

# Correlation of Solubility in Polydimethylsiloxane and Polyisobutylene Systems

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## Synopsis

Solubility data of organic probes in polydimethylsiloxane (PDMS) and polyisobutylene (PIB) obtained by inverse gas chromatography (IGC) were collected from the literature and analyzed. Applying the principle of corresponding states, empirical correlations were derived and presented for the estimation of solubilities of nonpolar and slightly polar probe molecules in these polymers. Estimation of other thermodynamic properties, such as activity coefficient of the solute, Henry's law constant, Flory-Huggins interaction parameter, and heat of solution through the use of these correlation equations, was demonstrated.

## INTRODUCTION

In polymer processing, the removal of volatile low molecular weight compounds from bulk polymers is often required. In the paint and coating industries, it is often necessary to know the vapor pressure (volatility) of the solvent over the film at high polymer concentrations during drying. The proper design of equipment and the selection of proper operating conditions to achieve these separations relies on an understanding of the solubility of low molecular weight compounds in polymers and the devolatilization process. While a thorough understanding of these phenomena is not yet available, attempts have been made to develop correlations for the prediction or estimation of the phase equilibria in various polymer/solvent systems.<sup>1-7</sup> In particular, correlations for predicting the solubility of various organics in low-density polyethylene,<sup>1-5</sup> polyvinyl acetate,<sup>6</sup> and polystyrene<sup>7</sup> have been presented. In this paper, solubility data reported in the literature for PDMS and PIB systems are analyzed, and correlations are developed to estimate the solubility of organic compounds in these polymers.

All of the data collected and analyzed in the present study were obtained via inverse gas chromatography (IGC) at infinite probe dilution and approximately 1 atm pressure. The available solubility data for PDMS/probe systems are those of Summers et al.<sup>8</sup> (13 probes at 25°C, 40°C, 55°C, and 70°C), Deshpande et al.<sup>9</sup> (12 probes at 60°C), Lichtenthaler et al.<sup>10,11</sup> (12 probes at 25°C, 40°C, 55°C, and 70°C), Hammers et al.<sup>12</sup> (10 probes at 20–160°C), Galin<sup>13</sup> (six probes at 40–180°C), and Ward et al.<sup>14</sup> (four probes at 160°C, 180°C, and 195°C). The available solubility data for PIB/probe systems include those of Hammers and Deligny<sup>15</sup> (12 probes at 40–140°C), Newman and Prausnitz<sup>16</sup> (four probes at 50°C, 75°C, 100°C, 125°C, and 150°C). Leung

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and Eichinger<sup>17</sup> (six probes at 25°C, 45°C, and 65°C), Lichtenthaler et al.<sup>11</sup> (three probes at 75, 100, and 125°C), and Leung and Eichinger<sup>18</sup> (seven probes at 25°C).

Solubility data may be presented in a variety of forms such as activity coefficient, Henry's law constant of the probe molecule, and Flory-Huggins interaction parameter. However, for IGC the experimentally observed specific retention volume  $V_g$  is a more direct and readily accessible measure of solubility. The specific retention volume can be related to the activity coefficient<sup>19</sup>  $\gamma_1^r$  and to the Flory-Huggins interaction parameter<sup>19</sup>  $\chi$ , through eqs. (1) and (2):

$$\ln \gamma_1^r = \ln \frac{22,414}{P_1^0 V_g M_1} - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (1)$$

where  $P_1^0$ ,  $B_{11}$ ,  $V_1$ , and  $M_1$  are the saturated vapor pressure, the second virial coefficient, the molar volume, and the molecular weight of the probe at the system temperature  $T$ ,

$$\chi = \ln \gamma_1^r - 1 - \ln \frac{v_1}{v_2} \quad (2)$$

where  $v_1$  and  $v_2$  are the specific volume of probe and stationary phase, respectively.

With the Henry's law constant<sup>16</sup>  $H_1^\infty$  and the heat of solution<sup>20</sup>  $\Delta H_s^\infty$ , the probe at infinite dilution in the polymer can be evaluated by eqs. (3) and (4):

$$H_1^\infty = \frac{22,414}{V_g M_1} \quad (3)$$

$$\Delta H_s^\infty = -R \left( \frac{\ln V_g}{1/T} \right) \quad (4)$$

Other thermodynamic properties such as partial molar heat of mixing, solubility parameter of polymer, and excess free energy of mixing can also be estimated.<sup>20</sup> Therefore, having a good estimate of  $V_g$  can lead to valuable thermodynamic information.

