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Solubility and Diffusivity of Cyclic Oligomers in Poly(dimethylsiloxane) Using Capillary Column Inverse Gas Chromatography[†]

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ABSTRACT: The solubility and diffusivity of octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), and dodecamethylcyclohexasiloxane (D_6) oligomers in poly(dimethylsiloxane) (PDMS) have been measured using inverse gas chromatography. Experiments were performed at 150, 175, and 200 °C. Solubility values were used to determine the Flory–Huggins interaction parameter for each species. The interaction parameter values were found to range from -0.15 to 0.15 over the temperature range of these measurements. Diffusion coefficient values were of order 10^{-6} cm^2/s and were found to be in reasonable agreement with the free volume theory of Vrentas and Duda.[1,2] An empirical relationship between diffusivity and solute molecular weight was developed at each temperature. Activation energies for diffusion were found to be 4.4 kcal/mol for D_4 and 7.1 kcal/mol for D_5 and D_6.

Introduction

Residual cyclic oligomers in poly(dimethylsiloxane) (PDMS) can create problems for products that are exposed to heat during use. Therefore, the polymer must be devolatilized prior to final product manufacture. In order to design a devolatilization scheme, the equilibrium and transport properties of these oligomers in PDMS must be known. In this study, these properties were measured using an inverse gas chromatography technique.

The thermodynamic properties of solutions of PDMS have been the subject of a number of investigations. These have involved the measurement of osmotic pressure, heats of mixing, and volume changes on mixing for solutions of PDMS in benzene, cyclohexane, and chlorobenzene,[3] in *n*-alkanes,[4] in several ketones,[5] and in octamethylcyclotetrasiloxane.[6] These studies were all conducted in solutions in which the polymer concentration was less than 30%. Polymer devolatilization processes involve polymer solutions in which the volatile solvent concentration approaches its infinite dilution limits. Under these conditions, the thermodynamic and transport properties may be significantly different than those in more concentrated solutions.

Gravimetric sorption/desorption techniques have been used to determine the solubility and diffusivity of volatile solvents in polymeric materials under conditions where the solute concentration is relatively dilute. However, relatively high solute concentrations are required to observe measurable weight changes. The difficulty in maintaining a constant, well-defined geometry for the polymer sample can also make the accurate determination of solute diffusivity extremely difficult.

In inverse gas chromatography (IGC), the polymer of interest is the stationary phase in a gas chromatography column. A pulse of solute is injected into the column and is carried through the column with an inert carrier gas. The solubility of the solute in the polymer dictates its retention time in the column. The width of the eluted solute peak is related to the diffusion coefficient of solute in the polymer. By using a capillary column, where the polymer is coated as a thin film on the inside of a capillary tube, the polymer geometry can be easily characterized. Therefore, development of the relationship between peak width and solute diffusivity is straightforward. Packed-column IGC was used by Summers *et al.*[7] and Lichenthaler *et al.*[8] to investigate the thermodynamic properties of various hydrocarbons in PDMS. Capillary column IGC has been used by Laurence and co-workers to measure properties of various solutes in polystyrene and poly(methyl methacrylate).[9-11]

Details of the theoretical model that relates the measured solute elution profile to the solubility and diffusivity in the polymer have been presented[9,10] and will not be derived in detail here. The model involves solving the continuity equations for solute in the gas and the polymer. By assuming plug flow in the gas phase and neglecting gas phase diffusion and dispersion, the solution is obtained using the method of Laplace transforms. At the column exit, the solution is

$$Y(s) = \exp\left[-s - \frac{2\sqrt{s}}{\alpha\beta}\tanh(\beta\sqrt{s})\right] \qquad (1)$$

where $Y(s)$ is the Laplace transform of cL/c_0v. The equilibrium partition coefficient, K, and diffusivity, D_p, are contained in the dimensionless parameters α and β:

$$\alpha = R_c/K\tau \qquad (2)$$

$$\beta^2 = \tau^2 v/D_p L \qquad (3)$$

where K is defined as the ratio of the solute concentration in the polymer relative to that in the surrounding gas.

