Correlation and Prediction of Gas–Liquid Partition Coefficients in Hexadecane and Olive Oil

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A cavity theory of solution has been used to derive an equation for the correlation and prediction of Ostwald solubility coefficients (as log L values) of solutes in hexadecane and olive oil:

$$\log L = a + bV + c(MR) + d\mu^2$$

The endoergic work of creating a cavity in the solvent is given by bV, where V is a solute volume, and the exoergic solute–solvent interactions are given by c(MR) and dμ^2, being dispersion and dipole-induced dipole (or dipole–dipole) effects, respectively; MR and μ are the solute molar refraction and dipole moment. When applied to 84 log L values for a wide variety of solutes in hexadecane, the standard deviation in log L is only 0.18 log units, and for 52 non-acidic solutes in olive oil the corresponding standard deviation is 0.23 log units. Comparison of calculated and observed log L values on olive oil for a number of hydrogen-bond-donor solutes shows that hydrogen bonding from the solute to the basic olive oil is negligible for solute $CHCl_3$, but contributes about 20% of the total solute–olive oil interaction energy for alcohol solutes, *viz.* ~2 kcal mol^{-1}.[†]

Recently, two general equations have been developed for the correlation and prediction of the effect of solutes on a wide variety of physicochemical and biochemical phenomena. For processes in condensed systems equation (1) is used;[1,2] SP is the property to be correlated and $(SP)_0$ is a constant. The other items refer to solute properties as follows: $\bar{V}_2$ is the solute molar volume and the term m$\bar{V}_2$ describes the endoergic process of cavity formation, π_2^* is the solute dipolarity, α_2 is the solute hydrogen-bond acidity, and β_2 is the solute hydrogen-bond basicity. These three solute terms describe the exoergic solute–solvent interactions.

$$SP = (SP)_0 + m\bar{V}_2/100 + s\pi_2^* + a\alpha_2 + b\beta_2 \quad (1)$$

Examples of processes correlated by equation (1) include octanol–water partition coefficients,[3] the solubility of liquid nonelectrolytes in water[4] and in blood,[5] the adsorption of nonelectrolytes from aqueous solution on carbon,[6] and the toxicity of aqueous solutions of nonelectrolytes towards *Photobacterium phosphoreum*.[7] Equation (1), however, is not so useful for processes in which solutes are transferred from the gas phase into a condensed phase, possibly because it contains no explicit term that covers dispersion interactions between the solute and the condensed phase. For such processes, the alternative equation (2) is preferred,[8] with the solute

$$SP = (SP)_0 + l(\log L^{16}) + s\pi_2^* + a\alpha_2 + b\beta_2 \quad (2)$$

parameter log L^{16} replacing the solute parameter $\bar{V}_2/100$. The former is simply[9] a function of the Ostwald solubility coefficient of a solute in hexadecane at 289 K, defined by equation (3). This

$$L^{16} = \frac{\text{concentration of solute in hexadecane}}{\text{concentration of solute in the gas phase}} \quad (3)$$

L^{16} value (as log L^{16}) may be regarded as a 'backing-off' term,[8] and is clearly related to the endoergic work of creating a cavity in the solvent and the exoergic solute–solvent dispersion interactions.[‡] No doubt L values in other nonpolar solvents would suffice as well as those in hexadecane, but L^{16} values were chosen because they can be determined very conveniently by gas–liquid chromatography, with hexadecane as the stationary phase.[9] Indeed, we have listed[9] no fewer than 240 values of log L^{16} at 298 K, covering a wide range of not-too-involatile solutes. Although this is probably the most extensive list of L values available for any non-aqueous solvent, equation (2) still suffers in general applicability, in comparison with equation (1), because log L^{16} values must be experimentally determined, whereas $\bar{V}_2$ values can be estimated (or can be replaced altogether by calculated intrinsic volumes, V_{IN}). We have already applied equation (2) successfully to the solubility of gases and vapours in polymers,[8] but it seems useful to investigate methods of estimating further log L^{16} values, as well as to examine any theoretical connection with cavity and dispersion effects; this is the main aim of the present work.

Together with our list of 240 log L^{16} values, we also recorded[9] no fewer than 140 values of solute Ostwald coefficients on olive oil at 310 K, denoted as log L^{oil}. These latter values have been used to correlate and to predict the solubilities of gases and vapours in biological systems,[10] and so methods of estimating these log L^{oil} values would also be of value.

