K. Hence, there is good agreement between experiment and theory for the third prediction listed above. Consequently, it can be concluded from the above data–theory comparison that the temperature dependence of the partition coefficient (above and below T_{g2}) predicted by the proposed theory is consistent with the temperature dependence deduced from experimental IGC data.

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References and Notes

(1) Vrentas, J. S.; Vrentas, C. M. *Macromolecules* **1991**, 24, 2404−2412.

(2) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(3) Standler, S. I. Chemical and Engineering Thermodynamics; John Wiley: New York, 1977.

(4) Arnould, D. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1989.

(5) Williams, D. R. G.; Allen, P. E. M.; Truong, V. T. *Eur. Polym. J.* **1986**, *22*, 911−919.

(6) Smith, L. S. A.; Schmitz, V. *Polymer* **1988**, 29, 1871−1878.

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