Stern et al.<sup>3</sup> utilized the principle of corresponding states and proposed a correlation between logarithmic solubility (expressed as mol sorbed/g amorphous polymer · atm) and  $(T_c/T)^2$  for low-density polyethylene. Stiel and Harnish<sup>7</sup> reported a relationship between  $V_g$  and  $(T_c/T)^2$  for molten polystyrene. Tseng et al.<sup>6</sup> found that the approach of Stiel and Harnish<sup>7</sup> held for correlating the solubility of a variety of organics in polyvinyl acetate. On the other hand, in order to relate  $V_g$  to  $(T_c/T)^2$  for molten and rubbery low-density polyethylene, it was necessary to multiply  $V_g$  by the critical pressure of the probe.<sup>5</sup> In light of these results, a similar study was carried out in the present work.

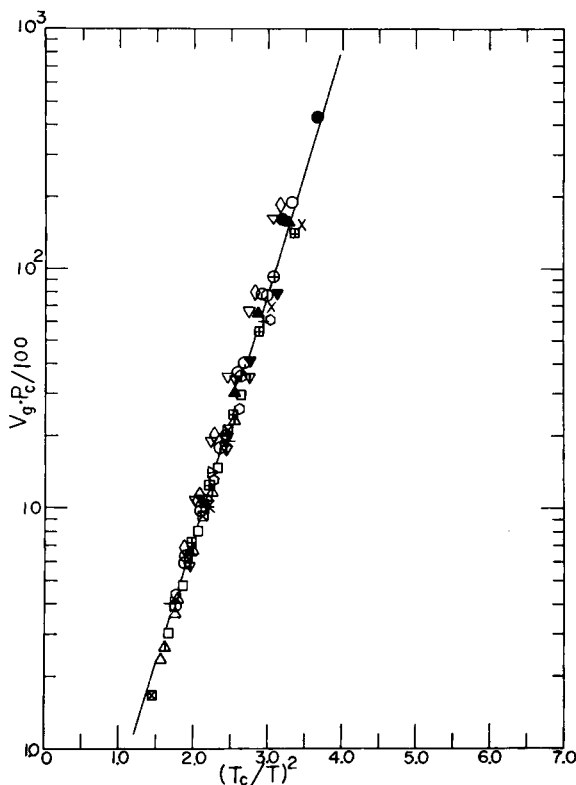


Fig. 1. Relationship between  $\ln(V_g \cdot P_c/100)$  and  $(T_c/T)^2$  for polyisobutylene/probe systems. Data taken from Ref. 15; ( $\Delta$ ) pentane; ( $\square$ ) hexane; ( $\odot$ ) heptane; ( $\circ$ ) octane; ( $\diamond$ ) nonane; ( $\nabla$ ) decane; ( $\triangle$ ) 2,3-dimethylbutane; ( $\nabla$ ) 2,2-dimethylpentane; ( $\oplus$ ) 2,5-dimethylhexane. Data taken from Ref. 16: ( $\circ$ ) benzene; ( $\boxplus$ ) toluene; ( $\boxtimes$ ) hexane; (+) cyclohexane. Data taken from Ref. 17: ( $*$ ) pentane; ( $\triangleright$ ) hexane; ( $\blacktriangle$ ) heptane; ( $\bullet$ ) octane; ( $\blacktriangledown$ ) benzene; ( $\times$ ) cyclohexane.

## RESULTS AND DISCUSSION

The solubility data, which was originally expressed as activity coefficient, Henry's law constant, or Flory-Huggins interaction parameter, were converted to specific retention volume  $V_g$  at standard state for the purpose of correlation. The required information for the conversion data (that is, density of probe and polymer, vapor pressure, and second virial coefficient) was obtained or computed from standard sources.<sup>21-26</sup>

In this study, the correlation parameters suggested by either Stern et al.<sup>3</sup> or Stiel and Harnish<sup>7</sup> could not adequately correlate the solubility of probes in PDMS and PIB systems. Regression analysis again<sup>5</sup> indicated the need to include the critical pressure of the probe,  $P_c$ , in the correlation model. The general correlation model applicable to PIB and PDMS systems is

$$\ln \left( \frac{V_g P_c}{100} \right) = a + b \left( \frac{T_c}{T} \right)^2 \quad (5)$$

TABLE I  
 Statistical Information for the Correlation Equations

System	Intercept $a$	Slope $b$	Correlation coefficient $R^2$
PIB/probe	$-2.754 \pm .175^a$	$2.372 \pm .069^a$	0.9750
PDMS/linear and branched aliphatic probes	$-2.50 \pm .166^a$	$2.323 \pm .044^a$	0.9826
PDMS/aromatic probe	$-2.284 \pm .099^a$	$2.143 \pm .031^a$	0.9964

<sup>a</sup> Within 95% confidence interval.

