An analysis of polymer–probe interactions in some hydrocarbon polymers using a new solvation equation*

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The new solvation equation:

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

has been applied to the solubility of 43 gaseous probes on each of nine hydrocarbon polymers using the data of Munk *et al.*. In this equation, L is the gas–liquid partition coefficient of a series of probes on a given polymer, and the explanatory variables are solute properties 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 gas–liquid partition coefficient of the probe on hexadecane at 25°C. Each of the nine equations, one for each polymer, had correlation coefficients of around 0.999 and standard derivations of around 0.025 log units. The solubility of the gaseous probes, as log L values, as well as the polymer–probe interaction parameter χ calculated by Munk, have been analysed in terms of particular polymer–probe interactions.

(Keywords: polymer–probe interactions; solubility; interaction parameter)

INTRODUCTION

The use of inverse gas chromatography (g.c.) to study polymer interactions is well established. The specific retention volume of a probe at the column temperature, V_G, may be related[1] to the Flory–Huggins interaction coefficient (χ) between the polymer stationary phase and the probe, or may be used[2] to calculate the gas–liquid partition coefficient of the probe via the simple relationship shown in equation (1). In this equation L is the gas–liquid partition coefficient of the probe defined by equation (2), and d_T is the density of the polymer at the column temperature T.

$$L = V_G d_T \qquad (1)$$

$$L = \frac{\text{concentration of the probe in solution}}{\text{concentration of the probe in the gas phase}} \qquad (2)$$

Munk *et al.*[1] have recently determined V_G values, and hence χ values, for 43 probes on nine hydrocarbon polymers as part of a systematic study of polymer–probe interactions. Since Munk[1] also listed d_T values, for the polymers at the experimental temperature of 100°C, values of L can simply be obtained for all the systems through equation (1).

It is the purpose of this paper to show that from the experimental values of V_G or L, a considerable amount of extra information on polymer–probe interactions can be obtained, and can be used to analyse quantitatively the variation of χ for a given probe with different polymers.

There is some difficulty here over the question of nomenclature. In inverse g.c., the probe is present at effectively zero concentration in the polymer, and hence would normally be regarded as the solute. Furthermore, the properties of the probe that will determine the value of L will refer to the probe as a simple monomeric entity. Properties of the probe as a bulk liquid (possibly associated) are not relevant to any discussion of gas–liquid partition coefficients of the probe. However, when V_G is converted to χ (through the vapour pressure of the probe), the χ value then refers to interactions between the polymer and the bulk liquid probe, which then becomes a solvent. Since the analysis is mostly

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concerned with L values, where the probe is acting as a solute, the nomenclature in which subscript 2 refers to the probe[3–5] is retained, and all solute probe parameters are denoted by subscript 2. The equation used[1] to obtain χ values then becomes,

$$\chi = \ln(RTV_1/V_G P_2^0 V_2) - 1 + V_2/M_1 V_1 - (B_{22} - V_2)P_2^0/RT \qquad (3)$$

where V_1 and M_1 are the specific volume and molecular weight of the polymer, respectively, and P_2^0, V_2 and B_{22} are the saturated vapour pressure of the pure bulk probe, the probe molar volume and the probe second virial coefficient, respectively. Note that ln and log are used for natural and decadic logarithms, respectively.