There have been numerous attempts to correlate gas–liquid partition coefficients, either as log L values or as log V_G values, but most of these attempts are of little general use, being restricted to certain specific classes of solute (see *e.g.* the review by Ecknig[11]). Ecknig and his co-workers[12] have used a semi-empirical method of estimating log V_G values, based on two parameters, φ and D. The former is a polar parameter that includes dipole–dipole interactions, hydrogen bonding, induction effects, *etc.*, and D is a non-polar dispersion parameter calculated from atomic group refractions. The calculation of φ

[†] 1 kcal = 4.184 kJ.

[‡] The standard free energy of solution of a gaseous solute is given by $\Delta G_s^0 = -RT \ln L$, with standard states of unit concentration in the gas phase and in solution.

Table 1. Values used in the calculations[a]

Solute	V_{adj}	V_{IN}	V_x	μ	MR	$\log L^{16}$	$\log L^{oil}$
Propane	88.1	36.0	53.1	0.00	15.95	1.050	0.742
Butane	100.4	45.8	67.2	0.00	20.63	1.615	1.267
Pentane	115.2	55.3	81.3	0.00	25.27	2.162	1.671
Hexane	130.5	64.8	95.4	0.00	29.89	2.668	2.130
Heptane	146.5	74.5	109.5	0.00	34.57	3.173	2.587
Octane	162.6	84.2	123.6	0.00	39.19	3.677	3.039
Nonane	178.7	93.9	137.7	0.00	43.84	4.182	3.480
Decane	194.9	103.6	151.8	0.00	48.43	4.686	3.914
Undecane	211.2	113.3	165.9	0.00	53.13	5.191	4.361
Dodecane	227.5	123.0	180.0	0.00	57.77	5.696	4.803
Hexadecane	292.9	161.7	236.3	0.00	76.36	7.714	6.572
Cyclopentane	104.1	50.0	70.4	0.00	23.13	2.447	1.995
Cyclohexane	118.1	59.8	84.5	0.00	27.73	2.913	2.439
Hept-1-ene	140.9	71.5	105.2	0.34	34.13	3.063	
Hex-1-ene	125.0	61.8	91.1	0.34	29.21	2.547	
Oct-1-ene	157.0	81.2	119.3	0.34	38.78	3.591	
Benzene	98.9	49.1	71.6	0.00	26.20	2.803	2.598
Toluene	116.3	59.2	85.7	0.36	31.06	3.344	3.075
Ethylbenzene	132.5	68.7	99.8	0.59	35.77	3.765	3.493
p-Xylene	133.3	67.1	99.8	0.00	36.00	3.858	3.531
n-Propylamine	82.4	43.3	63.1	1.40	19.40	2.141	
Aniline	101.1	56.2	81.6	1.56	30.60	3.993	
n-Pentylamine	115.5	62.3	91.3	1.37	28.72	3.086	
n-Butylamine	98.7	52.8	77.2	1.37	24.08	2.618	
Triethylamine	139.1	70.4	105.4	0.66	33.80	3.077	2.834
Pyridine	90.6	47.0	67.5	2.19	24.07	3.003	3.196
Dimethylformamide	77.0	44.4	64.7	3.82	19.92	3.173	3.458
Dimethylacetamide	93.0	54.3	78.8	3.81	24.38	3.717	3.896
Acetonitrile	52.2	27.1	40.4	3.92	11.08	1.560	
Propiononitrile	70.5	36.9	54.5	4.02	15.78	1.940	
Nitromethane	53.7	34.8	42.4	3.46	12.49	1.892	2.445
Nitroethane	71.9	44.5	56.5	3.70	17.10	2.367	2.750
1-Nitropropane	89.3	54.2	70.6	3.66	21.72	2.710	
Nitrobenzene	112.3	63.1	89.1	3.93	32.88	4.460	
Methyl formate	61.6	32.5	46.5	1.77	13.04	1.459	1.561
Methyl acetate	79.4	42.4	60.6	1.72	17.49	1.960	2.017
Ethyl acetate	97.9	52.1	74.7	1.78	22.25	2.376	2.360
Butyl acetate	131.6	71.6	102.9	1.80	31.50	3.379	3.196
Propanone	73.5	38.0	54.7	2.88	16.18	1.760	1.921
Butanone	89.5	47.7	68.8	2.76	20.68	2.287	2.358
Pentan-2-one	106.5	57.4	82.9	2.70	25.21	2.755	2.696
Pentan-3-one	105.8	57.4	82.9	2.82	25.22	2.811	2.717
Heptan-2-one	140.8	76.7	111.1	2.61	34.79	3.760	3.832
Heptan-4-one	139.7	76.7	111.1	2.74	34.38	3.820	
Hexan-2-one	123.5	67.0	97.0	2.65	29.98	3.262	3.214
Cyclohexanone	113.6	61.9	86.1	3.08	27.86	3.616	
Acetophenone	126.9	69.0	102.8	2.96	36.51	4.483	
Acetaldehyde	56.3	28.3	40.6	2.69	11.53	1.230	
Propionaldehyde	72.1	38.1	54.7	2.52	16.06	1.815	
Butyraldehyde	88.3	48.0	68.8	2.72	20.66	2.270	
Di-n-propyl ether	135.9	69.9	101.3	1.24	31.87	2.989	
Diethyl ether	103.8	50.5	73.1	1.15	22.49	2.061	1.813
Di-n-butyl ether	169.4	89.3	129.5	1.17	40.99	4.001	3.417
Anisole	118.6	63.0	100.3	1.38	32.89	3.926	
Tetrahydrofuran	91.1	45.5	68.8	1.63	19.97	2.534	2.389
Dioxane	95.2	49.1	68.1	1.63	21.68	2.797	2.830
Methanol	40.5	20.5	30.8	1.70	8.23	0.922	
Ethanol	58.4	30.5	44.9	1.69	12.92	1.485	
Propan-1-ol	74.8	40.2	59.0	1.68	17.49	2.097	
Propan-2-ol	76.6	40.3	59.0	1.66	17.62	1.821	
Butan-1-ol	91.5	49.9	73.1	1.66	22.15	2.601	
Pentan-1-ol	108.2	59.3	87.2	1.66	26.82	3.106	
Octan-1-ol	157.5	88.2	129.5	1.72	40.64	4.619	
2,2,2-Trifluoroethanol	72.3	37.6	50.2	2.52	13.19	1.224	
1-Chlorobutane	104.5	54.8	79.5	2.05	25.44	2.722	2.464
1-Chloropentane	120.9	64.5	93.6	2.16	30.12	3.223	2.990
Dichloromethane	64.0	33.6	49.4	1.60	16.34	2.019	2.136
Trichloromethane	80.5	42.7	61.7	1.01	21.46	2.480	2.582
Tetrachloromethane	96.5	51.4	73.9	0.00	26.43	2.823	2.527
1,2-Dichloroethane	80.1	44.2	63.5	1.86	21.31	2.573	2.614
Chloroethane	71.9	35.0	51.3	2.05	16.17	1.678	1.548

