

Hydrogen bonding. Part 45.† The solubility of gases and vapours in methanol at 298 K: an LFER analysis



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Values of the Ostwald solubility coefficient of gases and vapours in methanol solvent, L^{MeOH} , at 298 K have been determined for 23 solutes by an indirect method in which experimental partition coefficients between methanol and hexadecane were combined with literature data on Ostwald solubility coefficients in hexadecane. Another 70 L^{MeOH} values were obtained from literature data and the total 93 values were correlated by the Abraham equation to give the regression, where $n = 93$, $r^2 = 0.9952$, $sd = 0.13$ and $F = 3681$.

$$\log L^{\text{MeOH}} = -0.004 - 0.215 R_2 + 1.173 \pi_2^{\text{H}} + 3.701 \Sigma a_2^{\text{H}} + 1.432 \Sigma \beta_2^{\text{H}} + 0.769 \log L^{16} \quad (\text{i})$$

The solute descriptors in eqn. (i) are: R_2 an excess molar refraction, π_2^{H} the dipolarity/polarisability, Σa_2^{H} the overall hydrogen-bond acidity, $\Sigma \beta_2^{\text{H}}$ the overall hydrogen-bond basicity and $\log L^{16}$, where L^{16} is the Ostwald solubility coefficient on hexadecane at 298 K. The number of data points, or solutes, is n , the correlation coefficient is r , the standard deviation is sd and F is the F -statistic. Just as for the case of water solvent, solute dipolarity/polarisability, hydrogen-bond acidity and hydrogen-bond basicity all lead to an increase in $\log L$, although methanol is much less acidic than water. However, contrary to the solubility of vapours in water, the $\log L^{16}$ descriptor now also leads to an increase in $\log L$. Explanations for the different behaviour of water and methanol are given.

An analysis of $\log P$ values for the transfer of solutes from water to methanol also shows that bulk methanol is as strong a hydrogen-bond base as bulk water but is a much weaker hydrogen-bond acid.

A number of methods are available for the correlation and prediction of the solubility of gases and vapours in water, but comparatively little attention has been paid to solubilities in other associated solvents such as alcohols. The correlation and estimation of vapour solubilities in various solvents is important in chemical engineering processes, and is of theoretical significance as well. In this work we set out a database of vapour solubilities in methanol and then analyse them in order to elucidate the solute and solvent influences that affect solubility. We use the term 'vapour' to cover both permanent gases and vapours of compounds that are liquid or solid at 298 K.

We define vapour solubilities in terms of the Ostwald solubility coefficient, L , given by eqn. (1). This is identical to the

$$L = \frac{[\text{conc. of solute in solution}]}{[\text{conc. of solute in the gas phase}]} \quad (1)$$

gas-liquid partition coefficient, K . If concentrations in eqn. (1) are the same in solution and the gas phase, say mol dm^{-3} , then L is a dimensionless quantity. Our interest is in the value of L at zero solute concentration, L° , where there are no solute-solute interactions. Traditionally, the most common method of obtaining L° is through vapour-liquid equilibrium measurements,¹ but extrapolation to zero solute concentration is not easy in the case of asymmetric mixtures, and the method is difficult to apply to involatile solutes in volatile solvents. Another method is that of head-space analysis, in which the concentration of solute above a given solution is sampled and

analysed.²⁻⁴ Again, the most difficult systems to study by the head-space analysis method are those of a relatively involatile solute in a volatile solvent. This is also the case for the gas chromatographic method in which the solvent is the stationary phase.⁵ Thus for many volatile solvents such as water and methanol, some other method of obtaining L° would be useful.

For solvents that are immiscible with water, it is possible to obtain water-to-solvent partition coefficients from L° values in water and L° values in the solvent.⁵ Recently, we have used this method in another way and have shown⁶ that solubilities in water, as values of L^{W} , can be obtained from vapour solubilities in an alkane solvent, L^{ALK} , together with water-to-alkane partition coefficients, P^{ALK} , through eqn. (2).

$$P^{\text{ALK/W}} = L^{\text{ALK}}/L^{\text{W}} \quad (2)$$

We reasoned that a similar method could be used to obtain solubilities of vapours in methanol, L^{MeOH} , by combination of alkane-to-methanol partition coefficients, $P^{\text{MeOH/ALK}}$, with solubilities of vapours in the alkane, eqn. (3), using hexadecane

$$P^{\text{MeOH/ALK}} = L^{\text{MeOH}}/L^{\text{ALK}} \quad (3)$$

as the alkane. Such a method is convenient because there is no restriction on the determination of partition coefficients through involatility of solutes, and L^{ALK} (denoted as L^{16} when hexadecane is the alkane) values can be obtained by gas-liquid chromatography for a wide range of solutes including rather involatile compounds such as chrysene, perylene and benzo-pyrene.⁷ Interestingly, Schantz *et al.*⁸ obtained hexadecane-

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methanol partition coefficients for a number of alcohols and aromatic hydrocarbons, but did not use them to calculate L^{MeOH} . We shall refer to this later.