THE MODEL

The model used to discuss gas–liquid partition coefficients, is a simple cavity theory model. The process of dissolution of a gaseous solute is regarded as taking place in two stages: (1) a cavity must be formed in the polymer in an endoergic process, i.e. leading to negative values of $\log L$; and (2) the probe is inserted into the cavity, thus setting up various exoergic polymer–solute interactions, all of which lead to positive values of $\log L$. Note that the terms endoergic and exoergic refer to an increase or a decrease in Gibbs energy, respectively. We now consider the case where the polymer or solvent is constant, and a series of solute probes are studied. The formation of a cavity will be expected to be proportional to the size of the probe, either the probe volume or the probe surface area, but neither of these quantities are very useful as independent explanatory variables. Instead the solute parameter $\log L^{16}$ is used, where L^{16} is the solute gas–liquid partition coefficient on hexadecane[2] at 25°C. Although the $\log L^{16}$ paremeter will contain not only the cavity term but also a term in general van der Waals interactions, it has a marked advantage over volume or surface area in that $\log L^{16}$ is a Gibbs energy related quantity, exactly as $\log L$ the dependent variable. The various exoergic solute–solvent interactions in stage (2), above, are modelled by a number of solute parameters as explanatory variables. General dispersion or van der Waals interactions are included in the $\log L^{16}$ parameter, but more specific interactions involving π and n electron pairs are modelled by the solute excess molar refraction[3], R_2. There are two possible types of hydrogen bond interactions that can be set up, namely, polymer base–probe acid and polymer acid–probe base. The appropriate probe parameters are α_2^H and β_2^H the probe solute hydrogen-bond acidity and hydrogen-bond basicity, respectively[3–6]. Interactions of the dipole–dipole or dipole–induced dipole type are modelled by the solute dipolarity-polarizability parameter, π_2^H. Inclusion of all the above explanatory variables leads to the general solvation equation (4):

$$\log L = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \qquad (4)$$

Now because each explanatory variable in equation (4) refers to some particular interaction, the constants in this equation will then characterize the complimentary polymer property, so that equation (4) becomes symmetrical in polymer and probe properties. The r constant indicates the propensity of the polymer to interact with probe π and n electron pairs and is usually slightly positive, except for fluorinated polymers. The s constant relates to the interaction of the polymer with dipolar-polarizable probes, the a constant to the polymer hydrogen-bond basicity (because basic polymers will interact with acidic probes), and the b constant to the polymer hydrogen-bond acidity. The $l \log L^{16}$ term is a composite of endoergic cavity formation and exoergic general dispersion interactions[7]. The latter always dominates and hence the l constant is invariably positive. Similarly the exoergic interactions described by the $s\pi_2^H$, $a\alpha_2^H$ and $b\beta_2^H$ terms must always lead to positive s, a and b constants. The method therefore leads to a set of 'characteristic constants' c, r, s, a, b and l that quantitatively describe the solubility-related properties of a polymer in terms of specific polymer–probe interactions.

This approach is quite different to the solvatochromic method, pioneered by Kamlet *et al.*[8], and quite recently applied to polymers by Paley *et al.*[9]. In this latter method, information about polymer dipolarity, hydrogen-bond acidity and hydrogen-bond basicity is obtained through u.v. measurements on various indicator molecules dissolved in the bulk polymer. The solvatochromic method and our method seem to be rather complimentary, although the former has the limitation that, at present, the solvatochromic method is applicable only at 25°C. Our approach is different also to the solubility parameter method in that all the explanatory variables in equation (4), with the exception of the minor parameter R_2, are Gibbs energy related, being derived from equilibrium constants (as $\log L$). Thus equation (4) is a linear free (or Gibbs) energy relationship, of the correct form for the analysis of $\log L$ values.

The constants in equation (4) are found by the method of multiple linear regression analysis. All values of the probe explanatory variables are from our previous compilation[6] (with one exception) and are listed in *Table 1*. The exception is the value of $\log L^{16}$ for cyclohexadiene, which was obtained by back-calculation of Munk's results on the three solvents.

CORRELATIONS OF THE LOG L VALUES

The nine hydrocarbon polymers studied by Munk[1] are listed in *Table 2*, together with their densities[1] at 100°C.

