Comparison of Static with Gas Chromatographic Interaction Parameters and Estimation of the Solubility Parameter for Poly(dimethylsiloxane)

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ABSTRACT: Activity coefficients and interaction parameters determined from vapor sorption measurements are reported for chloroform and dichloromethane at infinite dilution in poly(dimethylsiloxane) (PDMS) at 303 K. These agree, within experimental error, with values obtained previously by gas–liquid chromatography (GLC) on the same polymer sample. The method developed by DiPaola-Baranyi and Guillet to evaluate a solubility parameter for a polymer stationary phase from GLC measurements has been applied successfully to the vapor sorption results for various solutes in PDMS and a value of the PDMS solubility parameter determined.

Gas–liquid chromatography (GLC) has proved to be a useful technique for the determination of a range of thermodynamic and other properties of polymers.[1] However, agreement between solution thermodynamic data at infinite dilution determined from GLC with a polymer as the stationary phase and those based on extrapolating finite concentration measurements from traditional static methods has not been consistent.[2] In particular, there has been considerable discussion concerning the results obtained when using poly(dimethylsiloxane) (PDMS). Summers et al.[3] found good agreement between their GLC results and the vapor sorption measurements of Chahal et al.[4] But Lichtenthaler et al.[5] found notable discrepancies between their GLC results and those of Summers et al., and an interlaboratory collaboration[6] failed to resolve the differences. Yet, a more recent interlaboratory collaboration did find good agreement between sorption measurements for various hydrocarbons at 303 K and GLC determinations on the same batch of polymer.[7] The vapor sorption of dichloromethane and chloroform at 303 K is now reported in order that the infinite dilution activity coefficients and interaction parameters determined can be compared with those obtained by GLC in the previous study on the same polymer.[7]

Although the solubility parameter is of limited use in solution thermodynamics, it remains a useful concept in polymer chemistry. However, polymer solubility parameters can be difficult to estimate. Guillet and co-workers have developed a method to calculate solubility parameters from GLC measurements and consistent results have been obtained for a number of systems.[8,9] The method has been applied to the results for the PDMS–solute systems studied at 303 K by vapor sorption and the analysis is reported here.

Experimental Section

Apparatus. The absorption measurements were made with a Sartorius Model 4102 vacuum microbalance in conjunction with a Texas Instruments quartz Bourdon pressure gauge allowing monitoring of weight and pressure changes to ±0.1 mg and ±0.01 torr, respectively. The apparatus and the techniques have been described previously.[10] The temperature at which the isotherms were recorded was monitored with a mercury-in-glass thermometer that had been calibrated with a platinum resistance thermometer and was controlled at 302.99 ± 0.01 K.

Materials. The chloroform and the dichloromethane were of Aristar grade obtained from BDH Ltd. (U.K.). Prior to use, ethanol stabilizer was removed by passage of the chloromethanes down a column of basic alumina. Analysis by GLC showed the resulting purity to be >99.9%. The PDMS was from the same batch as that used previously, having a number-average molecular weight of 89 000.[7] The polymer was coated onto Celite 545 AW support, of 100–120 mesh size from Phase Separations Ltd., to give a loading of about 20 wt % of polymer using ethyl acetate, which was then removed by evaporation. The dispersal of the polymer on the solid support was carried out in the microbalance sample bucket to ensure that the weight of the PDMS was known accurately.

Table I
Absorption of Solutes by PDMS at 303 K

solute	ϕ_1	P_1/torr	ln $^v\gamma_1$
chloroform	0.00683	8.30	1.6338
	0.01647	19.59	1.6113
	0.02830	32.77	1.5842
	0.04776	52.92	1.5387
	0.06692	71.01	1.4943
	0.09166	92.38	1.4413
	0.12032	113.74	1.3758
	0.14471	129.77	1.3221
dichloromethane	0.00786	26.23	1.8709
	0.01547	50.47	1.8471
	0.02354	75.15	1.8242
	0.03202	99.56	1.7969
	0.04116	124.69	1.7696
	0.05145	151.10	1.7375
	0.06139	175.43	1.7090
	0.07312	202.06	1.6743

Results and Discussion

The absorption measurements are shown in Table I as the volume fraction of solute absorbed ϕ_1 at a solute vapor pressure P_1. Activity coefficients $^v\gamma_1$ were calculated on the basis of volume fraction as before[7] using the equation

$$\ln {}^v\gamma_1 = \ln [P_1/(P_1^\circ\phi_1)] + [(V_1^\circ - B_{11}) \times (P_1^\circ - P_1)/RT] + [(B_{11}/RT)^2(P_1^{\circ 2} - P_1^2)/2] \quad (1)$$

A saturated vapor pressure P_1° of 240.80 torr,[11] a second virial coefficient B_{11} of −1.16 dm^3 mol^{-1},[12] and a molar volume V_1° of 81.18 cm^3 mol^{-1} [13] were used for chloroform. The corresponding values for dichloromethane were 525.88 torr,[11] −0.81 dm^3 mol^{-1},[12] and 64.98 cm^3 mol^{-1},[13] respectively.