In the present work we report the determination of L^{MeOH} values through eqn. (3), and we then analyse a compilation of L^{MeOH} values, including those we have determined and values from the literature, through the linear free energy relationship (LFER) shown in eqn. (4). Here, the dependent variable will be

$$\log SP = c + rR_2 + s\pi_2^{\text{H}} + a\Sigma a_2^{\text{H}} + b\Sigma\beta_2^{\text{H}} + l\log L^{16} \quad (4)$$

$\log L^{\text{MeOH}}$ for a series of solutes in methanol, and the independent variables are solute descriptors as set out in detail before.⁹ In brief, these are: R_2 an excess molar refraction, π_2^{H} the dipolarity/polarisability, Σa_2^{H} the overall hydrogen-bond acidity, $\Sigma\beta_2^{\text{H}}$ the overall hydrogen-bond basicity, and $\log L^{16}$, where L^{16} is the Ostwald solubility coefficient on hexadecane at 298 K.⁵ The coefficients in eqn. (4) are of interest, as they refer to properties of the solvent phase. In particular, we wish to compare the a coefficient (a measure of solvent hydrogen-bond basicity) and the b coefficient (a measure of solvent hydrogen-bond acidity) with those for water as a solvent,⁶ especially as there is disagreement over the relative hydrogen-bond basicities of water and alcohols.¹⁰

We can also combine the L^{MeOH} values with values of the Ostwald solubility coefficient in water at 298 K, L^{W} , to obtain partition coefficients for the transfer of solutes from pure water to pure methanol, $P^{\text{MeOH/W}}$, through eqn. (5). For the analysis

$$P^{\text{MeOH/W}} = L^{\text{MeOH}}/L^{\text{W}} \quad (5)$$

of the $P^{\text{MeOH/W}}$ values we use the alternative LFER given as eqn. (6), where the final descriptor in eqn. (4) has been replaced

$$\log SP = c + rR_2 + s\pi_2^{\text{H}} + a\Sigma a_2^{\text{H}} + b\Sigma\beta_2^{\text{H}} + vVx \quad (6)$$

by the McGowan volume, Vx , in units of $10^{-2} \text{ dm}^3 \text{ mol}^{-1}$.

Experimental

Procedure

The method used is a variant of the head-space gas chromatographic (HSGC) method described before.^{11,12} In brief, a cell was thermostatted at $298 \pm 0.1 \text{ K}$, charged with a dilute solution of a solute in either methanol or hexadecane solvent and allowed to equilibrate for 1 h. The vapour above the solution was sampled three or four times and analysed by HSGC. The second solvent, hexadecane or methanol, was then added to the cell from a digital burette controlled by a computer, the mixture allowed to equilibrate for 1 h, and the vapour sampled and analysed as before. The addition and analysis cycle was repeated five to seven times.

If the HSGC peak area due to the solute is denoted as A^0 and A^f before and after adding the second solvent, say hexadecane, then a plot of A^0/A^f vs. the volume of hexadecane added will yield a slope of $P^{\text{MeOH/16}}/V^{\text{MeOH}}$ where V^{MeOH} is the initial volume of methanol in the cell.¹¹

Results and discussion

The $P^{\text{MeOH/16}}$ values we have determined are in Table 1, as log $P^{\text{MeOH/16}}$, together with the corresponding log L^{16} values,^{6,9} and the calculated values of log L^{MeOH} through eqn. (3). We give also in Table 1 values of log L^{MeOH} calculated from literature data; most of these data are in the form of activity coefficients which we have converted into log L^{MeOH} values using saturated vapour pressures without correcting for gas imperfections. Agreement between our indirect values and those calculated from literature data is generally excellent. Hence possible diffi-

Table 1 Determination of log L^{MeOH} for solutes at 298 K

Solute	log P^a	log L^{16}	log L^{MeOH}	
			det. ^b	lit. ^c
Pentane	0.50	2.13	1.66	1.52 ^d
Hexane	0.61	2.67	2.06	2.04, ^d 2.04 ^e
Heptane	0.72	3.17	2.45	2.55 ^d
Octane	0.84	3.68	2.84	2.78, ^d 2.85 ^f
Nonane	0.95	4.18	3.23	
Trichloromethane	-0.53	2.48	3.10	
Tetrachloromethane	0.17	2.82	2.65	2.67 ^g
Dibutyl ether	0.28	3.92	3.64	
Tetrahydrofuran	-0.61	2.64	3.25	
Dioxane	-0.80	2.89	3.69	3.59, ^d 3.56 ^f
Propanone	-1.31	1.70	3.01	2.77 ^h
Butanone	-1.11	2.29	3.40	3.34, ^d 3.31, ^f 3.31 ^h
Pentan-2-one	-0.97	2.75	3.72	3.43 ^h
Propyl acetate	-0.71	2.82	3.53	
Butyl acetate	-0.58	3.35	3.93	
Acetonitrile	-1.37	1.74	3.11	2.81 ⁱ
Propionitrile	-1.52	2.08	3.61	
Nitromethane	-1.63	1.89	3.52	3.46, ^d 3.35, ^f 3.35 ^j
Pentan-1-ol	-2.49	3.11	5.60	
Trifluoroethanol	-2.97	1.22	4.19	
HFIP	-3.40	1.39	4.79	
Benzene	0.00	2.79	2.79	2.79 ^d
Toluene	0.15	3.33	3.18	3.17, ^d 3.20 ^d

^a Log $P^{\text{MeOH/16}}$, this work. ^b From eqn. (3), $\text{ALK} = 16$. ^c From literature sources as shown. ^d M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans. 2*, 1975, 1856. ^e H. Wolff and H. E. Hoppel, *Ber. Bunsenges. Phys. Chem.*, 1968, **72**, 710; 722. ^f Ref. 4. ^g E. Matteoli and L. Lepori, *J. Chem. Thermodynam.*, 1986, **18**, 1065. ^h R. A. Djerkic and R. J. Laub, *J. Liquid Chromatogr.*, 1988, **11**, 585. ⁱ B. G. Cox, A. J. Parker and W. E. Waghorne, *J. Am. Chem. Soc.*, 1973, **95**, 1010. ^j J. R. Khurma, O. Muthu, S. Munjal and B. D. Smith, *J. Chem. Eng. Data*, 1983, **28**, 113, 119.