The first application of the full equation (4) is to the 43 probes on each of the nine polymers. In all nine cases the b constant was small and slightly negative, and hence was eliminated from the equation. There is a small, but not insignificant, cross-correlation between β_2^H and π_2^H, see *Table 3*, so that a β_2^H term will tend to appear whenever a π_2^H term appears. However, the negative sign of the b constant precludes interaction. We therefore repeated all the regressions, excluding the $b\beta_2^H$ term, and obtained the results in *Table 4*. Here, the standard deviation is SD and R is the overall correlation coefficient. Although the regression equations are quite good, ethanol was out of line by several SDs on a number of phases (e.g. F and G). Alcohols are generally 'difficult' solutes on non-polar phases, since they can interact with the solid support and so cause tailing, and may also be sorbed through interfacial effects rather than by the bulk polymer[10]. Of the four alkan-1-ols studied, ethanol is the most likely to undergo these additional interactions. Since it has also a small V_G value, leading to extra possible errors, we are inclined to reject the ethanol values. To make sure all the regressions were

Table 1 The 43 probes used by Munk[1] and their solvation parameters

No.	Probe	R_2[a]	π_2^H	α_2^H	β_2^H	Log L^{16}
103	Propane	0.000	0.000	0.000	0.000	1.050
104	n-Butane	0.000	0.000	0.000	0.000	1.615
106	n-Pentane	0.000	0.000	0.000	0.000	2.162
109	n-Hexane	0.000	0.000	0.000	0.000	2.668
114	n-Heptane	0.000	0.000	0.000	0.000	3.173
126	n-Octane	0.000	0.000	0.000	0.000	3.677
145	n-Nonane	0.000	0.000	0.000	0.000	4.182
180	n-Decane	0.000	0.000	0.000	0.000	4.686
265	n-Undecane	0.000	0.000	0.000	0.000	5.191
601	Cyclopentane	0.263	0.100	0.000	0.000	2.515
701	Cyclohexane	0.305	0.100	0.000	0.000	3.007
800	Cylcoheptane	0.350	0.100	0.000	0.000	3.706
820	Cyclooctane	0.413	0.100	0.000	0.000	4.314
1340	Cyclohexene	0.395	0.200	0.000	0.100	3.021
1415	Cyclohexadiene	0.515	0.350	0.000	0.100	2.914
10001	Benzene	0.610	0.520	0.000	0.140	2.803
10002	Toluene	0.601	0.520	0.000	0.140	3.344
10003	Ethylbenzene	0.613	0.520	0.000	0.150	3.789
2501	Chloromethane	0.249	0.430	0.000	0.080	1.163
2502	Dichloromethane	0.387	0.570	0.100	0.050	2.019
2503	Trichloromethane	0.425	0.490	0.150	0.020	2.480
2504	Tetrachloromethane	0.458	0.380	0.000	0.000	2.823
2530	1-Chlorobutane	0.210	0.400	0.000	0.100	2.722
2550	1-Chloropentane	0.208	0.400	0.000	0.100	3.223
2560	1-Chlorohexane	0.201	0.400	0.000	0.100	3.710
2580	1-Chlorooctane	0.191	0.400	0.000	0.100	4.731
2506	1,1-Dichloroethane	0.322	0.490	0.100	0.100	2.316
2507	1,2-Dichloroethane	0.416	0.640	0.100	0.110	2.573
2508	1,1,1-Trichloroethane	0.369	0.410	0.000	0.090	2.733
2804	Trichloroethene	0.524	0.400	0.080	0.030	2.997
11601	Chlorobenzene	0.718	0.670	0.000	0.090	3.640
5501	Propanone	0.179	0.700	0.040	0.510	1.696
5502	Butanone	0.166	0.700	0.000	0.510	2.287
5110	Tetrahydrofuran	0.289	0.520	0.000	0.480	2.636
5200	Dioxan	0.329	0.750	0.000	0.640	2.892
6051	Methyl acetate	0.142	0.640	0.000	0.450	1.911
6052	Ethyl acetate	0.106	0.620	0.000	0.450	2.314
6053	n-Propyl acetate	0.092	0.600	0.000	0.450	2.819
6055	n-Butyl acetate	0.071	0.600	0.000	0.450	3.353
8002	Ethanol	0.246	0.420	0.370	0.480	1.485
8003	Propan-1-ol	0.236	0.420	0.370	0.480	2.031
8005	Butan-1-ol	0.224	0.420	0.370	0.480	2.601
8009	Pentan-1-ol	0.219	0.420	0.370	0.480	3.106

[a] In units of 10^{-1} cm^3 mol^{-1}

exactly comparable, ethanol was excluded from all the regressions, leading to the equations summarized in *Table 5*. The quality of the regression equations is now almost exactly the same for all nine polymers, and results in *Table 5* are preferred to those in *Table 4*.

