Solubility properties in polymers and biological media: 10. The solubility of gaseous solutes in polymers, in terms of solute–polymer interactions

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A general equation

$$SP = SP_0 + l \log L^{16} + s(\pi_2^* + d\delta_2) + a\alpha_2 + b\beta_2$$

has been used to describe solubility properties of a wide range of gaseous solutes in polymers. The property, SP, may be a log V_G value, an enthalpy of solution, etc., and the explanatory variables are solute parameters: L^{16} is the Ostwald solubility coefficient of the solute on hexadecane at 25°C, π_2^* is the solute dipolarity, δ_2 a polarizability correction term, α_2 the solute hydrogen-bond acidity, and β_2 the solute hydrogen-bond basicity. Solubilities may then be discussed in terms of the various solute–solvent interactions that are reflected by the coefficients of the various terms. These are cavity effects and dispersion forces (l), dipole–dipole and dipole–induced-dipole interactions (s), and hydrogen-bonding between solute acid and polymer base (a) or between solute base and polymer acid (b). For non-dipolar solutes in all non-aqueous solvent phases, and for weakly dipolar solutes in weakly dipolar phases, the general equation reduces to a more specific equation that includes only the term due to cavity effects and dispersion forces

$$SP = SP_0 + l \log L^{16}$$

(Keywords: poly(ethylene oxide); poly(methyl methacrylate); poly(vinyl acetate); polymer–solute interactions; hydrogen-bonding)

INTRODUCTION

The sorption and diffusion of gases and vapours into and through polymers is of considerable practical and theoretical importance. Construction of general equations that describe the sorption of gaseous solutes into polymers would represent a significant advance, especially if it were possible to ascertain whether or not equations that describe the behaviour of solutes in non-polymeric systems are equally applicable to polymers.

In previous parts of this series, and elsewhere, we have shown that the general solvatochromic equation

$$SP = SP_0 + m\bar{V}_2/100 + s(\pi_2^* + d\delta_2) + a\alpha_2 + b\beta_2 \qquad (1)$$

can be used to correlate and to predict numerous properties, SP, of non-electrolyte solutes in condensed phases[1–11]. Examples include octanol–water partition coefficients, K_{ow}, of 102 solutes given by[5]

$$\log K_{ow} = 0.20 + 2.74\bar{V}_2/100 - 0.92\pi_2^* - 3.49\beta_2 \qquad (2)$$

$$n = 102, \quad s.d. = 0.175, \quad r = 0.989$$

the solubilities of liquid solutes in water[6,11], the adsorption of solutes from aqueous solution onto carbon[9], and retention behaviour of solutes in reversed phase HPLC[7]. In equation (1), SP_0 is a constant, $\bar{V}_2$ is the solute molar volume at 20°C[+], π_2^* is a measure of solute dipolarity, δ_2 is a polarizability correction term, and α_2 and β_2 are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity respectively[8]. Note that we use the subscript 2 to denote a solute property and we shall use subscript 1 to denote a solvent property. In a particular solvent, one or more of the terms in equation (1) may be unimportant; for example, the term in solute hydrogen-bond acidity, $a\alpha_2$, is statistically not significant in equation (2).

We denote the number of data points as n, the standard deviation as s.d., and the overall correlation coefficient as r.

Recently, Galin[12] has used a similar multiparameter approach to investigate the enthalpy of solution at infinite dilution, ΔH_s^0, of gaseous solutes in liquid poly(ethylene oxide) (PEO), derived from gas–liquid chromatographic

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[+] A correction of 0.100 is added to $\bar{V}_2/100$ for cyclic compounds[5]

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measurements. Galin refers to the compounds studied as solvents, but since the results refer to the compounds at infinite dilution in PEO, it is more appropriate to use the term solutes. This is not a semantic argument, since the distinction is crucial to the choice of input parameters (α and β) used in the multiparameter regression equation. The best such regression equation found by Galin (for 26 out of the total of 44 solutes) is

$$-\Delta H_s/(\text{kcal mol}^{-1}) = 0.48 \times 10^{24} P + 1.73\mu + 4.29\alpha \quad (3)$$

$$n = 26, \qquad r = 0.957$$

where P is the solute polarizability, μ the solute dipole moment, and α the 'solute' hydrogen-bond acidity. Unfortunately, in equation (3) Galin has used our hydrogen-bond acidity parameter, α_1, which refers to the compound as a bulk, associated, liquid, whereas the correct parameter to be used is α_2, the solute hydrogen-bond acidity that refers to the compound as a monomeric species at infinite dilution (on occasions[11] we have used the term α_m rather than α_2).

