Thermodynamics of Solute Transfer from Water to Hexadecane

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New measurements of enthalpies of solution in hexadecane and in water (ΔH_s°), and gas–hexadecane Ostwald solubility coefficients (L_H) of neutral monomeric organic solutes are reported. These values, together with literature values of ΔH_s°, L_H, and gas–water Ostwald solubility coefficients (L_W), have been used to derive the Gibbs energies, enthalpies, and entropies of solute transfer from water to hexadecane (ΔG_{tr}°, ΔH_{tr}°, and ΔS_{tr}°), as well as water–hexadecane partition coefficients (as log P_H). Results have been examined by the method of multiple linear regression analysis, using the equation,

$$SP = c + d\delta_2 + s\pi_2^* + a\alpha_2 + b\beta_2 + vV_2$$

The $s\pi_2^*$ term is difficult to interpret, but the $a\alpha_2$ and $b\beta_2$ terms can be shown to arise through hydrogen bonding of solute molecules to the bulk water that is exothermic but rather disfavoured entropically. It is shown also that the vV_2 term arises due to a combination of cavity effects and general dispersion interactions in bulk water and bulk hexadecane.

The use of water–octanol partition coefficients is widespread in medicinal and pharmaceutical chemistry, and, indeed, forms part of the general rationale governing most quantitative structure–activity relationships (QSARs).[1] Although water-saturated octanol, according to this rationale, is a suitable model for biological membranes, other solvents, and hence other water–solvent partition coefficients, have also been used in QSARs. For example, Finkelstein[2] and, later, Franks and Lieb[3] used water–hexadecane partition coefficients, the latter workers specifically to test for hydrophobic binding sites in the luciferase enzyme. In these studies the required water–hexadecane partition coefficients were obtained by the traditional 'shake-flask' method. Unlike the water–octanol system, in which the mutual miscibility of the two solvents is quite high, the water–hexadecane system can be regarded as a system containing the two pure solvents (the solubility of water in hexadecane is 2×10^{-3} mol dm^{-3} and that of hexadecane in water is 4×10^{-4} mol dm^{-3}).[4] Hence water–hexadecane partition coefficients can be determined indirectly using equation (1), where L_W and L_H are the respective gas–solvent

$$P_H = L_H/L_W \qquad (1)$$

Ostwald solubility coefficients.† We,[4] and Shantz and Martire,[5] have shown almost simultaneously that values of P_H obtained indirectly *via* equation (1) are, indeed, identical with values determined by the direct 'shake-flask' method. Since the values of L_H can be measured very accurately by a gas-chromatographic method using hexadecane as the stationary phase,[4,5] it is possible from known aqueous solubilities of gases[6–10] to obtain P_H values relatively simply for a wide range of not-too-involatile solutes.

One of the aims of the present work is to set out values of P_H for the water–hexadecane partition of neutral, monomeric solutes, either as log P_H or as transfer Gibbs energies, ΔG_{tr}°, for as wide a range of solutes as possible. The second aim is to present values for the enthalpy, and hence, the entropy, of transfer of examples of these solutes. To date, there have been very few sets of ΔG_{tr}°, ΔH_{tr}°, and ΔS_{tr}° values for partition from water to a given solvent. The most substantial set of data is that of Riebesehl and Tomlinson,[11] who used a direct flow-microcalorimeter method to obtain ΔH_{tr}° values for transfer of 29 solutes from water to 2,2,4-trimethylpentane. We later analysed the thermodynamic results of Tomlinson and co-workers,[11,12] but found[13] that the data were not extensive enough to examine aliphatic and aromatic solutes separately. We have therefore obtained ΔH_{tr}° values through a combination of enthalpies of solution in water and in hexadecane separately, and set out ΔG_{tr}°, ΔH_{tr}°, and ΔS_{tr}° values for as many solutes as possible. We have, as well as our own calorimetrically determined ΔH_s° values, used literature data on ΔH_s° values in water and hexadecane, where possible, selecting calorimetrically determined values. Of course, for solutes that are gaseous at room temperature and pressure, ΔH_s° values have nearly always been obtained through the temperature variation of solubility—the so called van't Hoff method—but the method of direct calorimetry is to be preferred.

Experimental

Values of L_H for solutes on hexadecane at 298.15 K were obtained as described before.[4] The instruments used were either a Pye–Unicam 104 chromatograph fitted with a katharometer detector, for the determination of absolute L_H values, or a Perkin-Elmer F-11 chromatograph fitted with a flame detector, for the determination of relative L_H values to be converted into absolute values.

Enthalpies of solution in hexadecane and in water were measured as described previously,[14] with liquid solute samples of 10, 20, or 50 mm^3 injected through Teflon-faced silicone septa into vapour-tight, vacuum-jacketed solution calorimeters containing 80–110 cm^3 of solvent. For solutes which dissolve slowly the normal stirring speed of 300 rpm was increased to 600 rpm. Solutes and solvents, all of >99% purity, were dried with 4A molecular sieve, with the ex-

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† Note that L_H is the same as L,[16] the symbol we previously used.[4]

Table 1. Thermodynamics of transfer of solutes from water to hexadecane, and calculation of ΔG°_{tr} (mole fraction scale) and log P_H (molar scale) for water to hexadecane at 298 K.

