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## MEASUREMENT OF SOLUBILITY PARAMETERS BY GAS-LIQUID CHROMATOGRAPHY

G. J. PRICE and J. E. GUILLET\*

*Department of Chemistry, University of Toronto, Toronto M5S 1A1 (Canada)*

and

J. H. PURNELL

*Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP(U.K.)*

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### SUMMARY

Gas-liquid chromatography has been used to calculate thermodynamic data for a variety of probe molecules in three polymers at 25°C. The method of Guillet and co-workers has been applied to calculate solubility parameters,  $\delta$ , and good agreement was found with literature values. The results avoid extrapolation from higher temperatures and add further validity to the method. Discussion of the role of  $\delta$  in polymer solution thermodynamics is also given.

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### INTRODUCTION

Although of limited theoretical significance in solution thermodynamics, the concept of a solubility parameter,  $\delta$ , or a cohesive energy density (c.e.d.),  $\delta^2$ , as a measure of intermolecular forces remains useful for many practical applications<sup>1</sup>. The definition of  $\delta^2$  as an internal energy of vapourization per unit volume allows straightforward measurement of  $\delta$  for small molecule liquids but for polymers, this definition is of little or no use so that the physical meaning of the polymer solubility parameter,  $\delta_2$ , is doubtful.

Guillet and co-workers<sup>2-4</sup> have developed a technique for the estimation of  $\delta_2$  at infinite dilution from thermodynamic measurements made using gas-liquid chromatography (GLC) and have obtained consistent results for a number of polymers. However, GLC measurements have to be made well above the glass transition temperature,  $T_g$ , of the polymer<sup>5</sup> so that data have to be extrapolated to near ambient temperature for comparison with  $\delta_2$  values from classical techniques such as swelling equilibrium.

This paper presents results on polymers with low  $T_g$  values, polydimethylsiloxane (PDMS), polyisobutylene (PIB) and ethylene-propylene rubber (EPR), so that measurements could be made at room temperature allowing a direct comparison with literature values of  $\delta_2$ . The thermodynamic significance of the polymer solubility parameter is also examined further.

## EXPERIMENTAL

*Materials*

The probes used were obtained from a number of commercial sources and were of reagent grade or better.

The PDMS was an OV-101 stationary phase from Chromatographic Specialites, the EPR was a low-molecular-weight polymer from Aldrich and the PIB was a Kalene 800 sample of butyl rubber from Hardman (Toronto, Canada). The molecular weights and other physical properties are shown in Table I. The column packings were prepared in the usual way by coating Chromosorb G (80–100 mesh) from a suitable solvent. Column loadings in the region of 10% were used and were calculated by calcination for EPR and PIB, and by exhaustive solvent extraction to constant weight for PDMS.

*Apparatus*

The chromatograph used was designed for the application of finite concentration GLC techniques and has been described in detail previously<sup>6</sup>. For the present work, a carrier gas flow of pure helium was used for performing the usual infinite dilution measurements.

The column temperature was controlled and measured to  $\pm 0.01^\circ\text{C}$  using a water bath and high-precision thermometers. Probe samples in the region of 0.005–0.02  $\mu\text{l}$  or 5  $\mu\text{l}$  of air as a non-absorbing marker were injected using Hamilton syringes and the results reported here are the average of at least three values within experimental error. The necessary conditions for obtaining thermodynamic data by GLC, peak symmetry and absence of flow-rate and sample size effects, were satisfied directly with PDMS and EPR. This was as expected since the measurements were made well above  $T_g$  ( $T_g = 150\text{ K}$  for PDMS and 150–180 K for EPR)<sup>7</sup>. However, as noted by several workers<sup>5,8</sup> some non-equilibrium effects were noticed with PIB ( $T_g = 200\text{--}210\text{ K}$ )<sup>7</sup>. In this case a range of sample sizes and flow-rates was used and the values extrapolated to zero in each case.