Table 1. (*continued*)

Solute	V_{adj}	V_{IN}	V_x	μ	MR	log L^{16}	log L^{oil}
1-Chloropropane	88.2	44.7	65.4	2.05	20.81	1.997	2.076
1,1-Dichloroethane	84.2	43.9	63.5	2.06	21.15	2.350	2.272
Chlorobenzene	111.8	58.1	83.9	1.75	31.15	3.640	3.455
1,1-Dichloroethene	79.6	40.4	59.2	1.34	20.35	2.110	
Tetrachloroethene	102.0	57.8	83.7	0.00	30.33	3.584	3.219
1,1,2,2-Tetrachloroethane	105.2	61.7	88.0	1.32	30.63	3.826	4.121
Bromoethane	74.6	39.1	56.6	2.03	19.03	2.020	
1-Bromobutane	107.4	59.3	84.8	2.08	28.31	3.105	
Dibromomethane	69.6	43.3	60.0	1.43	21.91	2.849	
Tribromomethane	87.5	56.8	77.5	0.99	29.82	3.747	
1,2-Dibromoethane	86.2	53.1	74.0	0.92	26.99	3.399	3.556
Bromobenzene	115.0	62.4	89.2	1.70	33.94	4.035	4.141
1,1,1-Trichloroethane	99.6	51.0	75.8	1.78	26.15	2.690	2.471