Solute	Water[a]		Hexadecane[b]		Water ⟶ Hexadecane			log L_W	log L_H	log P_H
	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}			
Helium	7.03	−0.16	4.99	1.97[c]	−2.04	2.13	14.0	−2.023	−1.741	0.28
Neon	6.94	−0.92	4.77	1.62[c]	−2.17	2.54	15.8	−1.958	−1.575	0.38
Argon	6.27	−2.93	3.56	−0.19[c]	−2.71	2.74	18.3	−1.467	−0.688	0.78
Krypton	5.93	−3.74	2.91	−1.20[c]	−3.02	2.54	18.6	−1.213	−0.211	1.00
Xenon	5.60	−4.63	2.10	−2.41[c]	−3.50	2.22	19.2	−0.972	0.378	1.35
Radon	5.15	−5.74	1.42	−3.39[c]	−3.73	2.35	20.4	−0.646	0.877	1.52
Methane	6.27	−3.15	3.06	−0.95[c]	−3.21	2.20	18.1	−1.452	−0.323	1.14
Ethane	6.09	−4.66	1.95	−2.75[c]	−4.14	1.91	20.3	−1.336	0.492	1.83
Propane	6.23	−5.56	1.19	−3.81[c]	−5.04	1.75	22.8	−1.436	1.050	2.49
Butane	6.34	−6.20	0.42	−4.97[c]	−5.92	1.23	24.0	−1.518	1.615	3.13
2-Methylpropane	6.59	−5.78[d]	0.70	−4.48[c]	−5.89	1.30	24.1	−1.70	1.409	3.11
Pentane	6.60	−6.76	−0.33	−6.20	−6.93	0.56	25.1	−1.704	2.162	3.87
Hexane	6.76	−7.65	−1.02	−7.42	−7.78	0.23	26.9	−1.821	2.668	4.49
Heptane	6.95	−8.13	−1.71	−8.64	−8.66	−0.51	27.3	−1.962	3.173	5.14
Octane	7.15	−8.60	−2.40	−9.83	−9.55	−1.23	27.9	−2.109	3.677	5.79
Cyclopropane	5.02	−5.56[d]	0.83		−4.19			−0.55	1.314	1.86
Cyclopentane	5.48	−7.25	−0.72	−6.61[e]	−6.20	0.64	22.9	−0.88	2.447	3.33
Cyclohexane	5.50	−7.84[d]	−1.35	−7.53[e]	−6.85	0.31	24.0	−0.90	2.913	3.81
2,2-Dimethylpropane[f]	6.78		0.14		−6.64			−1.84	1.82	3.66
3,3-Diethylpentane[f]	6.50		−2.59		−9.09			−1.63	3.82	5.45
Tetramethylsilane[f]	7.32		−0.30		−7.62			−2.23	2.14	4.37
Tetraethylsilane[f]	7.04		−3.24		−10.33			−2.03	4.33	6.36
Tetramethyltin[f]	6.48		−1.36		−7.84			−1.62	2.92	4.54
Tetraethyltin[f]	6.75		−4.31		−11.06			−1.82	5.08	6.90
Ethene	5.55	−3.93[d]	2.23	−2.67[g]	−3.32	1.26	15.4	−0.94	0.289	1.23
Propene	5.59	−5.17[d]	1.33	−3.19[h]	−4.26	1.98	20.9	−0.97	0.946	1.92
But-1-ene	5.65	−5.77[d]	0.59		−5.06			−1.01	1.491	2.50
Pent-1-ene	5.94		−0.13		−6.07			−1.23	2.013	3.24
Hex-1-ene	5.85		−0.86		−6.71			−1.16	2.547	3.71
Hept-1-ene	5.93		−1.56		−7.49			−1.22	3.063	4.28
Oct-1-ene	6.19		−2.28		−8.47			−1.41	3.591	5.00
Non-1-ene	6.33		−2.84		−9.17			−1.51	4.00	5.51
Ethyne	4.26	−3.49[d]	2.41	1.67[i]	−1.85	5.16	23.5	0.01	0.150	0.14
Propyne	3.79	−3.73[j]	1.22		−2.57			0.35	1.025	0.68
But-1-yne	4.11	−3.71[j]	0.55		−3.56			0.12	1.52	1.40
Pent-1-yne	4.29		−0.12		−4.41			−0.01	2.01	2.02
Hex-1-yne	4.56		−0.80		−5.36			−0.21	2.51	2.72
Hept-1-yne	4.87		−1.47		−6.34			−0.44	3.00	3.44
Oct-1-yne	4.98		−2.13		−7.11			−0.52	3.48	4.00
Non-1-yne	5.32		−2.78		−8.10			−0.77	3.96	4.73
Benzene	3.39	−7.59	−1.20	−7.26	−4.59	0.33	16.5	0.65	2.803	2.15
Toluene	3.48	−8.67	−1.94	−8.58	−5.42	0.09	18.3	0.58	3.344	2.76
Ethylbenzene	3.61	−9.62	−2.52	−9.59	−6.13	0.03	20.7	0.48	3.765	3.28
Propylbenzene	3.75	−10.50	−3.14	−10.55	−6.89	−0.05	22.9	0.38	4.221	3.84
Butylbenzene	3.91	−10.55[m]	−3.17		−7.68			0.27	4.686	4.42
Pentylbenzene	4.04	−11.82[m]	−4.41		−8.45			0.17	5.152	4.98
Hexylbenzene	4.23	−12.60[m]	−5.04		−9.27			0.03	5.617	5.59
o-Xylene	3.36[k]	−9.01[n]	−2.75		−6.11			0.67	3.937	3.27
m-Xylene	3.56[l]	−9.37[n]	−2.65	−9.89	−6.21	−0.52	19.2	0.52	3.864	3.34
p-Xylene	3.54[k,l]	−9.49[n]	−2.64	−9.92	−6.18	−0.43	19.3	0.54	3.858	3.32
1,2,3-Trimethylbenzene	3.30[k,l]	−8.96[n]						0.71		
1,2,4-Trimethylbenzene	3.47[k,l]	−9.54[n]						0.59		
1,3,5-Trimethylbenzene	3.59[k]	−9.36[n]	−3.38	−11.13	−6.97	−1.77	17.4	0.50	4.399	3.90
Isopropylbenzene	3.81[k,l]	−9.46[n]	−2.98		−6.79			0.34	4.105	3.77
Naphthalene	1.87[k,o]	−11.20[o]	−4.67		−6.54			1.76	5.34	3.58
Fluorene	0.92[k]							2.46		
Phenanthrene	0.41							2.83		
Pyrene	−0.30							3.35		
Propanone	0.46	−9.90[p]	0.22	−5.14	−0.24	4.76	16.8	2.79	1.760	−1.03
Butanone	0.56	−10.91[p]	−0.50	−6.33	−1.06	4.58	18.9	2.72	2.287	−0.43
Pentan-2-one	0.75	−11.63[p]	−1.14	−7.42	−1.89	4.21	20.5	2.58	2.755	0.18
Hexan-2-one	0.98	−12.57[p]	−1.83	−8.55[q]	−2.81	4.02	22.9	2.41	3.262	0.85
Heptan-2-one	1.23	−13.43[p]	−2.51	−9.67	−3.74	3.76	25.1	2.23	3.760	1.53
Octan-2-one	1.39	−14.15[q]	−3.19	−10.73[q]	−4.58	3.42[q]	26.8	2.11	4.257	2.15
Nonan-2-one	1.78	−14.90[j]	−3.87	−11.80[q]	−5.65	3.10[q]	29.3	1.83	4.755	2.92
Decan-2-one	1.92		−4.56		−6.48			1.72	5.260	3.54
Undecan-2-one	2.11		−5.24		−7.35			1.58	5.760	4.18
Pentan-3-one	0.86[j]	−11.82[j]	−1.22		−2.08			2.50	2.811	0.31

Table 1 (*continued*)

