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ON THE PREDICTION OF POLYMER–PROBE χ AND Ω VALUES FROM INVERSE GAS-CHROMATOGRAPHIC DATA*

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Abstract—The solvation equation

$$\text{Log } V_G = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16}$$

has been applied to the solubility of 24 probes on poly(butadiene) at 353, 363 and 373 K using V_G values obtained by Romdhane and Danner by inverse gas-chromatography. In the above equation the explanatory variables are solute probe parameters as follows: R_2 is an excess molar refraction, π_2^H is the probe dipolarity/polarizability, α_2^H and β_2^H are the probe hydrogen-bond acidity and basicity, and L^{16} is the probe gas–liquid partition coefficient on hexadecane at 298 K. It is shown that log V_G can be predicted to ± 0.04 log units, using this equation, and that from the predicted log V_G values, the weight fraction activity coefficient, Ω^∞, can be predicted to around ± 0.04 log units, and the Flory–Huggins polymer-probe χ coefficient to within ± 0.10 units. The same general equation has also been applied to literature data on the solubility of 50 probes on poly(trifluoropropyl)methyl siloxane at 298 K, with similar results.

INTRODUCTION

The polymer–solvent interaction parameter, χ, is essential in any mean-field calculation of polymer–solvent thermodynamic properties, including construction of binary and ternary phase diagrams [1], and calculations of the extent of polymer swelling [2]. In addition, the χ-parameter contains information of the propensity and strength of the interactions between the polymer and the bulk solvent.

A number of techniques are available for the experimental determination of χ, including vapour pressure measurements [3], equilibrium swelling [2], scattering methods [4–6], and inverse gas-chromatographic measurements [7, 8]. Values of χ can also be obtained from binary and ternary phase diagrams, on fiitting the mean field theory to the experimental data [9, 10]. Because of the importance of the χ parameter, a number of predictive schemes have been developed, including those based on fragmentation methods, UNIFAC models, and relationships using the Hildebrand solubility parameter [11–13]. However, all these schemes have been restricted to systems with no strong specific interactions, and it is the purpose of this paper to develop a method that can, in principle, be applied to any set of solvents with a given polymer, no matter whether or not there are such specific interactions.

The use of gas chromatography to study properties of a stationary phase is now well established and is generally referred to as inverse gas chromatography (IGC). Retention data of a series of solute probes on a given stationary phase can be expressed as specific retention volumes at the column temperature, V_G. The V_G value is simply related to the Ostwald solubility coefficient of the gaseous probe in the stationary phase, L, via equation (1),

$$L = V_G \cdot \rho \tag{1}$$

where ρ is the density of the stationary phase at the column temperature; note that L is equivalent to the gas–liquid partition coefficient, K. When a polymer is used as the stationary phase, the probe–polymer Flory–Huggins interaction coefficient χ can be obtained from V_G using a standard equation [14–16], and in turn the polymer solubility parameter can be calculated from a series of χ values for test probes [14, 15]. The weight fraction activity coefficient of the liquid probe in the polymer at infinite dilution, Ω^∞, can also [16] be obtained from V_G.

We have already shown [17] that V_G or L values, as log V_G or log L, for a series of probes (including alcohols) on a given polymeric phase can be correlated and thence predicted using our solvation

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*Part 24 in the series *Hydrogen-bonding*.

equation (2), and we now examine whether or not Ω^∞ and χ values can similarly be treated.

$$\text{Log } SP = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + 1 \log L^{16} \quad (2)$$

In equation (2) the dependent variable SP can be L or V_G, and the explanatory variables are solute probe properties as follows: R_2 is an excess molar refraction, π_2^H is the solute dipolarity/polarizability, α_2^H and β_2^H are the solute hydrogen-bond acidity and basicity, and L^{16} is the Ostwald solubility coefficient of the solute probe on hexadecane at 298 K [18–20]. The constants in equation (2) are found by the method of multiple linear regression. Once these constants are known, then $\log L$, or $\log V_G$ can be predicted for any solute probe for which parameters are available. Note that the nomenclature we adopt is that subscript 2, as in equation (2), refers to the probe as a solute, and subscript 1 refers to the probe as a bulk liquid phase. In the examination of $\log V_G$ or $\log L$ values, the probe solute properties are relevant, because the probe is effectively at zero concentration in the polymer stationary phase.