[a] Volumes in $cm^3 mol^{-1}$; dipole moments in Debyes, and molar refractions as calculated in equation (5). All log L values taken from ref. 9.

and D is quite complicated,[12] but good agreement with experiment was obtained for retention data of 27 polar solutes on several solvent phases, using a separate equation (4) for each phase; the constants A_0, A_1, and A_2 are empirical coefficients.[13]

$$\log V_G = A_0 + A_1\varphi + A_2 D \quad (4)$$

Interestingly, Ecknig and his co-workers did not use any 'cavity term' in their calculations, although this is a central feature of the most general method used in gas solubility calculations, *i.e.* the scaled particle theory (SPT). Pierotti's version[14] of SPT is now commonly used to calculate gas–liquid partition coefficients, especially for the permanent gases. However, it is now clear that SPT is not so useful for the calculation of the solubility of larger solutes, even in nonpolar solvents such as hexane and benzene.[15] We have, therefore, chosen to use an empirical method of correlation, although based on the general concepts of cavity theories, such as SPT.

We start by considering the solubility of a gas to be governed by a cavity term related to the endoergic work of creating a suitably sized cavity in the solvent, plus exoergic interaction terms that reflect the various solute–solvent interactions set up on placing a solute in the cavity. For solution of a series of solutes in the same solvent, the cavity term will be proportioned to solute size. We have chosen three particular estimates: (i) the solute bulk molar volume at 293 K taken as $\bar{V}_2 = (MW)/\rho_2$, where MW is the solute molecular weight and ρ_2 the density (following previous workers,[1–7] we adjust the molar volume by addition of 10 $cm^3 mol^{-1}$ for each ring in the solute to give an adjusted molar volume, V_{adj}); (ii) the computer-calculated intrinsic volume, V_{IN}, of Leahy,[16] which has the advantage that V_{IN} values can be computed for any solute, even those that are solid at room temperature; and (iii) the calculated characteristic molecular volume, V_x, of McGowan.[17] Not only do the volumes V_x have the same advantage as V_{IN} over V_{adj}, they also have a decided advantage over intrinsic volumes in that the calculation of V_x is trivial.

For the solute–solvent interaction terms, we first consider the dispersion interaction term. Again, for a series of solutes in a given solvent, following the Kirkwood–Muller approach,[14] we can take this term to be proportional to the solute polarisability, P_2, and in particular to the electronic solute polarisability P_E. But this is simply the molar refraction, MR, given by the Lorenz–Lorentz equation (5), where η is the refractive index of

$$MR = \frac{\eta^2 - 1}{\eta^2 + 2} \cdot \frac{(MW)}{\rho_2} \quad (5)$$

the sodium D-line at 293 K.[18] If both solute and solvent are dipolar, then a dipole–dipole term proportional to $\mu_1^2\mu_2^2$ is necessary,[14] whereas for a nonpolar solvent a dipole-induced dipole term, $\mu_1^2P_2 + \mu_2^2P_1$, is needed. For a given solvent, μ_1^2 and P_1 are constant, so that the dipole–dipole term is just proportional to μ_2^2 and the dipole-induced dipole term reduces to (const.) P_2 + (const.)μ_2^2. Since P_2 is equated to MR, we have that a dipole–dipole term will involve just μ_2^2 and a dipole-induced dipole term will involve MR and μ_2^2. In either case, the total dipole effect plus the dispersion interaction will be given by a term in MR and a term in μ_2^2.

We can therefore collect all the solute–solvent interaction terms, together with a cavity term, and arrive at an empirical equation (6) for the correlation of log L values for a series of

$$\log L = a + bV + c(MR) + d\mu^2 \quad (6)$$

solutes in a given solvent.* In this equation, V can be V_{adj}, or V_{IN}, or V_x, and MR is defined by equation (5). The constants a—d are determined by multiple regression analysis.

