

Effect of the Polymer Glass Transition on the Chromatographic Retention Volumes

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ABSTRACT: Theoretical developments are presented that explain four experimental observations concerning the temperature dependence of chromatographic specific retention volumes. A theoretical framework is proposed for a method that can be used to determine the glass-transition temperature of the pure polymer and for a method of characterizing

the concentration dependence of the glass-transition temperature of a polymer-solvent system. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 793–796, 2005

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INTRODUCTION

Inverse gas chromatography has proven to be a useful method of studying the thermodynamic and mass-transfer characteristics of polymer-solvent systems. A study of the magnitude and temperature dependence of the interaction of a solvent with a stationary polymer phase allows the measurement of the properties of the polymer-solvent system and the properties of the pure polymer. For example, an elution curve of a solvent can be obtained by the measurement of the solvent concentration versus the time at the outlet of the chromatographic column. The moments of the elution curve can be used to determine both the mutual diffusion coefficient for a trace of the solvent in the polymer phase and the bulk solvent partition coefficient between the gas and polymer phases.¹ In addition, the temperature dependence of the specific retention volume can be determined, and this information can be used to investigate the glass-transition characteristics of the polymer and the polymer-solvent mixture.¹

Arnould¹ used a capillary chromatographic column to carry out a detailed study of the effect of the glass transition on the temperature dependence of the specific retention volume. Data were collected for the poly(methyl methacrylate) (PMMA)-methanol system and for five solvents diffusing in poly(*p*-methyl styrene) (PPMS). Specific retention volumes based on the mean retention times were determined from the data and were plotted on retention diagrams as $\ln V_g^0$ ver-

sus $1/T$ (K), where V_g^0 is the specific retention volume at 0°C and T is the temperature. From these retention diagrams, Arnould reported the following experimental observations:

1. In all cases, the retention diagrams were linear both above and below the glass-transition temperature of the system.
2. A change in the slope occurred at the glass-transition temperature, with a greater slope for data below the transition temperature.
3. Because of the low surface area characteristic of capillary columns, the contribution of surface adsorption to the retention process, in comparison with that of bulk absorption, was assumed to be negligible both above and below the glass-transition temperature. Hence, the observed change in the slope in the retention diagram at the glass-transition temperature indicated a change in the bulk-sorption temperature dependence at the lower temperatures, corresponding to a change in the heat of solution.
4. For the five PPMS-solvent systems studied, there were differences of several degrees in the measured glass-transition temperatures.

The objectives of this article are to provide a theoretical basis for these observations by Arnould and to use this theory to illustrate just what glass-transition parameters can be determined from retention-volume/temperature data. The theory is developed in the second section of this article, and its predictions are compared with experimental observations in the third section.

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THEORY

The specific retention volumes at 0°C (based on the mean retention times) for rubbery and glassy polymers, $(V_g^0)_R$ and $(V_g^0)_G$, respectively, can be related to the rubbery and glassy partition coefficients, K_R and K_G , respectively, by the following equations:¹

$$(V_g^0)_R = \frac{273.2K_R}{\rho_2 T} \quad (1)$$

$$(V_g^0)_G = \frac{273.2K_G}{\rho_2 T} \quad (2)$$

where ρ_2 is the density of the pure polymer and T is the column temperature (K). The partition coefficient represents the ratio of the solvent concentration in the polymer phase to the solvent concentration in the gas phase. If the gas phase is ideal and if the polymer-solvent system can be adequately represented by the Flory-Huggins theory,² the phase equilibrium for the rubbery polymer-solvent system can be described by the following equation in the limit of very small solvent concentrations:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(1 + \chi) \quad T \geq T_{g2} \quad (3)$$

where T_{g2} is the glass-transition temperature of the pure polymer, p_1 is the solvent partial pressure in the gas phase, p_1^0 is the vapor pressure of the pure solvent at T , ϕ_1 is the solvent volume fraction in the polymer phase, and χ is the interaction parameter of the Flory-Huggins theory. ϕ_1 can be expressed as follows:

$$\phi_1 = \rho_1 \hat{V}_1 \quad (4)$$

where ρ_1 is the solvent mass density in the polymer phase and \hat{V}_1 is the partial specific volume of the solvent in the limit of a zero solvent concentration. The ideal gas law yields the following expression for p_1 :

$$p_1 = \frac{\rho_{1g} RT}{M_1} \quad (5)$$

where ρ_{1g} is the solvent mass density in the gas phase and M_1 is the solvent molecular weight. Also, from the solvent equilibrium relationship, we can obtain

$$\rho_1 = K_R \rho_{1g} \quad (6)$$

The combination of eqs. (3)–(6) produces the following result:

$$\frac{1}{K_R} = \frac{M_1 p_1^0 \hat{V}_1 \exp(1 + \chi)}{RT} \quad (7)$$

The temperature dependence of p_1^0 can often be adequately described by the following integrated form of the Clausius-Clapeyron equation:³

$$\ln p_1^0 = E - \frac{H}{T} \quad (8)$$

where E and H are constants. Consequently, the substitution of eqs. (7) and (8) into eq. (1) produces the following result for $T \geq T_{g2}$:

$$\ln (V_g^0)_R = \ln \left[\frac{273.2R}{\rho_2 \hat{V}_1 M_1 \exp(1 + \chi)} \right] - E + \frac{H}{T} \quad (9)$$

If the temperature dependence of ρ_2 , \hat{V}_1 , and χ can be assumed to be small, then it follows that

$$\frac{\partial \ln (V_g^0)_R}{\partial \left(\frac{1}{T} \right)} = H \quad (10)$$

This method can also be used to derive a similar result for a glassy-polymer/solvent system by the addition of the following equations⁴ for the phase equilibrium of a glassy-polymer/solvent mixture in the limit of very small solvent concentrations:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(1 + \chi) e^F \quad T < T_{g2} \quad (11)$$

$$F = \frac{M_1 (\hat{C}_p - \hat{C}_{pg}) A}{RT} \left(\frac{T}{T_{g2}} - 1 \right) \quad (12)$$

where \hat{C}_p is the specific heat capacity at a constant pressure for the equilibrium liquid polymer and \hat{C}_{pg} is the specific heat capacity at a constant pressure for the glassy polymer. Equation (12) is based on the utilization of the following equation for the concentration dependence of the glass-transition temperature of the polymer-solvent system:

$$T_{gm} = T_{g2} - A\omega_1 \quad (13)$$

In this equation, T_{gm} is the glass-transition temperature of the polymer-solvent mixture at a particular solvent mass fraction, ω_1 is the solvent mass fraction, and A is a constant coefficient that depends on the nature of the solvent used to depress the glass-transition temperature of a particular polymer. This linear approximation should be valid at sufficiently low solvent concentrations. With the same procedure used to

derive eqs. (9) and (10) for the rubbery polymer, eqs. (11) and (12) yield the following results for $T < T_{g2}$:

$$\ln(V_g^0)_G = \ln \left[\frac{273.2R}{\rho_2 \hat{V}_1 M_1 \exp(1 + \chi)} \right] - E - \frac{M_1(\hat{C}_p - \hat{C}_{pg})A}{RT_{g2}} + \left[H + \frac{M_1(\hat{C}_p - \hat{C}_{pg})A}{R} \right] \frac{1}{T} \quad (14)$$

$$\frac{\partial \ln(V_g^0)_G}{\partial \left(\frac{1}{T} \right)} = H + \frac{M_1(\hat{C}_p - \hat{C}_{pg})A}{R} \quad (15)$$