RESULTS AND DISCUSSION

The data we use is that of Romdhane and Danner [16] on V_G values for 25 assorted probes on poly(butadiene) at 353, 363 and 373 K. The poly(butadiene) had $M_n = 22{,}600$, $M_w/M_n = 1.06$, and consisted [16] of 52 mol% *trans*-1,4, 40 mol% of *cis*-1,4, and 8 mol% of vinyl-1,2. The probes and their solute solvation parameters are in Table 1; note that the term $b\beta_2^H$ was not significant at any temperature. We found that methanol was out-of-line especially at 353 K, possibly due to either interfacial adsorption or interaction with the solid support, and we have excluded this probe from all our calculations. The remaining 24 probes yield excellent regression equations for $\log V_G$ at all three temperatures.

$$\text{Log } V_G(353) = -0.067 + 0.284R_2 + 0.344\pi_2^H + 0.437\alpha_2^H + 0.639 \log L^{16}$$

$$n = 24, \quad r = 0.9978, \quad \text{SD} = 0.045 \quad (3)$$

$$\text{Log } V_G(363) = -0.102 + 0.296R_2 + 0.327\pi_2^H + 0.387\alpha_2^H + 0.610 \log L^{16}$$

$$n = 24, \quad r = 0.9981, \quad \text{SD} = 0.041 \quad (4)$$

$$\text{Log } V_G(373) = -0.124 + 0.304R_2 + 0.301\pi_2^H + 0.369\alpha_2^H + 0.582 \log L^{16}$$

$$n = 24, \quad r = 0.9983, \quad \text{SD} = 0.037 \quad (5)$$

In these equations, n is the number of data points, r is the overall correlation coefficient, and SD is the standard deviation. In order to test equations (3–5) as predictors of $\log V_G$, we divided the 24 test probes into two sets of 12, using even numbered probes in one set and odd numbered probes in the other set. We then regressed each set separately; the two equations with the 363 K data are given as examples.

$$\text{Log } V_G(353, \text{even}) = -0.025 + 0.401R_2 + 0.284\pi_2^H + 0.426\alpha_2^H + 0.579 \log L^{16}$$

$$n = 12, \quad r = 0.9979, \quad \text{SD} = 0.046 \quad (6)$$

$$\text{Log } V_G(363, \text{odd}) = -0.155 + 0.204R_2 + 0.420\pi_2^H + 0.315\alpha_2^H + 0.624 \log L^{16}$$