First we consider gas–hexadecane partition coefficients, as log L^{16} values. We have available all the parameters in equation (6) for 84 solutes, including aliphatic compounds, aromatic compounds, hydroxylic compounds, *etc.* A complete list of parameters is given in Table 1. Regressions were carried out for all three size parameters, and a summary of the regression equations (6) is given in Table 2A. In all three cases, the signs of the coefficients are as expected: the negative coefficient b represents an endoergic cavity effect, and the positive coefficients c and d represent exoergic solute–solvent interactions. The correlations are all reasonably good, and further log L^{16} values can be calculated for use in equation (2); since log L^{16} is only one contributing term in this equation, even approximate log L^{16} values could suffice. In the set shown in Table 2A, and in all other solvent sets, use of V_{adj} leads to the best correlation. Most interestingly, the trivially calculated V_x parameter always yields a slightly better correlation than the computer-calculated V_{IN} values. In view of the interest in the use of Leahy's intrinsic volumes, it seems worthwhile to compare V_x and V_{IN} as solute parameters in other processes.

One worrying feature of the explanatory parameters in equation (6) is that for the wide range of 84 solutes (Table 1), the parameters V (V_{adj}, V_{IN}, or V_x) and MR are highly correlated, not surprisingly because the definition of MR actually involves $\bar{V}$ as $(MW)/\rho_2$. The regression coefficient between MR and V_{adj}, for example, is 0.972, so that these two parameters are not independent. However, dropping one or other of V_{adj} and MR results in a severe loss of correlation power. For the 84 solutes, an equation in V_{adj} and μ^2 only has s.d. = 0.542 and r = 0.873

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* We have used also a term in μ rather than in μ^2, but the difference in the correlations obtained is trivial.

Table 2. Summary of the general regression equation (6)[a]

	a	bV	c(MR)	d(μ^2)	n	s.d.	r
A. All solutes on hexadecane							
(i) V_{adj}	0.2927	−0.0263	0.1975	0.0451	84	0.185	0.986
	(0.0725)	(0.0021)	(0.0080)	(0.0052)			
(ii) V_{IN}	0.0574	−0.0456	0.1953	0.0650	84	0.258	0.973
	(0.0952)	(0.0074)	(0.0152)	(0.0074)			
(iii) V_x	0.0425	−0.0340	0.2041	0.0600	84	0.246	0.975
	(0.0903)	(0.0048)	(0.0145)	(0.0069)			
B. Aprotic solutes on hexadecane							
(i) V_{adj}	0.3020	−0.0254	0.1930	0.0531	52	0.181	0.988
	(0.0894)	(0.0028)	(0.0104)	(0.0071)			
(ii) V_{IN}	−0.0207	−0.0477	0.2001	0.0836	52	0.240	0.979
	(0.1108)	(0.0092)	(0.0194)	(0.0104)			
(iii) V_x	−0.0524	−0.0354	0.2094	0.0783	52	0.225	0.981
	(0.1040)	(0.0058)	(0.0180)	(0.0092)			
C. Aliphatic aprotic solutes on hexadecane							
(i) V_{adj}	0.2363	−0.0261	0.1973	0.0481	64	0.180	0.987
	(0.0803)	(0.0025)	(0.0097)	(0.0057)			
(ii) V_{IN}	−0.0281	−0.0580	0.2227	0.0743	64	0.260	0.973
	(0.1103)	(0.0128)	(0.0272)	(0.0096)			
(iii) V_x	−0.0555	−0.0462	0.2434	0.0701	64	0.230	0.979
	(0.0979)	(0.0071)	(0.0221)	(0.0078)			
D. Aprotic solutes on olive oil							
(i) V_{adj}	0.6468	−0.0384	0.2233	0.0869	52	0.233	0.973
	(0.1151)	(0.0035)	(0.0134)	(0.0092)			
(ii) V_{IN}	0.1594	−0.0695	0.2283	0.1318	52	0.342	0.941
	(0.1579)	(0.0130)	(0.0277)	(0.0148)			
(iii) V_x	0.1112	−0.0529	0.2456	0.1247	52	0.313	0.951
	(0.1448)	(0.0080)	(0.0250)	(0.0129)			

[a] n = no. of solutes; s.d. = standard deviation; r = multiple correlation coefficient. The standard errors of the regression coefficients are given in parentheses.

Table 3. Analysis of the contributing terms to values of log L^{16}, using the regression equation A(i)

Solute	V_{adj}	MR	μ^2	residual[a]
n-Hexane	−3.43	5.90	0	(−0.10)
Propanone	−1.93	3.20	0.37	(−0.17)
Heptan-2-one	−3.70	6.87	0.31	(0.00)
Ethyl acetate	−2.57	4.39	0.14	(0.12)
Methanol	−1.07	1.63	0.13	(−0.06)
Octan-1-ol	−4.14	8.03	0.13	(0.30)
Nitropropane	−2.35	4.29	0.60	(−0.12)

[a] As log L (calc.) + residual = log L (obs.).