Galin and Maslinko[13] subsequently analysed partial molal enthalpies of solution, ΔH^{∞}, of aprotic solutes on poly(vinylidene fluoride) in terms of the following equation

$$-\Delta H^{\infty}/(\text{kcal mol}^{-1}) = -0.18 \times 10^{24} P + 0.35\mu + 2.35\beta$$

$$n = 16, \qquad r = 0.992 \qquad (4)$$

in which β is our hydrogen-bond basicity parameter. For aprotic solutes β_1 and β_2 are identical, and so the difficulty referred to above does not apply.

Apart from the α-term in equation (3), we are in complete agreement with Galin in that the multiparameter approach, based on specific interaction terms, should provide important chemical information about the nature of solute–polymer interactions. The aim of the present work is to apply our own versions of multiparameter equations to the solubility of non-dipolar and dipolar solutes on polymeric phases.

RESULTS FOR NON-DIPOLAR SOLUTES

For solution of a series of non-dipolar solutes in a given phase, terms in α_2, β_2, μ, etc. will be effectively zero, and it is expected that multiparameter equations would collapse into equations with only one, or perhaps two, explanatory variables. Indeed, we have already shown[1] that the solubility of non-dipolar solutes in various polymeric phases, as $\log L$ where L is the Ostwald solubility coefficient, could be correlated and predicted through a set of simple linear equations of the following type:

$$\log L = d' + l' R_G \qquad (5)$$

where R_G is a solute parameter obtained by averaging solute solubilities in a range of simple solvents[14–16] and d' and l' are parameters that characterize the given polymeric phase. Equation (5), although simple, apparently extends to the solubility of all non-dipolar solutes in all non-aqueous solvents[1,14–16]. It is difficult, however, to incorporate R_G as an explanatory variable in multiparameter equations, and so we have devised a new solute parameter, $\log L^{16}$, where L^{16} is the solute Ostwald solubility coefficient in n-hexadecane at 25°C. Since $\log L^{16}$ is linear with R_G for non-dipolar solutes, all the sets of solubilities covered by equation (5) will also be covered by the general equation

$$SP = SP_0 + l \log L^{16} \qquad (6)$$

in which SP may be a $\log L$ term, or a $\log V_G$ term, or a ΔH_s° value; V_G is the retention volume of a solute on a given stationary phase.

We do not list the R_G equations, but give in *Table 1* a number of representative sets of solubilities or ΔH_s values for rather non-dipolar gases[17], together with their $\log L^{16}$ values[18]. Results of the correlations via equation (6) are given in *Table 2*. For the solubility regressions r varies from 0.998 down to only 0.958, but we feel certain that the comparatively poor correlation coefficients reflect considerable experimental errors in the solubility determinations. This is even more the case for the ΔH_s correlations, where the low r values and the very large s.d. values must be due primarily to experimental errors rather than the lack of fit of the model. For example if ΔH_s is obtained from $\log S$ or $\log L$ values at temperatures that differ by 30°C (say 20°C and 50°C) then an error of 0.1 unit in the $\log S$ or $\log L$ measurements will lead to an error of no less than 1.44 kcal mol^{-1} in the derived ΔH_s value. In addition, some of the solutes listed do have some polar character.

The success of the simple equation (6) in correlating especially $\log S$ and $\log L$ values means that it is now possible to predict further $\log S$ or $\log L$ values on the polymeric phases for the non-dipolar solutes for which $\log L^{16}$ values are known. Furthermore, the solution process for non-dipolar solutes on polymeric phases must be essentially similar to that in simple solvents such as n-hexadecane.

Although equation (6) is designed to apply to isothermal data, it is quite straightforward[1] to correct experimental $\log \mathrm{L}_i$ values obtained at temperatures T_i (K), scattered about a mean temperature T_m (K), through the following modified equation:

$$(T_i/T_m) \log L_i = SP_0 + l \log L^{16} \qquad (7)$$

Not only can equation (6) be applied to the prediction of new SP values for non-dipolar solutes, but also it can be used to identify solutes that interact with the polymer phase other than by dispersion forces. For example, in a plot of $\log S$ for solution in ethyl cellulose[17], with S in ml(s.t.p.) cm^{-3} cmHg^{-1} × 10^4, against $\log L^{16}$, the non-dipolar solutes, O_2, Ar, N_2, CO_2, C_2H_6 and C_3H_8, define a reasonable line with $r = 0.990$ and s.d. = 0.12, but the dipolar solutes NH_3 ($\mu = 1.5$ D) and SO_2 ($\mu = 1.6$ D) are appreciably more soluble than calculated from the non-dipolar regression. We deal with a general solubility equation for both non-dipolar and dipolar solutes in the next section.