Solute	Water[a]		Hexadecane[b]		Water ⟶ Hexadecane					
	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	$\log L_W$	$\log L_H$	$\log P_H$
Heptan-4-one	1.35[j]	−14.40[j]	−2.59		−3.94			2.14	3.820	1.68
Nonan-5-one	1.63[j]	−16.04	−3.71		−5.34			1.94	4.64	2.70
3-Methylbutan-2-one	1.03[j]		−1.01		−2.04			2.38	2.66	0.28
4-Methylpentan-2-one	1.21[j]		−1.54		−2.75			2.24	3.05	0.81
Cyclopentanone	−0.43[r]	−12.36	−1.64		−1.21			3.45	3.120	−0.33
Cyclohexanone	−0.64[s]	−12.90[t]	−2.31	−8.72	−1.67	4.18	19.6	3.60	3.616	0.02
Acetophenone	−0.31[j]	−12.64[t]	−3.50	−11.32	−3.19	1.32	15.1	3.36	4.483	1.12
Formaldehyde	1.52[u]		1.62		0.10			2.02	0.73	−1.29
Acetaldehyde	0.77[v]		0.94		0.17			2.57	1.230	−1.34
Propanal	0.83[v]		0.14		−0.69			2.52	1.815	−0.70
Butanal	1.09[v]		−0.48		−1.57			2.33	2.270	−0.06
Pentanal	1.24[v]		−1.16		−2.40			2.22	2.770	0.55
Hexanal	1.46[v]		−1.98		−3.44			2.06	3.370	1.31
Heptanal	1.60[v]		−2.65		−4.25			1.96	3.86	1.90
Octanal	1.98[v]		−3.35		−5.33			1.68	4.38	2.70
Nonanal	2.20[v]		−4.07		−6.27			1.52	4.90	3.38
2-Methylpropanal	1.41[w]		−0.19		−1.60			2.10	2.06	−0.04
Benzaldehyde	0.25[j]	−10.79[t]	−2.82	−9.84	−3.07	0.95	13.5	2.95	3.985	1.03
(*E*)-But-2-enal	0.05[j]		−0.89		−0.94			3.10	2.57	−0.53
Dimethyl ether	2.38[j]		1.33					1.39	1.09	−0.30
Diethyl ether	2.68[j]	−11.20[t]	−0.19	−6.02	−2.87	5.18	27.0	1.17	2.061	0.89
Dipropyl ether	3.11[j]		−1.46		−4.57			0.85	2.989	2.14
Di-isopropyl ether	3.74[x]		−0.87		−4.61			0.39	2.559	2.17
Dibutyl ether	3.44[x]		−2.84		−6.28			0.61	4.001	3.39
Tetrahydrofuran	0.80[j]	−11.31[t]	−0.84	−6.82	−1.64	4.49	20.6	2.55	2.534	−0.02
Tetrahydropyran	1.15[j]	−11.68[j]	−1.46					2.29	2.99	0.70
Anisole	1.82[y]	−9.90[t]	−2.74	−9.90	−4.56	0.00	15.3	1.80	3.926	2.13
Phenetole	2.05[y]		−3.03		−5.08			1.63	4.14	2.51
Methyl formate	1.49		0.63		−0.86			2.04	1.459	−0.58
Methyl acetate	1.13	−9.44[t] −10.16[j]	−0.05		−1.18			2.30	1.960	−0.34
Methyl propanoate	1.34		−0.74		−2.08			2.15	2.459	0.31
Methyl butanoate	1.44	−11.50[j]	−1.40		−2.84			2.08	2.943	0.86
Methyl pentanoate	1.70	−12.33[j]	−2.08		−3.78			1.88	3.442	1.56
Methyl hexanoate	1.78		−2.81		−4.59			1.83	3.984	2.15
Ethyl formate	1.70		0.03		−1.67			1.88	1.901	0.02
Ethyl acetate	1.33	−10.78[t]	−0.62	−6.69	−1.95	4.09	20.3	2.16	2.376	0.22
Ethyl propanoate	1.59		−1.31		−2.90			1.97	2.881	0.91
Ethyl butanoate	1.77		−1.99		−3.76			1.83	3.379	1.55
Ethyl pentanoate	1.77							1.83		
Ethyl hexanoate	2.03							1.64		
Ethyl heptanoate	1.95							1.70		
Propyl formate	1.79[x]		−0.67		−2.46			1.82	2.413	0.59
Propyl acetate	1.48		−1.31		−2.79			2.05	2.878	0.83
Propyl propanoate	1.83		−1.98		−3.81			1.79	3.370	1.58
Propyl butanoate	1.99[x]		−2.58		−4.57			1.67	3.81	2.14
Butyl acetate	1.63	−12.36[t]	−1.99	−9.20	−3.62	3.16	22.7	1.94	3.379	1.44
Pentyl acetate	1.76		−2.58		−4.34			1.84	3.81	1.97
Pentyl propanoate	2.16		−3.32		−5.60			1.55	4.350	2.80
Hexyl acetate	2.01[x]		−3.21		−5.22			1.66	4.27	2.61
Isopropyl formate	2.25[x]		−0.42		−2.67			1.48	2.23	0.75
Isopropyl acetate	1.63[x]		−0.97		−2.60			1.94	2.633	0.69
Isopropyl propanoate	2.05[x]		−1.51		−3.56			1.63	3.03	1.40
Isobutyl formate[z]	2.05[x]		−1.24		−3.29			1.63	2.83	1.20
Isobutyl acetate[z]	1.91[x]		−1.72		−3.63			1.73	3.180	1.45
Isoamyl formate[z]	2.14[x]		−1.95		−4.09			1.56	3.35	1.79
Isoamyl acetate[z]	2.06[x]		−2.48		−4.54			1.62	3.74	2.12
Isobutyl isobutyrate[z]	2.59[w]		−2.67		−5.25			1.24	3.88	2.64
Methyl benzoate	−0.01[x]	−12.44[t]	−3.70	−11.56	−3.69	0.88	15.3	3.14	4.634	1.49
Ethyl benzoate	0.63[y]							2.67		
Propylene carbonate	−3.29[aa]	0.39[ab]						5.54		
Water	−2.05[ac]	−10.51[ac]	2.26[ad]	−8.44[ae]	4.31	2.07	−7.5	4.64	0.260	−4.38
Methanol	−0.83	−10.78[p]	1.36	−3.19	2.19	7.59	18.1	3.74	0.922	−2.82
Ethanol	−0.73	−12.58[p]	0.59	−3.90	1.32	8.68	24.7	3.67	1.485	−2.19
Propan-1-ol	−0.58	−13.77[p]	−0.24	−5.06	0.34	8.71	28.1	3.56	2.097	−1.46
Butan-1-ol	−0.45	−14.75[p]	−0.93	−6.71	−0.48	8.04	28.6	3.46	2.601	−0.86
Pentan-1-ol	−0.30	−15.48[p]	−1.62	−7.46	−1.32	8.02	31.3	3.35	3.106	−0.24
Hexan-1-ol	−0.14	−16.28[p]	−2.31	−9.51	−2.17	6.77	30.0	3.23	3.610	0.38
Heptan-1-ol	0.06	−17.24[p]	−2.99	−10.62[q]	−3.05	6.62	32.4	3.09	4.115	1.02

Table 1 (*continued*)

	Water[a]		Hexadecane[b]		Water ⟶ Hexadecane					
Solute	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	log L_W	log L_H	log P_H
Octan-1-ol	0.18	−17.72[p]	−3.68	−11.73	−3.86	5.99	33.0	3.00	4.619	1.62
Nonan-1-ol	0.39		−4.37		−4.76			2.85	5.124	2.27
Decan-1-ol	0.63		−5.06		−5.69			2.67	5.628	2.96
Propan-2-ol	−0.48[af]	−14.05[t]	0.14	−5.35	0.62	8.70	27.1	3.48	1.821	−1.66
Butan-2-ol	−0.35[af]	−15.00[j]	−0.57		−0.22			3.39	2.338	−1.05
2-Methylpropan-1-ol	−0.23[af]	−14.38[j]	−0.65		−0.42			3.30	2.339	−0.90
2-Methylpropan-2-ol	−0.20[af]	−15.39[f]	−0.13	−5.50	0.07	9.89	32.9	3.28	2.018	−1.26
Pentan-2-ol	−0.12[x]		−1.26		−1.14			3.22	2.840	−0.38
2-Methylbutan-1-ol	−0.15[x]		−1.49		−1.34			3.24	3.011	−0.23
2-Methylbutan-2-ol	−0.16[x]	−16.44[ag]	−0.97		−0.86			3.25	2.630	−0.62
Pentan-3-ol	−0.08[j]	−15.77[j]						3.19		
3-Methylbutan-1-ol	−0.15[j]		−1.49					3.24	3.011	−0.23
Hexan-3-ol	0.20[j]	−16.63[j]	−2.07					2.98	3.440	0.46
4-Methylpentan-2-ol	0.53[x]							2.74		
2-Methylpentan-2-ol	0.34[x]		−1.72					2.88	3.181	0.30
2-Methylpentan-3-ol	0.38[x]							2.85		
Cyclopentanol	−1.22[j]	−15.98[j]	−1.84		−0.62			4.03	3.270	−0.76
Cyclohexanol	−1.20[j]	−16.85[j]	−2.39		−1.19			4.01	3.671	−0.34
Cycloheptanol	−1.21[j]	−17.82[j]						4.02		
Allyl alcohol	−0.76[x]		−0.10		0.66			3.69	1.996	−1.69
2,2,2-Trifluoroethanol	−0.03[j]	−12.01[t]	0.95	−4.99	0.98	7.02	20.3	3.15	1.224	−1.93
Hexafluoropropan-2-ol	0.51[j]	−13.65[j]	0.72	−5.28	0.21	8.37	27.4	2.76	1.392	−1.37
Benzyl alcohol	−2.07[y]	−16.00[t]	−3.44	−10.13	−1.37	5.87	24.3	4.65	4.443	−0.21
Phenol	−2.00[ah]	−13.65[ai]	−2.64		−0.64			4.60	3.856	−0.74
o-Cresol	−1.60[ai]	−14.52[ai]	−3.17		−1.57			4.30	4.242	−0.06
m-Cresol	−1.23[aj]		−3.29		−2.06			4.03	4.329	0.30
p-Cresol	−1.86[ai]	−14.29[ai]	−3.26		−1.40			4.50	4.307	−0.19
4-*t*-Butylphenol	−1.65[ai]	−15.25[ai]						4.34		
4-Bromophenol	−2.86[ai]	−16.27[ai]						5.23		
2-Nitrophenol	−0.15[ak]	−11.47[ak]	−3.77		−3.62			3.24	4.684	1.44
3-Nitrophenol	−5.36[j]	−16.18[j]						7.06		
4-Nitrophenol	−6.38[ai]	−18.04[ai] −16.40[j]						7.81		
3-Cyanophenol	−5.24[j]	−16.90[j]						6.97		
4-Cyanophenol	−5.90[j]	−16.80[j]						7.46		
3-Hydroxybenzaldehyde	−5.24[j]	−16.00[j]						6.97		
4-Hydroxybenzaldehyde	−6.20[j]	−16.30[j]						7.68		
2-Chlorophenol									4.937	
3-Chlorophenol		−12.03[j]								
4-Chlorophenol		−8.58[j]								
Formic acid		−11.09								
Acetic acid	−2.43[al]	−12.28	0.23		2.66			4.91	1.75	−3.16
Propanoic acid	−2.20[al]	−13.45	−0.50		1.70			4.74	2.29	−2.45
Butanoic acid	−2.08[al]	−14.50	−1.24		0.84			4.66	2.83	−1.83
Pentanoic acid	−1.90[am]	−15.32	−1.99		−0.09			4.52	3.38	−1.14
Hexanoic acid	−1.95[an]	−16.08	−2.72		−0.77			4.56	3.92	−0.64
Heptanoic acid	−1.89[an]	−16.96	−3.47		−1.58			4.52	4.46	−0.06
Octanoic acid	−1.78[q]	−17.75	−4.20		−2.42			4.44	5.00	0.56
3-Methylbutanoic acid	−1.82[w]		−1.88		−0.06			4.47	3.30	−1.17
Ammonia	−0.03[ao]	−8.42[ao]	2.25		2.28			3.15	0.269	−2.88
Methylamine	−0.29	−10.82						3.34		
Ethylamine	−0.23	−12.83	0.33		0.56			3.30	1.677	−1.62
Propylamine	−0.12	−13.38	−0.30	−5.73	−0.18	7.65	26.3	3.22	2.141	−1.08
Butylamine	0.03	−14.15	−0.95	−7.03	−0.98	7.12	27.2	3.11	2.618	−0.49
Pentylamine	0.18	−14.85	−1.59		−1.77			3.00	3.086	0.09
Hexylamine	0.32	−15.76	−2.23	−9.43	−2.55	6.33	29.8	2.90	3.557	0.66
Heptylamine	0.48		−2.91		−3.39			2.78	4.050	1.27
Octylamine	0.62		−3.55		−4.17			2.68	4.520	1.84
Isopropylamine		−13.37[ao]								
t-Butylamine		−14.16[ao]	−0.78	−6.25		7.91			2.493	
Cyclohexylamine	−0.32[w]							3.37		
Dimethylamine	−0.03[ao]	−12.69[ao]	0.44		0.47			3.15	1.60[q]	−1.55
Diethylamine	0.19[ao]	−15.37[t]	−0.65	−5.88	−0.84	9.49	34.6	2.99	2.395	−0.60
Dipropylamine	0.62[ao]	−17.26[ao]	−1.98		−2.60			2.68	3.372	0.69
Dibutylamine	1.03[ao]	−18.89[ao]						2.38		
Di-isopropylamine	1.06[ao]	−16.81[ao]	−1.33		−2.39			2.36	2.893	0.53
Trimethylamine	1.03[ao]	−12.60[ao]	0.41		−0.62			2.35	1.620	−0.73
Triethylamine	1.05[ap]	−16.64[ap]	−1.58	−8.16	−1.58	8.48	33.7	2.36	3.077	0.72
Aniline	−1.23[y]	−12.87[t]	−2.83	−9.99	−1.60	2.88	15.0	4.03	3.993	−0.04

