Hydrogen Bonding. Part 34. The Factors that Influence the Solubility of Gases and Vapours in Water at 298 K, and a New Method for its Determination

Michael H. Abraham,[a] Jenik Andonian-Haftvan,[a] Gary S. Whiting,[a] Albert Leo[b] and Robert S. Taft[c]
[a] *Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ*
[b] *Seaver Chemistry Laboratory, Pomona College, Claremont, CA 91711, USA*
[c] *Department of Chemistry, University of California, Irvine, CA 92717, USA*

The solubility of 408 gaseous compounds in water at 298 K has been correlated through eqn. (i), where the solubility is expressed as the Ostwald solubility coefficient, L^{w}, and the solute explanatory variables are R_2 an excess molar refraction, π_2^{H} the dipolarity/polarizability, $\Sigma\alpha_2^{H}$ and $\Sigma\beta_2^{H}$ the effective hydrogen-bond acidity and basicity, and V_x the McGowan characteristic volume. A similar equation using the log L^{16} parameter instead of V_x can also be used; L^{16} is the Ostwald solubility coefficient on hexadecane at 298 K.

$$\log L^{w} = -0.994 + 0.577R_2 + 2.549\,\pi_2^{H} + 3.813\Sigma\alpha_2^{H} + 4.841\Sigma\beta_2^{H} - 0.869\,V_x \qquad \text{(i)}$$

$$n = 408 \quad \rho = 0.9976 \quad \text{sd} = 0.151 \quad F = 16\,810$$

The main factors leading to increased solubility are solute π_2^{H}, $\Sigma\alpha_2^{H}$ and $\Sigma\beta_2^{H}$ values; conversely, the corresponding properties of water are dipolarity/polarizability, hydrogen-bond basicity and hydrogen-bond acidity. Solute size plays a minor role, and slightly decreases solubility, contrary to observations on all non-aqueous solvents. It is shown that this peculiar behaviour of water is due to (*a*) a greater increase in the unfavourable cavity effect with increase in solute size, for solvent water, and (*b*) a smaller increase in the favourable general dispersion interaction with size, for solvent water.

A new method for the determination of log L^{w} values is put forward, using the relationship $L^{w} = L^{16}/P$ where L^{16} is as above, and P is either the water–hexadecane partition coefficient or the water–alkane partition coefficient. For 14 solutes using the former P-value, agreement with values calculated through eqn. (i) is 0.08 log units on average and for 45 solutes using the latter P-value, the corresponding agreement is 0.15 log units, with log L^{w} values ranging up to 8 log units.

The solubility of non-electrolytes in water at ambient temperatures is not only of theoretical interest, but is of very considerable practical importance in such diverse areas as drug design,[1] environmental studies,[2] and olfactometry.[3] From the point of view of solute–solvent, *i.e.*, solute–water, interactions, it is necessary to differentiate between the solubility of liquids or solids on the one hand, and gases or vapours* on the other. The solubility of a liquid or a solid in water will not only involve solute–water and water–water interactions but also solute–solute interactions in the bulk liquid or solid. Hence the study of the solubility of gases will enable deductions about solute–solvent interactions to be made much more easily than from solubility studies made on liquids or solids. Indeed, quite different effects are often exhibited in the two systems. Thus Amidon and Anik[4] showed that there was quite a good connection between the solubility of aliphatic, aromatic and alkylaromatic hydrocarbons in water, as the pure (super cooled) liquids, and total surface area (TSA), but that there was almost no general connection between the solubility of the gaseous solutes and TSA. Privalov and Gill[5] observed that for the solubility of liquid non-polar non-electrolytes in water, the entropy of solution was always zero at a common temperature of around 413 K, but no such common temperature is found for the entropy of solution of gaseous non-polar non-electrolytes in water.[6] Even more relevant is the work of Kamlet *et al.*[7] on the solubility of liquid non-electrolytes in water. These workers showed that the two main factors influencing the solubility were the solute hydrogen-bond basicity and the solute volume, with solute hydrogen-bond acidity playing an insignificant role. Abraham *et al.*,[8] however, found that for the solubility of gaseous non-electrolytes in water a provisional equation had to include the solute hydrogen-bond acidity as a major term. We shall refer to this later, but point out now that the lack of hydrogen-bond acidity as an influence on the solubility of liquids in water is due to compensation between hydrogen-bond interactions within the bulk liquid acidic non-electrolytes and interactions of the solute hydrogen-bond acid–water hydrogen-bond base type. Only by consideration of the gaseous solubilities are the latter interactions correctly identified.

We therefore consider only the solubility of gaseous non-electrolytes in water at 298 K, in terms of the Ostwald solubility coefficient, eqn. (1). For solubility in water itself we use the term

$$L = \frac{\text{concentration of solute in solution}}{\text{concentration of solute in the gas phase}} \qquad (1)$$

L^{W}. As regards any regression equations for a series of solutes in water at 298 K, the standard states used affect only the intercept; we favour L^{W} only because Abraham and Fuchs *et al.*[9] list numerous L^{W} values that we shall make use of. Values of L^{W} can be obtained through direct measurement of vapour–liquid equilibria, but also by determination of the solubility of

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* We shall use the term 'gases' henceforth to refer to both permanent gases and the vapours of compounds that are liquids or solids at 298 K.

sparingly soluble liquids or solids, C_W. Then the concentration of solute in the gas phase is effectively that at the solute-saturated vapour pressure, P^o, so that the gas-phase solute concentration in mol dm^{-3} at 298 K is given by $C_G = P^o/24.45$; then L^W is calculated as C_W/C_G. Another indirect method (see later) involves combination of the water–hexadecane partition coefficient, P^{16}, with the gas–hexadecane partition coefficient (or Ostwald solubility coefficient), L^{16}, eqn. (2).

$$L^W = L^{16}/P^{16} \qquad (2)$$

There have been a number of compilations of L^W values, including the early work of Hine and Mookerjee,[10] the extensive collection of Cabani *et al.*,[11] the more recent data of Abraham and Fuchs *et al.*,[9,12] and the evaluation of L^W for compounds of environmental interest by Mackay and Shiu.[13] A number of organosulfur compounds have been examined by Przyjazny *et al.*,[14] Wilhelm *et al.*[15] have detailed the solubility of a number of permanent gases in water, and Abraham and Matteoli the *n*-alkanes.[6] Rytting *et al.*[16] have given L^W values for several homologous series.[16]

Rather surprisingly, there have been few attempts to correlate and then to predict the solubility of gases in water. Nirmalakhandan and Speece[17] used a number of descriptors that could be calculated from molecular structure, and reproduced the solubility data with a standard error of 0.262 log units for 180 compounds. More recently Jurs *et al.*[18] correlated the solubility of 63 gases in water using five theoretically determined solute descriptors in a linear regression equation with a correlation coefficient (ρ) of 0.978, a standard deviation (sd) of 0.375 log units, and an *F*-statistic (*F*) of 250. It was suggested by Jurs *et al.*[18] that the factors influencing solubility of gases in water were related to solute bulk, lipophilicity, and polarity. Hine and Mookerjee[10] set out a group contribution scheme, and a bond contribution scheme for the estimation of log L^W values (unfortunately denoted as log γ). For the former scheme, 69 group contributions reproduced 292 log L^W values with sd = 0.12 log units, and for the latter scheme 34 bond contributions reproduced 263 log L^W values with sd = 0.42 log units. A group contribution scheme was also devised by Cabani *et al.*,[11] who used 28 group contributions to reproduce 209 log L^W values to within 0.09 log units, possibly the best system of estimation of log L^W ever reported.* Unfortunately, neither the group-contribution method nor the bond-contribution method leads to much understanding of the factors that influence the solubility of gases in water.

Our method is based on the linear solvation energy relationships (LSERs) of Abraham,[19] eqn. (3) and eqn. (4). The solute descriptors are R_2, an excess molar refraction,[20] π_2^H, the solute dipolarity/polarisability,[21–23] $\Sigma\alpha_2^H$, the effective hydrogen-bond acidity,[19,20,24] $\Sigma\beta_2^H$, the effective hydrogen-bond basicity,[19,20,24] log L^{16} where L^{16} is the gas–hexadecane partition coefficient at 298 K,[21–23,25] and V_X, the characteristic volume of McGowan.[26] The dependent variable is log SP where SP is some solubility-related property of a series of solutes in a given system. In the present work, SP is L^W.

$$\log \mathrm{SP} = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + l\log L^{16} \quad (3)$$

$$\log \mathrm{SP} = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + vV_X \quad (4)$$

The constants or coefficients in eqn. (3) and eqn. (4) are obtained by the method of multiple linear regression analysis. Because of the way the descriptors in eqn. (3) and eqn. (4) have been formulated, these constants can be identified with particular properties of the solvent phase in question.[19] Thus *r* is the ability of the solvent to interact with π- and n-electron pairs, *s* is the solvent dipolarity/polarizability, *a* is the solvent hydrogen-bond basicity, *b* is the solvent hydrogen-bond acidity, *l* is the ability of a phase to distinguish between or to separate homologues, and *v* is the phase lipophilicity.[19] Generally, eqn. (3) is best applied to gas-condensed phase processes, and eqn. (4) to processes within condensed phases. Applications of eqn. (3) have included the characterisation of gas liquid chromatographic stationary phases,[27,28] the characterisation of solid adsorbents,[29] studies of the solubility of gases in polymers,[30] in soybean oil,[31] and in some common solvents,[32] and the selection of coatings for piezoelectric sorption detectors.[33] Eqn. (4) has been applied to a number of water–solvent partition coefficients,[34] and in a slightly modified earlier version to aqueous anaesthesia and the inhibition of firefly luciferase activity.[35]

It is the purpose of the present work to apply eqn. (3) and eqn. (4) to the solubility of a wide range of gases in water at 298 K in order to set up equations for the prediction of further log L^W values, and to analyse quantitatively the factors that influence the solubility of gases in water.

Results and Discussion

In Table 1 are set out calculations of L^W from solubilities in water, and solute-saturated vapour pressures, for the solid or liquid solute as appropriate. The method has often been used before,[10,13] but depends crucially on the availability of sufficiently good vapour pressure data. Solid or liquid solubilities were from a number of sources,[4,13,36–39] as were the vapour pressures,[4,13,40,41] care being taken to use only vapour pressures that were felt to be reliable.

Some years ago, Abraham and Fuchs *et al.*[9] calculated a number of water–hexadecane partition coefficients from known values of L^W and L^{16} through eqn. (2). Since then, a detailed analysis of various water–alkane partition coefficients has shown that eqn. (2) can, indeed, be used to obtain reliable values of P^{16}. But eqn. (2) can also be used to obtain L^W values from known values of L^{16} and P^{16}. To our knowledge, this is a new method of obtaining L^W values. Some results are in Table 2, mostly for aromatic compounds. The method can be greatly extended through the observation[34] that water–hexadecane and water–alkane partition coefficients are virtually identical, with the latter P^{alk} values obtained from various water–alkane systems. Then if $L^W = L^{16}/P^{alk}$, a new set of partition coefficients,[34,42] is available for the calculation of L^W values. Results are in Table 3, and lead to L^W values for a rather large number of aromatic compounds. Some of the L^W values, as log L^W, are very large, for example 7.54 (4-nitroaniline), 7.97 (4-nitrophenol) and 8.07 (benzamide), and would be extremely difficult to obtain by any direct method. Comparisons of the observed log L^W values by the indirect method, with calculated log L^W values using the LSER eqn. (4) are in Tables 2 and 3, and indicate that the indirect method is a useful and convenient way of obtaining log L^W values. Indeed, for rather involatile compounds we feel that the new method may be generally the most practical method of determining log L^W. The average deviation between determined and calculated values of log L^W is only 0.08 units for the 14 solutes in Table 2, and is 0.13 log units for the 42 solutes in Table 3, where the determined log L^W values go up to nearly 8 log units.