The coefficients  $a$  and  $b$  can be obtained from the intercept and slope by plotting  $\ln(V_g \cdot P_c/100)$  vs.  $(T_c/T)^2$ . Utilizing 118 data points for 13 probes in PIB,<sup>11,15-18</sup> a plot of  $\ln(V_g \cdot P_c/100)$  vs.  $(T_c/T)^2$  was constructed as shown in Figure 1. A single line through all of the data points produces the values  $a = -2.754 \pm 0.175$  and  $b = 2.372 \pm 0.069$ . The calculated correlation coefficient of 0.9750 indicates that the single straight line is reasonable (see Table I). A similar analysis of the available data<sup>8-14</sup> for PDMS/probe systems indicated the necessity of proposing two correlations based on the chemical nature of the organic probe. Plots utilizing 195 data points for 22 linear and branched aliphatic probes and 78 data points for nine aromatic probes in PDMS are shown in Figures 2 and 3, respectively. In general (with few exceptions) the data in all three figures can be well represented by the correlation given in eq. (5) as indicated by the statistical information given in Table I. By breaking the probe molecules into two classifications (that is, aliphatic and aromatic), the correlations for the PDMS-probe systems are improved (correlation coefficients of 0.9826 and 0.9964, respectively, compared to 0.970 when all data are considered together).

Statistical deviations from the correlation can be attributed to (i) effect of carrier gas flow rate, (ii) effect of polymer coating thickness, (iii) effect of sample injection size, (iv) effect of molecular weight and molecular weight distribution of the polymer, (v) method of data reduction, (vi) correction for finite carrier gas solubility in the polymer when the probe molecule has a small polymer solubility, and (vii) peak broadening due to the long equilibrium time required at low temperatures. All of these factors have been discussed in great detail in the literature.<sup>4,7,11,13,27-32</sup>

The effect of temperature on the solubility is clearly indicated in all of the figures; that is, solubility decreases as temperature increases. The effect of chemical nature of probes on the solubility is also readily observable. For nonpolar and slight polar probes interacting with these relatively nonpolar polymers, these correlations work well. The exceptional cases are those probes which possess either a strong dipole or a large molecular diameter. For a polar probe such as *o*-dichlorobenzene ( $\blacktriangle$ ) in PDMS as shown in Figure 3, specific dipole interactions likely are responsible for the relatively low solubility. This is expected and supported by the general rule of thumb, likes dissolve likes. It is known that the diffusion coefficient