Table 1 (*continued*)

	Water[a]		Hexadecane[b]		Water ⟶ Hexadecane					
Solute	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	log L_W	log L_H	log P_H
N,*N*-Dimethylaniline	0.82^{y}		−3.87	−11.56	−4.69			2.53	4.754	2.22
Pyridine	-0.42^{aq}	-11.93^{j}	−1.48	−7.80	−1.06	4.13	17.4	3.44	3.003	−0.44
2-Methylpyridine	-0.35^{aq}	-13.18^{j}	−2.07	−8.58	−1.72	4.60	21.2	3.39	3.437	0.05
3-Methylpyridine	-0.50^{aq}	-13.08^{j}	−2.30	−8.96	−1.80	4.12	19.9	3.50	3.603	0.10
4-Methylpyridine	-0.66^{aq}	-13.15^{j}	−2.28	−8.79	−1.62	4.36	20.1	3.61	3.593	−0.02
2-Ethylpyridine	-0.05^{aq}	-13.31^{aq}	−2.70		−2.65			3.17	3.90	0.73
3-Ethylpyridine	-0.33^{aq}	-12.78^{aq}	−3.01		−2.68			3.37	4.13	0.76
4-Ethylpyridine	-0.46^{aq}	-12.48^{aq}	−3.03		−2.57			3.47	4.14	0.67
2,3-Dimethylpyridine	-0.55^{aq}	-13.79^{aq}						3.53		
2,4-Dimethylpyridine	-0.59^{aq}	-14.51^{j}	−2.91		−2.32			3.56	4.05	0.49
2,5-Dimethylpyridine	-0.44^{aq}	-14.54^{j}	−2.91		−2.47			3.45	4.05	0.60
2,6-Dimethylpyridine	-0.32^{aq}	-14.81^{j}	−2.65		−2.33			3.37	3.86	0.49
3,4-Dimethylpyridine	-0.94^{aq}	-13.54^{aq}	−3.33		−2.35			3.82	4.36	0.54
3,5-Dimethylpyridine	-0.56^{aq}	-14.46^{j}	−3.18		−2.62			3.54	4.25	0.71
4-*t*-Butylpyridine	-0.19^{j}	-13.83^{j}	−3.86		−3.67			3.27	4.75	1.48
Nitromethane	0.25^{ar}	-8.54^{j}	0.04	−6.06	−0.21	2.48	9.0	2.95	1.892	−1.06
Nitroethane	0.56^{x}		−0.61		−1.17			2.72	2.367	−0.35
1-Nitropropane	0.93^{x}		−1.27		−2.20			2.45	2.85	0.40
1-Nitrobutane	1.18		−1.92		−3.10			2.27	3.33	1.06
1-Nitropentane	1.45^{w}		−2.59		−4.04			2.07	3.82	1.75
2-Nitropropane	1.14		−0.86		−2.00			2.30	2.550	0.25
Nitrobenzene	0.15^{x}	-11.60^{t}	−3.46	−10.91	−3.61	0.69	14.4	3.02	4.460	1.44
2-Nitrotoluene	0.68^{x}		−3.90		−4.58			2.63	4.78	2.15
3-Nitrotoluene	0.82		−4.16		−4.98			2.53	4.97	2.44
4-Nitrotoluene			−4.23						5.02	
Acetonitrile	0.38^{x}	-8.37^{t}	0.49	−4.56	0.11	3.81	12.4	2.85	1.560	−1.29
Propanonitrile	0.43^{x}	-9.48^{j}	−0.18		−0.61			2.82	2.050	−0.77
Butanonitrile	0.63^{x}	-10.15^{t}	−0.85		−1.48			2.67	2.540	−0.13
Pentanonitrile	0.75^{w}		−1.55		−2.30			2.58	3.057	0.48
Benzonitrile	0.16^{y}	-11.59^{t}	−2.84	−9.86	−3.00	1.73	15.9	3.01	4.004	0.99
Chloromethane	3.72	-5.53^{as}	1.03		−2.69			0.40	1.163	0.76
Chloroethane	3.64		0.33		−3.31			0.46	1.678	1.22
1-Chloropropane	3.94		−0.38		−4.32			0.24	2.202	1.96
1-Chlorobutane	4.11	-6.92^{at}	−1.09	−7.38	−5.20	−0.46	15.9	0.12	2.722	2.60
1-Chloropentane	4.21	-9.39^{at}	−1.78		−5.99			0.05	3.223	3.17
1-Chlorohexane	4.27	-8.86^{at}	−2.44		−6.71			0.00	3.71	3.71
1-Chloroheptane	4.56		−3.12		−7.68			−0.21	4.21	4.42
2-Chloropropane	4.03^{x}		−0.07		−4.10			0.18	1.970	1.79
2-Chlorobutane	4.27^{at}	-8.94^{at}						0.00		
1-Chloro-2-methylpropane			−0.88						2.566	
2-Chloro-2-methylpropane	5.36^{au}	-4.88^{au}	−0.41		−5.77			−0.80	2.217	3.02
2-Chloropentane	4.34^{x}							−0.05		
3-Chloropentane	4.31^{x}							−0.03		
Dichloromethane	$2.96^{k,x,at}$	-7.24^{av}	−0.14	−5.54	−3.10	1.70	16.1	0.96	2.019	1.06
Trichloromethane	$3.20^{k,x,at}$	-7.99^{f}	−0.76	−6.71	−3.96	1.28	17.6	0.79	2.480	1.69
Tetrachloromethane	4.35^{at}	-8.77^{av}	−1.23	−7.39	−5.58	1.38	23.3	−0.06	2.823	2.88
1,2-Dichloroethane	$2.48^{at,aw}$	-8.54^{av}	−0.89		−3.37			1.31	2.573	1.26
1,1-Dichloroethane	$3.42^{k,x,aw}$		−0.59		−4.01			0.62	2.350	1.73
1,1,1-Trichloroethane	$4.08^{x,at,aw}$		−1.05		−5.20			0.14	2.690	2.55
1,1,2-Trichloroethane	$2.28^{x,at}$		−1.87		−4.15			1.46	3.29	1.83
1,1,2,2-Tetrachloroethane	$1.80^{at,aw}$		−2.60		−4.48			1.81	3.826	2.02
1,1,1,2-Tetrachloroethane	2.99^{k}		−2.22		−5.21			0.94	3.55	2.61
Pentachloroethane	$2.88^{k,x}$							1.02		
Hexachloroethane	2.87^{x} 3.89^{k}									
1,2-Dichloropropane	$3.01^{x,at}$	-8.61^{at}	−1.27		−4.28			0.93	2.85	1.92
1,3-Dichloropropane	$2.38^{x,at}$	-7.78^{at}	−1.74		−4.12			1.39	3.194	1.80
1,4-Dichlorobutane	1.95^{at}	-6.22^{at}	−2.53		−4.48			1.70	3.775	2.08
Bromomethane	3.46	-6.10^{as}						0.60		
Bromoethane	3.54		−0.14		−3.68			0.54	2.020	1.48
1-Bromopropane	3.71		−0.95		−4.66			0.41	2.620	2.21
1-Bromobutane	3.87		−1.62		−5.49			0.29	3.105	2.82
1-Bromopentane	4.18		−2.31		−6.49			0.07	3.611	3.54
1-Bromohexane	4.45		−3.01		−7.46			−0.13	4.13	4.26
1-Bromoheptane	4.61		−3.66		−8.27			−0.25	4.60	4.85
1-Bromo-octane	4.79		−4.32		−9.11			−0.38	5.09	5.47
2-Bromopropane	3.79^{x}		−0.64		−4.43			0.35	2.391	2.04
2-Bromobutane			−1.38						2.933	
1-Bromo-2-methylpropane	4.24^{x}		−1.42		−5.66			0.02	2.961	2.94