RESULTS FOR DIPOLAR SOLUTES

The rationale behind our general equation (1) is that the term in $\bar{V}_2$ accounts for cavity effects, and the remaining terms deal with various interactions between the solute

Table 1 Solubilities (as log L, log S or log V_G) and enthalpies of solution (in kcal mol^{-1}) for non-polar solutes on various polymeric phases[a]

	log L^{16}	log L^A	log L^B	ΔH^B	log L^C	ΔH^C	log S^D	ΔH^D	log S^E	ΔH^E	log S^F	ΔH^F	log V_G^G
He	−1.741	−1.350					0.15	−1.8	−0.137	2.4	−0.432	1.5	
Ne	−1.575												
Ar	−0.688	−0.440					1.20	−0.1	0.875	0.8	0.518	−0.3	
Kr	−0.211				−0.347	−1.39							
Xe	0.378				0.255	−2.46							
H_2	−1.200	−0.924					0.69	0.8					
N_2	−0.978	−0.782			−1.155	−0.07	0.87	0.1	0.477	1.9	0.176	0.5	
O_2	−0.723	−0.467					1.18	−0.8	0.799	0.6	0.380	−0.4	
CO	−0.812						1.04	0.0	0.653	1.7	0.301	0.6	
CO_2	0.057	0.384					2.08	−2.8	1.531	0.1	1.137	−1.3	
N_2O	0.164				0.146	−2.77							
Methane	−0.323	−0.203					1.52	−1.3	1.176	0.4	0.833	−0.7	
Ethane	0.492								2.000	−1.5	1.591	−2.3	
Propane	1.050						2.90	−5.6	2.477	−2.1	2.041	−2.9	−0.208
Butane	1.615	1.215											
Isobutane	1.409												−0.066
Pentane	2.162		1.798	−6.88									0.255
Hexane	2.668												0.447
Heptane	3.173												0.681
Cyclopropane	1.314		1.064	−2.84	1.061	−4.78							
Cyclopentane	2.447												0.484
Cyclohexane	2.913												0.777
Ethene	0.289				0.104	−2.65							
Propene	0.946						3.15	−3.3	2.400	−2.1	2.033	−3.2	
Ethyne	0.150						2.22	−2.2					
Propyne	1.025								2.602	−2.6	2.204	−3.4	
SF_6	−0.450						1.48	−3.5	1.097	−0.5	0.724	−1.8	
Diethylether	2.061		1.861	−6.50	1.813	−7.10							
Divinylether	2.055				1.778	−7.41							
$CHCl{:}CCl_2$	3.130		2.594	−8.03	2.954	−9.27							
$CHClFCF_2OCHF_2$	2.300		1.760	−7.50	1.991	−7.31							
$CF_3CHClBr$	2.177		1.989	−7.00	2.342	−8.94							
$CHCl_2CF_2OCH_3$	2.864		2.724	−9.63	2.978	−9.37							
$CHCl_3$	2.480		2.243	−8.15	2.602	−9.30							0.505
$CF_3CH_2OCH{:}CH_2$	1.940				1.681	−7.50							
$CHF_2CF_2CH_2Br$	2.830				2.505	−7.89							
CF_3CHFBr	1.730				1.462	−4.54							
Benzene	2.803												0.889
Toluene	3.344												1.104
CH_2Cl_2	2.019												0.525

[a] Log L^{16} values from reference 18, other values as listed in *Table 2*

and the solvent phase through dipolar effects (π_2^*) or hydrogen-bond effects (α_2 and β_2). However, there is no explicit term in equation (1) which corresponds to a dispersion interaction. This does not seem to matter for processes that involve condensed phases, because the dispersion interaction in each phase will largely cancel, e.g. the partition of solutes between octanol and water described by equation (2). However, this term may not be neglected for the process of transferring a solute from the gas phase to solution, and so we thought it useful to modify equation (1) by incorporation of a term in log L^{16}. This term will include not only solute–solvent dispersion interactions but also the cavity effect, making the V_2 term redundant, and leaving the modified equation as

$$SP = SP_0 + l \log L^{16} + s(\pi_2^* + d\delta_2) + a\alpha_2 + b\beta_2 \qquad (8)$$

We now apply both equations (1) and (8) to the ΔH_s results obtained by Galin[12], as well as to other solubility properties such as log L or log V_G.