Experimental Section

The properties of three different cyclic oligomers were investigated—octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), and dodecamethylcyclohexasiloxane (D_6). These materials were obtained from the GE Silicones plant in Waterford, NY. The IGC column was prepared by the Restek Corp. using General Electric PDMS with an average molecular weight of 464 000. The polymer contained a vinyl cross-linking agent (0.2 mol %) that was not activated. Therefore, the material

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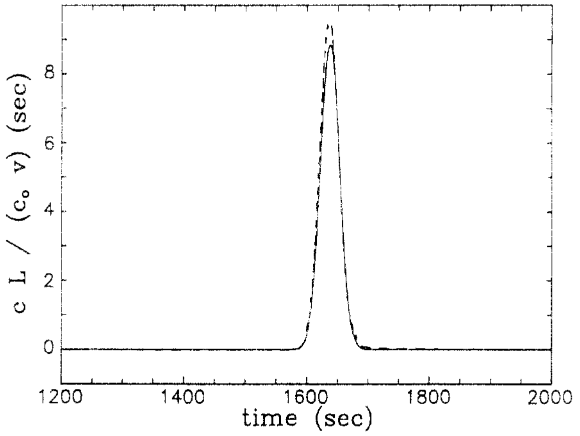

Figure 1. Comparison of experimental (- - -) and theoretical (—) elution profiles for D_4 at 150 °C. Flow rate = 2.0 cm^3/min, $L/v = 359.3$ s. The theoretical profile was obtained by numerical inversion of eq 1 with a fast Fourier transform algorithm using $\alpha = 0.563$ and $\beta = 0.0281$.

can be considered essentially linear. The nominal thickness of the polymer film was 7 μm, the column length was 60 m, and its radius was 265 μm (530 μm i.d.). The column was installed in a Hewlett Packard Model 5880 gas chromatograph equipped with a flame ionization detector. The injection system was modified to minimize dispersion during sample injection. Nitrogen was used as the carrier gas, and its flow rate was controlled using an MKS Model 247C mass flow controller. Less than 0.1 μL of liquid sample was introduced into the column using a 10-μL syringe. No significant difference in the elution profile was observed when the sample size was varied, indicating that infinite dilution conditions were maintained in the column. An injection of methane was used to determine the carrier flow rate. This was done periodically during a series of measurements. Data from the detector was directed through an Acro Systems data acquisition unit and recorded on a Dell personal computer. A basic program was used to analyze the elution profiles and determine α and β values for each experiment.

Experiments were performed at 150, 175, and 200 °C. For each solute at each temperature, measurements were performed at three or four different flow rates ranging from 2 to 10 cm^3/min. Replicate measurements were performed at each set of conditions. Experiments were first performed with D_4 and D_5 at each temperature. Following this series of measurements, experiments were performed with D_6 at each temperature. During this series of experiments, several measurements were repeated with D_4 and D_5. There was excellent agreement between the results obtained from these D_4 and D_5 measurements and the earlier D_4 and D_5 results. Therefore, it is reasonable to assume that the polymer was not changing because of its thermal history or exposure to these solvents.

Data Analysis

Two methods have been used to relate α and β to experimental concentration versus time data.[9,10] By taking advantage of the moment generating property of Laplace transforms, the moments of the observed concentration profile can be related to eq 1 without requiring an inversion of the transform:

$$\mu_k = \frac{\int_0^\infty t^k c(t)\, \mathrm{d}t}{\int_0^\infty c(t)\, \mathrm{d}t} = \frac{(-1)^k \left(\frac{L}{v}\right)^k \lim_{s \to 0} \frac{\mathrm{d}^k Y(s)}{\mathrm{d}s^k}}{\lim_{s \to 0} Y(s)} \qquad (4)$$

where μ_k is the kth normalized moment. Applying eq 4 to eq 1 with $k = 1$ yields the first normalized moment:

$$\mu_1 = \frac{L}{v}\left[1 + \frac{2}{\alpha}\right] \qquad (5)$$

The second centralized moment, $\mu_2{}^*$, is often more useful than the second normalized moment:

$$\mu_2{}^* = \mu_2 - \mu_1{}^2 = \frac{4}{3}\left(\frac{L}{v}\right)^2 \frac{\beta^2}{\alpha} \qquad (6)$$

where μ_2 was determined by applying eq 4 to eq 1 with $k = 2$.