The final list of the 408 log L^W values we have used is in Table 4. This represents the largest collection of log L^W values ever reported, even though we have deliberately excluded the known[6,15] values for the rare gases and the inorganic gases such

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* The analysis of Cabani *et al.*[11] is in terms of the standard Gibbs energy of hydration, $\Delta_h G^o$, but conversion to log L^W is trivial. Note that Cabani *et al.*[11] tabulated some 350 log L^W values.

Table 1 Calculation of log L^W from solubility data, at 298 K

Solute	log C_W	log C_G	log L^W	log L^W(calc.)[a]
Styrene	−2.54[36]	−3.45[41]	0.91	1.10
α-Methylstyrene	−3.01[36]	−3.92[41]	0.91	1.10
4-Isopropyltoluene	−3.60[36]	−4.10[4.41]	0.50	0.41
1,2,3-Trimethylbenzene	−3.20[4,13]	−4.09[41]	0.89	0.91
1,2,4-Trimethylbenzene	−3.33[4,13]	−3.96[41]	0.63	0.75
1,3,5-Trimethylbenzene	−3.22[4.13]	−3.88[41]	0.66	0.64
Naphthalene	−3.61[13,14.37,38]	−5.37[13,40]	1.76	2.15
1-Methylnaphthalene	−3.70[4,13,37,38]	−5.49[13.40]	1.79	1.98
Biphenyl	−4.33[13.37]	−6.28[13]	1.95	2.23
Indane	−3.03[37]	−4.10[40]	1.07	0.99
1,2,3-Trichlorobenzene	−3.76[37]	−4.67[13]	0.91	0.85
1,3,5-Trichlorobenzene	−4.44[37]	−5.01[13]	0.57	0.49
Trifluoromethylbenzene	−2.51[13]	−2.69[13,41]	0.18	0.05

[a] Using eqn. (4) with the constants in Table 5A.

Table 2 Calculation of log L^W from water–hexadecane and gas–hexadecane partition coefficients at 298 K[a]

Solute	log P^{16}	log L^{16}	log L^W	log L^W(calc.)[b]
2-Ethoxyethanol	−2.10[c]	2.81	4.91	4.89
4-Methylacetophenone	1.63[d]	5.08	3.45	3.51
Benzonitrile	0.95[e]	4.04	3.09	3.10
o-Toluidine	0.38[d]	4.44	4.06	4.13
p-Toluidine	0.36[d]	4.45	4.09	4.18
2-Chloroaniline	1.07[d]	4.67	3.60	3.59
3-Chloroaniline	0.64[d]	4.91	4.27	4.20
4-Chloroaniline	0.56[d]	4.89	4.33	4.33
2-Methoxyaniline	0.33[d]	4.82	4.49	4.54
3-Methoxyaniline	−0.33[d]	5.02	5.35	5.44
4-Methoxyaniline	−0.54[d]	4.95	5.49	5.56
2-Nitroaniline	0.22[d]	5.63	5.41	5.21
4-Chloro-3-methylphenol	0.31[d]	5.29	4.98	4.78
2-Iodophenol	0.41[d]	4.96	4.55	4.66

[a] All values of log L^{16} from refs. 21–23 and 25. [b] Using eqn. (4) with the constants in Table 5A. [c] M. Manabe, M. Koda and K. Shirahama, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3553. [d] Ref. 9. [e] E. D. Katz, C. H. Lochmuller and R. P. W. Scott, *Anal. Chem.*, 1988, **61**, 349.

as hydrogen, nitrogen, oxygen, *etc*., and have restricted the log L^W values to compounds for which we have all the descriptors in eqn. (4).* Our reason for excluding the rare gas and inorganic gas data, is that Abraham[43] has already shown that the log L^W values for these compounds fall into a quite separate category to log L^W values for organic solutes (see Fig. 1 in ref. 43). The solute descriptors used in eqn. (3) and eqn. (4) are also in Table 4, and have been taken from previous compilations, as described above.[19–26]

Details of the regression equation, using eqn. (4) are in Table 5, where n is the number of solutes, ρ is the overall correlation coefficient, sd is the standard deviation, and F is the Fisher F-statistic. Also given are the standard deviations in the various coefficients of the equation. It can be seen that eqn. (4) can reproduce log L^W values for the 408 solutes to 0.15 log units. This is very much better than the equations of Nirmalakhandon and Speece[17] and of Jurs *et al.*,[18] and is comparable to the group estimation schemes of Hine and Mookerjee[10] (sd = 0.12 for 292 solutes) and for Cabani *et al.*[11] (sd = 0.09 for 209 solutes, and sd = 0.13 log units for 276 solutes). However, the LSER eqn. (4) is more flexible than the group (or bond) contribution method. For example, neither scheme[10,11] contains any group containing a phosphorus atom; hence no log L^W values for any phosphorus compound can be estimated. But the LSER method does not exclude compounds in this way. Providing that descriptors can be obtained, log L^W can be estimated, using eqn. (4), for any compound.

The alternative LSER, eqn. (3), was also applied to the log L^W values in Table 4, and results are in Table 5. Only 392 solutes are included, because out of the 408 total solutes, we lack log L^{16} values for 16. As a method of correlating and predicting log L^W values, eqn. (3) is not as useful as eqn. (4). First of all, the regression eqn. (4) is the better of the two, as can be seen in Table 5, and secondly, the V_X descriptor can be calculated for any molecular structure very simply, whereas the log L^{16} descriptor has to be determined by experiment.

Some years ago, Kamlet *et al.*[7,44] used an LSER similar to eqn. (4) to correlate the solubilities of liquids and solids in water. They observed that the solubility did not depend at all on the solute hydrogen-bond acidity, in contrast with our observations on the solubility of gases. These two sets of results are not incompatible. Any solute that is a hydrogen-bond acid will neary always be a hydrogen-bond base, and will be subject to inter- or intra-molecular acid/base hydrogen-bonding in the neat liquid or solid. The effect of hydrogen-bond acidity in stabilising the neat liquid or solid could well just cancel out the effect of hydrogen-bond acidity in stabilising the aqueous solution, thus leading to no apparent effect of solute hydrogen-bond acidity at all. This illustrates the difficulty of reaching any conclusions on solute–solvent interactions from studies on the solubility of liquids or solids.

Kamlet *et al.*[7] also found a marked difference in their LSER equations for the solubility of aliphatic or aromatic compounds, which they attributed, in part, to 'vertical stacking' of the

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* For completeness we give at the end of Table 4, values for the inorganic gases, and values for a number of extra organic compounds. The latter include some polyaromatic hydrocarbons that are outliers (see later), and a few additional compounds that were recent additions. The total number of compounds in Table 4 is 439.

Table 3 Calculation of log L^W from water–alkane and gas–hexadecane partition coefficients at 298 K[a]

Solute	log P^{alk}	log L^{16}	log L^W	log L^W(calc.)[b]
Triethyl phosphate	−0.78	4.75	5.53	5.48
4-Methylbenzaldehyde	1.46	4.59	3.13	3.21
Methyl benzoate	1.82	4.70	2.88	2.89
Ethyl benzoate	2.41	5.08	2.67	2.74
Benzonitrile	0.95	4.04	3.09	3.10
2,6-Dimethylaniline	1.21	5.03	3.82	3.87
3-Nitroaniline	−0.61	5.88	6.49	6.42
4-Nitroaniline	−1.20	6.34	7.54	7.16
1-Naphthylamine	1.06	6.49	5.34	5.67
2-Naphthylamine	1.15	6.54	5.48	5.70
N-Methylaniline	1.04	4.48	3.44	3.75
Benzamide	−2.30	5.77	8.07	7.67
2,3-Dimethylphenol	0.43	4.95	4.52	4.41
2,4-Dimethylphenol	0.36	4.77	4.41	4.52
2,5-Dimethylphenol	0.43	4.77	4.34	4.44
2,6-Dimethylphenol	0.82	4.68	3.86	3.97
3,4-Dimethylphenol	0.21	4.98	4.77	4.78
3,5-Dimethylphenol	0.26	4.86	4.60	4.62
3-Ethylphenol	0.15	4.74	4.59	4.76
4-Ethylphenol	0.24	4.74	4.50	4.68
4-*n*-Propylphenol	0.86	5.19	4.33	4.55
2-Fluorophenol	−0.43	3.45	3.88	4.04
4-Fluorophenol	−0.70	3.84	4.54	4.69
2-Chlorophenol	0.84	4.18	3.34	3.68
3-Chlorophenol	−0.08	4.77	4.85	4.81
4-Chlorophenol	−0.39	4.77	5.16	5.03
4-Bromophenol	−0.08	5.14	5.22	5.31
2-Methoxyphenol	0.36	4.45	4.09	4.32
3-Methoxyphenol	−0.82	4.80	5.62	5.79
2-Nitrophenol	1.40	4.76	3.36	3.43
1-Naphthol	0.50	6.13	5.63	5.68
2-Naphthol	0.25	6.20	5.95	5.91
Benzyl alcohol	−0.64	4.22	4.86	4.86
2-Phenylethanol	−0.35	4.63	4.98	5.12
3-Phenylpropanol	0.10	5.18	5.08	5.12
3-Cyanopyridine	−0.79	4.16	4.95	4.93
4-Cyanopyridine	−0.59	4.03	4.42	4.66
3-Formylpyridine	−1.18	4.03	5.21	5.39
4-Formylpyridine	−0.88	4.26	5.14	4.99
3-Acetylpyridine	−1.18	4.88	6.06	5.96
4-Acetylpyridine	−0.93	4.66	5.59	5.55
Quinoline	1.26	5.46	4.20	3.92
N-Methylpiperidine	0.56	3.33	2.77	2.70

[a] Values of log P^{alk} from refs. 34 and 42, and values of log L^{16} from refs. 21–23 and 25. [b] Using eqn. (4) with the constants in Table 5A.

aromatic compounds in the neat liquids. In particular, the coefficients of Kamlet's π and β parameters were substantially changed. For aliphatic compounds $s = 1.09$ and $b = 5.23$ but for aromatic compounds $s = 0.00$ and $b = 3.85$.* We therefore repeated the LSER eqn. (3) and eqn. (4), using separate aliphatic and aromatic data sets, Table 5. On eqn. (4), the nearest equation to Kamlet's LSER, the differences in π_2^H and β_2^H are nowhere near those reported by Kamlet *et al.*,[7] so that it is indeed possible that the large differences found by Kamlet *et al.*,[7] are due to interactions in the bulk liquids or solids.

However, in both eqn. (3) and eqn. (4) there are aliphatic–aromatic differences that are larger than the combined errors in the coefficients, especially with eqn. (3). One reason for this could simply be that the aliphatic and the aromatic solute sets are not well matched. In Table 6 are given details of the coefficients for the aliphatic set (Aliph) and the aromatic set (Arom). Not only are the ranges of some of the coefficients different in the two sets, but so also are the means of the coefficients as well. Bearing this in mind, the aliphatic–aromatic differences with eqn. (4) do not seem to be very important. There are, however, substantial differences in the *r*- and *s*-coefficients with eqn. (3), although we have no explanation as to why these differences are much more pronounced than with eqn. (4).