We start with the ΔH_s values listed by Galin[12] for solution on poly(ethylene oxide). Of the 44 data points, Galin used 26 in equation (3), which yielded $r = 0.957$, albeit with an incorrect set of α values. Our approach is that if multiparameter equations are considered to be general equations for the investigation of solute–solvent interactions, they should be applied to as many data points as possible. All the required explanatory variables are available for 41 data points (the outstanding solutes being bis(2-methoxyethyl) ether, water, and 1,1,2-trichloroethane) and application of the various multiparameter equations yields the following:

$$-\Delta H_s = 3.34 + 0.30 \times 10^{24} P + 1.17\mu + 3.87\alpha_2$$
$$n = 41, \quad \text{s.d.} = 1.05, \quad r = 0.805 \qquad (9)$$

$$-\Delta H_s = 2.25 - 3.45 V_2/100 + 3.89(\pi_2^* - 0.01\delta_2) + 3.98\alpha_2 + 1.46\beta_2$$
$$n = 41, \quad \text{s.d.} = 1.12 \quad r = 0.786 \qquad (10)$$

$$-\Delta H_s = 2.33 + 1.46 \log L^{16} + 3.49(\pi_2^* - 0.24\delta_2) + 4.24\alpha_2 + 0.87\beta_2$$
$$n = 41, \quad \text{s.d.} = 0.86, \quad r = 0.880 \qquad (11)$$

As found for the non-dipolar solutes, values of s.d. are quite large, but again the large possible experimental error should be noted, e.g. for butanone, three values

Table 2 Correlations of solubilities and heats of solution of non-polar solutes in polymeric phases with $\log L^{16}$ values

Regression equation	n	s.d.	r
A Values of $\log L$ at 30°C on dimethylsiloxane silicone rubber containing 33% silica filler[26]			
$\log L^{A} = 0.071 \pm 0.052 + (0.787 \pm 0.04)\log L^{16}$	8	0.131	0.9886
B Values of $\log L$ at 30°C and ΔH on dimethylsiloxane silicone rubber containing 25% silica filler[27]			
$\log L^{B} = -0.118 \pm 0.265 + (0.918 \pm 0.112)\log L^{16}$	8	0.162	0.9583
$\Delta H^{B} = 0.38 \pm 1.52 - (3.22 \pm 0.64)\log L^{16}$	8	0.93	0.8982
C Values of $\log L$ at 37°C and ΔH on oil[28]			
$\log L^{C} = -0.156 \pm 0.067 + (1.006 \pm 0.034)\log L^{16}$	16	0.165	0.9918
$\Delta H^{C} = 2.05 \pm 0.34 - (2.44 \pm 0.18)\log L^{16}$	16	0.84	0.9655
D Values of $\log S$ in ml (s.t.p.) cm^{-3} $\mathrm{cmHg}^{-1} \times 10^{4}$ at 25°C and ΔH on poly-*cis*-isoprene 'natural rubber'[17]			
$\log S^{D} = 1.961 \pm 0.031 + (1.073 \pm 0.036)\log L^{16}$	12	0.098	0.9945
$\Delta H^{D} = -2.37 \pm 0.42 - (1.70 \pm 0.47)\log L^{16}$	12	1.29	0.7526
E Values of $\log S$ in ml (s.t.p.) cm^{-3} $\mathrm{cmHg}^{-1} \times 10^{4}$ at 25°C and ΔH on branched polyethylene 'Althon 14'[17]			
$\log S^{E} = 1.504 \pm 0.016 + (0.976 \pm 0.018)\log L^{16}$	12	0.054	0.9983
$\Delta H^{E} = -0.40 \pm 0.14 - (1.81 \pm 0.16)\log L^{16}$	12	0.48	0.9619
F Values of $\log S$ in ml (s.t.p.) cm^{-3} $\mathrm{cmHg}^{-1} \times 10^{4}$ at 25°C and ΔH on linear polyethylene 'Grex'[17]			
$\log S^{F} = 1.127 \pm 0.018 + (0.941 \pm 0.021)\log L^{16}$	12	0.061	0.9976
$\Delta H^{F} = -1.45 \pm 0.13 - (1.72 \pm 0.15)\log L^{16}$	12	0.46	0.9627
G Values of $\log V_G$ on molten polystyrene in ml (s.t.p.) g^{-1} polymer at 175°C[29]			
$\log V_G^{G} = -0.742 \pm 0.166 + (0.512 \pm 0.066)\log L^{16}$	11	0.149	0.9318