For elution profiles that are significantly skewed, a method for parameter estimation in the Fourier domain has been shown to be more accurate than the method of moments.[10] A least-squares parameter fit in the time domain is equivalent to minimizing the following function in the frequency domain:

$$\begin{aligned} F = \frac{1}{2t_{\max}}&[[A_{\exp,0}(\omega_0) - A_{\mathrm{th},0}(\omega_0)]^2 + \\ &[B_{\exp,0}(\omega_0) - B_{\mathrm{th},0}(\omega_0)]^2] + \frac{1}{t_{\max}}\sum_{n=1}^{N}[[A_{\exp,n}(\omega_n) - \\ &A_{\mathrm{th},n}(\omega_n)]^2 + [B_{\exp,n}(\omega_n) - B_{\mathrm{th},n}(\omega_n)]^2] \end{aligned} \qquad (7)$$

where the integral defining the Fourier transform has been replaced by a finite sum, A_n and B_n are the coefficients of a Fourier series expansion of $c(t)$, and the frequency ω_n is defined by

$$\omega_n = n\pi/t_{\max} \qquad (8)$$

The summation was truncated at $N = 100$, after which additional terms contribute negligibly to $c(t)$. Experimental A_n and B_n values were determined by numerical integration:

$$A_{\exp,n}(\omega_n) = \frac{1}{t_{\max}}\int_0^{t_{\max}} c(t) \cos(\omega_n t)\, \mathrm{d}t \qquad (9)$$

$$B_{\exp,n}(\omega_n) = \frac{1}{t_{\max}}\int_0^{t_{\max}} c(t) \sin(\omega_n t)\, \mathrm{d}t \qquad (10)$$

Theoretical A_n and B_n values were determined from the Laplace transform solution (eq 1) and

$$A_{\mathrm{th},n}(\omega_n) = \frac{1}{t_{\max}} \mathrm{Re}\{Y(i\omega_n)\} \qquad (11)$$

$$B_{\mathrm{th},n}(\omega_n) = \frac{1}{t_{\max}} \mathrm{Im}\{Y(i\omega_n)\} \qquad (12)$$

Initial guess values for α and β were determined from the first and second moments. A minimization procedure was then performed to find α and β that minimized the function in eq 7. A comparison of the experimental elution profile to the profile predicted by the theoretical model for one experiment is shown in Figure 1. The predicted elution profile was obtained by numerical inversion of eq 1 using a fast Fourier transform algorithm and the best fit values for α and β. The good agreement between the two profiles supports the validity of the model for this system.

Results

Solubility Measurements. The parameter α characterizes the thermodynamic properties of the solute–polymer mixture and therefore is expected to be independent of carrier flow rate. In all cases, the experimentally determined α values for a given set of conditions were in agreement within 5%. The coefficient K was determined from the average α value using eq 2. The specific retention volume, $V_g{}^\circ$, was determined using

$$V_g{}^\circ = \frac{273.2 v_2}{T} K \qquad (13)$$

The weight-fraction activity coefficient, $\Omega_1{}^\infty$, is related to

Table I. Thermodynamic Properties of Oligomeric Solutes

solute	T_c (K)	P_c (bar)	$\alpha_1 \times 10^3$ [d] (deg^{-1})	$v_{1,0}{}^*$ [e] (cm^3/g)
D_4	587[a]	14.1[a]	1.33	0.922
D_5	597[b]	11.6[c]	1.13	0.908
D_6	665[b]	9.9[c]	1.05	0.903

[a] Reference 20. [b] Estimated using eq 21 and $\Delta_T = 0.12$. [c] Estimated using eq 22 and $\Delta_P = 1.07$. [d] Derived using eqs 18–20. [e] Estimated using eq 30.

Table II. Summary of Thermodynamic Properties in PDMS

solute	T (°C)	K	$V_g°$	$\Omega_1{}^\infty$	χ_{12}	$\chi_{12}{}^*$
D_4	150	67.0	49.0	3.27	0.098	0.183
D_4	175	36.2	25.5	3.09	0.030	0.117
D_4	200	21.7	14.8	2.84	−0.068	0.023
D_5	150	155.4	113.6	3.05	0.049	0.103
D_5	175	76.3	53.7	2.93	0.0029	0.058
D_5	200	42.0	28.6	2.76	−0.067	−0.0069
D_6	150	385.1	281.5	2.72	−0.044	−0.0052
D_6	175	169.3	119.3	2.67	−0.072	−0.032
D_6	200	85.2	58.0	2.52	−0.136	−0.091

$V_g°$ by[9]

$$\ln(\Omega_1{}^\infty) = \ln\left[\frac{273.15R}{P_1°V_g°M_1}\right] - \frac{P_1°(B_{11} - v_1M_1)}{RT} \tag{14}$$

The Flory–Huggins interaction parameter, χ_{12}, is related to the weight-fraction activity coefficient:

$$\chi_{12} = \ln \Omega_1{}^\infty - \ln(v_1/v_2) - 1 \tag{15}$$

An alternative relation between the activity coefficient and the interaction parameter has also been proposed in which the specific volume ratio is replaced by a ratio of segment fractions based on hard-core volumes:[7]

$$\chi_{12}{}^* = \ln \Omega_1{}^\infty - \ln(v_1{}^*/v_2{}^*) - 1 \tag{16}$$

where $v_1{}^*$ and $v_2{}^*$ are specific hard-core volumes.