Table 4. Analysis of the contributing terms to values of log L^{oil} using equation D(i)

Solute	V_{adj}	MR	μ^2	HB
n-Hexane	−5.01	6.67	0	(0.29)
Propanone	−2.82	3.61	0.72	(−0.23)
Heptan-2-one	−5.36	7.77	0.59	(0.18)
Ethyl acetate	−3.76	4.97	0.28	(0.22)
Tetrachloromethane	−3.71	5.90	0	(−0.31)
Dimethylformamide	−2.96	4.45	1.27	(0.05)
Pyridine	−3.48	5.38	0.42	(0.24)
Triethylamine	−5.34	7.55	0.04	(−0.06)
Chloroform	−3.09	4.79	0.09	(0.14)
Methanol	−1.56	1.85	0.25	0.93
Ethanol	−2.24	2.89	0.25	1.07
Propan-1-ol	−2.87	3.91	0.25	1.22
Propan-2-ol	−2.94	3.94	0.24	0.93
Butan-1-ol	−3.51	4.95	0.24	1.27
2-Methylpropan-2-ol	−3.61	4.95	0.25	0.67

and an equation in MR and μ^2 has s.d. = 0.312 and r = 0.959, as compared with values of s.d. = 0.185 and r = 0.986 when V_{adj}, MR, and μ^2 are used. Furthermore, in equation (6) for 84 solutes, the confidence levels for the parameters V_{adj}, MR, and μ^2, are all over 99.9999% as judged by Student's *t*-test, so that it seems reasonable to use all these parameters. One method of deciding whether or not linearity of parameters leads to an unstable regression equation is to compare regression coefficients for various subsets of data. In Table 2B are given results for the same set of aprotic solutes as we used in the log L^{oil} regressions (see later), and Table 2C shows results for a specific subset of aliphatic aprotic solutes. It can be seen that the coefficients a—d remain the same over the three sets of data, and that values of s.d. and r are practically constant. We therefore feel that in spite of the collinearity of V and MR, both parameters are required, and that the resulting regression equation is perfectly stable.

The standard deviations in Table 2 reflect not only any intrinsic random error in equation (6), but also errors in log L^{16} and in the input parameters. Exner[18] has warned of the possible errors involved in the calculation of dipole moments, and inspection of various reported values of μ suggests that at least part of the overall s.d. value could arise through errors in the input μ values. However, the term in μ^2 is the smallest contributing term to log L^{16} over all the 84 solutes. In Table 3 is given a breakdown of terms contributing to log L^{16}: the dipole-induced dipole term makes only a minor contribution, even in the case of the most dipolar solutes (*e.g.* dimethylformamide), and the quite large negative cavity term (V_{adj}) is outweighed by the very positive dispersion interaction term (MR). Possibly, the reason why Ecknig and his co-workers[12] obtained good correlations without the use of a cavity term is that since V_{adj} is well correlated with MR, the cavity term in their equation (4) was actually subsumed into the 'dispersion' term.

We turn now to the solubility coefficients on olive oil, log L^{oil}. Since we have no parameters in equation (6) that take care of any hydrogen-bonding effects, and since olive oil (unlike hexadecane) is a hydrogen-bonding base, we omit from our correlation all solutes that are hydrogen-bonding acids. We are left with 52 aprotic solutes, for which the constants in the regression equation (6) are given in Table 2D. The regressions for olive oil are not as good as those for hexadecane (compare Table 2D with Table 2B) but might still be useful in predicting new log L^{oil} values. It is difficult to predict the magnitude of the coefficients b and c for olive oil against those for hexadecane, but certainly the coefficient of μ^2 should be larger in olive oil than in hexadecane, exactly as is observed (0.0869 as against 0.053 for the regression with V_{adj}). It might be thought that the log L^{16} values could be used to 'back-off' the log L^{oil} values as in

$$\log L^{oil} - \log L^{16} = 0.345 - 0.0130V_{adj} + 0.0303(\text{MR}) + 0.0338\mu^2 \quad (7)$$
$$n = 52 \quad r = 0.935 \quad \text{s.d.} = 0.127$$

equation (7), but the relatively small s.d. value is somewhat of an artefact since equation (7) is merely the difference of equations B(ii) and D(ii) in Table 2.