The value for helium is quite out of line. Omission of this point gives $n = 11$, s.d. $= 0.96$ and $r = 0.8855$

given[12] are 7.57, 7.65 and 8.25 kcal mol^{-1}*. Equation (11) is markedly better than the other two, and shows that the three main features of solute–(PEG) interactions are a dispersive–cavity term, a dipolar term, and a term corresponding to hydrogen-bond solute acidity (α_2). The β_2 term in equation (11) is statistically not significant. These conclusions are identical to those of Galin[12], based on equation (3) covering 26 selected solutes.

Not only are ΔH_s values available for PEG, but also $\log V_G$ values were obtained by Galin[12] and by Klein and Jeberien[19] at 70°C, with V_G in $\mathrm{cm}^3\,\mathrm{g}^{-1}$. Of 34 recorded[12,19] values, explanatory variables are known for 31 assorted solutes including hydrogen-bond bases and hydrogen-bond acids. Regressions for all 31 solutes are

$$\log V_G = 0.45 \pm 0.40 + 0.087 \pm 0.027 \times 10^{24} P + 0.41 \pm 0.11\mu + 0.78 \pm 0.31\alpha_2 \qquad (12)$$

$$n = 31, \quad \text{s.d.} = 0.46, \quad r = 0.651$$

$$\log V_G = -0.43 \pm 0.22 + 0.57 \pm 0.06 \log L^{16} + 1.68 \pm 0.26(\pi_2^* - 0.08\delta_2) + 0.97 \pm 0.17\alpha_2 + 0.39 \pm 0.28\beta_2 \qquad (13)$$

$$n = 31, \quad \text{s.d.} = 0.24, \quad r = 0.927$$

$$\log V_G = -0.41 \pm 0.41 + 1.29 \pm 0.26 V_2/100 + 1.85 \pm 0.44(\pi_2^* + 0.08\,\delta_2) + 0.78 \pm 0.026\alpha_2 + 0.53 \pm 0.42\beta_2 \qquad (14)$$

$$n = 31, \quad \text{s.d.} = 0.36, \quad r = 0.821$$

Again, the $\log L^{16}$ equation yields much the better correlation, although by our usual standards $r = 0.927$ would be regarded as only a fair correlation value. Interestingly, although the signs of the coefficients in the $\log V_G$ and $-\Delta H_s$ correlations are the same, the magnitude of those in the $\log V_G$ correlations are lower by factors of 3 or 4. If the $\log V_G$ coefficients are multiplied by $2.303RT$, yielding a factor of 1.57, the scale of the coefficients is then the same, but still those in $2.303RT \log V_G$ are lower by a factor of just over 2. As is often the case, there is a partial compensation by the $T\Delta S_s^\circ$ term of ΔH_s. This is as expected, because any interactions that increase solubility (i.e. increase $\log V_G$) will give rise to negative ΔH_s values and to negative ΔS_s values due to loss of translational entropy on, for example, hydrogen-bond formation. However, the same factors that influence ΔH_s also influence $\log V_G$, namely solute dispersion–cavity effects, solute dipolarity, and solute hydrogen-bond acidity; again the β_2 term in equation (13) is not significant.

As mentioned in the introduction, equation (4) has been used[13] to correlate partial molal enthalpies of mixing, ΔH^∞ values. There is a fundamental difference between ΔH_s and ΔH^∞: the former refers to solution of a gas, equation (15), and the latter to solution of the liquid solute, equation (16)[19]

$$\text{solute (gas)} \xrightarrow{\Delta H_s} \text{solute (solution at zero concentration)} \qquad (15)$$

$$\text{solute (pure liquid)} \xrightarrow{\Delta H^\infty} \text{solute (solution at zero concentration)} \qquad (16)$$

Since there are no solute–solute interactions in the gaseous state, ΔH_s includes only solute–solvent effects. However, ΔH^∞ represents the difference between solute–solute effects in the pure liquid solute and solute–solvent effects in solution. There is therefore no comparison to be made between regression coefficients for ΔH_s and those for ΔH^∞. In our view, equation (8) and similar equations should really apply to ΔH_s because these equations contain no term that refers to solute–solute interactions.