Table 2 Calculation of log L^{MeOH} using the log P values of Schantz *et al.*⁸

Solute	log P^a	log L^{16}	log L^{MeOH}	
			calc. ^b	lit. ^c
Benzene	-0.03	2.79	2.74	2.79, ^d 2.79 ^d
Toluene	0.13	3.32	3.19	3.17, ^d 3.18, ^d 3.20 ^d
Ethylbenzene	0.17	3.78	3.61	3.54 ^e
Propylbenzene	0.35	4.23	3.88	3.89 ^e
Butylbenzene	0.50	4.73	4.23	4.22 ^e
Biphenyl	0.23	6.01	5.78	
Butan-1-ol	-1.96	2.60	4.56	
Pentan-1-ol	-1.82	3.11	4.93	5.60 ^d
Hexan-1-ol	-1.68	3.61	5.29	
Heptan-1-ol	-1.45	4.12	5.57	
Octan-1-ol	-1.27	4.62	5.89	
Nonan-1-ol	-1.13	5.12	6.25	

^a Log $P^{\text{MeOH/16}}$, ref. 8. ^b Calculated from eqn. (3), $\text{ALK} = 16$. ^c From literature sources as shown. ^d Table 1. ^e Cheung and P. W. Carr, *J. Chromatogr.*, 1990, **500**, 215.

culties over mutual solubility of the methanol and hexadecane phases seem not to be of consequence. This is in accord with the work of Dallas and Carr¹² who determined Ostwald solubility coefficients for alkylbenzenes in hexadecane and in hexadecane saturated with methanol, and showed that there was no measurable effect of methanol in the hexadecane. In Table 2 is a similar calculation of log L^{MeOH} using the log $P^{\text{MeOH/16}}$ values of Schantz *et al.*⁸ at 298 K. There is good agreement with literature data, and with our results in Table 1, except for pentan-1-ol. We have no explanation of this, and for consistency with the other alcohols, we take the Schantz *et al.*⁸ value. Very recently, Berthod *et al.*¹³ have measured heptane-methanol partition coefficients using countercurrent chromatography. Mutual solubility is quite marked in this system,¹³ being 10.4 mol% heptane in methanol and 2.0 mol% methanol in heptane at 293 K. Com-

Table 3 Calculation of $\log L^{\text{MeOH}}$ using the $\log P$ values of Berthod *et al.*¹³

Solute	$\log P^a$	$\log L^{\text{ALK}}$	$\log L^{\text{MeOH}}$	
			calc.	lit.
Benzene	0.02	2.79	2.77	2.79, ^a 2.79, ^a 2.74 ^b
Toluene	0.12	3.32	3.20	3.17, ^a 3.18, ^a 3.20, ^a 3.19 ^b
Ethylbenzene	0.18	3.78	3.60	3.54, ^b 3.61 ^b
Propylbenzene	0.26	4.23	3.97	3.88, ^b 3.89 ^b
Butylbenzene	0.34	4.73	4.39	4.22, ^b 4.23 ^b
Hexylbenzene	0.49	5.72	5.23	

^a Table 1. ^b Table 2.

pare values⁸ for the hexadecane–methanol system of 4.2 mol% hexadecane in methanol and 0.3 mol% methanol in hexadecane at 298 K. Details of the calculation of $\log L^{\text{MeOH}}$ from the data of Berthod *et al.*¹³ are in Table 3. There is good agreement with other values, although there is a trend of too great an increase of $\log L^{\text{MeOH}}$ with increasing size of solute. In these calculations we have made the approximation that $\log L^{\text{oo}}$ for the solutes in heptane are the same as those for the solutes in hexadecane. This approximation was used before, however, and led to reasonable results.⁶

Finally, we collect in Table 4 all the $\log L^{\text{MeOH}}$ values we have obtained. For the solutes in Tables 1, 2 and 3, where more than one value is recorded, we took a straight average except for pentan-1-ol (see above) and pentane (where our value is more in line with the homologous series of alkanes than the alternative value in Table 1). The general LFER, eqn. (4), was applied to the 93 $\log L^{\text{MeOH}}$ values in Table 4 to yield eqn. (7), where $n = 93$,

$$\log L^{\text{MeOH}} = -0.004 - 0.215 R_2 + 1.173 \pi_2^{\text{H}} + 3.701 \Sigma a_2^{\text{H}} + 0.026 R_2 + 0.061 \pi_2^{\text{H}} + 0.077 \Sigma a_2^{\text{H}} + 0.088 \Sigma \beta_2^{\text{H}} + 0.769 \log L^{16} + 0.084 R_2 + 0.011 \Sigma \beta_2^{\text{H}} \quad (7)$$

$r^2 = 0.9952$, $sd = 0.13$ and $F = 3681$. The required solute descriptors have nearly all been published before.^{5-7,9,†}