Table 1 (*continued*)

	Water[a]		Hexadecane[b]		Water ⟶ Hexadecane					
Solute	ΔG°_s	ΔH°_s	ΔG°_s	ΔH°_s	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	log L_W	log L_H	log P_H
2-Bromo-2-methylpropane	5.12[au]	−6.07[au]	−0.95		−6.07			−0.62	2.616	3.24
Dibromomethane	2.31[x]		−1.27		−3.58			1.44	2.849	1.41
Tribromomethane	2.14[y]		−2.51		−4.65			1.56	3.747	2.19
1,2-Dibromoethane	1.94[x]		−2.01		−3.95			1.71	3.999	1.69
Iodomethane	3.37	−6.19[j]								
Iodoethane	3.54		−0.89		−4.43			0.54	2.573	2.04
1-Iodopropane	3.74		−1.65		−5.39			0.39	3.130	2.74
1-Iodobutane	4.03		−2.33		−6.36			0.18	3.628	3.45
1-Iodopentane	4.14		−3.01		−7.15			0.10	4.13	4.03
1-Iodohexane	4.35		−3.68		−8.03			−0.06	4.62	4.68
1-Iodoheptane	4.54		−4.32		−8.86			−0.20	5.09	5.29
Di-iodomethane	1.77[y]		−2.64	−9.31	−4.41			1.84	3.853	2.01
Fluoromethane	4.06[as]	−4.33[as]								
CCl_2FCClF_2	6.05[x]		−0.28		−6.33			−1.30	2.123	3.42
CF_3CHFBr (Tefluorane)	4.78[ax]		0.74		−4.04			−0.37	1.37	1.74
$CF_3CHClBr$ (Halothane)	4.13[ax]		−0.35		−4.51			0.08	2.177	2.10
CHF_2OCF_2CHFCl (Enfluorane)			0.36						1.653	
$CH_3OCF_2CHCl_2$ (Methoxyfluorane)	3.15[ax]		−1.29		−4.44			0.82	2.864	2.04
$CHF_2OCHClCF_3$ (Isofluorane)	4.37[ax]		0.47		−3.90			−0.07	1.576	1.65
$CF_3CH_2OCH{=}CH_2$ (Fluoroxene)	4.14[ax]		0.71		−3.43			0.10	1.40	1.30
Chloroethene	4.20[as]	−5.87[as]						0.05		
1,1-Dichloroethene	4.52[at]	−9.18[at]	−0.26		−4.78			−0.18	2.110	2.29
cis-1,2-Dichloroethene	3.57[ax]		−0.72		−4.29			0.51	2.450	1.94
trans-1,2-Dichloroethene	3.50[ax]		−0.59		−4.09			0.57	2.350	1.78
Trichloroethene	3.83[ax]	−9.23[at]	−1.47		−5.30			0.32	2.997	2.68
Tetrachloroethene	4.37[ax]	−9.41[at]	−2.27	−9.18	−6.64	0.23	23.0	−0.07	3.584	3.65
Allyl chloride	3.69[x]		−0.26		−3.95			0.42	2.109	1.69
Allyl bromide	3.42[y]		−0.80		−4.22			0.63	2.510	1.88
Allyl iodide			−1.49						3.01	
Benzyl chloride	2.35[y]	(3.47)[ay]	−3.23	(1.62)	−5.58	−1.85	12.5	1.41	4.290	2.88
Benzyl bromide	1.90[y]		−3.74		−5.64			1.74	4.66	2.92
Fluorobenzene	3.48[az]	−7.53[t]	−1.26	−7.42	−4.74	0.11	16.3	0.58	2.84	2.26
Chlorobenzene	3.13[k]	−10.40[av]	−2.35	−9.14	−5.48	1.26	22.6	0.84	3.640	2.80
2-Chlorotoluene	3.13[at]		−3.06		−6.19			0.84	4.16	3.32
3-Chlorotoluene									4.16	
4-Chlorotoluene									4.19	
1,2-Dichlorobenzene	2.77[k]		−3.39		−6.16			1.10	4.405	3.30
1,3-Dichlorobenzene	3.14[k]		−3.37		−6.51			0.83	4.39	3.56
1,4-Dichlorobenzene	2.95[k,x]		−3.38		−6.33			0.97	4.40	3.43
Bromobenzene	2.81[k]		−2.89		−5.80			1.07	4.035	2.97
2-Bromotoluene			−3.55						4.52	
3-Bromotoluene			−3.57						4.54	
4-Bromotoluene	2.88[x]		−3.57		−6.45			1.02	4.54	3.52
Iodobenzene	2.53[k]		−3.63		−6.16			1.28	4.58	3.30
Methanethiol[ba]	2.91	−6.16						1.00		
Ethanethiol[ba]	3.13	−6.80	−0.34		−3.47			0.84	2.173	1.34
Propanethiol[ba]	3.21	−7.10	−1.04		−4.25			0.78	2.685	1.91
Butanethiol[ba]	3.27	−7.58	−1.31		−4.58			0.73	2.880	2.15
Dimethyl sulphide[ba]	2.72	−7.49	−0.43		−3.15			0.63	2.238	1.61
Diethyl sulphide[ba]	2.81	−8.87	−1.62		−4.43			1.07	3.104	2.03
Dipropyl sulphide[ba]	2.99	−7.58	−3.00		−5.99			0.94	4.120	3.18
Di-isopropyl sulphide[ba]	3.06	−9.56	−2.29		−5.35			0.89	3.600	2.71
Dimethyl disulphide[ba]	2.43	−7.58	−2.22		−4.65			1.35	3.549	2.20
Diethyl disulphide[ba]	2.63	−7.36	−3.12		−5.75			1.20	4.210	3.01
Thiophene[ba]	2.85	−7.15	−1.40	−7.15	−4.25	0.00	14.3	1.04	2.943	1.90
2-Methylthiophene[ba]	2.90	−7.55	−1.89		−4.79			1.01	3.302	2.30
Thiophenol	1.72[x]		−3.00		−4.72			1.87	4.118	2.25