We can still use the 'all solute' regression equations to investigate the factors that influence the solubility of gaseous solutes in water at 298 K. The three main effects are solute dipolarity/polarizability, solute hydrogen-bond acidity and solute hydrogen-bond basicity that all bring about an increase in solubility, with the solute excess molar refraction also increasing solubility but to a lesser extent. Thus, conversely, we can say that bulk water is quite dipolar, and is a strong hydrogen-bond acid and a strong hydrogen-bond base. The *s*-constant, a measure of solvent dipolarity/polarizability, is just as large for water [2.55 on eqn. (4) and 2.74 on eqn. (3)] as for the amide *N*-formylmorpholine (2.57).[19] The *a*-constant which is a measure of solvent hydrogen-bond basicity is 3.81 or 3.90 for water, 4.32 for *N*-formylmorpholine,[19] and 3.74 for tri(2-ethylhexyl) phosphate.[19] From preliminary equations for the solubility of gases in methanol and ethanol,[45] the *a*-constant for water is a little larger than the *a*-constants for the alcohols, but the *b*-constant for water is very much larger than those for the alcohols. Hence bulk water is very basic, as seen also by the amide and phosphate comparisons, but is also very acidic,

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* The descriptors π and β were defined somewhat differently to our π_2^H and $\Sigma\beta_2^H$ descriptors, but for the present purpose we can take it that they describe similar solute properties.

Table 4 Values of log L^W at 298 K for solutes, and their descriptors

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x	log L^{16}	log L^W	Ref.
Methane	0.000	0.00	0.00	0.00	0.2495	−0.323	−1.46	6
Ethane	0.000	0.00	0.00	0.00	0.3904	0.492	−1.34	6
Propane	0.000	0.00	0.00	0.00	0.5313	1.050	−1.44	6
n-Butane	0.000	0.00	0.00	0.00	0.6722	1.615	−1.52	6
2-Methylpropane	0.000	0.00	0.00	0.00	0.6722	1.409	−1.70	9
n-Pentane	0.000	0.00	0.00	0.00	0.8131	2.162	−1.70	6
2-Methylbutane	0.000	0.00	0.00	0.00	0.8131	2.013	−1.75	11
2,2-Dimethylpropane	0.000	0.00	0.00	0.00	0.8131	1.820	−1.84	9
n-Hexane	0.000	0.00	0.00	0.00	0.9540	2.668	−1.82	6
2-Methylpentane	0.000	0.00	0.00	0.00	0.9540	2.503	−1.84	10
3-Methylpentane	0.000	0.00	0.00	0.00	0.9540	2.581	−1.84	10
2,2-Dimethylbutane	0.000	0.00	0.00	0.00	0.9540	2.352	−1.84	10
2,3-Dimethylbutane	0.000	0.00	0.00	0.00	0.9540	2.495	−1.72	13
n-Heptane	0.000	0.00	0.00	0.00	1.0949	3.173	−1.96	6
2-Methylhexane	0.000	0.00	0.00	0.00	1.0949	3.001	−2.15	13
3-Methylhexane	0.000	0.00	0.00	0.00	1.0949	3.044	−1.99	13
2,2-Dimethylpentane	0.000	0.00	0.00	0.00	1.0949	2.796	−2.11	13
2,3-Dimethylpentane	0.000	0.00	0.00	0.00	1.0949	3.016	−1.85	13
2,4-Dimethylpentane	0.000	0.00	0.00	0.00	1.0949	2.809	−2.08	13
3,3-Dimethylpentane	0.000	0.00	0.00	0.00	1.0949	2.946	−1.88	13
n-Octane	0.000	0.00	0.00	0.00	1.2358	3.677	−2.11	6
3-Methylheptane	0.000	0.00	0.00	0.00	1.2358	3.510	−2.18	13
2,2,4-Trimethylpentane	0.000	0.00	0.00	0.00	1.2358	3.106	−2.12	13
2,3,4-Trimethylpentane	0.000	0.00	0.00	0.00	1.2358	3.481	−1.88	13
n-Nonane	0.000	0.00	0.00	0.00	1.3767	4.182	−2.30	13
2,2,5-Trimethylhexane	0.000	0.00	0.00	0.00	1.3767	3.567	−2.15	13
n-Decane	0.000	0.00	0.00	0.00	1.5176	4.686	−2.32	12
Cyclopropane	0.180	0.15	0.00	0.00	0.4227	1.314	−0.55	9
Cyclopentane	0.263	0.10	0.00	0.00	0.7045	2.477	−0.88	9
Methylcyclopentane	0.225	0.10	0.00	0.00	0.8454	2.816	−1.17	10
n-Propylcyclopentane	0.225	0.10	0.00	0.00	1.1272	3.803	−1.56	13
n-Pentylcyclopentane	0.220	0.10	0.00	0.00	1.4090		−1.87	13
Cyclohexane	0.305	0.10	0.00	0.00	0.8454	2.964	−0.90	9
Methylcyclohexane	0.244	0.10	0.00	0.00	0.9863	3.323	−1.25	10
cis-1,2-Dimethylcyclohexane	0.281	0.10	0.00	0.00	1.1272	3.795	−1.16	11
trans-1,4-Dimethylcyclohexane	0.191	0.10	0.00	0.00	1.1272	3.538	−1.55	13
Ethene	0.107	0.10	0.00	0.07	0.3474	0.289	−0.94	9
Propene	0.103	0.08	0.00	0.07	0.4883	0.946	−0.97	9
But-1-ene	0.100	0.08	0.00	0.07	0.6292	1.491	−1.01	9
Pent-1-ene	0.093	0.08	0.00	0.07	0.7701	2.047	−1.23	9
(*z*)-Pent-2-ene	0.141	0.08	0.00	0.07	0.7701	2.211	−0.96	13
3-Methylbut-1-ene	0.063	0.08	0.00	0.07	0.7701	1.910	−1.34	10
2-Methylbut-2-ene	0.159	0.08	0.00	0.07	0.7701	2.226	−0.96	10
Hex-1-ene	0.078	0.08	0.00	0.07	0.9110	2.572	−1.16	9
2-Methylpent-1-ene	0.090	0.08	0.00	0.07	0.9110	2.588	−1.08	11
Hept-1-ene	0.092	0.08	0.00	0.07	1.0519	3.063	−1.22	9
(*E*)-Hept-2-ene	0.119	0.08	0.00	0.07	1.0519		−1.23	13
Oct-1-ene	0.094	0.08	0.00	0.07	1.1928	3.568	−1.41	9
Non-1-ene	0.090	0.08	0.00	0.07	1.3337	4.073	−1.51	9
Buta-1,3-diene	0.320	0.23	0.00	0.10	0.5862	1.543	−0.45	15
2-Methylbuta-1,3-diene	0.313	0.23	0.00	0.10	0.7271	2.101	−0.50	10
2,3-Dimethylbuta-1,3-diene	0.352	0.23	0.00	0.14	0.8680	2.690	−0.29	10
Penta-1,4-diene	0.185	0.20	0.00	0.10	0.7271		−0.68	13
Hexa-1,5-diene	0.191	0.20	0.00	0.10	0.8680		−0.74	10
Cyclopentene	0.335	0.20	0.00	0.10	0.6615	2.402	−0.41	10
Cyclohexene	0.395	0.20	0.00	0.10	0.8024	3.021	−0.27	10
1-Methylcyclohexene	0.391	0.20	0.00	0.10	0.9433	3.483	−0.49	10
Cyclohepta-1,3,5-triene	0.764	0.46	0.00	0.18	0.8573	3.442	0.73	10
Propyne	0.183	0.25	0.13	0.15	0.4453	1.025	0.35	9
But-1-yne	0.178	0.23	0.13	0.15	0.5862	1.520	0.12	9
Pent-1-yne	0.172	0.23	0.13	0.10	0.7271	2.010	−0.01	9
Hex-1-yne	0.166	0.23	0.13	0.10	0.8680	2.510	−0.21	9
Hept-1-yne	0.160	0.23	0.13	0.10	1.0089	3.000	−0.44	9
Oct-1-yne	0.155	0.23	0.13	0.10	1.1498	3.521	−0.52	9
Tetrafluoromethane	−0.280	−0.20	0.00	0.00	0.3203	−0.800	−2.29	15
Chloromethane	0.249	0.43	0.00	0.08	0.3719	1.163	0.40	9
Dichloromethane	0.387	0.57	0.10	0.05	0.4943	2.019	0.96	9
Trichloromethane	0.425	0.49	0.15	0.02	0.6167	2.480	0.79	9
Tetrachloromethane	0.458	0.38	0.00	0.00	0.7391	2.823	−0.06	9
Chloroethane	0.227	0.40	0.00	0.10	0.5128	1.678	0.46	9
1,1-Dichloroethane	0.322	0.49	0.10	0.10	0.6352	2.316	0.62	9
1,2-Dichloroethane	0.416	0.64	0.10	0.11	0.6352	2.573	1.31	9
1,1,1-Trichloroethane	0.369	0.41	0.00	0.09	0.7576	2.733	0.14	9
1,1,2-Trichloroethane	0.499	0.68	0.13	0.08	0.7576	3.290	1.46	9
1,1,2,2-Tetrachloroethane	0.595	0.76	0.16	0.12	0.8800	3.803	1.81	9