In eqn. (7), n is the number of data points (solutes), r is the regression correlation coefficient, sd is the standard deviation in the dependent variable, defined as $[\Sigma(y_{\text{obs}} - y_{\text{calc}})^2/(n - 1)]^{0.5}$ and F is the F -statistic. The sd value for each of the coefficients is given below the coefficient, and the t ratios for the coefficients are 3.5(r), 15.2(s), 42.0(a), 17.0(b) and 70.4(l). Bearing in mind the disparate sources of the data, the statistics in eqn. (7) are as good as could be expected. We have checked for any cross-correlations between the descriptors; the correlation matrix in r^2 is given below:

	R_2	π_2^{H}	Σa_2^{H}	$\Sigma \beta_2^{\text{H}}$
π_2^{H}	0.456			
Σa_2^{H}	0.013	0.014		
$\Sigma \beta_2^{\text{H}}$	0.004	0.259	0.052	
$\log L^{16}$	0.411	0.348	0.003	0.111
V_x	0.187	0.127	0.009	0.070

The greatest cross-correlations are those between R_2 and π_2^{H} with $r^2 = 0.456$, and between R_2 and $\log L^{16}$ with $r^2 = 0.411$, so that we can take the descriptors in eqn. (7) to be reasonably

† A complete list of descriptors, together with observed and calculated values of $\log L^{\text{MeOH}}$ and $\log P^{\text{MeOH}/16}$ (see later) is available as supplementary data (SUPPL. NO 57380, pp. 4) from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available via the RSC Web page (<http://www.rsc.org/authors>). The supplementary data is also available on the RSC's web server (<http://www.rsc.org/suppdata/perkin2/1998/1385/>).

Table 4 Values of $\log L^{\text{MeOH}}$ at 298 K

Solute	$\log L^{\text{MeOH}}$	Solute	$\log L^{\text{MeOH}}$
Helium	-1.45 ^{a,b}	Hexan-2-one	3.82 ⁿ
Neon	-1.31 ^{a,b}	Heptan-2-one	4.38 ^{n,p}
Argon	-0.57 ^a	Heptan-3-one	4.26 ^p
Krypton	-0.19 ^b	Heptan-4-one	4.23 ^p
Xenon	0.32 ^c	Methyl acetate	2.92 ⁿ
Radon	0.68 ^a	Propyl acetate	3.53 ^g
Hydrogen	-1.02 ^a	Butyl acetate	3.93 ^g
Oxygen	-0.60 ^d	Methyl propanoate	3.17 ^{n,q}
Nitrogen	-0.81 ^b	Methyl butanoate	3.55 ⁿ
Nitrous oxide	0.51 ^a	Methyl pentanoate	3.91 ⁿ
Carbon monoxide	-0.65 ^a	Methyl hexanoate	4.28 ⁿ
Carbon dioxide	0.52 ^e	Acetonitrile	2.96 ^g
Sulfur dioxide	2.08 ^a	Propionitrile	3.61 ^g
Methane	-0.27 ^f	Ammonia	2.26 ^a
Ethane	0.38 ^f	Dimethylamine	2.57 ^a
Propane	0.84 ^f	Diethylamine	3.73 ^a
Butane	1.27 ^f	Triethylamine	3.84 ^f
2-Methylpropane	1.07 ^f	Nitromethane	3.42 ^g
Pentane	1.66 ^g	Water	4.07 ^a
2,2-Dimethylpropane	1.40 ^f	Methanol	3.60 ^s
Hexane	2.05 ^g	Ethanol	3.89 ^s
Heptane	2.50 ^g	Propan-1-ol	4.36 ^s
Octane	2.82 ^g	Butan-1-ol	4.56 ^t
Nonane	3.23 ^g	Pentan-1-ol	4.93 ^t
3,3-Diethylpentane	3.15 ^f	Hexan-1-ol	5.29 ^t
Cyclopentane	1.92 ^f	Heptan-1-ol	5.57 ^t
Cyclohexane	2.43 ^f	Octan-1-ol	5.89 ^t
Ethene	0.41 ^h	Nonan-1-ol	6.25 ^t
Ethyne	1.04 ⁱ	Trifluoroethanol	4.19 ^g
Tetrafluoromethane	-0.73 ^b	HFIP	4.79 ^g
Dichloromethane	2.55 ^j	Ethanthiol	2.20 ^u
Trichloromethane	3.10 ^g	Sulfur hexafluoride	-0.21 ^b
Tetrachloromethane	2.66 ^g	Benzene	2.77 ^v
1,1-Dichloroethane	2.16 ^k	Toluene	3.19 ^v
Iodomethane	2.35 ^f	Ethylbenzene	3.58 ^v
Iodoethane	2.62 ^f	Propylbenzene	3.91 ^v
CCl ₂ FCCl ₂ F	2.76 ^l	Isopropylbenzene	3.80 ^v
Diethyl ether	2.39 ^m	Butylbenzene	4.28 ^v
Dibutyl ether	3.64 ^g	<i>tert</i> -Butylbenzene	4.05 ^w
Tetrahydrofuran	3.25 ^g	Hexylbenzene	5.23 ^v
Dioxane	3.62 ^g	Chlorobenzene	3.67 ^x
Propionaldehyde	2.79 ⁿ	Biphenyl	5.78 ^v
Butyraldehyde	3.18 ^o	Naphthalene	5.14 ^y
Pentanal	3.57 ⁿ	Anthracene	7.25 ^y
Propanone	2.89 ^g	Phenanthrene	7.24 ^y
Butanone	3.34 ^g	Methyl <i>tert</i> -butyl ether	2.77 ^z
Pentan-2-one	3.58 ^g		