$$n = 12, \quad r = 0.9994, \quad \text{SD} = 0.028 \quad (7)$$

Table 1. Probe parameters

Probe name	Probe No.	R_2	π_2^H	α_2^H	β_2^H	$\log L^{16}$
Hexane	1	0.000	0.000	0.000	0.000	2.668
Cyclohexane	2	0.305	0.100	0.000	0.000	3.007
Methylene chloride	3	0.387	0.570	0.100	0.050	2.019
Chloroform	4	0.425	0.490	0.150	0.020	2.480
Carbon tetrachloride	5	0.458	0.380	0.000	0.000	2.823
1,2-Dichloroethane	6	0.416	0.640	0.100	0.110	2.573
Tetrahydrofuran	7	0.289	0.520	0.000	0.480	2.636
Acetone	8	0.179	0.700	0.040	0.510	1.696
Methyl-ethyl ketone	9	0.166	0.700	0.000	0.510	2.287
Methyl-isobutyl ketone	10	0.111	0.650	0.000	0.510	3.089
Cyclohexanone	11	0.403	0.860	0.000	0.520	3.792
Ethyl acetate	12	0.106	0.620	0.000	0.450	2.314
Acetonitrile	13	0.237	0.900	0.090	0.300	1.739
N,*N*-dimethylformamide	14	0.367	1.330	0.000	0.660	3.173
Isopropyl alcohol	15	0.212	0.360	0.330	0.560	1.764
Butyl alcohol	16	0.224	0.420	0.370	0.480	2.601
Benzene	17	0.610	0.520	0.000	0.140	2.786
Toluene	18	0.601	0.520	0.000	0.140	3.325
Ethylbenzene	19	0.613	0.510	0.000	0.150	3.778
p-Xylene	20	0.613	0.520	0.000	0.170	3.839
n-Butylbenzene	21	0.600	0.510	0.000	0.150	4.730
Benzaldhyde	22	0.820	0.990	0.000	0.420	3.985
Aniline	23	0.995	0.960	0.260	0.530	3.993
Benzyl alcohol	24	0.803	0.900	0.390	0.500	4.249
Methanol	25	0.278	0.440	0.430	0.470	0.970

Table 2. Calculated and observed values of log V_G at 363 K

Probe name	Probe No.	V_G	log V_G Obs	log V_G Pred	Pred − Obs
Hexane	1	31.80	1.502	1.520	0.0174
Cyclohexane	2	68.40	1.835	1.826	−0.0091
Methylene chloride	3	27.10	1.433	1.504	0.0707
Chloroform	4	57.30	1.758	1.732	−0.0262
Carbon tetrachloride	5	77.30	1.888	1.901	0.0129
1,2-Dichloroethane	6	71.10	1.852	1.836	−0.0159
Tetrahydrofuran	7	57.40	1.759	1.765	0.0059
Acetone	8	18.70	1.272	1.246	−0.0258
Methyl-ethyl ketone	9	37.50	1.574	1.565	−0.0092
Methyl-isobutyl ketone	10	101.00	2.004	2.068	0.0637
Cyclohexanone	11	432.00	2.635	2.576	−0.0591
Ethyl acetate	12	39.90	1.601	1.571	−0.0300
Acetonitrile	13	27.00	1.431	1.371	−0.0605
N,N-Dimethylformamide	14	187.00	2.272	2.458	0.1862
Isopropyl alcohol	15	17.60	1.246	1.325	0.0792
Butyl alcohol	16	66.70	1.824	1.807	−0.0171
Benzene	17	80.60	1.906	1.980	0.0741
Toluene	18	182.00	2.260	2.261	0.0009
Ethylbenzene	19	358.00	2.554	2.553	−0.0008
p-Xylene	20	406.00	2.609	2.548	−0.0605
n-Butylbenzene	21	1420.00	3.152	3.099	−0.0532
Benzaldehyde	22	826.00	2.917	2.915	−0.0020
Aniline	23	1011.00	3.005	3.053	0.0485
Benzyl alcohol	24	1622.00	3.210	3.161	−0.0491
Methanol	25	19.50	1.290	—	—

Equation (6) can then be used to predict values of log V_G for the 12 odd numbers, as shown in Table 2. There is good agreement between observed and predicted values, with an average deviation of 0.041 log units and a standard deviation of 0.052 log units. Similarly, equation (7) can be used to predict log V_G for the 12 even numbers (see Table 2), with an average deviation of 0.038 and a standard deviation of 0.064 log units. Taking all 24 results together yields an average deviation of 0.039 and a standard deviation of 0.057 log units in log V_G. An exactly similar analysis can be carried out using the log V_G values at 353 K and at 373 K; a summary of all the results is given in Table 3. These confirm our previous conclusion [17] that equation (2) can account satisfactorily for log V_G values for a wide variety of solutes on polymers as stationary phases. We note that in theory, equations (4), (6) and (7) should be identical. They are not, because random errors in log V_G and in the probe parameters will not be the same in the full data set and in the two subsets. This difficulty is increased when the number of data points becomes rather small, as is the case with the two subsets that each contain only 12 data points. However, predictions of log V_G are reasonable, no matter which of the three equations are used.