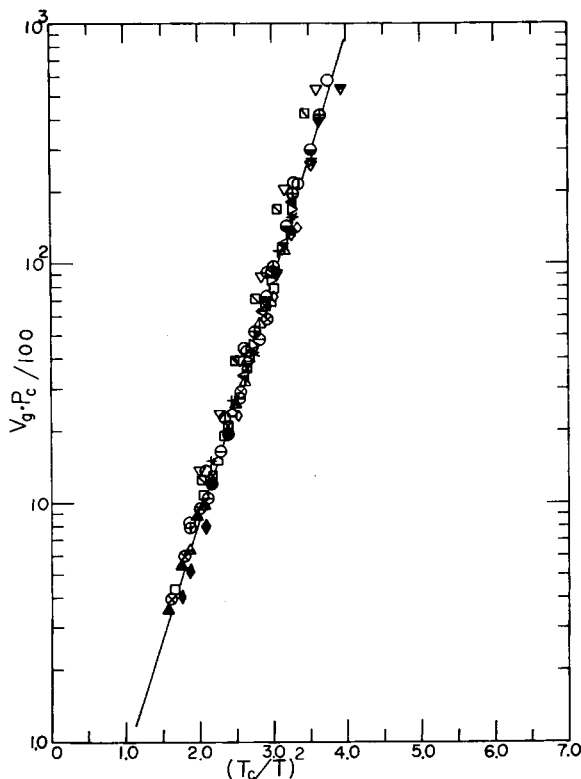


Fig. 2. Relationship between  $\ln(V_g \cdot P_c/100)$  and  $(T_c/T)^2$  for PDMS/aliphatic and branched probe systems. Data taken from Ref. 8: (●) hexane; (\*) heptane; (▼) octane; (▲) 2-methylhexane. Data taken from Ref. 10: (▲) pentane; (⊞) hexane; (△) heptane; (⊕) octane; (□) cyclopentane; (⊖) 2-methylpentane; (◄) 2-methylhexane; (⊖) 2-methylheptane; (►) 3-methylhexane; (◇) 2,2,4-trimethylpentane. Data taken from Ref. 12: (▲) pentane; (□) hexane; (⊖) heptane; (○) octane; (▽) nonane; (⊞) decane; (○) 2,3-dimethylbutane; (+) 2,5-dimethylhexane. Data taken from Ref. 14: (◆) decane.

decreases as the temperature decreases and the size of penetrant increases. Consequently, for large probes such as octane, nonane, and decane, especially in the low temperature range, slow diffusion may result in thermodynamic nonequilibrium and give rise to the relatively large deviation for these molecules in Figure 2. It should be noted that for PDMS/probe systems the data reported by Hammers et al.<sup>12</sup> were higher than others and the variance ranged from 7% to 15% as indicated in Table II. Further examination of the data presented by Hammers et al.<sup>12</sup> showed deviations from a linear relationship between  $\ln V_g$  and  $1/T$  at low temperatures. This result gives a good indication that thermodynamic equilibrium was not achieved. Comparison between literature data and values computed by the correlation equations is given in Table II.

The usefulness of these correlation equations to evaluate thermodynamic properties is illustrated by using PIB system as an example. By using eq. (5) and data listed in Table I, one can obtain an expression for specific retention volume as

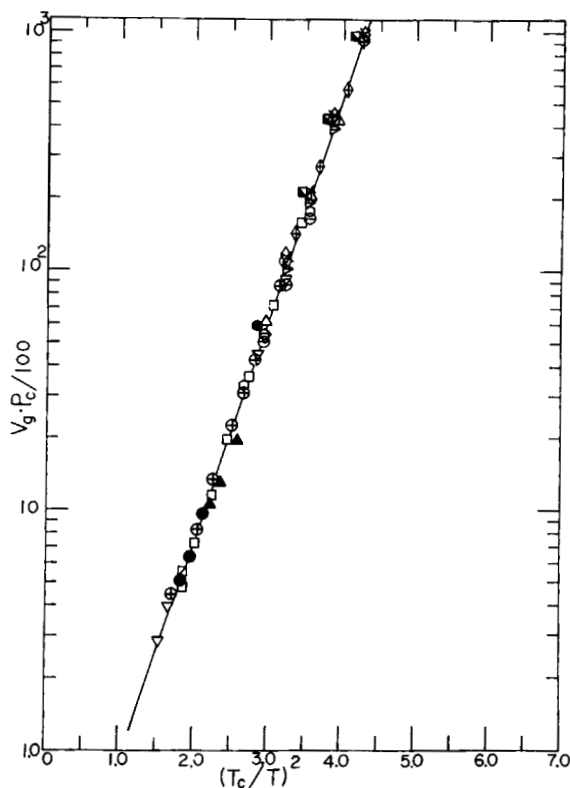


Fig. 3. Relationship between  $\ln(V_g \cdot P_c/100)$  and  $(T_c/T)^2$  for PDMS/aromatic probe systems. Data taken from Ref. 8: ( $\ominus$ ) benzene; (+) *p*-xylene; ( $\oplus$ ) ethylbenzene. Data taken from Ref. 9: ( $\bullet$ ) benzene. Data taken from Ref. 10: ( $\circ$ ) benzene; ( $\triangle$ ) toluene; ( $\blacklozenge$ ) *o*-xylene; ( $\diamond$ ) *m*-xylene; ( $\times$ ) *p*-xylene; ( $\circ$ ) ethylbenzene; ( $\blacksquare$ ) mesitylene. Data taken from Ref. 13: ( $\nabla$ ) benzene; ( $\oplus$ ) toluene; ( $\square$ ) ethylbenzene. Data taken from Ref. 14: ( $\boxplus$ ) toluene; ( $\blacktriangle$ ) *o*-dichlorobenzene; ( $\bullet$ ) chlorobenzene.