^a Solubility data project series. ^b S. Bo, R. Battino and A. Wilhelm, *J. Chem. Eng. Data.*, 1993, **38**, 611. ^c G. L. Pollack, J. F. Hinn and J. J. Enyeart, *J. Chem. Phys.*, 1984, **81**, 3239. ^d R. Battino, T. R. Rettich and T. Tominaga, *J. Phys. Chem. Ref. Data*, 1983, **12**, 163. ^e E. Wilhelm and R. Battino, *Chem. Rev.*, 1973, **73**, 1. ^f Footnote *d*, Table 1. ^g Table 1. ^h S. Zeck and H. Knapp, *Int. J. Thermophys.*, 1985, **6**, 643. ⁱ Y. Miyano and W. Hayduk, *Can. J. Chem.*, 1981, **59**, 746. ^j Footnote *j*, Table 1. ^k A. Kovac, J. Svoboda and L. Undrus, *Chem. Zvesti.*, 1985, **39**, 729. ^l V. Dohnal and M. Novotna, *Fluid Phase Equilib.*, 1985, **23**, 303. ^m R. Srivastava, G. Natarajan and B. D. Smith, *J. Chem. Eng. Data*, 1986, **31**, 8. ⁿ Footnote *h*, Table 1. ^o Interpolated value, from the other alkanals. ^p R. G. Rubin, J. A. R. Renuncio and M. D. Pena, *J. Chem. Thermodynam.*, 1983, **15**, 779. ^q J. Polak and C.-Y. Lu, *J. Chem. Eng. Data*, 1972, **17**, 4. ^r K. Nakanishi, R. Toba and H. Shirai, *J. Chem. Eng. Jpn.*, 1969, **2**(1), 4. ^s Calculated using $\gamma = 1$, *cf.* other alkanols. ^t Table 2. ^u P. W. Rousseau and J. Y. Kim, *AIChE Symposium*, 1987, **256**, 42. ^v Tables 1, 2 and 3. ^w Footnote *e*, Table 2. ^x P. J. Maher and B. D. Smith, *J. Chem. Eng. Data*, 1979, **24**, 363. ^y Calculated in this work from solubilities and vapour pressures. ^z E. Velasco, M. J. Cocero and F. Mato, *J. Chem. Eng. Data*, 1990, **35**, 21.

independent. The solute propionitrile is an outlier on eqn. (7) by over three standard deviations; we retain propionitrile, but omission of this data point would make little difference to the final result. Because the solute descriptors used to construct eqn. (7) have been published previously, we can view the 93 values of $\log L^{\text{MeOH}}$ as a test set of data. The success of eqn. (4)

Table 5 Coefficients in eqn. (4) for solvents at 298 K

Solvent	<i>c</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>
Methanol	0.00	-0.22	1.17	3.70	1.43	0.769
Water ^a	-1.21	0.82	2.74	3.90	4.81	-0.213
3-Ethylphenol ^b	-1.08	-0.20	0.87	1.80	3.42	0.899
NFM ^c	-0.53	0.00	2.57	4.32	0.00	0.730
2-EHP ^c	-0.07	-0.26	0.91	3.47	0.00	0.955
CH ₂ I ₂ ^d	-0.74	0.32	1.34	0.83	1.19	0.866
CHCl ₃ ^d	0.10	-0.35	1.26	0.60	1.18	0.994
CCl ₄ ^d	0.23	-0.20	0.35	0.07	0.27	1.041
CH ₂ ClCH ₂ Cl ^d	-0.01	-0.28	1.72	0.73	0.59	0.926
Hexadecane ^e	0.00	0.00	0.00	0.00	0.00	1.000

^a Ref. 6. ^b M. H. Abraham, I. Hamerton, J. B. Rose and J. W. Grate, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1417. ^c Ref. 9; NFM = *N*-formylmorpholine and 2-EHP = tris(2-ethylhexyl) phosphate. ^d M. H. Abraham, J. Andonian-Haftvan, J. P. Osei-Owusu, P. Sakellariou, J. S. Urieta, M. C. Lopez and R. Fuchs, *J. Chem. Soc., Perkin Trans. 2*, 1993, 299. ^e By definition.

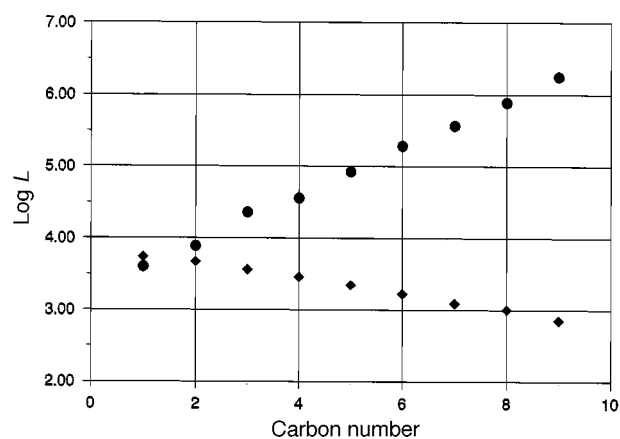
Table 6 Values of the Kamlet–Taft solvatochromic parameters α_1 and β_1 for water and some alcohol solvents