Table 4 *Continued*

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x	log L^{16}	log L^W	Ref.
1,1,1,2-Tetrachloroethane	0.542	0.63	0.10	0.08	0.8800	3.641	0.94	9
Pentachloroethane	0.648	0.66	0.17	0.06	1.0024	4.267	1.02	9
1-Chloropropane	0.216	0.40	0.00	0.10	0.6537	2.202	0.24	9
2-Chloropropane	0.177	0.35	0.00	0.12	0.6537	1.970	0.18	9
1,2-Dichloropropane	0.371	0.60	0.10	0.11	0.7761	2.857	0.93	9
1,3-Dichloropropane	0.408	0.74	0.00	0.17	0.7761	3.101	1.39	9
1-Chlorobutane	0.210	0.40	0.00	0.10	0.7946	2.722	0.12	9
2-Chlorobutane	0.189	0.35	0.00	0.12	0.7946	2.540	0.00	9
2-Chloro-2-methylpropane	0.142	0.25	0.00	0.12	0.7946	2.217	−0.80	9
1,4-Dichlorobutane	0.413	0.95	0.00	0.17	0.9170		1.70	9
1-Chloropentane	0.208	0.40	0.00	0.10	0.9355	3.223	0.05	9
1-Chlorohexane	0.201	0.40	0.00	0.10	1.0764	3.777	0.00	9
1-Chloroheptane	0.194	0.40	0.00	0.10	1.2173	4.282	−0.21	9
1,1-Dichloroethane	0.362	0.34	0.00	0.05	0.5922	2.110	−0.18	9
(*Z*)-1,2-Dichloroethene	0.436	0.61	0.11	0.05	0.5922	2.439	0.86	10
(*E*)-1,2,-Dichloroethene	0.425	0.41	0.09	0.05	0.5922	2.278	0.57	9
Trichloroethene	0.524	0.40	0.08	0.03	0.7146	2.997	0.32	9
Tetrachloroethene	0.639	0.42	0.00	0.00	0.8370	3.584	−0.07	9
1-Chloroprop-2-ene	0.327	0.56	0.00	0.05	0.6106	2.109	0.42	9
Bromomethane	0.399	0.43	0.00	0.10	0.4245	1.630	0.60	9
Dibromomethane	0.714	0.67	0.10	0.10	0.5995	2.886	1.44	9
Tribromomethane	0.974	0.68	0.15	0.09	0.7745	3.784	1.56	9
Bromoethane	0.366	0.40	0.00	0.12	0.5654	2.120	0.54	9
1,2-Dibromoethane	0.747	0.76	0.10	0.17	0.7404		1.71	9
1-Bromopropane	0.366	0.40	0.00	0.12	0.7063	2.620	0.41	9
2-Bromopropane	0.332	0.35	0.00	0.14	0.7063	2.390	0.35	9
1-Bromobutane	0.360	0.40	0.00	0.12	0.8472	3.105	0.29	9
1-Bromo-2-methylpropane	0.337	0.37	0.00	0.12	0.8472	2.960	0.02	9
2-Bromo-2-methylpropane	0.305	0.25	0.00	0.14	0.8472	2.616	−0.62	9
1-Bromopentane	0.356	0.40	0.00	0.12	0.9881	3.611	0.07	9
1-Bromohexane	0.349	0.40	0.00	0.12	1.1290	4.130	−0.13	9
1-Bromoheptane	0.343	0.40	0.00	0.12	1.2699	4.663	−0.25	9
1-Bromooctane	0.339	0.40	0.00	0.12	1.4108	5.090	−0.38	9
Iodomethane	0.676	0.43	0.00	0.13	0.5077	2.106	0.65	11
Iodoethane	0.640	0.40	0.00	0.15	0.6486	2.573	0.54	9
1-Iodopropane	0.634	0.40	0.00	0.15	0.7895	3.130	0.39	9
1-Iodobutane	0.628	0.40	0.00	0.15	0.9304	3.628	0.18	9
1-Iodopentane	0.621	0.40	0.00	0.15	1.0713	4.130	0.10	9
1-Iodohexane	0.615	0.40	0.00	0.15	1.2122	4.620	−0.06	9
1-Iodoheptane	0.608	0.40	0.00	0.15	1.3531		−0.20	9
Halothane	0.102	0.38	0.15	0.03	0.7410	2.177	0.08	9
Teflurane	−0.070	0.21	0.20	0.00	0.6360	1.370	−0.37	9
Diethyl ether	0.041	0.25	0.00	0.45	0.7309	2.015	1.17	9
Di-*n*-propyl ether	0.008	0.25	0.00	0.45	1.0127	2.954	0.85	9
Diisopropyl ether	0.000	0.19	0.00	0.45	1.0127	2.482	0.39	9
Di-*n*-butyl ether	0.000	0.25	0.00	0.45	1.2945	3.924	0.61	9
Methoxyflurane	0.109	0.67	0.17	0.05	0.8700	2.864	0.82	9
Isoflurane	−0.240	0.50	0.10	0.10	0.8010	1.576	−0.07	9
Tetrahydrofuran	0.289	0.52	0.00	0.48	0.6223	2.636	2.55	9
2-Methyltetrahydrofuran	0.241	0.48	0.00	0.53	0.7632	2.820	2.42	11
2,5-Dimethyltetrahydrofuran	0.204	0.38	0.00	0.58	0.9041	2.980	2.14	11
Tetrahydropyran	0.275	0.47	0.00	0.55	0.8288	3.057	2.29	9
1,4-Dioxane	0.329	0.75	0.00	0.64	0.6810	2.892	3.71	11
Formaldehyde	0.220	0.70	0.00	0.33	0.2652	0.730	2.02	9
Acetaldehyde	0.208	0.67	0.00	0.45	0.4061	1.230	2.57	9
Propionaldehyde	0.196	0.65	0.00	0.45	0.5470	1.815	2.52	9
Butyraldehyde	0.187	0.65	0.00	0.45	0.6879	2.270	2.33	9
Isobutyraldehyde	0.144	0.62	0.00	0.45	0.6879	2.120	2.10	9
Pentanal	0.163	0.65	0.00	0.45	0.8288	2.851	2.22	9
Hexanal	0.146	0.65	0.00	0.45	0.9697	3.357	2.06	9
Heptanal	0.140	0.65	0.00	0.45	1.1106	3.865	1.96	9
Octanal	0.160	0.65	0.00	0.45	1.2515	4.361	1.68	9
Nonanal	0.150	0.65	0.00	0.45	1.3924	4.856	1.52	9
(*E*)-But-2-enal	0.387	0.80	0.00	0.49	0.6449	2.570	3.10	9
(*E*)-Hex-2-enal	0.404	0.80	0.00	0.45	0.7860	3.400	2.70	11
(*E*)-Oct-2-enal	0.400	0.80	0.00	0.45	1.0680		2.52	11
Propanone	0.179	0.70	0.04	0.51	0.5470	1.696	2.79	9
Butanone	0.166	0.70	0.00	0.51	0.6879	2.287	2.72	9
Pentan-2-one	0.143	0.68	0.00	0.51	0.8288	2.755	2.58	9
Pentan-3-one	0.154	0.66	0.00	0.51	0.8288	2.811	2.50	9
3-Methylbutan-2-one	0.134	0.65	0.00	0.51	0.8288	2.692	2.38	9
Hexan-2-one	0.136	0.68	0.00	0.51	0.9676	3.262	2.41	9
4-Methylpentan-2-one	0.111	0.65	0.00	0.51	0.9676	3.089	2.24	9
Heptan-2-one	0.123	0.68	0.00	0.51	1.1106	3.760	2.23	9
Heptan-4-one	0.113	0.66	0.00	0.51	1.1106	3.705	2.14	9

Table 4 *Continued*

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x	log L^{16}	log L^W	Ref.
Octan-2-one	0.108	0.68	0.00	0.51	1.2515	4.257	2.11	9
Nonan-2-one	0.119	0.68	0.00	0.51	1.3924	4.735	1.83	9
Nonan-5-one	0.103	0.66	0.00	0.51	1.3924	4.698	1.94	9
Decan-2-one	0.108	0.68	0.00	0.51	1.5333	5.245	1.72	9
Undecan-2-one	0.101	0.68	0.00	0.51	1.6742	5.732	1.58	9
Cyclopentanone	0.373	0.86	0.00	0.52	0.7202	3.221	3.45	9
Cyclohexanone	0.403	0.86	0.00	0.56	0.8611	3.792	3.60	9
Methyl formate	0.192	0.68	0.00	0.38	0.4648	1.285	2.04	9
Ethyl formate	0.146	0.66	0.00	0.38	0.6057	1.845	1.88	9
n-Propyl formate	0.132	0.63	0.00	0.38	0.7466	2.433	1.82	9
Isopropyl formate	0.091	0.60	0.00	0.40	0.7466	2.230	1.48	9
Isobutyl formate	0.095	0.60	0.00	0.40	0.8875	2.789	1.63	9
Isoamyl formate	0.092	0.60	0.00	0.40	1.0284	3.306	1.56	9
Methyl acetate	0.142	0.64	0.00	0.45	0.6057	1.911	2.30	9
Ethyl acetate	0.106	0.62	0.00	0.45	0.7466	2.314	2.16	9
n-Propyl acetate	0.092	0.60	0.00	0.45	0.8875	2.819	2.05	9
Isopropyl acetate	0.055	0.57	0.00	0.47	0.8875	2.546	1.94	9
n-Butyl acetate	0.071	0.60	0.00	0.45	1.0284	3.353	1.94	9
Isobutyl acetate	0.052	0.57	0.00	0.47	1.0284	3.161	1.73	9
n-Pentyl acetate	0.067	0.60	0.00	0.45	1.1693	3.844	1.84	9
Isoamyl acetate	0.051	0.57	0.00	0.47	1.1693	3.740	1.62	9
n-Hexyl acetate	0.056	0.60	0.00	0.45	1.3102	4.351	1.66	9
Methyl propanoate	0.128	0.60	0.00	0.45	0.7466	2.431	2.15	9
Ethyl propanoate	0.087	0.58	0.00	0.45	0.8875	2.807	1.97	9
n-Propyl propanoate	0.070	0.56	0.00	0.45	1.0284	3.338	1.79	9
n-Pentyl propanoate	0.050	0.56	0.00	0.45	1.3102	4.331	1.55	9
Methyl butanoate	0.106	0.60	0.00	0.45	0.8875	2.893	2.08	9
Ethyl butanoate	0.068	0.58	0.00	0.45	1.0284	3.271	1.83	9
n-Propyl butanoate	0.050	0.56	0.00	0.45	1.1693	3.783	1.67	9
Methyl pentanoate	0.108	0.60	0.00	0.45	1.0284	3.392	1.88	9
Ethyl pentanoate	0.049	0.58	0.00	0.45	1.1693	3.769	1.83	9
Methyl hexanoate	0.080	0.60	0.00	0.45	1.1693	3.874	1.83	9
Ethyl hexanoate	0.043	0.58	0.00	0.45	1.3102	4.251	1.64	9
Isobutyl isobutanoate	0.000	0.50	0.00	0.47	1.3102	3.885	1.24	9
Acetonitrile	0.237	0.90	0.04	0.33	0.4042	1.739	2.85	9
Propanonitrile	0.162	0.90	0.02	0.36	0.5451	2.082	2.82	9
1-Cyanopropane	0.188	0.90	0.00	0.36	0.6860	2.548	2.67	9
1-Cyanobutane	0.177	0.90	0.00	0.36	0.8269	3.108	2.58	9
Ammonia	0.139	0.35	0.14	0.62	0.2084	0.680	3.15	9
Methylamine	0.250	0.35	0.16	0.58	0.3493	1.300	3.34	9
Ethylamine	0.236	0.35	0.16	0.61	0.4902	1.677	3.30	9
n-Propylamine	0.225	0.35	0.16	0.61	0.6311	2.141	3.22	9
n-Butylamine	0.224	0.35	0.16	0.61	0.7720	2.618	3.11	9
n-Pentylamine	0.211	0.35	0.16	0.61	0.9129	3.139	3.00	9
n-Hexylamine	0.197	0.35	0.16	0.61	1.0538	3.655	2.90	9
n-Heptylamine	0.197	0.35	0.16	0.61	1.1947	4.166	2.78	9
n-Octylamine	0.187	0.35	0.16	0.61	1.3356	4.520	2.68	9
Cyclohexylamine	0.326	0.56	0.16	0.58	0.9452	3.796	3.37	9
Dimethylamine	0.189	0.30	0.08	0.66	0.4902	1.600	3.15	9
Diethylamine	0.154	0.30	0.08	0.68	0.7720	2.395	2.99	9
Di-*n*-propylamine	0.124	0.30	0.08	0.68	1.0538	3.351	2.68	9
Diisopropylamine	0.053	0.24	0.08	0.71	1.0538	2.893	2.36	9
Di-*n*-butylamine	0.107	0.30	0.08	0.68	1.3356	4.349	2.38	9
Trimethylamine	0.140	0.20	0.00	0.67	0.6311	1.620	2.35	9
Triethylamine	0.101	0.15	0.00	0.79	1.0538	3.040	2.36	9
Nitromethane	0.313	0.95	0.06	0.32	0.4237	1.892	2.95	9
Nitroethane	0.270	0.95	0.02	0.33	0.5646	2.414	2.72	9
1-Nitropropane	0.242	0.95	0.00	0.31	0.7055	2.894	2.45	9
2-Nitropropane	0.216	0.92	0.00	0.32	0.7055	2.550	2.30	9
1-Nitrobutane	0.227	0.95	0.00	0.29	0.8464	3.415	2.27	9
1-Nitropentane	0.212	0.95	0.00	0.29	0.9873	3.938	2.07	9
n-Butylacetamide	0.360	1.30	0.40	0.74	1.0695		6.83	*a*
N,*N*-Dimethylformamide	0.367	1.31	0.00	0.73	0.6468	3.173	5.73	*b*
Acetic acid	0.265	0.65	0.61	0.45	0.4648	1.750	4.91	9
Propanoic acid	0.233	0.65	0.60	0.45	0.6057	2.290	4.74	9
Butanoic acid	0.210	0.62	0.60	0.45	0.7466	2.830	4.66	9
Pentanoic acid	0.205	0.60	0.60	0.45	0.8875	3.380	4.52	9
3-Methylbutanoic acid	0.178	0.57	0.60	0.50	0.8875	3.140	4.47	9
Hexanoic acid	0.174	0.60	0.60	0.45	1.0284	3.920	4.56	9
Water	0.000	0.45	0.82	0.35	0.1673	0.260	4.64	9
Methanol	0.278	0.44	0.43	0.47	0.3082	0.970	3.74	9
Ethanol	0.246	0.42	0.37	0.48	0.4491	1.485	3.67	9
Propan-1-ol	0.236	0.42	0.37	0.48	0.5900	2.031	3.56	9
Propan-2-ol	0.212	0.36	0.33	0.56	0.5900	1.764	3.48	9
Butan-1-ol	0.224	0.42	0.37	0.48	0.7309	2.601	3.46	9