By-and-large the regression equations in *Table 5* correlate the log *L* values to about 0.025 log units, with *R* on average around 0.9992 in value. The equations are thus good enough to estimate log *L* values for probes for which the necessary probe parameters are available. Several of the polymers (A–E) give rise to very similar regression constants, but polymers F–I do show some differences. The most marked is the hydrogen-bond basicity shown by polymer I, where the *a* constant is 0.201 ± 0.038 units. In all other cases the *a* constant was very small and slightly negative, and so was disregarded.

It is possible to break down the log *L* values for the polymer–gaseous probe solubilities, noting that the larger is log *L* the more soluble is the probe, into various polymer–probe interactions via equation (4). On our model, the constants *r*, *s* and *a* (*b* is always insignificant) will reflect dispersion interactions involving probe π and n electrons, dipole–induced dipole and polarizability interactions, and probe acid–polymer base interactions,

Table 2 The hydrocarbon polymers investigated by Munk[1]

Code	Polymer	d_2 (100°C)[a]
A	Octacosane	0.756
B	Dotriacontane	0.761
C	Hexatriacontane	0.768
D	Atactic polypropene	0.825
E	Atactic polypropene	0.816
F	Hydrogenated poly(1,2-butadiene) or polyethylene	0.822
G	Hydrogenated poly(2,3-dimethyl-1,4-butadiene)	0.816
H	Poly(isobutene)	0.859
I	Poly(1,2-butadiene) or poly(vinylethene)	0.847

[a] Polymer densities at 100°C, from Ref. 1, in g cm^{-3}

Table 3 Values of the correlation coefficient between the variables for the 43 probes

	R_2	π_2^H	α_2^H	β_2^H
π_2^H	0.480			
α_2^H	0.045	0.169		
β_2^H	−0.052	0.679	0.428	
Log L^{16}	0.048	−0.265	−0.265	−0.317

Table 4 A summary of regression equations for the 43 probes on each of the nine polymers in terms of log L at 100°C

Polymer	c	r	s	a	l	SD[a]	r[b]
A	−0.225	0.155	0.023	(0)	0.666	0.026	0.9992
	−0.016[c]	0.024	0.020		0.005		
B	−0.244	0.170	0.027	(0)	0.667	0.028	0.9991
	−0.017	0.025	0.021		0.005		
C	−0.248	0.188	0.014	(0)	0.663	0.028	0.9990
	0.017	0.025	0.021		0.005		
D	−0.313	0.168	0.069	(0)	0.643	0.027	0.9990
	0.014	0.020	0.017		0.004		
E	−0.284	0.156	0.081	(0)	0.643	0.022	0.9994
	0.014	0.020	0.017		0.004		
F	−0.307	0.225	0.039	(0)	0.634	0.040	0.9978
	0.025	0.037	0.031		0.007		
G	−0.382	0.250	0.067	(0)	0.651	0.041	0.9978
	0.026	0.038	0.032		0.007		
H	−0.448	0.226	0.110	(0)	0.643	0.037	0.9982
	0.023	0.034	0.028		0.007		
I	−0.285	0.131	0.361	0.130	0.626	0.029	0.9988
	0.018	0.026	0.022	0.042	0.005		

[a] Overall standard deviation in log L

[b] Overall correlation coefficient

[c] The standard deviation in the given coefficient

Table 5 A summary of regression equations for the 43 probes excluding ethanol on each of the nine polymers in terms of log L at 100°C