Comparison of Vapor Sorption and GLC Results. Interaction parameters χ were calculated as before[14] from the following form of the Flory–Huggins expression

$$\ln {}^v\gamma_1 = (1 - V_1^\circ/V_2^\circ)(1 - \phi_1) + (1 - \phi_1)^2\chi \quad (2)$$

using a value of 92.18 dm^3 mol^{-1} for the molar volume V_2° of the PDMS.[7] The interaction parameters were extrapolated to infinite dilution (i.e., $\phi_2 = 1$) by linear regression to determine the volume fraction activity coefficients at infinite dilution, $^v\gamma_1^\infty$. The corresponding activity coefficients based on weight fraction $^w\gamma_1^\infty$ were calculated by

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Table II
Infinite Dilution Activity Coefficients and Interaction Parameters for PDMS at 303 K

	vapor sorption			GLC[a]	
	${}^{v}\gamma_1^{\infty}$	${}^{w}\gamma_1^{\infty}$	χ^{∞}	${}^{w}\gamma_1^{\infty}$	χ^{∞}
chloroform	5.210	3.421	0.652	3.366	0.640
dichloromethane	6.660	4.919	0.897	4.937	0.901

[a] As reported in ref 7.

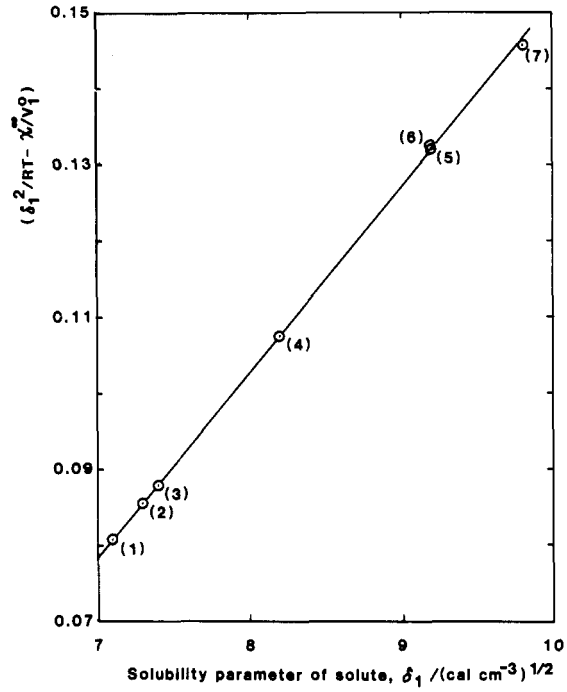

Figure 1. Determination of poly(dimethylsiloxane) solubility parameter δ_2 at infinite dilution. Slope = $2\delta_2/RT$. Solutes: (1) *n*-pentane, (2) *n*-hexane, (3) *n*-heptane, (4) cyclohexane, (5) benzene, (6) chloroform, and (7) dichloromethane.

using the ratio of the component densities (ρ_2/ρ_1) according to

$${}^{w}\gamma_1^{\infty} = {}^{v}\gamma_1^{\infty}(\rho_2/\rho_1) \quad (3)$$

The resulting values at infinite dilution of the interaction parameters and activity coefficients are compared in Table II with the GLC results determined previously for these systems.[7] The differences in χ^{∞} amount to 1.8% for chloroform and 0.5% for dichloromethane. While the difference found with chloroform is greater than the differences found with the alkane solutes studied before, it is well within the combined experimental error of the two methods and so supports the previous conclusion that when used under proper circumstances, GLC with polymer stationary phases can give results agreeing with those from static methods.

Determination of the PDMS Solubility Parameter. Combination of the regular solution and Flory–Huggins theories leads to the following expression for χ^{∞}:

$$\chi^{\infty} = [(\delta_1 - \delta_2)^2 V_1^{\circ}/RT] + \chi_S^{\infty} \quad (4)$$

The interaction parameter is regarded as having an enthalpic part χ_H and an entropic part χ_S. The enthalpic part is accounted for in terms of the solubility parameters for the two components δ_1 and δ_2. DiPaola-Baranyi and Guillet showed that the equation may be arranged to give

$$(\delta_1^2/RT - \chi^{\infty}/V_1^{\circ}) = (2\delta_2/RT)\delta_1 - (\delta_2^2/RT + \chi_S^{\infty}/V_1^{\circ}) \quad (5)$$

A plot of the function on the left side of the equation vs. the solute solubility parameter δ_1 should be linear, enabling δ_2 to be calculated from the gradient. The results for the chloroalkanes reported here with those for the alkanes reported previously are plotted in Figure 1 and show the predicted linear relationship. Solubility parameters for the various solutes were taken from ref 15 and refer to a temperature of 25 °C. However, they are not very dependent on temperature and have been used with the χ^{∞} and V_1° values at 303 K without correction for the temperature difference. A value of 7.33 (cal cm^{-3})$^{1/2}$ was calculated for the PDMS solubility parameter, δ_2, which may be compared with estimates by other methods of 7.3–7.6 (cal cm^{-3})$^{1/2}$.[16]

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Registry No. chloroform, 67-66-3; dichloromethane, 75-09-2.

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