Application of equation (2) to values of log Ω^∞ and to values of χ yielded, however, very poor correlations for the 24 solutes studied before. For the data at 363 K we find for example,

$$\text{Log}\,\Omega^\infty(363) = -0.525 - 0.519R_2 + 0.287\pi_2^H + 1.171\alpha_2^H + 0.563\beta_2^H + 0.008\log L^{16}$$

$$n = 24, \quad r = 0.8500, \quad \text{SD} = 0.191 \qquad (8)$$

$$\chi(363) = -0.163 - 0.988R_2 + 1.152\pi_2^H + 3.136\alpha_2^H + 0.538\beta_2^H - 0.027\log L^{16}$$

$$n = 24, \quad r = 0.9139, \quad \text{SD} = 0.300 \qquad (9)$$

Table 3. Prediction of log V_G using equation (2)

T(K)		Even numbers	Odd numbers	Total
353	Av. deviation[a]	0.039	0.044	0.039
	St. deviation[b]	0.066	0.055	0.059
363	Av. deviation	0.038	0.041	0.039
	St. deviation	0.064	0.052	0.057
373	Av. deviation	0.037	0.036	0.036
	St. deviation	0.060	0.047	0.052

[a] $|\text{Pred} - \text{Obs}|/n$.

[b] $[(\text{Pred} - \text{Obs})^2/n - 1]^{1/2}$.

Now the definition of log Ω^∞ and χ involves not only the probe V_G value, but also the saturated vapour pressure of the bulk liquid probe at the column temperature. We have seen that the solute probe V_G values, as log V_G, are connected to a set of solute probe parameters, as in equation (2), but the relevant parameters linked to the probe saturated vapour pressure will be those characteristic of the bulk liquid probe and not those of the solute probe. Hence, in principle, two distinct sets of probe properties must be used in order to correlate log Ω^∞ or χ, and it is not surprising that only one set of probe properties gives rise to poor correlations. It might be possible to use both solute probe parameters and bulk liquid probe parameters in the same correlation, but this would involve a plethora of explanatory variables. We prefer to proceed by an indirect method as follows.

Both log Ω^∞ and χ, are obtained from the experimental V_G values, using a number of additional parameters such as the probe saturated vapour pressure, second viral coefficient and molar volume, and the polymer number average molecular weight and density [16]. We can then simply predict log Ω^∞ and χ using the predicted V_G values to calculate log Ω^∞ and χ as usual [16]. Professor Danner has kindly supplied [21] all the ancillary data he used in the calculation of log Ω^∞ and χ from V_G, and in Table 4