Polymer	c	r	s	a	l	SD[a]	r[b]
A	−0.216	0.156	0.021	(0)	0.663	0.025	0.9992
	0.016[c]	0.023	0.019		0.005		
B	−0.230	0.171	0.024	(0)	0.663	0.024	0.9993
	0.015	0.015	0.022		0.004		
C	−0.235	0.189	0.012	(0)	0.659	0.024	0.9992
	0.016	0.022	0.019		0.004		
D	−0.298	0.170	0.067	(0)	0.639	0.022	0.9993
	0.014	0.020	0.017		0.004		
E	−0.276	0.157	0.080	(0)	0.640	0.020	0.9994
	0.013	0.019	0.016		0.004		
F	−0.279	0.228	0.034	(0)	0.626	0.028	0.9989
	0.018	0.025	0.021		0.005		
G	−0.351	0.253	0.062	(0)	0.643	0.026	0.9991
	0.017	0.024	0.020		0.005		
H	−0.425	0.228	0.107	(0)	0.637	0.028	0.9989
	0.018	0.026	0.022		0.005		
I	−0.275	0.133	0.355	0.201	0.623	0.023	0.9992
	0.015	0.021	0.018	0.038	0.004		

[a] Overall standard deviation in log L

[b] Overall correlation coefficient

[c] The standard deviation in the given coefficient

Table 6 A breakdown of log L values for some gaseous probes on polymers B, G, H and I in terms of solute–solvent interactions, using equation (4)[a]

	Polymer			
Solute probe	B	G	H	I
n-Butane				
c	−0.230	−0.351	−0.425	−0.275
rR_2	0	0	0	0
$s\pi_2$	0	0	0	0
$a\alpha_2^H$	0	0	0	0
$l \log L^{16}$	1.071	1.038	1.029	1.006
Total	0.841	0.687	0.604	0.731
n-Decane				
c	−0.230	0.351	−0.425	−0.275
rR_2	0	0	0	0
$s\pi_2^H$	0	0	0	0
$a\alpha_2^H$	0	0	0	0
$l \log L^{16}$	3.107	3.013	2.985	2.919
Total	2.877	2.662	2.560	2.644
Toluene				
c	−0.230	−0.351	−0.425	−0.275
rR_2	0.062	0.152	0.137	0.080
$s\pi_2^H$	0.012	0.032	0.056	0.185
α_2^H	0	0	0	0
$l \log L^{16}$	2.217	2.150	2.130	2.083
Total	2.061	1.983	1.898	2.073
Chlorobenzene				
c	−0.230	−0.351	−0.425	−0.275
rR_2	0.123	0.182	0.164	0.095
$s\pi_2^H$	0.016	0.042	0.072	0.238
$a\alpha_2^H$	0	0	0	0
$l \log L^{16}$	2.413	2.341	2.319	2.268
Total	2.322	2.214	2.300	2.326
Butanone				
c	−0.230	−0.351	−0.425	−0.275
rR_2	0.028	0.042	0.038	0.022
$s\pi_2^H$	0.017	0.043	0.075	0.249
$a\alpha_2^H$	0	0	0	0
$l \log L^{16}$	1.516	1.471	1.157	1.425
Total	1.331	1.205	1.145	1.421
Butan-1-ol				
c	−0.230	−0.351	−0.425	−0.275
rR_2	0.038	0.057	0.051	0.030
$s\pi_2^H$	0.010	0.026	0.045	0.149
$a\alpha_2^H$	0	0	0	0.074
$l \log L^{16}$	1.724	1.672	1.657	1.620
Total	1.542	1.404	1.328	1.598

[a] In all cases the $b\beta_2^H$ term is not significant (see text)

Table 7 Values of the Flory–Huggins interaction parameter χ for various probes on polymers, calculated by Munk[1]