However, there are further data sets on gas→solvent equilibria, as V_G values, to which equations (1) and (8) may be applied. In every case, equation (8) is superior to equation (1), and so we give results only in terms of the former equation. Dincer[20] has obtained V_G values for 34 solutes on poly(methyl methacrylate) at 150°C. Explanatory parameters are known for 29 solutes, the following equation being found:

$$\log V_G = -0.70 \pm 0.16 + 0.36 \pm 0.05 \log L^{16} + 1.40 \pm 0.15(\pi_2^* - 0.16\delta_2) + 0.73 \pm 0.17\alpha_2 - 0.18 \pm 0.18\beta_2 \qquad (17)$$

$$n = 29, \quad \text{s.d.} = 0.13, \quad r = 0.9327$$

Note that the term in β_2 is statistically not significant.

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* Note that in all cases we took a strict average of the quoted[12] values.

Several workers have measured $\log V_G$ values for solutes on poly(vinyl acetate) at various temperatures. Ward *et al.*[21] have collected and analysed results in terms of the quantity T_c/T, where T_c is the solute critical temperature, and T is the experimental temperature. The regression takes the form

$$\log V_G = a + b(T_c/T)^2 \tag{18}$$

and Ward *et al.*[21] found good correlations provided that solutes were grouped into families. Thus for 21 strongly polar solutes (95 data points)* $r = 0.9916$, for 5 aromatic solutes (44 data points) another regression equation with different slopes and intercepts gives $r = 0.9984$, and for a third different regression equation for 16 non-polar and non-aromatic solutes (53 data points) $r = 0.9388$. Although equations such as (18) are useful for the prediction of V_G values, they are clearly not general equations and cannot yield information about solute–polymer interactions. Out of the 42 solutes studied by Ward *et al.*[21], we have obtained from the references given by Ward *et al.*[21] values of V_G for 38 solutes, all at 135°C. Without selecting any families of solutes at all, we applied our general equation to the solubility data at 135°C to yield the following regression equation:

$$\begin{aligned}\log V_G = & -0.64 \pm 0.08 + 0.38 \pm 0.02 \log L^{16} \\ & + 1.32 \pm 0.16(\pi_2^* - 0.01\delta_2) + 1.19 \pm 0.19\alpha_2 \\ & + 0.36 \pm 0.21\beta_2 \end{aligned} \tag{19}$$

$$n = 38, \quad \text{s.d.} = 0.15, \quad r = 0.9710$$

As found above in other correlations of solubility data on polymers, the s.d. and r values in equations (17) and (19) are poor by our usual standards. However, experimental errors in the determinations appear to be larger than expected. For example, five determinations of $\log V_G$ for cyclohexane solute yield s.d. = 0.14 at 135°C, and seven such determinations for benzene solute give an s.d. of 0.09. Bearing in mind that errors in $\log V_G$ may average as much as 0.1 unit, equations (17) and (19) are probably as good as expected for 'all-solute' correlations. Since Ward *et al.*[21] give no numerical data, we list in *Table 3* the $\log V_G$ values at 135°C that we have used.

A rather different polymer has been studied by Dangayach and Bonner[22], who measured V_G° in ml g^{-1} for 34 solutes at 150°C and 31 solutes at 170°C on polysulphone. Of these solutes, explanatory variables are available for 30 using $\log L^{16}$, the regression at 150°C being given by

$$\begin{aligned}\log V_G = & -0.45 \pm 0.19 + 0.103 \pm 0.62 \log L^{16} + 0.79 \\ & \pm 0.17(\pi_2^* + 0.43\delta_2) + 0.03 \pm 0.12\alpha_2 + 0.67 \pm 0.19\beta_2 \end{aligned} \tag{20}$$

$$n = 30, \quad \text{s.d.} = 0.16, \quad r = 0.906$$

These results are unusual in that the dispersion–cavity term $\log L^{16}$ is statistically not significant, the main interactions involving solute dipolarity (π_2^*) and hydrogen-bond basicity (β_2).