In order to use eqs 13–16 to calculate χ_{12} and $\chi_{12}{}^*$ from the measured values of K, the solute vapor pressure, the specific volume, and the hard-core volume of the solute and polymer must be known. In addition, the solute critical properties must be known in order to estimate B_{11}. The vapor pressure of each solute at each temperature was estimated using a correlation reported by Wilcock:[12]

$$\log P_1° = 7.07 - \frac{1190}{T} + \left[0.265 - \frac{294}{T}\right]x \tag{17}$$

where the vapor pressure is in mmHg, T is the absolute temperature in K, and x is the number of silicon atoms in the solute. The polymer density at a given temperature was estimated from the molar volume at 25 °C (75.6 cm^3/mol) and the thermal expansion coefficient (0.068 cm^3/(mol K)).[13] The mole basis used for these values is 1 mol of polymer repeating unit. The solute specific volume in eq 15 refers to the specific volume of liquid and was estimated using the following expressions:[14]

for D_4:

$$v_1 = 1.0209[1 + 1.197 \times 10^{-3}(T - 273) + 1.352 \times 10^{-6}(T - 273)^2] \tag{18}$$

for D_5:

$$v_1 = 1.0175[1 + 1.178 \times 10^{-3}(T - 273) + 5.789 \times 10^{-7}(T - 273)^2] \tag{19}$$

for D_6:

$$v_1 = 1.0115[1 + 1.087 \times 10^{-3}(T - 273) + 5.121 \times 10^{-7}(T - 273)^2] \tag{20}$$

where v_1 is in cm^3/g. Equations 18–20 were obtained by fitting data collected at 0–80 °C and were assumed to be valid at the temperatures of these experiments.

The critical temperature and pressure of D_4 are known and are listed in Table I. However, the critical properties of D_5 and D_6 are not known. For these materials, T_c and P_c were estimated using Lydersen's method:[15]

$$T_c = T_b[0.567 + \sum\Delta_T - (\sum\Delta_T)^2]^{-1} \tag{21}$$

$$P_c = M_1(0.34 + \sum\Delta_P)^{-2} \tag{22}$$

where T_c is in K, P_c is in bar, and T_b is the normal boiling point. The quantities $\Sigma\Delta_T$ and $\Sigma\Delta_P$ are summations of group contribution increments. Values of Δ_T and Δ_P are tabulated for various hydrocarbon groups.[15] As an alternative approach, we have calculated values for Δ_T and Δ_P for each repeating unit in the oligomer ring using the known values of T_c and P_c for D_4 and eqs 21 and 22. These values were found to be $\Delta_T = 0.12$ and $\Delta_P = 1.07$ and were then used to estimate T_c and P_c for D_5 and D_6. A 5–10% difference was found between the estimates for T_c and P_c using these values for Δ_T and Δ_P and those estimated using Lydersen's critical property increments. However, the difference in χ_{12} determined using these different critical property values was considerably less than 5%. The estimated values for T_c and P_c are listed in Table I.

The second virial coefficient was estimated from the critical temperature and pressure using a correlation proposed by Tsonopoulos:[16]

$$B_{11} = \frac{RT_c}{P_c}\left[0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^{\,2}} - \frac{0.0121}{T_r^{\,3}} - \frac{0.000607}{T_r^{\,8}}\right] \tag{23}$$

where a second term involving the acentric factor was neglected because of the uncertainty in estimating its value.

The specific hard-core volume, $v_2{}^*$, for PDMS has been reported by Shih and Flory[17] over the temperature range of interest in this study. These values were used in eq 16 when calculating $\chi_{12}{}^*$. For the oligomer solutes, eq 4 from Shih and Flory[17] was used to estimate $v_1{}^*$ from the thermal expansion coefficient. The thermal expansion coefficient for each oligomer was derived from eqs 18–20.