Although we have specifically excluded hydrogen-bonding acids from the olive-oil solvent set, we can use our general equation (6) to estimate the effect of hydrogen-bonding on log L^{oil}. We know from equations A(i) and C(ii) in Table 2 that identical equations result from regressions on hexadecane that include and exclude hydrogen-bonding acids. Hence with some confidence we can assume that equation D(i) in Table 2, constructed for aprotic solutes, will also apply to the non-hydrogen-bonding terms for solution of hydrogen-bonding acids. Hence log L^{oil}(obs.) − log L^{oil}[calc. *via* equation D(i)] should provide a measure of the hydrogen-bonding term for these solutes in olive oil. In Table 4 is an analysis of contributing terms for some aprotic solutes on olive oil, following Table 3 exactly; also given are the calculated terms including the hydrogen-bonding term for some hydroxylic solutes. For the aprotic solutes the differences between observed and calculated values are parenthesised in the final column; these are in accord with the standard deviation of 0.23 log units given by equation D(i) in Table 2. The difference for chloroform of only 0.14 is zero within the correlational uncertainty and shows how very weak is monomeric chloroform as a hydrogen-bonding acid. However, the obtained differences for the alcohols all have the correct (positive) sign, and are well outside the standard deviation, thus indicating a substantial, but not large, contribution from hydrogen-bonding. Differences within the alcohol series are not significant, and we can conclude that the hydrogen bond between acidic alcohol and basic olive oil contributes about 20% of the total exoergic interaction energy, that is about 2 kcal mol^{-1}.

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References

1 M. H. Abraham, R. M. Doherty, M. J. Kamlet, and R. W. Taft, *Chem. Br.*, 1986, **22**, 551.
2 M. J. Kamlet, R. M. Doherty, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *Chem.tech.*, 1986, 566.
3 R. W. Taft, M. H. Abraham, G. R. Famini, R. M. Doherty, J.-L. M. Abboud, and M. J. Kamlet, *J. Pharm. Sci.*, 1985, **74**, 807.
4 M. J. Kamlet, R. M. Doherty, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Pharm. Sci.*, 1986, **75**, 338.
5 M. J. Kamlet, D. J. Abraham, R. M. Doherty, R. W. Taft, and M. H. Abraham, *J. Pharm. Sci.*, 1986, **75**, 350.
6 M. J. Kamlet, R. M. Doherty, M. H. Abraham, and R. W. Taft, *Carbon*, 1985, **23**, 549.
7 M. J. Kamlet, R. M. Doherty, G. D. Veith, R. W. Taft, and M. H. Abraham, *Environ. Sci. Technol.*, 1986, **20**, 690.
8 M. H. Abraham, P. L. Grellier, R. A. McGill, R. M. Doherty, M. J. Kamlet, T. N. Hall, R. W. Taft, P. W. Carr, and W. J. Koros, *Polymer*, 1987, **28**, 1363.
9 M. H. Abraham, P. L. Grellier, and R. A. McGill, *J. Chem. Soc., Perkin Trans. 2*, 1987, 797.
10 M. H. Abraham, M. J. Kamlet, R. W. Taft, R. M. Doherty, and P. K. Weathersby, *J. Med. Chem.*, 1985, **28**, 865.
11 W. Ecknig, *Z. Chem.*, 1985, **25**, 240.
12 T. Kleinert and W. Ecknig, *J. Chromatogr.*, 1984, **315**, 75.
13 T. Kleinert, W. Ecknig, and J. Novak, *J. Chromatogr.*, 1984, **315**, 85.
14 R. A. Pierotti, *Chem. Rev.*, 1976, **76**, 717.
15 M. H. Abraham and A. Nasehzadeh, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 321.
16 D. Leahy, *J. Pharm. Sci.*, 1986, **75**, 629.
17 M. H. Abraham and J. C. McGowan, *Chromatographia*, 1987, **23**, 243.
18 O. Exner, 'Dipole Moments in Organic Chemistry,' Thieme, Stuttgart, 1975.

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