Copolymers can also be included in our system: Dincer and Bonner[23] have obtained V_G values for 43 solutes at 150 and 161°C on an ethylene–vinyl acetate copolymer containing 29 wt% vinyl acetate. Explanatory variables are available for most of the solutes; the regression equation at 150°C is:

$$\begin{aligned}\log V_G = & -0.23 \pm 0.09 + 0.428 \pm 0.028 \log L^{16} + 0.46 \\ & \pm 0.07(\pi_2^* + 0.05\delta_2) + 0.13 \pm 0.06\alpha_2 - 0.13 \pm 0.09\beta_2 \end{aligned} \tag{21}$$

$$n = 37, \quad \text{s.d.} = 0.09, \quad r = 0.958$$

GENERAL DISCUSSION

Of the two general regression equations, (1) and (8), that we have used, equation (8) is always superior. Although equation (1) may be useful in predicting $\log V_G$ or other solubility values for gaseous solutes on polymers, we limit this discussion to the use of equation (8), as a general equation, and to the use of the restricted equation (6).

For non-dipolar solutes on any non-aqueous solvent, and for solutes of rather low dipolarity on rather low dipolarity solvents, the simple equation (6) represents a reasonably accurate method of correlating and predicting gaseous solubilities. The only explanatory variable used, $\log L^{16}$, reflects a combination of cavity and dispersion terms.

A summary of the coefficients in equation (8) for the polymers studied here, and for some non-polymeric solvent phases[18], is presented in *Table 4*. Of the materials listed, all are either monomer liquids or rubbery polymers above the glass transition temperature, with the exception of poly(sulphone) which has a T_g value of about 190°C[22]. We should point out that our approach is unambiguous for solution of solutes in non-polymeric liquids and in rubbery polymers, but would not be expected to apply to the solution of solutes (especially small solutes) in glassy polymers[24,25]. The presence of 'free sites' in glassy polymers can lead to enhanced solubility of small solutes. Furthermore, because the glassy polymer contains packing defects that provide these 'free sites', the dependence of solubility on the cavity dispersion term would be expected to be much less than for solution in rubbery polymers or in non-polymeric liquids. This is certainly so for the glassy polymer, poly(sulphone), where the $l \log L^{16}$ term is small and only just statistically significant. We therefore exclude poly(sulphone) from this general discussion on our approach based on equation (8).

The cavity–dispersive interaction term $l \log L^{16}$ is lower than unity for all the solvent phases, but the effect of temperature differences is not known. At any given temperature, cavity effects will be negative and dispersion effects positive, the balance between the two giving rise to larger or smaller net values of l. The $s\pi_2^*$ term represents dipolarity contributions of the dipole–dipole or dipole–induced-dipole type: the larger the value of s the more dipolar is the solvent phase. The polymeric phases are usually quite dipolar, cf. the triester, olive oil[18]. If the solvent phase is itself a hydrogen-bond base, then acid–base interactions will occur with acidic solutes, as shown by the $a\alpha_2$ term. As expected for polyethers or polyesters, all the polymers act as hydrogen-bond bases, to about the same extent as the triester, olive oil. The general chemical sense of our equation (8) is shown by the near-zero coefficient b in the $b\beta_2$ term. This term will arise through

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* The number of data points is much larger than the number of solutes, because each $\log V_G$ measurement at each temperature is a new data point.

Table 3 Solute parameters and values of log V_G for gaseous solutes on poly(vinyl acetate) at 135°C