Equation (15) is based on the assumption that the temperature dependence of ρ_2 , \hat{V}_1 , χ , \hat{C}_p , and \hat{C}_{pg} is small. The combination of eqs. (10) and (15) gives the following result valid for small solvent concentrations:

$$\frac{\partial \ln(V_g^0)_G}{\partial \left(\frac{1}{T} \right)} - \frac{\partial \ln(V_g^0)_R}{\partial \left(\frac{1}{T} \right)} = \frac{M_1(\hat{C}_p - \hat{C}_{pg})A}{R} \quad (16)$$

Heat effects for the sorption process can be calculated by the definition of a solubility coefficient (s):⁴

$$s = \left(\frac{C}{p_1} \right)_{\omega_1=0} \quad (17)$$

where C is the concentration of the sorbed solvent [$\text{cm}^3(\text{STP})/\text{cm}^3$ of polymer]. A molar heat of solution ($\Delta\tilde{H}$) can then be defined as follows:⁴

$$\Delta\tilde{H} = RT^2 \frac{\partial \ln s}{\partial T} \quad (18)$$

Consequently, for solvent sorption in rubbery polymers, eqs. (3), (17), and (18) give

$$\ln s_R = -\ln p_1^0 - \ln \left(\frac{M_1 \hat{V}_1}{22,400} \right) - (1 + \chi) \quad (19)$$

$$(\Delta\tilde{H})_R = -\frac{RT^2}{p_1^0} \frac{\partial p_1^0}{\partial T} \quad (20)$$

For solvent sorption in glassy polymers, eqs. (11), (12), (17), and (18) give

$$\ln s_G = -\ln p_1^0 - \ln \left(\frac{M_1 \hat{V}_1}{22,400} \right) - (1 + \chi) - \frac{M_1(\hat{C}_p - \hat{C}_{pg})A}{R} \left(\frac{1}{T_{g2}} - \frac{1}{T} \right) \quad (21)$$

$$(\Delta\tilde{H})_G = -\frac{RT^2}{p_1^0} \frac{\partial p_1^0}{\partial T} - M_1(\hat{C}_p - \hat{C}_{pg})A \quad (22)$$

In the derivation of these equations, it has been assumed that the temperature dependence of \hat{V}_1 , χ , \hat{C}_p , and \hat{C}_{pg} is negligible.

It is generally accepted⁵ that T_{g2} must be dependent on the timescale of the process used to measure it. Slower measurement experiments lead to lower values of T_{g2} . Inverse chromatography experiments involve unsteady sorption and desorption in a thin film of thickness L . The characteristic diffusion time (θ_D) for the sorption or desorption process is simply

$$\theta_D = \frac{L^2}{D} \quad (23)$$

where D is the mutual diffusion coefficient at $\omega_1 = 0$ and $D(\omega_1 = 0)$ is equal to the self-diffusion coefficient of the solvent at $\omega_1 = 0$. If inverse chromatography experiments are carried out with a series of solvents in the same polymer with the same film thickness L , then θ_D will be higher for the solvents with the smaller diffusion coefficients. Consequently, for two solvents B and C, T_{g2} measured with solvent B should be less than T_{g2} measured with solvent C if D for solvent C is greater than D for solvent B.

DISCUSSION

Because the temperature dependence of ρ_2 , \hat{V}_1 , and χ is assumed to be small, it is evident from eq. (9) that a retention diagram is linear above T_{g2} with the slope given by eq. (10). Also, because the temperature dependence of ρ_2 , \hat{V}_1 , χ , \hat{C}_p , and \hat{C}_{pg} is assumed to be small, it follows from eq. (14) that a retention diagram is linear below T_{g2} with the slope given by eq. (15). Consequently, the theoretical predictions are consistent with the first experimental observation. It is also evident from eqs. (9) and (14) that the two straight lines intersect at $T = T_{g2}$, and so the temperature at which the intersection occurs is necessarily equal to the glass-transition temperature of the pure polymer. Hence, retention diagrams provide a simple way of determining polymer glass-transition temperatures.