[a] Values of ΔG°_s and ΔH°_s, in kcal mol^{-1} mole fraction scale, for gaseous solutes taken from refs. 8 and 9 unless shown otherwise. [b] This work, or from ref. 4, unless shown otherwise. [c] M. H. Abraham and E. Matteoli, unpublished survey. [d] S. F. Dec and S. J. Gill, *J. Solution Chem.*, 1984, **13**, 27. [e] Note that van't Hoff enthalpies from A. Kuantes and G. W. A. Rijinders in 'Gas Chromatography 1958,' ed. D. H. Desty, Butterworths, London, 1958, are −5.95 and −6.87, respectively. [f] From data given by M. H. Abraham, P. L. Grellier, and R. A. McGill, *J. Chem. Soc., Perkin Trans. 2*, 1987, 797. [g] Value for solution in dodecane by the van't Hoff method. Data from A. Sahgad, H. M. La, and W. Hayduk, *Can. J. Chem. Eng.*, 1978, **56**, 354. [h] By the van't Hoff method, P. J. Lin and J. F. Parcher, *J. Chromatogr. Sci.*, 1982, **20**, 33. [i] By the van't Hoff method, data from Y. Migano and W. Hayduk, *Can. J. Chem. Eng.*, 1981, **59**, 746. [j] Ref. 7. [k] Ref. 10. [l] G. L. Amidon and S. T. Anik, *J. Chem. Eng. Data*, 1981, **26**, 28. [m] J. W. Owens, S. P. Wasik, and H. De Voe, *J. Chem. Eng. Data*, 1986, **31**, 47. [n] I. Sanemasa, M. Araki, T. Deguchi, and H. Nagai, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1054. [o] R. D. Wauchope and R. Haque, *Can. J. Chem.*, 1972, **50**, 133. [p] Data from ref. 8 slightly adjusted using more recent ΔH°_v values from V. Majer and V. Svoboda, 'Enthalpies of Vaporization of Organic Compounds,' Blackwell, Oxford, 1985. [q] Estimated

Table 1 (*continued*)

value, this work. [r] Estimated value by J. P. Guthrie and P. A. Cullimore, *Can. J. Chem.*, 1979, **57**, 240. [s] K. R. Brower, J. Peslak, and J. Elrod, *J. Phys. Chem.*, 1969, **73**, 207. [t] This work. [u] C. J. Marsh and R. C. Pemberton, *National Physical Laboratory*, *Report Chem. III*, 1980. [v] R. G. Buttery, L. C. Ling, and D. G. Guadagni, *J. Agric. Food Chem.*, 1969, **17**, 385. These values are for the unhydrated aldehydes; see ref. in footnote *u*. [w] J. E. Amoure and R. G. Buttery, *Chem. Senses Flavour*, 1978, **3**, 57. [x] Ref. 6. [y] From liquid solubilities and vapour pressures as calculated in this work. [z] Isobutyl is 2-methylpropyl; isoamyl is 3-methylbutyl; isobutyrate is 2-methylpropanoate. [aa] Calculated from vapour–liquid equilibria. [ab] Enthalpy of solution of the pure liquid from B. C. Cox, A. J. Parker, and W. E. Waghorne, *J. Am. Chem. Soc.*, 1973, **95**, 1010. [ac] Parameters for the vaporisation of pure water. [ad] Value from ref. 2. Other values that may be calculated are 2.17 from S. D. Christian, R. French, and K. O. Yeo, *J. Phys. Chem.*, 1973, **74**, 813, and 2.27 from P. Schatzberg, *J. Phys. Chem.*, 1963, **67**, 776. [ae] H. Saito and K. Shinoda, *J. Colloid Interfac. Chem.*, 1970, **32**, 647. [af] J. H. Rytting, L. P. Huston, and T. Higuchi, *J. Pharm. Sci.*, 1978, **67**, 615. [ag] K. Bocek, *J. Chromatogr.*, 1979, **162**, 209. [ah] M. F. Abd-El-Bary, M. F. Hamoda, S. Tanisho, and N. Wakao, *J. Chem. Eng. Data*, 1986, **31**, 229. [ai] G. H. Parsons, C. H. Rochester, and C. E. Wood, *J. Chem. Soc.*, *Perkin Trans. 2*, 1972, 136. [aj] Calculated from the known partition coefficient and log L_H values. [ak] K. Schoene and J. Steinhanses, *Fresenius Z. Anal. Chem.*, 1985, **321**, 538. The ΔH° value is by the van't Hoff method. [al] J. A. V. Butler and C. N. Ramchandani, *J. Chem. Soc.*, 1935, 952. [am] Average of values from ref. in footnote *w* (-1.88) and calculated from partition coefficients of R. Aveyard and R. W. Mitchell, *Trans. Faraday Soc.*, 1970, **66**, 37, corrected in this work for dimerization in hexadecane (-1.92). [an] From partition coefficients, see ref. in footnote *am*. [ao] E. M. Arnett and F. M. Jones, *Prog. Phys. Org. Chem.*, 1974, **11**, 263. [ap] M. H. Abraham and A. Nasehzadeh, *J. Chem. Thermodyn.*, 1981, **13**, 549. [aq] R. J. L. Andon, J. D. Cox, and E. F. G. Herington, *J. Chem. Soc.*, 1954, 3118. [ar] J. H. Park, A. Hussam, P. Couasnon, D. Fritz, and P. W. Carr, *Anal. Chem.*, 1987, **59**, 1970. [as] E. Wilhelm, R. Battino, and R. J. Wilcock, *Chem. Rev.*, 1977, **77**, 219. [at] D. L. Leighton and J. M. Cole, *J. Chem. Eng. Data*, 1981, **26**, 382. [au] M. H. Abraham, P. L. Grellier, A. Nasehzadeh, and R. A. C. Walker, *J. Chem. Soc.*, *Perkin Trans. 2*, 1988, 1717. [av] From ΔH_s° (liq) by J. W. Larsen and L. Magid, *J. Phys. Chem.*, 1974, **78**, 834, and R. de Lisi, M. Goffredi, and V. T. Liveri, *J. Chem. Soc.*, *Faraday Trans. 1*, 1980, 1660, together with ΔH_v°. [aw] R. S. Barr and D. M. T. Newshan, *Fluid Phase Eq.*, 1987, **35**, 189. [ax] M. H. Abraham, M. J. Kamlet, R. W. Taft, R. M. Doherty, and P. K. Weathersby, *J. Med. Chem.*, 1985, **28**, 865. [ay] This is ΔH_s° (liq) from R. Ohnishi and K. Tanabe, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 2647, by the van't Hoff method. Our own listed value for ΔH_s° in hexadecane is also for the liquid solute. [az] P. Bernal, S. D. Christian, and E. E. Tucker, *J. Solution Chem.*, 1986, **15**, 947. [ba] A. Przyjazny, W. Janicki, W. Chrzanowski, and R. Staszewski, *J. Chromatogr.*, 1983, **280**, 249.

ception of methanol (3A), nitromethane (3A), and water. ΔH_s° values were independent of concentration in the measurement range.

Discussion

Most of the gas solubility data in water were taken from key references,[6–8] two of which [7,8] include values for the enthalpy of solution in water. The L_H values used were mostly those we have determined either previously[4] or in this work, but we also calculated a number of values using literature data for closely related solvents such as squalane,[15–17] $C_{87}H_{176}$,[18,19] octacosane,[20] and heptadecane.[21] In Table 1 are collected values of log L_W and log L_H, together with the calculated log P_H values, *via* equation (1). The log P_H values all refer to the molar concentration scale, as is usual for partition coefficients. We have, where necessary, recalculated gas solubilities using standard states of 1 atm (gas) and unit mole fraction (solution), so that the ΔG_{tr}° values in Table 1 refer to the mole fraction concentration scale, a more appropriate scale when calorimetrically determined enthalpies of solution are involved. Our enthalpies of solution of liquid solutes were converted into ΔH_s° values for gaseous solutes, using enthalpies of vaporization at 298 K, care being taken to ensure that the same ΔH_v° values were used for solution into water and hexadecane. The observed ΔH_s° values, and the deduced ΔH_{tr}° and ΔS_{tr}° are collected in Table 1. Additional log P_H values are given in Table 2.