Values for K, $V_g°$, $\Omega_1{}^\infty$, χ_{12}, and $\chi_{12}{}^*$ are summarized in Table II. A plot of χ_{12} versus $1/T$ is shown in Figure 2, and a plot of $\chi_{12}{}^*$ versus $1/T$ is shown in Figure 3. The temperature dependence of the interaction parameter is related to the partial molar heat of mixing at solute infinite dilution.[19] For χ_{12} versus $1/T$:

$$\Delta\bar{h}_1{}^\infty = \bar{h}_1{}^\infty - h_1° = RT^2(\alpha_2 - \alpha_1) + R\frac{\partial\chi_{12}}{\partial(1/T)} \tag{24}$$

where $\bar{h}_1{}^\infty$ is the partial molar enthalpy of solute in the polymer at infinite dilution, $h_1°$ is the enthalpy of pure liquid solute, and α_1 and α_2 are the thermal expansion coefficients of the solute and polymer. For $\chi_{12}{}^*$ versus $1/T$:

$$\Delta\bar{h}_1{}^\infty = R\frac{\partial\chi_{12}{}^*}{\partial(1/T)} \tag{25}$$

The thermal expansion coefficient of PDMS has been

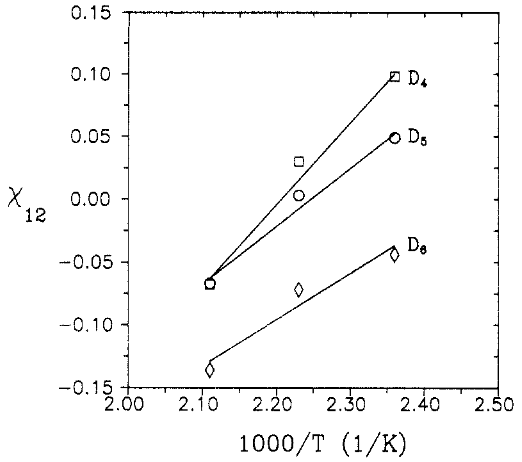

Figure 2. Flory–Huggins interaction parameters for D_4, D_5, and D_6 in PDMS. The specific volumes of the solute and polymer were used when calculating χ_{12} (eq 15).

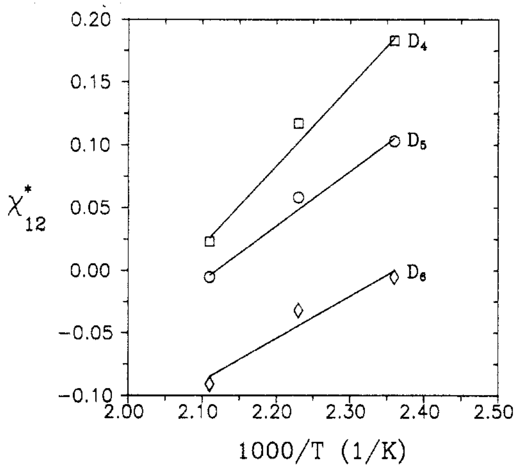

Figure 3. Flory–Huggins interaction parameters for D_4, D_5, and D_6 in PDMS. The specific hard-core volumes of the solute and polymer were used when calculating χ_{12}^* (eq 16).

Table III. Experimentally Determined Heats of Dilution

	$\Delta\bar{h}_1^\infty$ (kcal/mol)	
solute	using χ_{12} (eq 24)	using χ_{12}^* (eq 25)
D_4	1.16	0.32
D_5	0.85	0.22
D_6	0.69	0.17

reported by Shih and Flory[17] over the temperature range of 20–200 °C. Using these values for α_2 and α_1 values derived from eqs 18–20, the heat of dilution was determined using the slopes of the lines in Figures 2 and 3 and eqs 24 and 25. These values are compared in Table III. The difference between χ_{12} and χ_{12}^* lies in the expression used for describing the combinatorial entropy. Because of the chemical similarity between the polymer and solute for these systems, one would expect their mixtures to be quite athermal. Because the heat of dilution determined using χ_{12}^* is 3–4 times smaller than that determined using χ_{12}, it appears that using segment fractions rather than volume fractions provides a more accurate description of the combinatorial entropy, as was argued by Shih and Flory.[17] More recently, Lichenthaler *et al.*[8] have presented a modification to the Flory–Huggins entropy formula that incorporates molecular size and shape differences between polymer segments and solute molecules in describing the combinatorial entropy. However, in order to test the validity of this approach, independent heat of mixing data are required. Such data are not available for the systems investigated here.