Table 4 *Continued*

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x	log L^{16}	log L^W	Ref.
2-Methylpropan-1-ol	0.217	0.39	0.37	0.48	0.7309	2.413	3.30	9
Butan-2-ol	0.217	0.36	0.33	0.56	0.7309	2.338	3.39	9
2-Methylpropan-2-ol	0.180	0.30	0.31	0.60	0.7309	1.963	3.28	9
Pentan-1-ol	0.219	0.42	0.37	0.48	0.8718	3.106	3.35	9
Pentan-2-ol	0.195	0.36	0.33	0.56	0.8718	2.840	3.22	9
Pentan-3-ol	0.218	0.36	0.33	0.56	0.8718	2.860	3.19	9
2-Methylbutan-1-ol	0.219	0.39	0.37	0.48	0.8718	3.011	3.24	9
3-Methylbutan-1-ol	0.192	0.39	0.37	0.48	0.8718	3.011	3.24	9
2-Methylbutan-2-ol	0.194	0.30	0.31	0.60	0.8718	2.630	3.25	9
Hexan-1-ol	0.210	0.42	0.37	0.48	1.0127	3.610	3.23	9
Hexan-3-ol	0.200	0.36	0.33	0.56	1.0127	3.343	2.98	9
2-Methylpentan-2-ol	0.169	0.30	0.31	0.60	1.0127	3.081	2.88	9
4-Methylpentan-2-ol	0.167	0.33	0.33	0.56	1.0127	3.179	2.74	9
2-Methylpentan-3-ol	0.207	0.33	0.33	0.56	1.0127	3.240	2.85	9
Heptan-1-ol	0.211	0.42	0.37	0.48	1.1536	4.115	3.09	9
Octan-1-ol	0.199	0.42	0.37	0.48	1.2950	4.619	3.00	9
Nonan-1-ol	0.193	0.42	0.37	0.48	1.4354	5.124	2.85	9
Decan-1-ol	0.191	0.42	0.37	0.48	1.5763	5.628	2.67	9
Cyclopentanol	0.427	0.54	0.32	0.56	0.7630	3.241	4.03	9
Cyclohexanol	0.460	0.54	0.32	0.57	0.9040	3.758	4.01	9
Cycloheptanol	0.513	0.54	0.32	0.58	1.0450	4.407	4.02	9
Prop-2-en-1-ol	0.342	0.44	0.44	0.47	0.5470	1.951	3.69	9
2-Methoxyethanol	0.269	0.50	0.30	0.84	0.6487	2.490	4.96	11
2-Ethoxyethanol	0.237	0.50	0.30	0.83	0.7900	2.815	4.91	Table 2
2-Propoxyethanol	0.212	5.00	0.30	0.83	0.9310		4.70	11
2-Butoxyethanol	0.201	0.50	0.30	0.83	1.0720	3.806	4.59	11
2,2,2-Trifluoroethanol	0.015	0.60	0.57	0.25	0.5022	1.224	3.16	11
HFP	−0.240	0.55	0.77	0.10	0.6962	1.392	2.76	11
Ethanethiol	0.392	0.35	0.00	0.24	0.5539	2.173	0.84	9
n-Propanethiol	0.385	0.35	0.00	0.24	0.6948	2.685	0.78	9
n-Butanethiol	0.382	0.35	0.00	0.24	0.8357	3.111	0.73	9
Diethyl sulfide	0.373	0.38	0.00	0.32	0.8357	3.104	1.07	9
Di-*n*-propyl sulfide	0.358	0.38	0.00	0.32	1.1175	4.120	0.94	9
Diisopropyl sulfide	0.328	0.32	0.00	0.37	1.1175	3.600	0.89	9
Diethyl disulfide	0.670	0.48	0.00	0.29	0.9990	4.210	1.20	9
Sulfur hexafluoride	−0.600	−0.20	0.00	0.00	0.4643	−0.120	−2.23	15
Triethyl phosphate	0.000	1.00	0.00	1.06	1.3934	4.750	5.53	Table 3
N-Methylpiperidine	0.318	0.34	0.00	0.70	0.9452	3.330	2.85	11
N-Acetylpyrrolidine	0.550	1.63	0.00	0.92	0.9609		7.19	*a*
Morpholine	0.434	0.79	0.06	0.91	0.7221		5.26	11
N-Methylmorpholine	0.333	0.74	0.00	0.90	0.8630		4.64	11
Benzene	0.610	0.52	0.00	0.14	0.7164	2.786	0.63	9
Toluene	0.601	0.52	0.00	0.14	0.8573	3.325	0.65	9
Ethylbenzene	0.613	0.51	0.00	0.15	0.9982	3.778	0.58	11
o-Xylene	0.663	0.56	0.00	0.16	0.9982	3.939	0.66	11
m-Xylene	0.623	0.52	0.00	0.16	0.9982	3.839	0.61	11
p-Xylene	0.613	0.52	0.00	0.16	0.9982	3.839	0.59	11
n-Propylbenzene	0.604	0.50	0.00	0.15	1.1391	4.230	0.39	11
Isopropylbenzene	0.602	0.49	0.00	0.16	1.1391	4.084	0.22	11
1,2,3-Trimethylbenzene	0.728	0.61	0.00	0.19	1.1391	4.565	0.89	Table 1
1,2,4-Trimethylbenzene	0.677	0.56	0.00	0.19	1.1391	4.441	0.63	Table 1
1,3,5-Trimethylbenzene	0.649	0.52	0.00	0.19	1.1391	4.344	0.66	Table 1
2-Ethyltoluene	0.680	0.55	0.00	0.18	1.1391	4.346	0.76	13
4-Ethyltoluene	0.630	0.51	0.00	0.18	1.1391	4.289	0.70	13
n-Butylbenzene	0.600	0.51	0.00	0.15	1.2800	4.730	0.29	10
Isobutylbenzene	0.580	0.47	0.00	0.15	1.2800	4.500	−0.12	13
sec-Butylbenzene	0.603	0.48	0.00	0.16	1.2800	4.506	0.33	10
tert-Butylbenzene	0.619	0.49	0.00	0.16	1.2800	4.413	0.32	13
4-Isopropyltoluene	0.607	0.49	0.00	0.19	1.2800	4.590	0.50	Table 1
n-Pentylbenzene	0.594	0.51	0.00	0.15	1.4209	5.230	0.17	9
n-Hexylbenzene	0.591	0.50	0.00	0.15	1.5618	5.720	0.03	9
Styrene	0.849	0.65	0.00	0.16	0.9552	3.856	0.91	Table 1
α-Methylstyrene	0.851	0.64	0.00	0.19	1.0961	4.292	0.91	Table 1
Biphenyl	1.360	0.99	0.00	0.22	1.3242	6.014	1.95	Table 1
Naphthalene	1.340	0.92	0.00	0.20	1.0854	5.161	1.76	Table 1
1-Methylnaphthalene	1.344	0.90	0.00	0.20	1.2263	5.789	1.79	Table 1
1,3-Dimethylnaphthalene	1.387	0.92	0.00	0.20	1.3672	6.236	1.81	11
1,4-Dimethylnaphthalene	1.400	0.91	0.00	0.20	1.3672	6.339	2.07	11
2,3-Dimethylnaphthalene	1.431	0.95	0.00	0.20	1.3672	6.291	2.04	11
2,6-Dimethylnaphthalene	1.329	0.91	0.00	0.20	1.3672	6.226	1.93	11
1-Ethylnaphthalene	1.371	0.87	0.00	0.20	1.3672	6.136	1.76	11
Indane	0.829	0.62	0.00	0.17	1.0305	4.590	1.07	Table 1
Acenaphthene	1.604	1.04	0.00	0.20	1.2586	6.469	2.31	11
Fluorene	1.588	1.03	0.00	0.20	1.3565	6.922	2.46	13
Fluorobenzene	0.477	0.57	0.00	0.10	0.7341	2.788	0.59	13