Solvent	α_1	β_1^a
Water	1.02 ^b	0.14 ^c
		0.18 ^d
		0.31 ^e
		0.42 ^f
Methanol	0.99 ^b	0.57 ^f
		0.43 ^g
		0.62 ^c
		0.70 ^c
Ethanol	0.79 ^g	0.66 ^g
		0.79 ^h
		0.79 ^h
		0.71 ^g
Octanol	0.85 ^b	0.73 ^c
		0.92 ^h
		0.90 ^h
Wet octanol	0.70 ⁱ	0.86 ⁱ
		0.79 ⁱ
		0.96 ⁱ
		0.95 ⁱ

^a The first column gives values with 4-nitroaniline indicator and the second column values with 4-nitrophenol indicator. ^b R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2886. ^c M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377. ^d T. Yokoyama, R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 3233. ^e Obtained by a kinetic method, L. Valgimigli, K. U. Ingold and J. Luszyk, *J. Am. Chem. Soc.*, 1996, **118**, 3545. ^f Y. Marcus and Y. Migron, *J. Phys. Chem.*, 1991, **95**, 400. ^g R. M. C. Goncalves, A. M. N. Simoes, L. M. P. C. Albuquerque, M. Roses, C. Rafols and E. Bosch, *J. Chem. Res. (M)*, 1993, 1380; (S) 1993, 214. ^h M. Roses, J. Ortega and E. Bosch, *J. Solution Chem.*, 1995, **24**, 51. ⁱ A. J. Dallas and P. W. Carr, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2155.

in correlating a quite new and extensive set of data confirms the generality of this equation.

From eqn. (7), the main factors that influence the solubility of gases and vapours in methanol at 298 K are solute dipolarity, hydrogen-bond acidity (markedly), hydrogen-bond basicity, and the $\log L^{16}$ descriptor, which all lead to an increase in solubility. Correspondingly, we can now deduce various properties of the methanol solvent. It must have some dipolarity, very considerable hydrogen-bond basicity, some hydrogen-bond acidity, and is quite hydrophobic ($l = 0.769$ as compared to $l = 1.000$ for hexadecane at 298 K). In order to compare methanol with other solvents, we summarise in Table 5 the characteristic coefficients for various solvents at 298 K. Bulk methanol does not behave as a very polarisable/dipolar solvent, with $s = 1.17$ only. Water and NFM (*N*-formylmorpholine) are more polar, and solvents such as diiodomethane and trichloromethane have larger s coefficients, no doubt because they are much more polarisable. Methanol, however, is a very strong hydrogen-bond base ($a = 3.70$), as strong as water and tris(2-ethylhexyl) phosphate, but not quite as strong as the amide NFM. Perhaps surprisingly, methanol does not behave as a very strong hydrogen-bond acid ($b = 1.43$), being much weaker than water or 3-ethylphenol.

**Fig. 1** A plot of the solubility, as $\log L$, for alkan-1-ol vapours in methanol (●) and in water (◆) against the alkan-1-ol carbon number

These conclusions are contrary to those reached through studies of solvatochromic effects, as summarised in Table 6. The Kamlet–Taft hydrogen-bond acidity of water is slightly greater than that of methanol, from the solvatochromic studies, but from the b coefficients in Table 5 we infer that the hydrogen-bond acidity of water is very much larger than that of methanol. Various values for the solvatochromic hydrogen-bond basicity of water have been recorded, Table 6, partly depending on the nature of the indicator probe used. However, the solvatochromic hydrogen-bond basicity of water is always less than that of methanol, whereas from the a coefficients in Table 5, there is very little difference in the hydrogen-bond basicity of the two solvents.

A similar discrepancy occurs in comparison of solvatochromic studies and water–octanol partitions. All workers are agreed that from analyses of partition coefficients, water and (wet) octanol have similar hydrogen-bond basicities,^{14–17} but solvatochromic studies, Table 6, indicate that octanol and wet octanol have much larger hydrogen-bond basicities than water. Our analysis of gas–methanol partition coefficients, and comparison with gas–water partition coefficients, has led to exactly the same conclusion as found from analyses of water–alcohol partitions,¹⁸ namely that bulk water and alcohols have nearly the same hydrogen-bond basicity, but that bulk alcohols are much weaker hydrogen-bond acids than is solvent water.

Finally, we note once again the extraordinary l coefficient of water as compared to values for non-aqueous solvents. For solutions of gases and vapours in water, an increase in size (*i.e.* an increase in $\log L^{16}$) invariably leads to a slight decrease in solubility, but for all non-aqueous solvents an increase in solute size leads to a very large increase in solubility. As we have explained before,⁶ the negative l coefficient in the case of water is due to (i) a greater increase in the unfavorable cavity effect with increase in solute size, and (ii) a smaller increase in the favorable general dispersion interaction with increase in solute size. The present results on solubility in methanol confirm this explanation, in that it is now clear that the result for water has nothing to do with a self-associated solvent as such, because the l coefficient for methanol, a highly self-associated solvent, is large and positive.