Equation (16) indicates that there is a change in the slope at $T = T_{g2}$ and that the slope is greater for data below the polymer glass-transition temperature because A is greater than 0 and $\hat{C}_p - \hat{C}_{pg}$ is greater than 0. These theoretical predictions are consistent with the second experimental observation. Also, because the theoretical sorption equations both above and below T_{g2} do not consider surface adsorption, the change in the slope simply reflects a difference in the bulk-sorption processes in the rubbery and glassy states. This difference is reflected in the predicted difference of the

heats of solution for sorption in rubbery and glassy polymers, as shown in eqs. (20) and (22). This prediction is consistent with the third experimental observation.

The concentration dependence of T_{gm} for a particular polymer-solvent system can be computed with eq. (13) (at least for sufficiently small solvent mass fractions) if T_{g2} and A are known. It has already been noted that T_{g2} can be measured with data on the temperature dependence of specific retention volumes. The same data can be used to compute A from eq. (16) if a $\hat{C}_p - \hat{C}_{pg}$ value is available for the polymer of interest. For example, when data for the PMMA-methanol system¹ are analyzed with eq. (13), a value of $A = 1300$ K can be calculated. Values of A determined by other methods are listed in Table I along with the value of A calculated from the temperature dependence of the retention volumes for the PMMA-methanol system. The value of A for the PMMA-methanol system is comparable in magnitude to some of the other A values that are listed, and so the proposed method of determining A is a reasonable alternative to other methods.

The glass-transition data of Arnould¹ for five PPMS-solvent systems are presented in Table II. This table includes the experimental value of T_{g2} for each of the five systems and the experimental diffusion coefficient (D) at $T \approx 383$ K, a temperature reasonably close to the measured values of T_{g2} . On the basis of the previous discussion, we expect the value of T_{g2} to decrease as D decreases, and so the T_{g2} values should satisfy the following inequalities:

$$T_{g2}(M) > T_{g2}(A) \approx T_{g2}(MA) > T_{g2}(EA) > T_{g2}(B) \quad (24)$$

where M is methanol, A is acetone, MA is methyl acetate, EA is ethyl acetate, and B is benzene. The

TABLE I
Values of A for the Polymer-Penetrant Systems

Polymer	Penetrant	A (K)	Reference
PMMA	Methanol	1300	This study
PMMA	Water	1100	6
Polystyrene	Carbon dioxide	690	7
Polystyrene	Benzene	370	5
Polystyrene	Carbon disulfide	720	5
Polycarbonate	Carbon dioxide	1110	4

TABLE II
Glass-Transition Data for the PPMS-Solvent Systems¹

Solvent	D at 383 K (cm ² /s)	Experimental T_{g2} (°C)
Methanol	2.28×10^{-7}	104
Acetone	1.03×10^{-8}	103
Methyl acetate	8.71×10^{-9}	103
Ethyl acetate	2.23×10^{-9}	100
Benzene	1.11×10^{-9}	100

experimental data listed in Table II lead to the following inequalities:

$$T_{g2}(M) > T_{g2}(A) = T_{g2}(MA) > T_{g2}(EA) = T_{g2}(B) \quad (25)$$

Because the predicted ordering of T_{g2} [eq. (24)] is nearly equivalent to the experimental ordering of T_{g2} [eq. (25)], it appears that the differences in the T_{g2} values noted in the fourth experimental observation can be explained by the use of eq. (23) to compute θ_D .

CONCLUSIONS

It has been shown that four experimentally obtained observations concerning the temperature dependence of chromatographic specific retention volumes can be explained by the theoretical developments proposed here. Also, a theoretical framework has been proposed for a method of determining the glass-transition temperature of the pure polymer and for a method of characterizing the concentration dependence of the glass-transition temperature of a polymer-solvent system. The results of this study should be applicable to any amorphous polymer-solvent system.

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