The expected error in the log L_H values is very small, probably no more than 0.03 log unit, However, there are substantial differences in recorded values for log L_W, even for moderately volatile solutes. Thus for halogenated alkanes, the log L_W values given by Hine and Mookerjee[6] and by Mackay and Shiu[10] differ randomly by *ca.* 0.1 log unit, and for hexachloroethane the two recorded values differ by a full log unit (2.87 and 3.89, respectively). Enthalpies of solution, although in the best instances* capable of leading to ΔH_{tr}° values with an error of only some 0.05 kcal mol^{-1}, can also be subject to very large errors. We can suggest that the expected error in ΔG_{tr}° will be *ca.* 0.2 kcal mol^{-1}, that in ΔH_{tr}° around 0.5 kcal mol^{-1}, and that in ΔS_{tr}° *ca.* 2 cal K^{-1} mol^{-1}. However, occasionally much larger experimental errors may arise, and this should be borne in mind when results are discussed. We note that the thermodynamics of transfer from water to hexadecane are very similar to those for transfer to 2,2,4-trimethylpentane, as found by Tomlinson *et al.*[12] A comparison for a number of solutes is in Table 3. Within any reasonable error, it seems as though ΔH_{tr}° values are identical for the two transfers, and that ΔG_{tr}° values average at about the same, with rather more random variation. It seems that without introducing too much error, values of ΔH_{tr}° and ΔG_{tr}° for transfer to 2,2,4-trimethylpentane, Table 3, could be taken as those for transfer to hexadecane.

Tomlinson *et al.*[12] examined the possibility of enthalpy–entropy correlations for transfer to 2,2,4-trimethylpentane through the statistically correct method of plotting ΔG_{tr}° *vs.* ΔH_{tr}°. They found that there was no general correlation between ΔG_{tr}° and ΔH_{tr}°, although linear relationships were observed for various homologous series. Using a more extended data set, we can confirm the findings of Tomlinson *et al.*[12] Aliphatic series such as the alkanes, ketones, and alcohols form separate linear plots. However, aromatic or halogeno-substituted compounds always lie off the plots for the unsubstituted series. This rather complicated enthalpy–Gibbs energy interplay is hardly surprising in view of the varied solute–solvent interactions that are possible.

One method for the examination of solute–solvent interactions is that of multiple linear regression analysis, especially as developed by Abraham, Doherty, Kamlet, Taft, and their coworkers.[22–25] The solubility of a gaseous solute in a solvent is regarded as being made up of an endoergic cavity term, that arises through breaking of solvent–solvent interactions, together with a number of exoergic terms that arise through different solute–solvent interactions. For a number of solutes in a given solvent phase, equations (2) and (3) are valid.[22–25]

$$\mathrm{SP} = c + d\delta_2 + s\pi_2^* + a\alpha_2 + b\beta_2 + vV_2 \qquad (2)$$

$$\mathrm{SP} = c + d\delta_2 + s\pi_2^* + a\alpha_2 + b\beta_2 + l\log L_H \qquad (3)$$

Equation (2) is recommended for processes within condensed phases, such as the water–hexadecane partition coefficients we

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* These are nearly always with calorimetrically determined enthalpies of solution of liquid solutes that dissolve readily in water and hexadecane and are not subject to extensive self-association. Note that any error in ΔH_v° cancels out. 1 kcal = 4.184 kJ.

Table 2. Directly determined log P_H values for compounds not in Table 1.[a]

Solute	ΔG°_{tr}/kcal mol^{-1}	log P_H	Ref.
Butane-1,4-diol	4.30	−4.37	2
Hexane-1,6-diol	2.80	−3.27	2
Formamide	5.31	−5.10	2
Acetamide	4.73	−4.68	2
Butyramide	3.05	−3.44	2
Isobutyramide	3.03	−3.43	2
Urea	5.79	−5.46	2
4-Pentylpyridine	−5.26	2.64	*b*
4-Hexylpyridine	−6.12	3.27	*b*
4-Heptylpyridine	−7.00	3.92	*b*
4-Octylpyridine	−7.89	4.57	*b*
4-Nonylpyridine	−8.76	5.21	*b*
4-Decylpyridine	−9.62	5.84	*b*
Paraldehyde	−1.98	0.24	3
2-Chlorophenol	(−1.52) −1.45	−0.15	*c*
4-Chlorophenol	(−0.70) −0.63	−0.75	*c*
4-Chloro-3-methylphenol	(−2.14) −2.07	0.31	*c*
2-Iodophenol	(−2.28) −2.21	0.41	*c*
o-Toluidine	−2.17	0.38	*d*
p-Toluidine	−2.14	0.36	*d*
2-Methoxyaniline	−2.10	0.33	*d*
4-Methoxyaniline	−0.92	−0.54	*d*
2-Chloroaniline	−3.11	1.07	*d*
3-Chloroaniline	−2.53	0.64	*d*
4-Chloroaniline	−2.42	0.56	*d*
2-Nitroaniline	−1.95	0.22	*e*
Acetophenone	−3.18	1.12[g]	*f*
4-Methoxyacetophenone	−2.88	0.90	*f*
3-Methylacetophenone	−4.00	1.72	*f*
4-Methylacetophenone	−3.88	1.63	*f*
4-Fluoroacetophenone	−3.29	1.20	*f*
3-Chloroacetophenone	−4.40	2.01	*f*
4-Chloroacetophenone	−3.89	1.85	*f*
3-Trifluoromethylacetophenone	−4.49	2.08	*f*
3-Nitroacetophenone	−2.38	0.53	*f*
4-Nitroacetophenone	−2.59	0.69	*f*
Biphenyl	−7.37	4.19	5

[a] Values of log P_H on the molar scale and ΔG°_{tr} on the mol fraction scale as in Table 1. [b] K. C. Yeh and W. I. Higuchi, *J. Pharm. Sci.*, 1976, **65**, 82. [c] Parenthesised values are for transfer to dodecane, from D. E. Burton, K. Clarke, and G. W. Gray, *J. Chem. Soc.*, 1964, 1314. The listed values for ΔG°_{tr} and log *P* have been slightly adjusted to correspond to transfer to hexadecane, by comparison for phenols for which both transfers are known. [d] W. Kemula, H. Buchowski, and W. Pawlowski, *Rocz. Chem.*, 1968, **48**, 1951. [e] W. Kemula, H. Buchowski, and J. Terepat, *Bull. Acad. Sci. Polon.*, 1961, **9**, 595. [f] Values for transfer to dodecane, from J. Toullec, M. El-Alaoui, and P. Kleffert, *J. Org. Chem.*, **48**, 4808. [g] Note the same value (Table 1) for transfer to hexadecane.

wish to analyse. We shall therefore consider only equation (2) and not equation (3), preferred for gas–solvent partition coefficients. In equation (2), δ_2 is a solute polarisability correction term taken as zero except for polyhalogeno aliphatics (0.5) and aromatics (1.0), π^*_2 is the solute dipolarity, α_2 the solute hydrogen-bond acidity, β_2 the solute hydrogen-bond basicity, and V_2 is the solute volume. The constants *c*, *d*, *s*, *a*, *b*, and *v* are found by multiple linear regression analysis, and can be used to deduce the factors that are important in the particular process. If we consider specifically the water–hexadecane partition, with SP = log P_H as defined *via* equation (1), then the values of the *s*-constant will depend on the differences in dipolarity between water and hexadecane; a negative *s*-constant will indicate that water is more dipolar than hexadecane and hence more able to undergo solvent–solute dipole–dipole interactions. In a similar vein, the *a*-constant will reflect the hydrogen-bond basicity of water, that is its ability to hydrogen bond with solutes that are hydrogen-bond acids (hexadecane cannot), whilst the *b*-constant will reflect the hydrogen-bond acidity of water. The vV_2 term covers cavity effects, the larger the solute the more solvent–solvent interactions must be broken to make a suitably sized cavity. Hence the *v*-constant should provide an assessment of the difference in cavity effects between water and hexadecane.