Table 4 *Continued*

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x	log L^{16}	log L^W	Ref.
Benzotrifluoride	0.225	0.48	0.00	0.10	0.9100	2.894	0.18	Table 1
Chlorobenzene	0.718	0.65	0.00	0.07	0.8388	3.657	0.82	11
1,2-Dichlorobenzene	0.872	0.78	0.00	0.04	0.9612	4.518	1.00	10
1,3-Dichlorobenzene	0.847	0.73	0.00	0.02	0.9612	4.410	0.72	10
1,4-Dichlorobenzene	0.825	0.75	0.00	0.02	0.9612	4.435	0.74	10
1,2,3-Trichlorobenzene	1.030	0.86	0.00	0.00	1.0836	5.419	0.91	Table 1
1,2,4-Trichlorobenzene	0.980	0.81	0.00	0.00	1.0836	5.248	0.82	13
1,3,5-Trichlorobenzene	0.980	0.73	0.00	0.00	1.0836	5.045	0.57	Table 1
1,2,3,4-Tetrachlorobenzene	1.180	0.92	0.00	0.00	1.2060	6.171	0.98	13
1,2,3,5-Tetrachlorobenzene	1.160	0.85	0.00	0.00	1.2060	5.922	1.19	13
1,2,4,5-Tetrachlorobenzene	1.160	0.86	0.00	0.00	1.2060	5.926	0.98	13
2-Chlorotoluene	0.762	0.65	0.00	0.07	0.9797	4.173	0.84	9
Bromobenzene	0.882	0.73	0.00	0.09	0.8914	4.041	1.07	9
4-Bromotoluene	0.879	0.74	0.00	0.09	1.0323	4.586	1.02	9
Iodobenzene	1.188	0.82	0.00	0.12	0.9746	4.502	1.28	9
Methyl phenyl ether	0.708	0.74	0.00	0.29	0.9160	3.890	1.80	9
Ethyl phenyl ether	0.681	0.70	0.00	0.32	1.0569	4.242	1.63	9
Benzaldehyde	0.820	1.00	0.00	0.39	0.8730	4.008	2.95	9
4-Methylbenzaldehyde	0.862	1.00	0.00	0.42	1.0139	4.592	3.13	Table 3
Acetophenone	0.818	1.01	0.00	0.49	1.0139	4.501	3.36	9
4-Methylacetophenone	0.842	1.00	0.00	0.52	1.1548	5.081	3.45	Table 2
Methyl benzoate	0.733	0.85	0.00	0.48	1.0726	4.704	2.88	Table 3
Ethyl benzoate	0.689	0.85	0.00	0.46	1.2135	5.075	2.67	Table 3
Benzonitrile	0.742	1.11	0.00	0.33	0.8711	4.039	3.09	Table 2
o-Toluidine	0.966	0.92	0.23	0.45	0.9571	4.442	4.06	Table 2
p-Toluidine	0.923	0.95	0.23	0.45	0.9571	4.452	4.09	Table 2
2,6-Dimethylaniline	0.972	0.89	0.20	0.46	1.0980	5.028	3.82	Table 3
2-Chloroaniline	1.033	0.92	0.25	0.31	0.9386	4.674	3.60	Table 2
3-Chloroaniline	1.053	1.10	0.30	0.30	0.9386	4.909	4.27	Table 2
4-Chloroaniline	1.060	1.13	0.30	0.32	0.9386	4.889	4.33	Table 2
2-Methoxyaniline	0.988	1.03	0.23	0.50	1.0158	4.818	4.49	Table 2
3-Methoxyaniline	1.027	1.22	0.25	0.55	1.0158	5.023	5.35	Table 2
4-Methoxyaniline	1.050	1.19	0.23	0.61	1.0158	4.949	5.49	Table 2
2-Nitroaniline	1.180	1.37	0.30	0.36	0.9904	5.627	5.41	Table 2
3-Nitroaniline	1.200	1.71	0.40	0.35	0.9904	5.880	6.49	Table 3
4-Nitroaniline	1.220	1.91	0.42	0.38	0.9904	6.343	7.54	Table 3
1-Naphthylamine	1.670	1.26	0.20	0.57	1.1850	6.490	5.34	Table 3
2-Naphthylamine	1.670	1.28	0.22	0.55	1.1850	6.540	5.48	Table 3
N-Methylaniline	0.948	9.00	0.17	0.43	0.9571	4.478	3.44	Table 3
N,*N*-Dimethylaniline	0.957	0.84	0.00	0.42	1.0980	4.701	2.53	9
Nitrobenzene	0.871	1.11	0.00	0.28	0.8906	4.557	3.02	9
2-Nitrotoluene	0.866	1.11	0.00	0.28	1.0315	4.878	2.63	9
3-Nitrotoluene	0.874	1.10	0.00	0.28	1.0315	5.097	2.53	9
Benzamide	0.990	1.50	0.49	0.67	0.9728	5.767	8.07	Table 3
Phenol	0.805	0.89	0.60	0.31	0.7751	3.766	4.85	11
o-Cresol	0.840	0.86	0.52	0.31	0.9160	4.218	4.31	9
p-Cresol	0.820	0.87	0.57	0.32	0.9160	4.312	4.50	9
2,3-Dimethylphenol	0.850	0.81	0.53	0.36	1.0569	4.952	4.52	Table 3
2,4-Dimethylphenol	0.843	0.80	0.53	0.39	1.0569	4.770	4.41	Table 3
2,5-Dimethylphenol	0.840	0.79	0.54	0.37	1.0569	4.774	4.34	Table 3
2,6-Dimethylphenol	0.860	0.79	0.39	0.39	1.0569	4.680	3.86	Table 3
3,4-Dimethylphenol	0.830	0.86	0.56	0.39	1.0569	4.980	4.77	Table 3
3,5-Dimethylphenol	0.820	0.84	0.57	0.36	1.0569	4.856	4.60	Table 3
3-Ethylphenol	0.810	0.91	0.55	0.37	1.0569	4.741	4.59	Table 3
4-Ethylphenol	0.800	0.90	0.55	0.36	1.0569	4.737	4.50	Table 3
4-*n*-Propylphenol	0.793	0.88	0.55	0.37	1.1978	5.185	4.33	Table 3
4-*tert*-Butylphenol	0.810	0.89	0.56	0.39	1.3387	5.264	4.34	9
2-Fluorophenol	0.660	0.69	0.61	0.26	0.7928	3.453	3.88	Table 3
4-Fluorophenol	0.670	0.97	0.63	0.23	0.7928	3.844	4.54	Table 3
2-Chlorophenol	0.853	0.88	0.32	0.31	0.8975	4.178	3.34	Table 3
3-Chlorophenol	0.909	1.06	0.69	0.15	0.8975	4.773	4.85	Table 3
4-Chlorophenol	0.915	1.08	0.67	0.21	0.8975	4.775	5.16	Table 3
4-Chloro-3-methylphenol	0.920	1.02	0.65	0.23	1.0384	5.290	4.98	Table 2
4-Bromophenol	1.080	1.17	0.67	0.20	0.9501	5.135	5.23	9
2-Iodophenol	1.360	1.00	0.40	0.35	1.0335	4.964	4.55	Table 2
2-Methoxyphenol	0.837	0.91	0.22	0.52	0.9747	4.449	4.09	Table 3
3-Methoxyphenol	0.879	1.17	0.59	0.38	0.9747	4.803	5.62	Table 3
3-Hydroxybenzaldehyde	0.990	1.38	0.74	0.40	0.9317		6.97	11
4-Hydroxybenzaldehyde	1.010	1.40	0.77	0.44	0.9317	5.533	6.48	11
3-Cyanophenol	0.930	1.55	0.77	0.28	0.9298	5.181	7.08	11
4-Cyanophenol	0.940	1.63	0.79	0.30	0.9298	5.420	7.46	11
2-Nitrophenol	1.015	1.05	0.05	0.37	0.9493	4.760	3.36	Table 3
3-Nitrophenol	1.050	1.57	0.79	0.23	0.9493	5.692	7.06	11
4-Nitrophenol	1.070	1.72	0.82	0.26	0.9493	5.876	7.81	11
1-Naphthol	1.520	1.05	0.61	0.37	1.1440	6.130	5.63	Table 3

Table 4 *Continued*

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	V_x	$\log L^{16}$	$\log L^W$	Ref.
2-Naphthol	1.520	1.08	0.61	0.40	1.1440	6.200	5.95	Table 3
Benzyl alcohol	0.803	0.87	0.33	0.56	0.9160	4.221	4.86	Table 3
2-Phenylethanol	0.811	0.91	0.30	0.65	1.0569	4.628	4.98	Table 3
3-Phenylpropanol	0.821	0.90	0.30	0.67	1.1978	5.180	5.08	Table 3
Thiophenol	1.000	0.80	0.09	0.16	0.8799	4.110	1.87	9
Phenyl methyl sulfide	1.068	0.92	0.00	0.26	1.0280	4.659	2.00	10
Pyridine	0.631	0.84	0.00	0.52	0.6753	3.022	3.44	9
2-Methylpyridine	0.598	0.75	0.00	0.57	0.8162	3.422	3.40	9
3-Methylpyridine	0.631	0.81	0.00	0.54	0.8162	3.631	3.50	9
4-Methylpyridine	0.630	0.82	0.00	0.55	0.8162	3.640	3.62	9
2,3-Dimethylpyridine	0.657	0.77	0.00	0.62	0.9571	4.045	3.54	9
2,4-Dimethylpyridine	0.634	0.76	0.00	0.63	0.9571	4.006	3.57	9
2,5-Dimethylpyridine	0.633	0.74	0.00	0.62	0.9571	3.986	3.46	9
2,6-Dimethylpyridine	0.607	0.70	0.00	0.62	0.9571	3.760	3.37	9
3,4-Dimethylpyridine	0.676	0.85	0.00	0.61	0.9571	4.317	3.83	9
3,5-Dimethylpyridine	0.659	0.79	0.00	0.60	0.9571	4.214	3.55	9
2-Ethylpyridine	0.613	0.70	0.00	0.59	0.9571	3.844	3.18	9
3-Ethylpyridine	0.640	0.79	0.00	0.57	0.9571	4.093	3.37	9
4-Ethylpyridine	0.634	0.80	0.00	0.57	0.9571	4.124	3.47	9
2-Chloropyridine	0.738	1.03	0.00	0.37	0.7977	3.875	3.22	11
3-Chloropyridine	0.732	0.83	0.00	0.41	0.7977	3.783	2.94	11
3-Cyanopyridine	0.750	1.26	0.00	0.62	0.8300	4.164	4.95	Table 3
4-Cyanopyridine	0.750	1.21	0.00	0.59	0.8300	4.033	4.42	Table 3
3-Formylpyridine	0.817	1.16	0.00	0.76	0.8319	4.258	5.21	Table 3
4-Formylpyridine	0.796	1.12	0.00	0.70	0.8319		5.14	Table 3
3-Acetylpyridine	0.795	1.17	0.00	0.90	0.9728	4.880	6.06	Table 3
4-Acetylpyridine	0.771	1.13	0.00	0.84	0.9728	4.660	5.59	Table 3
Quinoline	1.268	0.97	0.00	0.54	1.0443	5.457	4.20	Table 3
2-Methylpyrazine	0.629	0.86	0.00	0.67	0.7751	3.254	4.04	11
2-Ethylpyrazine	0.629	0.90	0.00	0.65	0.9160		4.00	11
2-Isobutylpyrazine	0.620	0.87	0.00	0.65	1.1978		3.70	11
Thiophene	0.687	0.56	0.00	0.15	0.6411	2.819	1.04	9
2-Methylthiophene	0.688	0.56	0.00	0.16	0.7820	3.308	1.01	9
Dimethyl ether	0.000	0.27	0.00	0.41	0.4491		1.40	*c* (1.29)[d]
Methyl ethyl ether	0.020	0.25	0.00	0.45	0.5900		1.54	*c* (1.32)[d]
Methyl *tert*-butyl ether	0.024	0.19	0.00	0.45	0.8718		1.62	*c* (0.92)[d]
3,3-Dimethylbutan-2-one	0.106	0.62	0.00	0.51	0.9697		2.28	*c* (2.27)[d]
2,4-Dimethylpentan-3-one	0.072	0.60	0.00	0.51	1.1106		2.01	11 (2.08)[d]
Methyl cyclopropyl ketone							3.38	*c*
Methyl cyclohexyl ketone							2.86	*c*
Methyl trimethylacetate	0.049	0.54	0.00	0.45	1.0284		1.76	*c* (1.70)[d]
Cyclopropyl CO_2Me							3.01	*c*
Cyclohexyl CO_2Me							2.42	*c*
Dimethyl sulfide	0.404	0.38	0.00	0.29	0.5540		1.18	11 (1.13)[d]
Methyl ethyl sulfide	0.390	0.38	0.00	0.28	0.6948		1.10	*c* (0.95)[d]
Dimethyl sulfoxide	0.522	1.74	0.00	0.88	0.6130		7.41	*c* (7.47)[d]
4-Methoxyacetophenone							3.23	*c*
N-Methylpiperidine	0.318	0.39	0.00	0.69	0.9452		2.77	Table 3 (2.73)[d]
Anthracene	2.290	1.34	0.00	0.26	1.4540	7.568	2.90	Table 10 (3.74)[d]
Phenanthrene	2.055	1.29	0.00	0.26	1.4540	7.632	2.85	Table 10 (3.48)[d]
Pyrene	2.808	1.71	0.00	0.29	1.5846	8.833	3.32	13 (5.01)[d]
Helium	0.000	0.00	0.00	0.00	0.0680	−1.741	−2.02	6
Neon	0.000	0.00	0.00	0.00	0.0850	−1.575	−1.96	6
Argon	0.000	0.00	0.00	0.00	0.1900	−0.688	−1.47	6
Krypton	0.000	0.00	0.00	0.00	0.2460	−0.211	−1.21	6
Xenon	0.000	0.00	0.00	0.00	0.3290	0.378	−0.97	6
Radon	0.000	0.00	0.00	0.00	0.3840	0.877	−0.65	6
Hydrogen	0.000	0.00	0.00	0.00	0.1086	−1.200	−1.72	*e*
Deuterium	0.000	0.00	0.00	0.00	0.1100	−1.200	−1.73	*e*
Oxygen	0.000	0.00	0.00	0.00	0.1830	−0.723	−1.51	*e*
Nitrogen	0.000	0.00	0.00	0.00	0.2222	−0.978	−1.80	*e*
Nitrous oxide	0.068	0.35	0.00	0.10	0.2810	0.164	−0.23	*e*
Carbon monoxide	0.000	0.00	0.00	0.04	0.2220	−0.836	−1.62	15
Carbon dioxide	0.150	0.42	0.00	0.10	0.2809	0.057	−0.08	15

[a] P. R. Gibbs, A. Radzicka and R. Wolfenden, *J. Am. Chem. Soc.*, 1991, **113**, 4714. [b] From vapour–liquid equilibria at 313 K by J. Zielkiewicz and A. Konitz, *J. Chem. Thermodyn.*, 1991, **23**, 59, using an enthalpy of liquid DMF of −3.92 kcal mol^{-1} from B. G. Cox, A. J. Parker and W. E. Waghorne, *J. Am. Chem. Soc.*, 1973, **95**, 1010. [c] A. Bagno, V. Lucchini and G. Scorrano, *J. Phys. Chem.*, 1991, **95**, 345. [d] Calculated values using eqn. (4) with the constants in Table 5A. [e] From the Solubility Data Project Series.

being a much stronger hydrogen-bond acid than the alcohols.[45]

A most unusual feature of eqn. (3) and eqn. (4) when applied to $\log L^W$ values, is the negative sign of the *l*- and the *v*-constant, indicating that for solubility in water of gases, the larger the gas the smaller (slightly) the solubility. This is quite unlike the situation for non-aqueous solvents, where invariably the larger the gas the larger is the solubility.[19,32,45] Thus the *l*-constant in

Table 5 Constants in the regression equations for log L^W, with their standard deviations

No.	Solute set	c	r	s	a	b	v	n	p	sd	f
A[a]	All solutes	−0.994	0.577	2.549	3.813	4.841	−0.869	408	0.997 6	0.151	16 810
		0.031	0.032	0.037	0.040	0.040	0.031				
B[a]	Aliphatic	−1.073	0.848	2.461	3.827	4.910	−0.817	266	0.997 4	0.145	9 863
		0.035	0.052	0.044	0.061	0.048	0.033				
C[a]	Aromatic	−0.982	0.367	2.819	3.724	4.630	−0.864	142	0.997 6	0.142	5 607
		0.096	0.067	0.073	0.056	0.070	0.087				
D[b]	All solutes	−1.271	0.822	2.743	3.904	4.814	−0.213[c]	392	0.996 2	0.185	10 229
		0.030	0.045	0.047	0.050	0.051	0.011				
E[b]	Aliphatic	−1.344	1.250	2.605	3.886	4.915	−0.203[c]	254	0.996 0	0.170	6 223
		0.034	0.065	0.054	0.073	0.059	0.011				
F[b]	Aromatic	−1.399	0.433	3.118	3.783	4.588	−0.168[c]	138	0.996 6	0.168	3 853
		0.091	0.100	0.082	0.068	0.068	0.030				

[a] Eqn. (4). [b] Eqn. (3). [c] Coefficient of log L^{16}.