## RESULTS AND DISCUSSION

The primary GLC datum, the specific retention volume,  $V_g^0$ , was calculated from the usual expression<sup>9</sup>

TABLE I  
PHYSICAL PROPERTIES OF THE POLYMERS AT 25°C

<i>Polymer</i>	<i>Molecular weight</i>	<i>Density (g cm<sup>-3</sup>)</i>	<i>Column load (wt. %)</i>
PDMS	30 000	0.965	10.2
PIB	40 000	0.917	8.9
EPR	24 500	0.910	9.8

TABLE II  
PHYSICAL PROPERTIES OF THE PROBES AT 25°C

	Vapour pressure (Torr)	Density (g cm <sup>-3</sup> )	2nd Virial coefficient (cm <sup>3</sup> mol <sup>-1</sup> )	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )
Pentane	512.48	0.6214	1260	116.10
Hexane	150.42	0.6549	1935	131.59
Heptane	45.72	0.6795	2861	147.46
Octane	13.98	0.6985	4188	179.91
Cyclohexane	97.29	0.7738	1717	108.76
Benzene	94.90	0.8738	1478	89.40
Toluene	28.44	0.8623	2375	106.85
Carbon tetrachloride	115.25	1.5843	1520	97.10
Chloroform	194.18	1.4799	1207	80.67
Methylene chloride	435.86	1.3163	857	64.53

$$V_g^0 = [F(t_R - t_M)]/w \quad (1)$$

where  $w$  is the weight of polymer used,  $t_R$  and  $t_M$  are the retention times of the probe and marker, respectively, and  $F$  is the flow-rate of carrier gas, fully corrected to standard temperature and pressure in the usual manner<sup>9</sup>.

Infinite dilution activity coefficients rationalized on a weight fraction basis,  $\Omega_1^\infty$ , and Flory-Huggins interaction parameters,  $\chi^\infty$ , were calculated using<sup>10</sup>

$$\ln \Omega_1^\infty = \ln \left( \frac{273.15 R}{P_1^0 M_1 V_g^0} \right) - \frac{P_1^0}{RT} (B_{11} - V_1^0) \quad (2)$$

$$\chi^\infty = \ln \Omega_1^\infty - \ln (\rho_1/\rho_2) - [1 - (V_1^0/V_2^0)] \quad (3)$$

In eqns. 2 and 3  $P_1^0$ ,  $B_{11}$  and  $M_1$  are the saturated vapour pressure, second virial coefficient and molecular weight of the probe at column temperature,  $T$ , respectively, while  $\rho$  and  $V^0$  represent the density and molar volume. In calculating the results, values for these physical properties were taken from a number of sources<sup>11-15</sup> and are shown in Tables I and II. The results calculated from eqns. 1-3 are given in Table III.

Bearing in mind the small temperature difference, the results for EPR are in good agreement with those of Ito and Guillet<sup>3</sup> measured at 30°C. Reasonable agreement is also seen for the PIB results compared to literature values<sup>16-18</sup>. The small divergence may be explained by the non-equilibrium effects noted above. Several workers have measured thermodynamic data for PDMS by GLC and obtained conflicting results although a more recent comparison of GLC values with those extrapolated from static equilibrium measurements showed good agreement<sup>19</sup>. The results from this study agree well with those of the latter work.

Although the interaction parameter was originally introduced to account for enthalpic mixing effects, later work recast it as a free energy parameter allowing

TABLE III  
 SPECIFIC RETENTION VOLUMES,  $V_g^0$  ( $\text{cm}^3 \text{g}^{-1}$ ), INFINITE DILUTION ACTIVITY COEFFICIENTS,  $\Omega_1^\infty$ , AND INTERACTION PARAMETERS,  $\chi^\infty$ , FOR PROBES AT 25°C

	PDMS			PIB			EPR		
	$V_g^0$	$\ln \Omega_1^\infty$	$\chi^\infty$	$V_g^0$	$\ln \Omega_1^\infty$	$\chi^\infty$	$V_g^0$	$\ln \Omega_1^\infty$	$\chi^\infty$
Pentane	77.4	1.822	0.382	54.8	2.091	0.702	72.5	1.887	0.505
Hexane	219.5	1.803	0.415	184.0	1.983	0.646	217.4	1.816	0.487
Heptane	604.7	1.824	0.473	575.3	1.873	0.573	632.2	1.779	0.468
Octane	1633.5	1.833	0.511	1781.1	1.793	0.521	1973.7	1.691	0.426
Cyclohexane	390.4	1.683	0.461	338.8	1.922	0.476	473.8	1.489	0.327
Benzene	359.1	1.864	0.764	405.1	1.646	0.874	452.7	1.633	0.592
Toluene	1053.4	1.824	0.710	1062.1	1.816	0.754	1364.7	1.565	0.511
Carbon tetrachloride	371.5	0.960	0.455	387.4	0.918	0.465	450.4	0.768	0.322
Chloroform	226.6	1.190	0.616	262.9	1.041	0.520	289.8	0.944	0.430
Methylene chloride	95.0	1.599	0.907	137.2	1.232	0.593	145.9	1.170	0.539