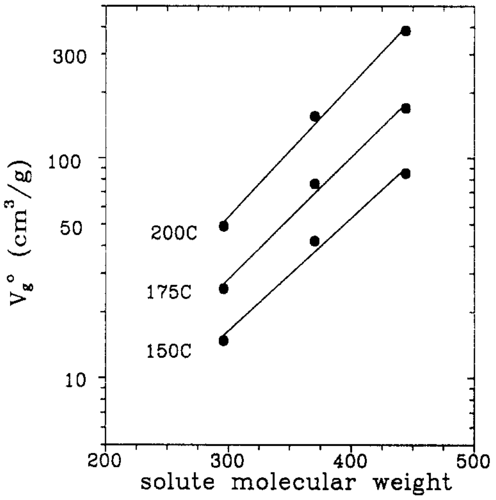

Figure 4. Specific retention volume (V_g°) as a function of solute molecular weight. Parameters for the best fit line at each temperature are listed in Table IV.

Table IV. Parameters for V_g° and D_p versus Solute Molecular Weight (Equations 26 and 31)

temp (°C)	*a*	*b*	*c*	*d*
150	1.47	1.12×10^{-2}	4.74×10^{-1}	2.19
175	1.16	1.04×10^{-2}	2.56×10^{-2}	1.62
200	0.956	9.23×10^{-3}	6.37×10^{-3}	1.33

Table V. Diffusion Coefficients in PDMS

	$D_p \times 10^6$ (cm^2/s)		
solute	150 °C	175 °C	200 °C
D_4	1.84	2.46	3.19
D_5	1.04	1.80	2.55
D_6	0.76	1.27	1.85

The relationship between the specific retention volume and solute molecular weight was determined by fitting the results to an equation of the form

$$V_g^\circ = ae^{bM_1} \quad (26)$$

A semilog plot of V_g° versus molecular weight is shown in Figure 4, and the values for *a* and *b* at each temperature are summarized in Table IV. Equation 26 can be used to estimate the solubility of other cyclic oligomers in PDMS.

Diffusion Coefficient Measurements. For each solute at each temperature, a plot of β^2 versus v/L was prepared. A straight line through the origin is expected, and in all cases, excellent linearity was observed. The diffusion coefficient was calculated from the slope of the line using eq 3. The diffusion coefficient values for D_4, D_5, and D_6 determined in this study are summarized in Table V.

A semilog plot of D_p versus $1/T$ is presented in Figure 5. The activation energy for diffusion was determined from the slope of the line for each solute. These values were found to be 4.4 kcal/(g mol) for D_4 and 7.1 kcal/(g mol) for D_5 and D_6.

The free-volume theory of Vrentas and Duda[1] for diffusion in polymers provides the following relationship for the solute and temperature dependence of the diffusion coefficient at infinite dilution of solute:

$$D_p = D_0 \exp\left(-\frac{E^*}{RT}\right) \exp\left(-\frac{\gamma \hat{V}_2^* \xi / K_{12}}{K_{22} + T - T_{g2}}\right) \quad (27)$$

The parameters K_{22} and $\gamma\hat{V}_2/K_{12}$ are related to the Williams–Landel–Ferry constants of the polymer, C_1^g and

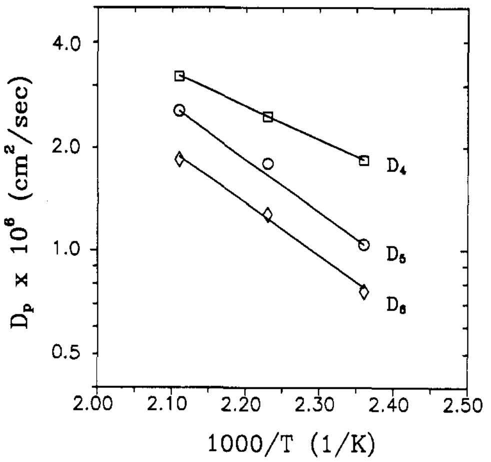

Figure 5. Diffusion coefficients of D_4, D_5, and D_6 in PDMS.

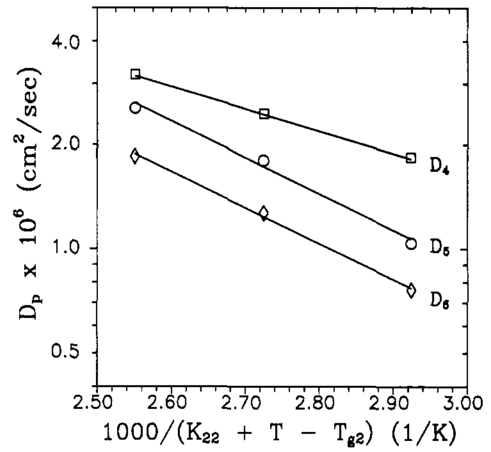

Figure 6. Temperature dependence of the solute diffusion coefficient according to the free-volume theory of Vrentas and Duda[1] (eq 27).