Table 4. Predicted, observed values of χ and $\log \Omega^{\infty}$ at 363 K

	χ			$\log \Omega^{\infty}$		
Probe No.	Obs	Pred	Pred − Obs	Obs	Pred	Pred − Obs
1	0.459	0.419	0.404	0.793	0.776	−0.017
3	0.459	0.297	−0.162	0.493	0.423	−0.071
5	0.119	0.089	−0.030	0.255	0.242	−0.013
7	0.243	0.230	−0.013	0.567	0.561	−0.006
9	0.961	0.983	0.022	0.925	0.934	0.009
11	0.737	0.873	0.137	0.741	0.800	0.059
13	1.938	2.077	0.139	1.360	1.421	0.060
15	1.913	1.731	−0.182	1.343	1.265	−0.079
17	0.239	0.068	−0.171	0.566	0.492	−0.074
19	0.141	0.143	0.002	0.521	0.522	0.001
21	0.105	0.228	0.123	0.506	0.560	0.053
23	1.239	1.127	−0.112	0.922	0.873	−0.049
2	0.234	0.256	0.022	0.617	0.626	0.010
4	0.135	0.195	0.060	0.295	0.321	0.026
6	0.571	0.607	0.037	0.556	0.572	0.016
8	1.175	1.233	0.058	1.028	1.054	0.025
10	0.769	0.621	−0.148	0.835	0.771	−0.064
12	0.740	0.808	0.069	0.779	0.809	0.030
14	1.763	1.335	−0.429	1.188	1.001	−0.186
16	1.772	1.812	0.040	1.262	1.279	0.017
18	0.159	0.158	−0.002	0.532	0.531	−0.001
20	0.078	0.135	0.057	0.498	0.552	0.024
22	1.015	1.024	0.009	0.817	0.820	0.002
24	1.885	1.997	0.112	1.189	1.238	0.049

From log V_G values predicted using equation (6).
From log V_G values predicted using equation (7).

we give the "observed" $\log \Omega^{\infty}$ and χ as obtained from the observed V_G values, together with the predicted $\log \Omega^{\infty}$ and χ values obtained from the V_G values predicted from equations (6) and (7), using data at 363 K as an example. Note that our "observed" $\log \Omega^{\infty}$ and χ values are occasionally marginally different to those listed by Romdhane and Danner [3].

The predicted χ values for the odd numbers in Table 4 have been obtained from the predicted log V_G values for the odd numbers are shown in Table 2. The average deviation is 0.094 units and the standard deviation is 0.119 units. For the corresponding observed and predicted values for the even numbers, the average deviation is 0.087 units and the standard deviation is 0.147 units, whilst taking all 24 probes together the average deviation in χ is 0.090 units, and the standard deviation 0.131 units. Similarly the predicted $\log \Omega^{\infty}$ values obtained from the two sets of predicted log V_G values are listed in Table 4 also. The two separate sets lead to average deviations of 0.041 and 0.038 log units and standard deviations of 0.052 and 0.063 log units, with overall deviations for the 24 probes as 0.039 (average) and 0.057, and are summarized in Table 5. It should be pointed out that all our results refer to actual predictions and not to correlations, via the two predictive equations (6) and (7).

Inspection of Table 5 shows that our method of prediction of χ through the prediction of log V_G leads to predicted χ values that are within about ±0.10 units, for actual χ values that cover a range of 1.86 units and average 0.785 units (at 363 K). The method thus seems good enough to use to obtain χ values for probes that cannot easily be investigated by IGC. For example, probes may be eluted too quickly or too slowly to be conveniently studied, and in these cases our method can lead to quite reliable predicted χ values, provided that the necessary probe parameters are available. The predicted $\log \Omega^{\infty}$ values seem also to be reliable, and again can be obtained for probes via the predicted log V_G values.

In order to show the versatility of our method, we now consider a very different polymer, that is OV-202 a commercially available poly(trifluoropropyl)methylsiloxane that is liquid at room temperature. Values of log V_G have been obtained [22] for 50 varied solutes on OV-202 at 298 K and application of the general equation (2) leads to [22];

$$\text{Log } V_G = -0.489 - 0.480 R_2 + 1.298 \pi_2^H + 0.441 \alpha_2^H + 0.705 \beta_2^H + 0.807 \log L^{16}$$

$$n = 50, \quad r = 0.9967, \quad \text{SD} = 0.071 \qquad (10)$$

Table 5. Prediction of χ and $\log \Omega^{\infty}$

		χ			$\log \Omega^{\infty}$		
T(K)		Odd Nos	Even Nos	Total	Odd Nos	Even Nos	Total
353	Av. deviation	0.092	0.094	0.093	0.068	0.041	0.040
	St. deviation	0.121	0.157	0.137	0.053	0.040	0.060
363	Av. deviation	0.094	0.087	0.090	0.041	0.038	0.039
	St. deviation	0.119	0.147	0.131	0.052	0.063	0.057
373	Av. deviation	0.084	0.086	0.085	0.036	0.037	0.037
	St. deviation	0.109	0.138	0.122	0.047	0.060	0.053