$$\ln V_g = 1.851 - \ln P_c + 2.372(T_c/T)^2 \quad (6)$$

By substituting eq. (6) into eqs. (1), (3), and (4), the activity coefficient, Henry's law constant, and heat of solution of the probe at infinite dilution can be rewritten as

$$\ln \gamma_1^{\infty} = \ln \frac{22,414 \cdot P_c}{P_1^0 M_1} - \frac{P_1^0}{RT} (B_{11} - V_1) - 1.851 - 2.372 \left( \frac{T_c}{T} \right)^2 \quad (7)$$

$$H_1^{\infty} = \frac{22,414}{M_1 \cdot e^{1.851 - \ln P_c + 2.372(T_c/T)^2}} \quad (8)$$

$$\Delta H_s^{\infty} = -4.744 \cdot RT(T_c/T)^2 \quad (9)$$

A comparison of Henry's law constant, activity coefficient, heat of solution of the probes, and the Flory-Huggins interaction parameter between average literature data and values computed from eqs. (2), (7), (8), and (9) is

TABLE II  
Comparison between Literature Data and  $V_g$  Values Computed in This Study

		60°C			100°C						
		PIB System									
Probes	Ref.	60°C		100°C		This study	This study				
		15	16 <sup>a</sup>	17 <sup>a</sup>	This study			11	15	16	
Hexane	49.74	51.46	52.50	53.34	16.80	16.27	16.80				
Benzene	89.14	88.38	99.51	112.94	29.70	30.32	26.85				
Cyclohexane	107.88	105.62	104.63	110.13	33.10	33.93	26.85				
PDMS System											
		60°C			70°C						
Probes	Ref.	60°C		70°C		This study	This study				
		8 <sup>a</sup>	9	10 <sup>a</sup>	12			13	8	10	12 <sup>a</sup>
Hexane	56.33	60.91	61.04	64.76	59.9	61.31	41.05	44.38	48.51	43.66	44.99
Octane	259.42	332.14	320.09	375.07	—	292.33	194.9	210.44	256.79	—	198.14
2-Methyl pentane	43.91	—	47.22	—	—	49.11	32.21	35.20	—	—	36.47
Benzene	88.55	105.46	94.37	—	91.60	94.08	63.43	68.36	—	66.24	66.27
Ethylbenzene	435.04	—	472.10	—	446.1	446.5	286.4	308.76	—	296.03	292.71

<sup>a</sup> Represents data obtained by interpolation from  $a \ln V_g$  vs.  $1/T$  plot.

TABLE III  
Comparison of Henry's Law Constant, Activity Coefficient, Heat of Solution, and Flory-Huggins Interaction Parameter between the Averaged Literature Data and Values Computed from This Study for PIB Systems at 100°C

Probe	$H_1^\infty$ (atm)		$\gamma_1^\infty$		$-\Delta H_s^\infty$ (cal/mol)		$\chi$	
Hexane	15.65	14.90 <sup>a</sup>	7.08	6.75 <sup>a</sup>	6660	7260 <sup>a</sup>	0.53	0.48 <sup>a</sup>
Benzene	9.91	10.00 <sup>a</sup>	5.90	5.96 <sup>a</sup>	7245	7980 <sup>a</sup>	0.67	0.68 <sup>a</sup>
Cyclohexane	8.08	9.12 <sup>a</sup>	4.99	5.63 <sup>a</sup>	7350	7935 <sup>a</sup>	0.40	0.50 <sup>a</sup>

<sup>a</sup> Values computed from this study.

given in Table III. It is observed that the values computed from the equations derived by using the proposed correlation equation agree well with the average literature data as shown in Tables II and III. Other properties such as partial molar heat of mixing of the probe, solubility parameter of polymer, and excess free energy of mixing can also be estimated.

### SUMMARY

Utilizing solubility data for PIB-probe and PDMS-probe systems reported in the literature, three correlation equations were proposed. These equations are useful in predicting thermodynamic properties when no data other than critical pressure and critical temperature is available. In general, these equations are not recommended for polar probes, for large molecular probes, and for temperatures below 40°C.

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