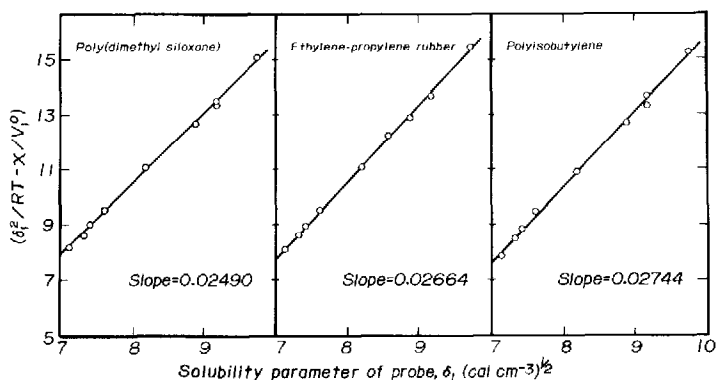


Fig. 1. Calculation of polymer solubility parameters at 25°C: (a) poly(dimethyl siloxane), (b) ethylene-propylene rubber, (c) polyisobutylene.

separation into an entropic contribution  $\chi_S^\infty$  in addition to the enthalpy contribution,  $\chi_H^\infty$ .

$$\chi^\infty = \chi_H^\infty + \chi_S^\infty \quad (4)$$

Combining regular solution theory<sup>20</sup>, which uses the solubility parameter to estimate enthalpy effects, with eqn. 4 leads to

$$\chi^\infty = \frac{V_1^0 (\delta_1 - \delta_2)^2}{RT} + \chi_S^\infty \quad (5)$$

where  $\delta_1$  and  $\delta_2$  are the solubility parameters of the probe and polymer, respectively. Expanding the term in parentheses and rearranging yields<sup>2</sup>,

$$\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1^0} = \left(\frac{2\delta_2}{RT}\right) \delta_1 - \left(\frac{\delta_2^2}{RT} - \frac{\chi_S^\infty}{V_1^0}\right) \quad (6)$$

Hence, a plot of the term on the left hand side of eqn. 6 versus  $\delta_1$  should yield a linear relationship with slope  $(2\delta_2/RT)$ .

Fig. 1 shows the results for the three polymers plotted in the form suggested by eqn. 6. As predicted the plots show excellent linear correlation (regression coefficients  $> 0.99$ ) in each case. The values of the derived polymer solubility parameters are given in Table IV along with literature data for comparison<sup>7</sup>. The PDMS result

TABLE IV  
SOLUBILITY PARAMETERS ( $\text{cal cm}^{-3}$ )<sup>1/2</sup> AT 25°C

	Current work	Literature <sup>7</sup>
PDMS	7.38	7.3–7.6
PIB	7.90	7.7–8.1
EPR	8.13	7.9–8.4

agrees very well with the value of  $7.33 \text{ (cal cm}^{-3}\text{)}^{\frac{1}{2}}$  measured by the same method as used here with static equilibrium data<sup>21</sup>. Table IV shows that, as has been found previously, results obtained by GLC and by more classical methods are in excellent agreement. However, in this work, GLC measurements were made in the temperature range where the classical methods are useful rather than being extrapolated from, in some cases, considerably higher temperatures. Thus the method used here is again shown to give useful results for  $\delta$  and gives further credence to results obtained previously. However, it should be noted that the solubility parameter measured here is at infinite dilution of solvent (probe) whereas conventional techniques are usually useful for dilute polymer solutions. Since Regular Solution and basic Flory-Huggins theories do not allow for concentration dependent interaction parameters although there is ample experimental evidence that  $\chi$  does vary with concentration, the relationship, if any, between  $\delta_2$  in the different regions of concentration is unclear.

The data analysis used in this work has yielded consistent results for a large range of probes and a number of polymers, a correlation which is worthy of further comment and speculation.