Table 6 Maximum and minimum values of descriptors in aliphatic and aromatic subsets

	R_2		π_2^H		$\Sigma\alpha_2^H$		$\Sigma\beta_2^H$		V_x	
	Aliph.	Arom.	Aliph.	Arom.	Aliph.	Arom.	Aliph.	Arom.	Aliph.	Arom.
Max[a]	0.97	1.60	1.63	1.91	0.77	0.82	1.06	0.90	1.674	1.562
Min[a]	−0.60	0.23	−0.20	0.47	0.00	0.00	0.00	0.00	0.250	0.641
Mean[a]	0.21	0.88	0.42	0.89	0.08	0.17	0.31	0.33	0.866	1.024
Max[b]	0.97	1.67	1.31	1.91	0.77	0.82	1.06	0.90	5.732[c]	6.922
Min[b]	−0.60	0.23	−0.20	0.47	0.00	0.00	0.00	0.00	−0.800[c]	2.786
Mean[b]	0.21	0.88	0.41	0.89	0.08	0.17	0.30	0.32	2.848[c]	4.683

[a] Eqn. (4). [b] Eqn. (3). [c] Values for log L^{16}.

eqn. (3) can range from 0.730 (*N*-formylmorpholine)[19] to 0.866 (methylene diiodide)[32] and 1.041 (tetrachloromethane)[32] at 298 K. This peculiar behaviour of water is not unexpected, and is in line with previous results on the methylene increment to log L values for the solubility of gaseous alkanes in a number of solvents.[42,46,47] The methylene increment, Δ log L, ranges from 0.54 for *n*-hexane to 0.41 for methanol, and down to 0.26 for ethylene glycol, but is -0.13 for solvent water.[47] Calculations of Abraham and Nazehzadeh[48] using scaled particle theory, SPT,[49] suggest that if the methylene increment, Δ log L is broken down into a cavity term Δ log L_{CAV} and a dispersion interaction term Δ log L_{DISP}, then for solution in water at 298 K, Δ log $L_{CAV} = -0.9$ and Δ log $L_{DISP} = +0.8$ solution giving Δ log $L = -0.1$ as observed. But for solution in *n*-hexane at 298 K, Δ log $L_{CAV} = -0.5$ and Δ log $L_{DISP} = +1.1$, giving Δ log $L = +0.6$, again as observed. Thus two factors lead to the small negative values of the *l*-constant (and the *v*-constant) in Table 5: (*i*) the unfavourable endoergic cavity effect increases more rapidly with increase in solute size when water is the solvent, and (*ii*) the favourable exoergic solute–solvent interaction term due to general dispersion interactions, increases less rapidly with increase in solute size when water is the solvent. The l log L^{16} term in eqn. (3) and the $v \cdot V_X$ term in eqn. (4) always include both cavity effects and general dispersion interactions. For all non-aqueous solvents, the latter effect is the larger and so the *l*- or *v*-constant is positive (in a regression with log L^W). In the case of water, the two effects almost cancel out, and lead to a slightly negative *l*- or *v*-constant, with the cavity effect just dominating.

Finally, we can use the constants given in Table 5 to analyse the various factors that influence gaseous solubility at 298 K. These factors can be obtained by a term-by-term analysis using either eqn. (3) or eqn. (4), and will refer to (*i*) interactions due to the presence of π- and n- electron pairs, rR_2, (*ii*) dipolar/polarizability interactions, $s\pi_2^H$, (*iii*) hydrogen-bonding between solute acid and solvent water as a base, $a\Sigma\alpha_2^H$, (*iv*) hydrogen-bonding between solute base and solvent water as an acid, $b\Sigma\beta_2^H$ and (*v*) combined cavity and general dispersion interactions, vV_X or l log L^{16}. We can calculate the cavity effect using SPT and then deduce the general dispersion interaction by difference using either the vV_X or the l log L^{16} term. Note that the dispersion term calculated in this way differs marginally from that used for the *n*-alkanes, because the latter has been obtained by difference from the overall log L^W value. In the SPT calculations, which must refer to standard states of 1 mol dm^{-3} in the gas phase and in solution, we have estimated the required hard-sphere diameters of solutes by comparison of their V_X values with V_X for alkanes of known[48] diameter. In Table 7 are results for a few representative solutes, using eqn. (4) with the constants of Table 5A. Although eqn. (3) is of the more correct form than eqn. (4) for combination with a cavity term calculated as ΔG°_{CAV} or log K_{CAV}, we use eqn. (4) because it is rather more general. In any case, the differences are trivial.

It is clear from Table 7 that the main interaction leading to increased solubility of gases in water, is the general dispersion interaction. Although Abraham and Fuchs[50] have shown that this is the case for gaseous solubility in hexadecane and in olive oil, it is still rather surprising for a liquid such as water, with a particularly low refractive index. However, since the general dispersion interaction and the cavity term very largely cancel

Table 7 A term-by-term analysis of the factors that influence log L^W values for gases in water at 298 K[a]

Solute	c	rR_2	$s\pi_2^H$	$a\Sigma\alpha_2^H$	$b\Sigma\beta_2^H$	Disp.[b]	Cav.[b]	Total Cal.[c]	 Obs.[d]
Ethane	−1.0	0.0	0.0	0.0	0.0	4.8	−5.1	−1.3	−1.3
n-Propane	−1.0	0.0	0.0	0.0	0.0	6.0	−6.5	−1.5	−1.4
n-Hexane	−1.0	0.0	0.0	0.0	0.0	7.9	−8.7	−1.8	−1.8
Butan-2-one	−1.0	0.1	1.8	0.0	2.5	7.0	−7.6	2.8	2.7
Propanoic acid	−1.0	0.1	1.6	2.3	2.2	6.6	−7.1	4.7	4.7
Ethanol	−1.0	0.1	1.1	1.4	2.3	5.3	−5.7	3.5	3.7
HFP	−1.0	−0.1	1.4	2.9	0.5	7.0	−7.6	3.1	2.8
N-Butylacetamide	−1.0	0.2	3.3	1.5	3.6	8.2	−9.1	6.7	6.8
Benzene	−1.0	0.3	1.3	0.0	0.7	7.1	−7.7	0.7	0.6
2-Chlorophenol	−1.0	0.5	2.2	1.2	1.5	7.7	−8.5	3.6	3.3
4-Chlorophenol	−1.0	0.5	2.8	2.6	1.0	7.7	−8.5	5.1	5.2
2-Nitrophenol	−1.0	0.6	2.7	0.2	1.8	7.9	−8.7	3.5	3.4
4-Nitrophenol	−1.0	0.6	4.4	3.1	1.3	7.9	−8.7	7.6	7.8
Benzamide	−1.0	0.6	3.8	1.9	3.2	8.0	−8.8	7.7	8.1
Pyridine	−1.0	0.4	2.1	0.0	2.5	6.9	−7.5	3.4	3.4

[a] Using eqn. (4), Table 5A. [b] As described in the text. These two terms together make up the vV_x term in eqn. (4). [c] This is the calculated log L^W value on eqn. (4) [d] Table 4.

out, the main factors that lead to *differences* in solubility between various gaseous solutes are the solute dipolarity/polarizability, and the solute hydrogen-bond acidity and basicity. Thus for butan-2-one, the $s\pi_2^H$ and the $b\beta_2^H$ terms account for a contribution to log L^W of 4.3, *i.e.*, a factor of some 20 000 over an alkane of the same size. Carboxylic acids are interesting because although they are strongly acidic ($\Sigma\alpha_2^H$ = 0.60) they are also quite basic ($\Sigma\beta_2^H$ = 0.45) and the $a\Sigma\alpha_2^H$ and $b\Sigma\beta_2^H$ terms make almost the same contribution of around 2.2 log units each. Again, hexafluoropropan-2-ol (HFP) and ethanol have about the same solubility, even though HFP is much the stonger acid with the $a\Sigma\alpha_2^H$ term of 2.9 as compared with 1.4 log units for ethanol. But ethanol is quite basic ($\Sigma\beta_2^H$ = 0.48) as compared with HFP ($\Sigma\beta_2^H$ = 0.10) and the $b\Sigma\beta_2^H$ term for ethanol is so much larger than that for HFP, that ethanol is even a little more soluble than HFP.

Compounds with intramolecular hydrogen bonds, such as 2-chlorophenol and 2-nitrophenol, are less soluble than their counterparts 4-chlorophenol and 4-nitrophenol; hence 2-nitro- and 4-nitro-phenol can be separated by steam distillation, the former being the more volatile. Internal hydrogen-bonding not only reduces the acidity of the phenolic hydroxy group, but reduces the dipolarity of the molecule and increases the basicity of the oxygen atom in the hydroxy group. All these factors are involved in the increase of log L^W for 4-chlorophenol over 2-chlorophenol, with the α_2^H term making most difference (1.4 log units to the overall increase of 1.5 log units). In the case of the nitrophenols, the $a\Sigma\alpha_2^H$ term again makes most difference (2.9 log units), but the $s\pi_2^H$ term also contributes some 1.7 log units to the overall difference of 4.1 log units. Such analyses can be carried out for any of the solutes, or combinations of solutes listed in Table 4. It is not necessary in these analyses to dissect the vV_X or l log L^{16} terms into dispersion and cavity effects, and a simplified analysis can be carried out by using the total vV_X term instead of the dispersion/cavity terms in Table 7.

It is of interest to compare the dissection of log L^W values into components, *via* eqn. (4), with the electrostatic Gibbs energy of solvation calculated by Honig *et al.*[51] and by Pettitt *et al.*[52] We therefore convert the electrostatic Gibbs energy into the equivalent log L^W contribution, and give in Table 8 the calculated contributions to log L^W. Note that three different calculation procedures were used by Honig *et al.*,[51] leading to the range of contributions given in Table 8. There is reasonable agreement between the calculated electrostatic contributions and the sum of electrostatic effects using eqn. (4), *i.e.*, ($s\pi_2^H$ + $a\Sigma\alpha_2^H$ + $b\Sigma\beta_2^H$) or (rR_2 + $s\pi_2^H$ + $a\Sigma\alpha_2^H$ + $b\Sigma\beta_2^H$). Since the rR_2 term contributes only a few tenths of a log unit, it makes little difference whether or not this term is included.