Table VI. Free-Volume Theory Parameters

solute	$D_0 \exp(-E^*/RT)$ (cm^2/s)	$\gamma \hat{V}_2^* \xi / K_{12} \times 10^{-3}$ (K)
D_4	1.38×10^{-4}	1.48
D_5	1.23×10^{-3}	2.41
D_6	8.33×10^{-4}	2.39

C_2^g:

$$\frac{\gamma \hat{V}_2^*}{K_{12}} = 2.303 C_1^g C_2^g \qquad (28)$$

$$K_{22} = C_2^g \qquad (29)$$

where $C_1^g = 6.1$ and $C_2^g = 69$ K for PDMS.[13] For temperatures close to T_{g2}, the energy term, $\exp(-E^*/RT)$, can be absorbed in the preexponential constant, D_0. The glass transition temperature for PDMS is 150 K.[13] Although the temperature of the diffusion measurements is significantly above T_{g2}, the range of temperatures is fairly narrow. Therefore, it is reasonable to combine the preexponential and energy terms into one factor. A semilog plot of D_p versus $1/(K_{22} + T - T_{g2})$ is presented in Figure 6. Values for $D_0 \exp(-E^*/RT)$ and $\gamma \hat{V}_2^* \xi / K_{12}$ were determined for each solute using linear regression and are listed in Table VI.

The parameter $\gamma \hat{V}_2^* \xi / K_{12}$ is related to the size of the diffusing solute. According to the free-volume theory of Vrentas and Duda,[2] a plot of $\gamma \hat{V}_2^* \xi / K_{12}$ versus the molar volume at 0 K should yield a straight line through the origin. Haward has proposed a number of expressions that can be used to estimate liquid specific volume or density at 0 K.[18] The most convenient expression to use

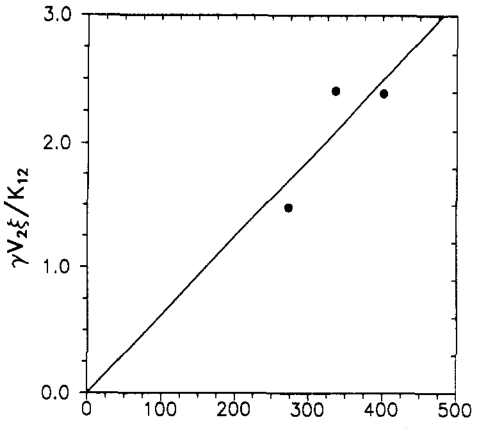

Figure 7. Free-volume parameter $\gamma \hat{V}_2^* \xi / K_{12}$ as a function of solute molar volume. Values for $\gamma \hat{V}_2^* \xi / K_{12}$ were obtained from the slope of each line in Figure 6.

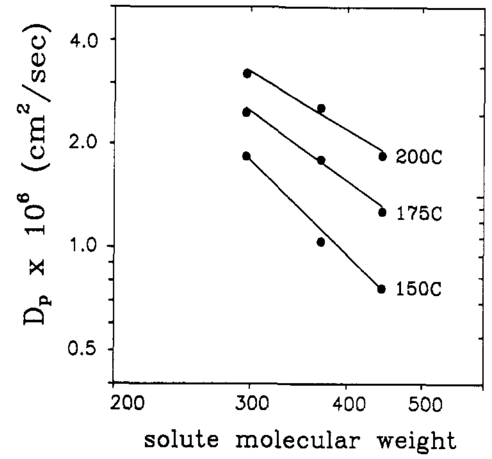

Figure 8. Diffusion coefficient as a function of solute molecular weight (eq 31). Parameters for the best fit line at each temperature are listed in Table IV.

for the solvents studied here is

$$v_{1,0}^* = 0.709 v_b \qquad (30)$$

where $v_{1,0}^*$ is the specific volume at 0 K and v_b is the specific volume at the normal boiling point. Equation 17 was used to determine the boiling point at atmospheric pressure for each solute, and eqs 18–20 were used to estimate v_b. The specific volume at 0 K was then estimated using eq 30, and the values for each solute are listed in Table I. The results obtained in this study are plotted in this manner in Figure 7. The limited amount of data presented makes it difficult to use the results of this study as a definitive test of this theory. However, the results presented do show reasonable agreement with the straight line expected from the free-volume theory.