Table 6. Values of χ and $\log \Omega^{\infty}$ from observed values of $\log V_G$ on OV-202 at 298 K

Probe	Log V_G	χ	$\log \Omega^{\infty}$
Isopropyl alcohol	1.822	3.22	2.03
Butyl alcohol	2.582	3.14	1.98
Cyclohexane	1.862	1.98	1.50
n-Butylbenzene	3.772	1.74	1.35
Methylene chloride	1.632	1.55	1.08
Chloroform	1.972	1.33	0.93
Benzene	2.272	1.25	1.13
Toluene	2.732	1.22	1.12
Tetrahydrofuran	2.362	0.60	0.84

Although the SD of 0.071 is larger than in equation (3), for example, the quality of the regressions are about the same, with the Fisher F-statistic being 1327 for equation (10) compared to 1076 for equation (3). Thus the general equation (2) applies just as well to a functionally substituted polymer at 298 K, as to a hydrocarbon polymer at 363 K. From the observed $\log V_G$ values at 298 K, we can calculate χ and $\log \Omega^{\infty}$ in the usual way [16]. Some representative values are in Table 6. As might be expected for a rather polar polymer, the nonpolar cyclohexane is incompatible with OV-202 ($\chi = 1.98$) whereas it is quite compatible with poly(butadiene) at 363 K ($\chi = 0.23$). The best probe for OV-202 at 298 K out of those in Table 6 is tetrahydrofuran with $\chi = 0.60$ from the observed $\log V_G$ value.

From the regression equation (10) and the corresponding probe parameters, it is possible to predict $\log V_G$ for numerous other probes, and then to calculate χ and $\log \Omega^{\infty}$ values. In Table 7 are values thus obtained for several probes not examined before [22]. A number of such probes seem to be compatible with OV-202 at 298 K, particularly cyclohexanone and *N*,*N*-dimethylformamide. This is a simple illustration of how a rather large number of probes can be surveyed, once the solvation equation (2) has been set up, and how χ and $\log \Omega^{\infty}$ values can be estimated indirectly, through the predicted values of $\log V_G$.

Finally, we point out that although we have used only two polymers as examples of the applicability of our new method for the estimation of χ and $\log \Omega^{\infty}$, it is now reasonably clear that the key equation (2) is of general applicability. For example, we have used equation (2) to analyse $\log V_G$ values (or their equivalent $\log L$ values) on 14 very different polymeric phases at 298 K [22], and on a number of polymeric gas-chromatographic stationary phases at 373 K [19]. Once the regression equation is established for any polymer, then further $\log V_G$ values, and thence χ and $\log \Omega^{\infty}$ values, can be estimated as we have shown.

Table 7. Values of χ and $\log \Omega^{\infty}$ from calculated values of $\log V_G$ on OV-202 at 298 K, using equation (10)

Probe	Log V_G	χ	$\log \Omega^{\infty}$
Benzyl alcohol	4.201	3.67	2.08
Aniline	3.877	2.50	1.60
p-Xylene	3.103	1.39	1.19
Acetone	2.065	1.04	1.08
Ethyl acetate	2.450	0.75	0.90
Cyclohexanone	3.889	0.41	0.72
N,*N*-Dimethylformamide	4.118	0.37	0.71

CONCLUSIONS

The same general equation (2) that can be used to identify polymer–probe interactions [17], can be used to predict $\log V_G$ values of probes to around 0.04 log units. Although the solvation equation cannot be applied directly to the correlation and thence prediction of χ and $\log \Omega^{\infty}$ values, these important quantities can be predicted in an indirect manner, via the prediction of $\log V_G$ values.

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