The s , a and b coefficients for solvent water, see Table 5, are very large and positive,⁶ so that small functionally substituted solutes will have quite large $\log L^W$ values. However, as any homologous series is ascended, the $\log L^W$ values will become progressively rather smaller. Thus $\log L^W$ is 3.15 for ammonia, but is reduced to 2.68 for *n*-octylamine, and $\log L^W$ gradually decreases from 3.74 for methanol to 2.85 for nonan-1-ol,⁶ see Fig. 1. On the other hand, small functionally substituted solutes will have large values in methanol, but homologues will have even larger $\log L^{\text{MeOH}}$ values as shown also in Fig. 1. We can thus predict that solutes such as HOCH₂CH₂OH will have

Table 7 A term-by-term analysis on eqn. (4) of the solubility of solute vapours in water and methanol at 298 K

Term						Total
	rR_2	$s\pi_2^H$	$a\Sigma a_2^H$	$b\Sigma\beta_2^H$	$l\log L^{16}$	
<i>Solvent water^a</i>						
Ethanol	0.20	1.15	1.44	2.31	-0.32	3.51
Heptan-1-ol	0.17	1.15	1.44	2.31	-0.88	2.92
Triethylamine	0.08	0.41	0.00	3.80	-0.65	2.37
<i>Solvent methanol^b</i>						
Ethanol	-0.05	0.49	1.37	0.68	1.14	3.63
Heptan-1-ol	-0.05	0.49	1.37	0.68	3.17	5.66
Triethylamine	-0.02	0.18	0.00	1.12	2.34	3.62

^a The constant term is -1.27; observed values are 3.67 for ethanol, 3.09 for heptan-1-ol and 2.36 for triethylamine. ^b The constant term is 0.00; observed values are 3.89 for ethanol, 5.57 for heptan-1-ol and 3.67 for triethylamine.

larger log L values in water than in methanol, *i.e.* they will be more soluble in water, but homologues of type $\text{HO}(\text{CH}_2)_n\text{OH}$ will be more soluble in methanol, exactly as for the alkanols shown in Fig. 1. Plots such as those in Fig. 1 are the simplest demonstration of the hydrophobic effect, without any complications due to solute-solute interactions that inevitably arise when solubilities of liquids in solvents are considered.¹⁹

The factors that influence the solubility of vapours in water and methanol can be shown through a term-by-term analysis of the respective solvation equations, based on eqn. (4). In Table 7 are the contributions to log L made by each term in the equation for the solutes ethanol and heptan-1-ol. In solvent water, the increased solubility of ethanol over heptan-1-ol (by 0.59 log units) is due to the negative $l\log L^{16}$ term. In solvent methanol, the larger alcohol heptan-1-ol is more soluble than solute ethanol by 2.03 log units, entirely due to the effect of the $l\log L^{16}$ term. If we compare the solubility of heptan-1-ol in water and methanol, the increased solubility in methanol is again entirely due to the $l\log L^{16}$ term, with a difference of no less than 4.05 log units in favour of solubility in methanol. This completely overwhelms the other large difference, that in the $b\Sigma\beta_2^H$ term; by itself, this term would result in heptan-1-ol being more soluble in water by 1.64 log units, through the greater hydrogen-bond acidity of water. Similar breakdowns of log L values into components can be made for any of the solutes listed in Table 4. We give in Table 7 values for a typical hydrogen-bond base, triethylamine. Although the much greater hydrogen-bond acidity of water over methanol increases the solubility of triethylamine in water over methanol by some 2.7 log units, once again the very large $l\log L^{16}$ in methanol counteracts this completely.

It is worth noting that the $l\log L^{16}$ term, which for many solutes will be numerically the largest term for solubility in methanol, is composed of a cavity term opposing solution, and a general dispersion interaction term that favours solution. The former will produce a negative contribution to $l\log L^{16}$, so that the general dispersion term will be even more positive than $l\log L^{16}$. Thus in the case of heptan-1-ol in solvent methanol, by far the largest solute-solvent interaction will be that of general dispersion. Levine²⁰ has pointed out that for non-ionic molecules, the dominant term in intermolecular interactions will be that of dispersion, except for small highly polar molecules. Our findings agree with Levine's comment completely.

The method of determining log L values for vapours in methanol through eqn. (3) has led to 23 new values that are compatible with those obtained by traditional methods. Application of the solvation equation, eqn. (4), to 93 values of log L^{MeOH} has resulted in eqn. (5) that correlates these values to 0.13 log units, and which can now be used to estimate further log L^{MeOH} values. This equation is not just a statistical fitting

Table 8 Coefficients in eqn. (6) for water-solvent partitions^a

Solvent	c	r	s	a	b	v
Methanol (dry)	0.33	0.30	-0.67	0.08	-3.39	3.51
Isobutanol (wet)	0.23	0.51	-0.63	0.02	-2.26	2.76
Pentanol (wet)	0.18	0.57	-0.79	0.02	-2.84	3.25
Hexanol (wet)	0.14	0.72	-0.98	0.14	-3.21	3.40
Octanol (wet)	0.09	0.56	-1.05	0.03	-3.46	3.81
Decanol (wet)	0.01	0.48	-0.97	0.02	-3.80	3.95
Hexadecane	0.09	0.67	-1.62	-3.59	-4.87	4.43

^a From ref. 10, except for methanol (this work). Note that for the wet alcohols, the b coefficient refers to the $\Sigma\beta_2^o$ descriptor.

equation, but can be used to investigate the particular solute-solvent interactions that influence the solubility of gases and vapours.