The Flory-Huggins relation for the thermodynamic activity of a solvent in a solution,  $a_1$  (*i.e.*, the ratio of the solution fugacity to that of a standard state, usually taken as pure solvent), is

$$\ln a_1 = \ln \phi_1 + [1 - (1/r)]\phi_2 + \chi\phi_2^2 \quad (7)$$

where  $r$  is the ratio of the molar volumes of polymer and solvent. Useful activity coefficients for polymer solutions may be defined in terms of volume fraction,  $\phi$ , or of weight fraction,  $w$ , as earlier in the text.

$$a_1 = \phi_1^v \gamma_1 = w_1 \Omega_1 \quad (8)$$

where  ${}^v\gamma_1$  is the activity coefficient on a volume fraction basis. Mole fraction based activity coefficients are of little use for polymer solutions since they require precise knowledge of molecular weights<sup>10</sup>. It is readily shown that, at infinite dilution,

$$\Omega_1^\infty = {}^v\gamma_1^\infty (\rho_2/\rho_1) \quad (9)$$

Hence, from eqn. 3 with the assumption that  $r \gg 1$  as is the case for most polymers.

$$\begin{aligned} \chi^\infty &= \ln \Omega_1^\infty + \ln (\rho_2/\rho_1) - 1 \\ &= \ln {}^v\gamma_1^\infty - 1 \end{aligned} \quad (10)$$

By analogy with an excess free energy in small molecule solutions, which accounts for all mixing interactions other than the ideal entropy, and following Flory's definition<sup>22</sup>, a residual partial molar free energy of mixing,  ${}^\phi\Delta G_1^{R,\infty}$ , can be used to account for all interactions not included in the combinatorial entropy of mixing given by the Flory-Huggins expression.

$$\begin{aligned} {}^\phi\Delta G_1^{R,\infty} &= RT \ln {}^v\gamma_1^\infty \\ &= RT (\chi^\infty + 1) \end{aligned} \quad (11)$$

Hence

$$\chi^\infty = \frac{\phi \Delta G_1^{R,\infty} - RT}{RT} \quad (12)$$

$$\approx \frac{\phi \Delta G_1^{R,\infty} - PV}{RT} \quad (13)$$

$$\approx \frac{\phi \Delta A_1^{R,\infty}}{RT} \quad (14)$$

assuming ideal behaviour of the probe vapour where  $A$  represents a Helmholtz free energy. It should be noted that eqns. 11–14 will be valid only for polymer solutions.

Thus, the infinite dilution interaction parameter as defined here has the form of a Helmholtz free energy or work function corresponding to the work required to remove a probe molecule from infinite dilution in the polymer compared to its removal from the pure liquid.

Since

$$\Delta A = \Delta U - T\Delta S \equiv RT \chi^\infty \quad (15)$$

then a more appropriate way of splitting  $\chi^\infty$  may be into an entropic contribution and one due to internal energy rather than enthalpy.

$$\chi^\infty = \chi_{\bar{v}}^\infty + \chi_{S'}^\infty \quad (16)$$

where the prime on  $\chi_{S'}^\infty$  differentiates it from the same quantity in eqn. 4.

Since the probe solubility parameter  $\delta$  may be found from

$$\delta^2 = \Delta U^{\text{vap}}/V_1^0 \quad (17)$$

it is also an internal energy parameter. Thus, inspection of eqn. 6 shows that  $\delta_2^\infty$  is calculated from a combination of parameters representing changes in internal energies. This may provide at least a partial explanation of the consistency of results calculated according to eqn. 6 since  $\delta_2^\infty$  is obtained from the slope while  $\chi_{S'}^\infty$  (or  $\chi_{\bar{v}}^\infty$ ) appears only in the intercept.

Lipson and Guillet<sup>4</sup> have commented on the physical significance of  $\chi_S$  values which were calculated from the intercepts of eqn. 6 but no general agreement of results has been found. It is possible that eqn. 5 needs to be recast in the form

$$\chi^\infty = \frac{V_1^0 (\delta_1 - \delta_2)^2}{RT} + \chi_{S'}^\infty + \chi_{PV}^\infty$$

where  $\chi_{PV}$  accounts for pressure–volume effects. These effects would be included in the  $\chi_S$  calculated as above and so may go some way toward explaining some inconsistencies found in previous discussions. It is also pertinent to note that more recent rigorous theories of the thermodynamics of polymer solutions<sup>22–24</sup> treat  $\chi$  as a residual chemical potential with pressure–volume effects included by considering equation of state effects.

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