	Polymer			
Probe	B	G	H	I
n-Butane	0.322	0.483	0.646	0.390
n-Decane	0.096	0.268	0.481	0.296
Toluene	0.271	0.423	0.603	0.194
Chlorobenzene	0.388	0.507	0.703	0.283
Butanone	1.309	1.427	1.546	0.982
Butan-1-ol	2.172	2.290	2.449	1.757

respectively. These will all be relative to corresponding interactions with n-hexadecane as the solvent. The $l \log L^{16}$ term includes the very important general dispersion interactions plus the cavity effect. In *Table 6* is set out a breakdown for a number of representative probes in polymer B as a representative of polymers A–E, and polymers G, H and I. For polarizable and dipolar probes there are small terms in rR_2 and $s\pi_2^H$ with polymer B, i.e. there are some effects in comparison with n-hexadecane, but not large. With polymer G there are increased rR_2 and $s\pi_2$ terms, but not large enough to counteract the very negative c constant. Hence all probes are less soluble in G than in B. In the case of polymer I, non-polar solutes such as n-butane and n-decane are less soluble than in polymer B, but polarizable (toluene), dipolar (butanone) or hydrogen-bond acidic (butan-1-ol) probes are more soluble in I than in B. The main terms leading to an increase in log L are the $s\pi_2^H$ and $a\alpha_2^H$ terms. Now polymer I, poly (1,2-butadiene) will contain the alkene functional group, known[6] to be slightly polarizable and slightly basic, and so the increased solubility of some probes in I against B is related to the chemical constitution of the polymers. The c constant itself influences, through equation (4), the log L values of probes. Thus all log L values in H will tend to be less than in B because of the more negative c constant in H. Formally, the c constant represents the log L value for a non-polar probe with $\log L^{16} = 0$, e.g. an alkane between methane ($\log L^{16} = -0.323$) and ethane ($\log L^{16} = 0.492$).

INTERPRETATION OF THE χ VALUES

Values of log L for a gaseous probe in a polymer can be considered to be the result of two main effects, an endoergic polymer cavity term and a set of exoergic polymer–probe interaction terms. However, because χ is calculated from V_G and the saturated vapour pressure of the probe, equation (3), there will now be four main effects that contribute to χ, namely, an endoergic polymer cavity term and a set of exoergic polymer–probe interaction terms (as above), plus the two corresponding terms that refer to the pure liquid probe – the liquid probe cavity term and various probe–probe interaction terms. This is why χ values are always much more difficult to interpret than log L values. As can be seen from the defining equation (3), the χ values result from a combination of V_G the retention volume of the probe at infinite dilution in the polymer, with P_2^0 the saturated vapour pressure of the bulk liquid probe and hence include two completely different sets of probe properties.

In order to interpret a matrix of χ values for different probes on different polymers, it is necessary to consider all the four main effects, above. However, if only χ values for a given probe in a set of polymers are examined, effects relating to the pure liquid probe cancel out, and we should be able to explain the variation in χ in the same way as we explain the variation in log L for a given probe in a set of polymers. Munk[1] calculated χ values for all 43 probes on all the nine polymers, but we shall simply illustrate the method for the probe butan-1-ol in the various polymers. Munk[1] showed that the χ values for butan-1-ol were quite similar for polymers A–G, 2.21 ± 0.05, but was larger for polymer H at 2.45, and much lower for polymer I at only 1.76 units. Inspection of the regression equations in *Table 5* shows that for polymers A–G there are but minor effects in the characteristic constants. Hence butan-1-ol interacts with these seven polymers in a very similar way. For polymer H, the c constant is the most negative of all the polymers at -0.425 units; this leads to a small log L value for butan-1-ol in polymer H, due to an endoergic cavity effect. In the case of polymer G, the regression equation, *Table 5*, shows that both dipolar interactions and polymer (base)–probe (acid) hydrogen-bond interactions can be set up. Butan-1-ol is a probe capable of this, hence log L will be larger, the probe will be more soluble in the polymer and χ will be correspondingly smaller.

CONCLUSIONS

Polymer–probe interactions can be identified and assessed quantitatively through the new solvation equation (4), under conditions in which the probe functions as a solute at effectively zero concentration in the bulk polymer. A noticeable feature of equation (4) is that it is a linear Gibbs energy equation and hence of the correct form for the correlation of log L values. The Flory–Huggins polymer–probe interaction coefficient is generally more difficult to interpret than log L values because it relates to two quite different sets of probe properties. However, for the case of a given probe in a series of polymers, χ values can be interpreted in the same way as log L values through the new solvation equation.

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