The dependence of the diffusion coefficient on solute molecular weight was determined by fitting the results to an equation of the form:

$$D_p = c M_1^d \qquad (31)$$

A log–log plot of D_p versus molecular weight is shown in Figure 8. The values for c and d at each temperature are summarized in Table IV. Equation 31 is an empirical relation that can be used to estimate the diffusivity of other cyclic oligomers in poly(dimethylsiloxane).

Summary

Capillary column inverse gas chromatography has been used to determine the thermodynamic and transport

properties of cyclic oligomers in PDMS. Two different Flory–Huggins expressions were used to calculate the interaction parameter from the weight fraction activity coefficient, one in which a specific volume ratio is used in describing the combinatorial entropy and one in which a segment fraction ratio is used. The heat of mixing was calculated from the temperature dependence of the interaction parameter for each expression. Heat of mixing values determined from interaction parameters calculated using the segment fraction ratio were considerably smaller than those calculated using a ratio of specific volumes. Because these systems are expected to be quite athermal, it appears that the segment fraction approach provides a more accurate description of the solute–polymer interactions for these systems.

Diffusion coefficient values were of order 10^{-6} cm^2/s and were found to be in reasonable agreement with the free-volume theory of Vrentas and Duda.[1,2] Activation energies for diffusion were found to be 4.4 kcal/mol for D_4 and 7.1 kcal/mol for D_5 and D_6. An empirical relationship between the diffusivity and solute molecular weight was developed at each temperature.

Nomenclature

A_n	Fourier coefficient
B_n	Fourier coefficient
B_{11}	second virial coefficient for solute in the gas phase (cm^3/mol)
c	solute concentration in the gas phase (g/cm^3)
c_0	solute concentration in the injected sample (g/cm^3)
C_1^g, C_2^g	Williams–Landel–Ferry constants for the polymer
D_0	preexponential constant in the free-volume theory (eq 27)
D_p	solute diffusivity in the polymer (cm^2/s)
Δh_1^∞	solute partial molar enthalpy in the polymer at infinite dilution (kcal/mol)
h_1°	pure solute molar enthalpy (kcal/mol)
E^*	critical energy per mole needed to overcome attractive forces (eq 26)
K	solute partition coefficient between the polymer and gas phases
K_{12}, K_{22}	free-volume parameters of the polymer (eqs 27 and 28)
L	column length (cm)
M_1	solute molecular weight (g/mol)
P_1°	vapor pressure of pure solute (bar)
P_c	critical pressure (bar)
R	gas constant
R_c	column radius (cm)
s	Laplace parameter (sec^{-1})
t	time (sec)
t_{max}	time for peak to completely elute from column (sec)
T	temperature (K)
T_b	normal boiling temperature (K)
T_c	critical temperature (K)
T_{g2}	glass transition temperature of polymer (K)
T_r	reduced temperature (T/T_c)
v	gas velocity in column (cm/sec)
v_b	specific volume at the normal boiling point (cm^3/g)
v_1	solute specific volume (cm^3/g)
v_1^*	solute specific hard core volume (cm^3/g)
$v_{1,0}^*$	solute specific volume at 0 K (cm^3/g)
v_2	polymer specific volume (cm^3/g)
v_2^*	polymer specific hard core volume (cm^3/g)
V_g°	specific retention volume in column (cm^3/g)
$\hat{V}_2^*$	specific critical hole free volume of polymer required for a jump
x	number of silicon atoms in oligomer (equation 17)
Y	Laplace transform of cL/c_0v
α	dimensionless parameter defined in eq 2
α_1, α_2	thermal expansion coefficient of solute (1) and polymer (2) (cm^3/(g K))
β	dimensionless parameter defined in eq 3
γ	overlap factor for free volume
Δ_T, Δ_P	group contribution increments for critical property estimation
μ_k	kth normalized moment of the elution profile
μ_k^*	kth centralized moment of the elution profile
ξ	ratio of the critical volume of the solvent jumping unit to the critical molar volume of the jumping unit of the polymer
τ	polymer film thickness in the column (cm)
χ_{12}, χ_{12}^*	Flory–Huggins interaction parameter for solute in polymer
Ω_1^∞	weight fraction activity coefficient at infinite dilution of solute in polymer
ω_n	frequency in Fourier series expansion

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