Table 8 Comparison of electrostatic contributions to log L^W calculated by Honig *et al.*[51] and Pettitt *et al.*,[52] with those obtained through eqn. (4)

Solute	Ref. 51	Ref. 52	Eqn. (4)[a]	Eqn. (4)
Water	4.3–6.8		5.9	5.9
Methanol	3.7–4.7	5.2	5.1	5.2
Ethanol	3.2–4.6		4.8	4.9
Propan-2-ol	3.0–4.7		4.9	5.0
Propanone	3.9–4.3	3.7	4.3	4.4
Methyl acetate	1.9–6.5	3.2	3.8	3.9
Acetamide	6.4–9.7	8.2	8.6	8.9
(*E*)-*N*-Methylacetamide	7.3–10.0		8.4	8.6
(*Z*)-*N*-Methylacetamide	6.8–7.5			
N,*N*-Dimethylacetamide	4.6–6.5		7.2	7.4
Acetic acid	3.8–9.1	6.0	6.1	6.2
Benzene		2.2	2.0	2.3
Toluene	0.4–1.5		2.0	2.3
Phenol	4.3–6.8	6.5	6.0	6.5

[a] Calculated as ($s\pi_2^H$ + $a\Sigma\alpha_2^H$ + $b\Sigma\beta_2^H$). [b] Calculated as (rR_2 + $s\pi_2^H$ + $a\Sigma\alpha_2^H$ + $b\Sigma\beta_2^H$).

Honig *et al.*[51] also show (graphically) the calculated and experimental total solvation energies, $\Delta_sG°$, which are related to L by $\Delta_sG° = -RT \ln L$. It would be of interest to compare these results of Honig *et al.*[51] with our results but it is, unfortunately, difficult to deduce the exact origin of the experimental $\Delta_sG°$ values used by Honig *et al.*[51] Thus the solvation energies for methylacetamide and dimethylacetamide were said to be taken from Jorgensen and Gao[53] who list no experimental values at all. The solvation energies for phenol, acetic acid and acetamide were taken from Radzicka and Wolfenden[54] who refer in turn to the 1981 paper of Wolfenden *et al.*[55] Nowhere is phenol mentioned, and the $\Delta_sG°$ value listed by Wolfenden *et al.*[55] for acetic acid (−10.95 kcal mol^{-1}) is a completely incorrect calculation from the Henry's constant given by Butler and Ramchandani,[56] the correct $\Delta_s G^\circ$ value being -6.70 kcal mol^{-1}.* We note also that the $\Delta_s G^\circ$ values listed[55] for *N*-methylguanidine (-11.19 kcal mol^{-1}) and *N*-propylguanidine (-19.92 kcal mol^{-1}) are incompatible; replacement of a methyl group by an *n*-propyl group leads to a reduction in log *L* of only around 0.25, corresponding to an increase in ΔG° of 0.35 kcal mol^{-1}, not a decrease of 8.7 kcal mol^{-1}.

Since the *L*-values determined by Wolfenden *et al.*[54,55,57] refer to a number of biologically interesting molecules, we collect their experimental results in Table 9, and compare them with values we can calculate through eqn. (4). There is fair agreement with experiment, except for propionic acid where the log *L* value of 7.48 (obtained from the quoted[55] $\Delta_s G^\circ$ value of -10.20 kcal mol^{-1}) is nearly 3 log units too large. The above analysis illustrates how difficult it is to obtain log *L* values for rather involatile compounds, and how useful it is to check experimental values for such compounds against those calculated *via* eqn. (4). Quite recently, Hoff *et al.*[58] and Carr *et al.*[59] have determined log L^W values at 298 K, Carr *et al.*[59] by a variant of the new method we described earlier. The results of Hoff *et al.*[58] are in excellent agreement with those listed in Table 4, as shown in Table 10 that contains all their results. Nearly all the results of Carr *et al.*[59] are also in good agreement with those in Table 4, although there are a few compounds where agreement is poor: tetrachloromethane, diisopropyl ether, di-*n*-butyl ether and fluorobenzene. But note that the peculiar use of percentage differences as applied to log L^W values by Carr *et al.*[59] leads to discrepancies that are more apparent than real when the log L^W values are close to zero. The solutes for which there are considerable differences in the actual log L^W values are in Table 10, together with a selection of other results from Carr *et al.*[59] Inspection of Table 10 shows that it is almost impossible to choose between different log L^W values for the same solute on any rational basis, at least if the difference is no more than around 0.2 or 0.3 log units. The greatest discrepancy is for diisopropyl ether (1.01 or 0.39 log units), where an average value of 0.70 seems the most reasonable.

Table 9 Comparison of some experimental log *L* values with those calculated through eqn. (4)

Solute	Obs.	Calc.[a]
Acetic acid	4.96[57] (8.03)[55]	4.87 (4.91)[b]
Propionic acid	7.48[55]	4.74 (4.74)[b]
Acetamide	7.12[57]	7.50
Propionamide	6.88[55]	7.40
N-Methylacetamide	7.39[57]	7.00
N,*N*-Dimethylacetamide	6.27[57]	5.70
3-Methylindole	4.33[55]	4.20
4-Methylimidazole	7.51[55]	—
N-Methylguanidine	8.20[55]	—
N-Propylguanidine	14.60[55]	

[a] Eqn. (4) with the constants in Table 5A. [b] Experimental value from Table 1.

Finally, we deal with the only set of compounds that are not well correlated through eqn. (4), namely the polyaromatic hydrocarbons (PAHs). Some calculated and observed log L^W values are in Table 11, using eqn. (4) with the constants in Table 5A. If the constants in the 'aromatic only' regression are used, Table 5B, the calculated log L^W values are not quite so large, *e.g.*, anthracene (3.58), phenanthrene (3.36) and pyrene (4.84), but still much larger than the observed values. In general, the larger the PAH, the greater the discrepancy between observed and calculated log L^W values.

The most obvious reasons for such discrepancies are either that the descriptors used are incorrect, or that the experimental values are in error. However, the same descriptors listed in Table 11 lead to calculated partition coefficients for PAHs that are in excellent agreement with experiment.[34] In two particular cases, that of anthracene and naphthalene, it is possible to check the directly determined log L^W values by various indirect procedures, Table 12. For anthracene, three independent experimental methods lead to log L^W values of 3.00, 3.12 and 3.32, whereas the calculated log L^W value is 3.74 (Table 5A) or 3.58 (Table 5C). For naphthalene, the three methods lead to log L^W values of 1.76, 1.78 and 1.83, as compared with calculated

Table 10 Comparison of some log L^W values

Solute	Hoff *et al.*[58]	Carr *et al.*[59]	Table 4	Calc.[a]
Dichloromethane	1.00		0.96	0.88
Trichloromethane	0.80		0.79	0.63
Tetrachloromethane	−0.05	−0.24	−0.06	−0.40
1,2-Dichloroethane	1.31		1.31	1.24
1,1,1-Trichloroethane	0.12		0.14	0.04
Trichloroethane	0.42		0.32	0.08
Tetrachloroethene	0.19		−0.07	−0.23
1-Bromobutane	0.06		0.29	0.08
Diisopropyl ether		1.01	0.39	0.60
Di-*n*-butyl ether		0.73	0.61	0.70
Methyl formate	2.00		2.04	2.29
Propanone	2.82		2.79	2.94
Nonan-2-one		2.01	1.83	2.07
Isobutyronitrile		2.37		2.34[b]
Benzene	0.62	0.63	0.63	0.74
Toluene	0.50	0.60	0.65	0.61
Fluorobenzene		0.44	0.59	0.58
Chlorobenzene	0.81	0.80	0.82	0.69
1,2-Dichlorobenzene	0.92	1.07	1.00	0.86
3-Nitrotoluene		2.84	2.53	2.63

[a] On eqn. (4). [b] With $R_2 = 0.156$, $\pi_2^H = 0.87$, $\Sigma\alpha_2^H = 0.00$, $\Sigma\beta_2^H = 0.36$ and $V_x = 0.8269$.

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* The value of $\Delta_s G^\circ$ for *n*-butylamine (-9.52 kcal mol^{-1}) has also been incorrectly calculated[55] from data in ref. 56, the correct value being -4.38 kcal mol^{-1}.

Table 11 Calculated and observed log L^W values for some aromatic hydrocarbons at 298 K

Solute	R_2	π_2^H	$\Sigma\beta_2^H$	V_x	log L^W			
					Calc.[a]	Ref. 11	Ref. 13	Ref. 4
Benzene	0.610	0.52	0.14	0.716	0.74	0.63	0.65	0.64
Toluene	0.601	0.52	0.14	0.857	0.61	0.65	0.57	0.61
Naphthalene	1.340	0.92	0.20	1.085	2.15	1.75	1.76	1.76
1-Methylnaphthalene	1.344	0.90	0.20	1.226	1.98	1.79	1.74	—
Acenaphthene	1.604	1.05	0.20	1.259	2.48	2.31	2.01	—
n-Butylbenzene	0.600	0.51	0.15	1.280	0.27	0.29	0.28	−0.04
Fluorene	1.588	1.06	0.20	1.357	2.41	—	2.46	—
1-Ethylnaphthalene	1.371	0.88	0.20	1.367	1.82	1.76	—	—
1,3-Dimethylnaphthalene	1.387	0.92	0.20	1.367	1.93	1.81	—	—
Anthracene	2.290	1.34	0.26	1.454	3.74	3.10	2.62	2.92
Phenanthrene	2.055	1.29	0.26	1.454	3.48	2.90	2.79	2.87

[a] Eqn. (4) with constants in Table 5A.

Table 12 Determination of log L^W for anthracene and naphthalene by indirect methods, at 298 K

	Indirect	Indirect	Direct	Calc. eqn. (4)
Anthracene				
log P^{alk}	4.25[a]	4.45[b]		
log L^{16}	7.57[c]	7.57[c]		
log L^W	3.32[d]	3.12[d]	3.00[e]	3.74[f]
Naphthalene				
log P^{alk}	3.38[a]	3.33[g]		
log L^{16}	5.16[c]	5.16[c]		
log L^W	1.78[d]	1.83[d]	1.76[e]	2.15[f]

[a] Observed log P^{alk}, The Pomona College Medicinal Chemistry Project. [b] From the molar solubility in water, 3.7 × 10^{-7} mol dm^{-3} in ref. 13 and the average molar solubility in hexane, heptane and octane, 1.05 × 10^{-2} mol dm^{-3} from ref. 39. [c] Ref. 22. [d] From the preceding two rows. [e] Table 11. [f] Using the constants in Table 5A. [g] Calculated value in ref. 34.

values of 2.15 (Table 5A) or 2.09 (Table 5C). We have therefore not been able to resolve the problem of the PAHs, and can only suggest that eqn. (4) should not be used to estimate log L^W values for the higher PAHs.

Conclusions

Our main conclusion is that the same solute descriptors that have been used with the LSER eqn. (3) and eqn. (4) to analyse and interpret a large variety of processes,[27–35] can be used with the same general equations to correlate the aqueous solubility of a very wide range of gaseous solutes. The equations thus constructed, Table 5, can be used to estimate further log L^W values for solutes for which the relevant descriptors are available, and can be used to interpret aqueous solubility in terms of specific solute–solvent interactions. This is possible, because, unlike most correlation equations, eqn. (3) and eqn. (4) can be interpreted term-by-term using well-established chemical principles.

We have also shown that log L^W values can be obtained by a new method, using a combination of water–hexadecane or water–alkane partition coefficients with gas–hexadecane partition coefficients. Comparison of the log L^W obtained in this way with those calculated through eqn. (4) shows excellent agreement, even for compounds with very large log L^W values, and indicates that this new method may be the preferred procedure to obtain log L^W for particular classes of solute.

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