As shown above, we can calculate log $P^{\text{MeOH/W}}$ values through eqn. (5), using log L^W values compiled previously.^{6,21} All the 93 required values of log L^W were available, and the 93 values of log $P^{\text{MeOH/W}}$ could be correlated through eqn. (6) to yield eqn. (8), where $n = 93$, $r^2 = 0.9880$, $sd = 0.16$ and $F = 1440$.

$$\log P^{\text{MeOH/W}} = 0.329 + 0.299 R_2 - 0.671 \pi_2^H + 0.080 \Sigma a_2^H - 0.040 \quad 0.065 \quad 0.090 \quad 0.103 \\ 3.389 \Sigma \beta_2^H + 3.512 Vx \quad (8) \\ 0.097 \quad 0.050$$

The statistics of eqn. (8) are not as good as those of eqn. (7); this is to be expected because the log $P^{\text{MeOH/W}}$ values will be subject to errors both in log L^{MeOH} and log L^W . The t ratios for the coefficients are 4.6(r), 7.5(s), 0.8(a), 35.0(b) and 69.9(v). Cross-correlations between the descriptors are the same as for eqn. (7), except for the Vx descriptor as shown in the matrix above. Eqn. (8) is reasonably good, and affords another comparison of the solvent properties of methanol and water. The coefficients in eqn. (8) now reflect differences in properties of methanol and water. The most striking effects are the almost zero value of the a coefficient, the large negative value of the b coefficient, and the large positive value of the v coefficient. These indicate (i) that methanol and water solvents have the same hydrogen-bond basicity, (ii) that methanol solvent is a much weaker hydrogen-bond acid than water solvent, and (iii) that methanol is much more hydrophobic than water. All this is consistent with our deductions from eqn. (7), and consistent with equations¹⁰ for partitions between water and various (wet) alcohols, see Table 8.

In Table 8 are also given the coefficients for partition from water to hexadecane, as an illustration of the size of the a and b coefficients for a completely nonacidic and nonbasic organic solvent. For all the water-alcohol partitions, whether to dry methanol or wet alcohols, the r and s coefficients do not vary very much. This is no doubt due to a combination of dipolarity (greater for water and the lower alcohols) and polarizability (greater for the higher alcohols). Quite remarkably, the a coefficient is effectively zero for all the water-alcohol partitions, and yet for partition from water to hexadecane the value is very negative (-3.59 units). This can only mean that water, wet alcohols and dry methanol have the same hydrogen-bond basicity. On the other hand, the b coefficient for the wet alcohols becomes progressively less negative as the alcohol becomes smaller, and the amount of water in the alcohol phase becomes larger. That is, the hydrogen-bond acidity of the wet alcohols approaches that of water as the alcohol becomes smaller. Dry methanol has about the same hydrogen-bond acidity as wet hexanol or wet octanol. However, this is much less than that for water; the b coefficient of -3.39 is 70% towards the hexadecane b coefficient of -4.87 units. The v coefficient, rather like the l coefficient in eqn. (4), is a measure of the solvent hydrophobicity, but now relative to water as zero. As expected, the larger

the alcohol and the less water there is in the alcohol phase, the larger is the hydrophobicity. On our scale, dry methanol solvent has nearly the same hydrophobicity as wet hexanol solvent. The general conclusions derived from examination of eqn. (8) are thus the same as those from eqn. (7).

There remains the problem as to why LFERs that deal with partition between water and solvents or between the gas phase and solvents lead to one set of conclusions on the hydrogen-bond acidity and basicity of methanol and other alcohols, whereas the solvatochromic method leads to considerably different conclusions. The LFERs indicate that methanol is much less acidic than water, but has the same hydrogen-bond basicity. The solvatochromic method assigns a similar hydrogen-bond acidity to methanol and water, and rates methanol as a stronger hydrogen-bond base. We suggest that these differences might arise from the fundamentally different processes involved in partition and solvatochromism. The dependent variables in eqn. (7) and eqn. (8), and in any equation that deals with partition coefficients as $\log P$ values, are Gibbs free energy quantities. The Σa_2^H and $\Sigma \beta_2^H$ descriptors are also Gibbs free energy quantities because they are linearly related to equilibrium constants (as $\log K$). Hence the a and b coefficients are exactly equivalent to the slope, m , in a strict Gibbs free energy equation [eqn. (9)],

$$\Delta G^\circ(\text{I}) = m\Delta G^\circ(\text{II}) + c \quad (9)$$

where $\Delta G^\circ(\text{I})$ and $\Delta G^\circ(\text{II})$ are the standard Gibbs free energy changes for processes (I) and (II), in which reactants and products are in equilibrium with their surroundings. On the other hand, solvatochromic properties refer to differences in spectroscopic energy between a ground state and an excited state. Firstly, spectroscopic energy is not a Gibbs energy. Secondly, because of the Franck–Condon principle, the arrangement of solvent molecules around the excited state will be the same as the arrangement around the ground state. The ground state will be in equilibrium with the solvent, but the excited state will not be in equilibrium with the solvent, because the latter has not been allowed to reach its equilibrium position. For solvents that have little inherent ‘order’ or ‘structure’, this non-equilibrium solvation may not be very important. But for solvents such as alcohols and especially water, the equilibrium position of solvent molecules around an excited state that differs from the ground state in dipole moment, acidity or basicity will not be the same as the equilibrium position around the ground state, and non-equilibrium solvation may be highly significant.

There is thus no fundamental reason why solvent properties from solvatochromic measurements should be well matched with solvent properties deduced from LFERs through the m

coefficient in eqn. (9), or the a and b coefficients in eqn. (7) and eqn. (8).

In conclusion, we have constructed an equation for the correlation and prediction of $\log L^{\text{MeOH}}$ values that can also be used to establish important chemical properties of methanol solvent. An equation for $\log P^{\text{MeOH/W}}$ for transfer from water to methanol yields very similar information. The hydrogen-bond acidity and hydrogen-bond basicity of methanol with respect to water and other alcohols, deduced from either equation, do not agree with the corresponding solvatochromic properties of water and alcohols.

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