Solute	δ_2	π_2^*	α_2	β_2	log L^{16}	$V/100$	log V_G
Methanol	0.000	0.400	0.330	0.400	0.922	0.405	1.032
Ethanol	0.000	0.400	0.330	0.450	1.485	0.584	1.218
1-Propanol	0.000	0.400	0.330	0.450	2.097	0.748	1.435
2-Propanol	0.000	0.400	0.330	0.510	1.821	0.765	1.030
1-Butanol	0.000	0.400	0.330	0.450	2.601	0.915	1.441
Cyclohexanol	0.000	0.400	0.330	0.510	3.671	1.140	1.997
n-Hexane	0.000	0.000	0.000	0.000	2.668	1.307	0.310
n-Heptane	0.000	0.000	0.000	0.000	3.173	1.465	0.530
Ethane	0.000	0.000	0.000	0.000	0.492	0.660	−0.579
Ethene	0.000	0.080	0.000	0.080	0.289		−0.503
n-Octane	0.000	0.000	0.000	0.000	3.677	1.626	0.922
n-Nonane	0.000	0.000	0.000	0.000	4.182	1.787	0.919
n-Decane	0.000	0.000	0.000	0.000	4.686	1.949	1.114
n-Undecane	0.000	0.000	0.000	0.000	5.191	2.112	1.310
n-Dodecane	0.000	0.000	0.000	0.000	5.696	2.275	1.498
Cyclohexane	0.000	0.000	0.000	0.000	2.913	1.180	0.673
Benzene	1.000	0.590	0.000	0.100	2.803	0.989	1.137
Toluene	1.000	0.540	0.000	0.110	3.344	1.163	1.343
PhCl	1.000	0.710	0.000	0.070	3.640	1.118	1.777
1,2-Dichloroethane	0.500	0.810	0.000	0.100	2.573	0.787	1.356
$CHCl_3$	0.500	0.580	0.050	0.100	2.480	0.805	1.179
CCl_4	0.500	0.280	0.000	0.100	2.823	0.968	0.953
n-BuCl	0.000	0.450	0.000	0.100	2.722	1.044	0.909
PhBu-n	1.000	0.420	0.000	0.120	4.686	1.661	1.834
Dioxan	0.000	0.550	0.000	0.740	2.797	0.953	1.576
THF	0.000	0.580	0.000	0.550	2.534	0.911	1.091
2-Propanone	0.000	0.710	0.000	0.480	1.760	0.734	0.972
2-Butanone	0.000	0.670	0.000	0.480	2.287	0.895	1.147
Acetaldehyde	0.000	0.670	0.000	0.420	1.230	0.566	0.708
MeCOOH	0.000	0.450	0.710	0.540	3.290	0.572	1.970
Cyclohexanone	0.000	0.760	0.000	0.530	3.420	1.135	1.951
Ethyl acetate	0.000	0.550	0.000	0.450	2.376	0.978	1.132
n-Butyl acetate	0.000	0.500	0.000	0.450	3.379	1.316	1.396
MeCN	0.000	0.750	0.000	0.370	1.560	0.521	1.311
$EtNO_2$	0.000	0.820	0.000	0.250	2.367	0.715	1.664
2,2,4-Trimethylpentane	0.000	0.000	0.000	0.000	3.120	1.651	0.500
1-Heptene	0.000	0.080	0.000	0.070	3.063	1.409	0.816
MeCl	0.000	0.400	0.000	0.100	1.163	0.551	0.387
Vinyl chloride	0.000	0.550	0.000	0.450		0.924	1.035

Table 4 Coefficients in the general solubility equation (8) for log S or log V_G on polymer phases

Solvent phase	t (°C)	$l \log L^{16}$	$s\pi_2^*$	$a\alpha_2$	$b\beta_2$
n-Hexadecane[a]	25	1	0	0	0
Olive oil[b]	37	0.84	0.68	1.10	(0.19)
Poly(ethylene oxide)[c]	70	0.57	1.68	0.97	(0.39)
Poly(methyl methacrylate)[c]	150	0.36	1.40	0.73	(0.18)
Poly(vinyl acetate)[c]	135	0.38	1.32	1.19	(0.36)
Poly(sulphone)[c]	150	(0.10)	0.79	(0.03)	0.67
Poly(sulphone)[c]	170	0.10	0.52	(0.13)	0.81
Ethylene-vinyl acetate[c]	150	0.43	0.46	0.13	−(0.13)
Ethylene-vinyl acetate[c]	161	0.38	0.42	(0.10)	−(0.11)

[a] By definition
[b] From reference 18
[c] This work

hydrogen-bonding of solute bases with hydrogen-bond acid solvents. Since none of the solvent phases in *Table 4* possesses acidic groups, the *b* coefficient should be zero, as observed within statistical error.

The general equation (8) thus provides a quantitative assessment, through the coefficients *l*, *s*, *a* and *b*, of the magnitude of solute–solvent interactions as well as of the nature of the interactions. Regressions using equation (8) reproduce experimental log V_G values, or other measures of gas solubility, with a standard deviation that approaches the experimental error of the measurements, and hence can be used to predict further log V_G or other values for solutes with known solvatochromic parameters.

Finally, but very importantly, we show that correlation equations used to investigate the solubility of gaseous solvents in non-polymeric solvents are applicable as such to a variety of polymeric materials. It is now possible, as we shall do in the future, to compare interactions between solutes and (rubbery) polymers with those between solutes and pure solvents in a qualitative and quantitative manner.

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