In equation (2), the solute explanatory variables were taken as follows: δ_2 defined as above; π^*_2 as listed before;[22–25] α_2 as α^H_2, the new solute hydrogen-bond acidity parameter;[26] β_2 as β^H_2, the new solute hydrogen-bond basicity parameter,[27,28] supplemented by a few recently determined[29] 'effective' or 'summation' β^H_2 values for multifunctional bases; V_2 as McGowan's intrinsic volume V_x.[30] The equation that we use to correlate log P_H and also the thermodynamic functions of transfer is therefore as follows, where V_x is in units of (cm^3 mol^{-1})/100.

$$\mathrm{SP} = c + d\delta_2 + s\pi^*_2 + a\alpha^H_2 + b\beta^H_2 + vV_x \qquad (4)$$

If we include all of the data of Tomlinson *et al.*[12] in Table 3, as well as our calculated values in Tables 1 and 2, we have 270 compounds for which we have all the required explanatory variables. Details of the regression equations are in Table 4, where *n* is the number of solutes, *r* the overall correlation coefficient, and sd the standard deviation. Bearing in mind the probable average experimental error in log P_H of about 0.1, and also the experimental errors in the various explanatory variables, an overall standard deviation of *ca.* 0.2 log units is as good as can be expected. Thus the regression equation for 270 compounds, with $r = 0.9884$ and sd = 0.28, is quite acceptable. The constants in equation (4) are all chemically reasonable, with *s*, *a*, and *b* all being very negative, and *v* being very positive. Thus solute dipolarity, hydrogen-bond acidity, and hydrogen-bond basicity, all lead to a preference for water, whereas solute volume leads to a preference for hexadecane. As mentioned in the introduction, we were interested in results for aliphatic compounds and aromatic compounds taken separately; details of the found regressions are also in Table 4. A comparison of the 'aliphatics only' with the 'aromatics only' regression does suggest that there are small, but possibly significant differences, with the constants *a*, *b*, and *v* all being numerically smaller for the aromatic regression. Interestingly, Kamlet and co-workers[31,32] found that for aqueous solubility of liquids and solids, different regression equations were required for aliphatic and aromatic compounds,[31] but for water–octanol partition coefficients (log P_{OCT})[32] the same regression equation could accommodate both types of solutes [equation (5)].

$$\log P_{OCT} = 0.35 + 0.36\,\delta_2 - 1.04\,\pi^*_2 + 0.10\,\alpha_m - 3.84\,\beta_m + 5.35\,V_I \qquad (5)$$

Because equation (5) is cast in terms of α_m and β_m (related to α^H_2 and β^H_2 but not entirely equivalent) and also of Leahy's intrinsic volume, V_I,[33] we felt it useful to examine log P_{OCT} for the set of solutes assembled in Tables 1–3 using equation (4). The results are in Table 5. The *v*-constant in Table 5 is much smaller than in equation (5), but this is to be expected since V_x/V_I is only *ca.* 0.68.[30] The other constants in Table 5 are all reasonably consistent with those in equation (5), and, as found by Kamlet and co-workers,[32] there is little difference between aliphatic and aromatic solutes.

It is instructive to compare the constants in equation (4) for water–hexadecane with water–octanol, for the 'all solutes' correlations:

	c	*d*	*s*	*a*	*b*	*v*
water–hexadecane	0.26	0.51	−1.45	−3.92	−5.21	4.32
water–octanol	0.20	0.49	−1.24	−0.28	−3.32	3.85

Table 3. Comparison of thermodynamics of transfer from water to hexadecane and to 2,2,4-trimethylpentane, molar scale at 298 K.

Solute	Hexadecane[a]			2,2,4-Trimethylpentane[11,12]		
	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}	ΔG°_{tr}	ΔH°_{tr}	ΔS°_{tr}
Butanone	0.59	4.58	13	0.25	4.54	14
Ethanol	2.99	8.68	19	2.72	8.36	19
Hexan-1-ol	−0.52	6.77	24	−0.74	6.57	24
Aniline	0.05	2.88	9	0.28	3.25	10
Nitrobenzene	−1.96	0.69	9	−1.95	0.67	9
Methyl benzoate	−2.03	0.88	10	−2.49	0.82	11
Phenol	1.01			1.31	4.64	11
p-Cresol	0.26			0.54	4.51	13
4-Chlorophenol	1.02			0.66	4.11	12
3-Methoxyphenol				1.48	4.46	10
4-Methylaniline				−0.46	3.53	13
4-Chloroaniline				−0.65	2.46	10
N-Methylaniline				−1.41	2.52	13
Methyl phenyl sulphone				1.25	3.21	7
Methyl phenyl sulphoxide				2.03	5.60	12
Ethyl benzoate				−2.76	0.74	12
Benzyl alcohol	0.29	5.87	19	1.04	6.15	17
2-Phenylethanol				0.49	6.03	19
3-Phenylpropan-1-ol				−0.25	6.41	22
Acetophenone	−1.53	1.32	10	−1.52	2.11	12
Benzaldehyde	−1.41	0.95	8	−1.43	0.99	8
Anisole	−2.90	0.00	10	−2.76	0.00	9
Pyridine	0.60	4.13	12	0.56	4.08	12

[a] From Tables 1 and 2, after conversion into the molar scale.

Table 4. Regression analysis of water–hexadecane partition coefficients, using equation (4).[a]

Solute set	*c*	*d*	*s*	*a*	*b*	*v*	*n*	*r*	sd
All solutes	0.26 ± 0.06	0.51 ± 0.05	−1.45 ± 0.09	−3.92 ± 0.11	−5.21 ± 0.09	4.32 ± 0.06	270	0.9884	0.28
Aliphatics only	0.27 ± 0.07	0.48 ± 0.17	−1.45 ± 0.10	−4.11 ± 0.14	−5.39 ± 0.13	4.39 ± 0.07	203	0.9890	0.28
Aromatics only	0.94 ± 0.19	—	−1.31 ± 0.17	−3.65 ± 0.13	−4.74 ± 0.17	3.85 ± 0.16	67	0.9913	0.21

[a] Compounds listed in Tables 1–3, with log P_H on the molar scale.

Table 5. Regression analysis of water–octanol partition coefficients,[a] using equation (4).

Solute set	*c*	*d*	*s*	*a*	*b*	*v*	*n*	*r*	sd
All solutes	0.20 ± 0.06	0.49 ± 0.04	−1.24 ± 0.08	−0.28 ± 0.08	−3.32 ± 0.08	3.85 ± 0.06	307	0.9790	0.26
Aliphatic only	0.28 ± 0.06	0.24 ± 0.15	−1.28 ± 0.09	−0.48 ± 0.13	−3.42 ± 0.11	3.84 ± 0.06	215	0.9740	0.27
Aromatic only	0.53 ± 0.17	—	−0.91 ± 0.15	−0.17 ± 0.09	−3.30 ± 0.14	3.74 ± 0.14	92	0.9782	0.22

[a] Compounds listed in Tables 1–3, with log P_{OCT} on the molar scale.

The most striking features of the two sets of constants are (i) the dipolarity of wet octanol is surprisingly small, with *s* (octanol) almost as negative as *s* (hexadecane); (ii) the basicity of wet octanol must be almost the same as that of water, since *a* (octanol) is only −0.28 as compared with *a* (hexadecane) of −3.92; (iii) the hydrogen-bond acidity of wet octanol is appreciably less than that of water: *cf.* *b* (hexadecane) = −5.21, *b* (octanol) = −3.21; and (iv) the cavity effect (or probably a combined cavity effect plus dispersion interactions) for wet octanol is not far away from that for hexadecane. Obviously, results on more water–solvent partitions are needed to quantify these effects, but already it can be seen that equation (4) will yield information about various solute–solvent interactions.

Having now to hand not only values of log P_H (equivalent to ΔG°_{tr} on the molar scale) but also ΔH°_{tr}, we can now set out ΔG°_{tr}, ΔH°_{tr}, and ΔS°_{tr} on the mole fraction scale, Table 1, and regress a unified set of transfer parameters for the same solutes. We have 86 such solutes for which the required explanatory variables are known, and summarise results of the regressions in Table 6. The constants in the ΔG°_{tr} regression (other than *c*) then yield the log P_H constants on division by −1.364; there is reasonable agreement between the 86 solute correlation in Table 6 and the 270 solute correlation in Table 4. The sd values in Table 6 are roughly as expected for correlations of ΔH°_{tr} (±0.5 kcal mol^{-1}) and ΔS°_{tr} (±2 kcal K^{-1} mol^{-1}), being 0.94 kcal mol^{-1} and 2.7 cal K^{-1} mol^{-1} respectively.

There are a number of extraordinary features of the results given in Table 6; it is useful to take the main parameters in turn. The *s*-constants, viewed as dipolarity effects, are almost impossible to interpret. Whereas an increase in solute dipolarity (π_2^*) reduces transfer to hexadecane in terms of ΔG°_{tr} or log P_H, it actually aids transfer in terms of ΔH°_{tr}. One difficulty here is that the π_2^* parameter involves not only dipolarity, but also polarisability effects; furthermore, there is an interplay between δ_2, the polarisability correction term, and π_2^*. The solute hydrogen-bond acidity term, $a\alpha_2^H$, can be plausibly interpreted

Table 6. Regression analysis of ΔG°_{tr}, ΔH°_{tr}, and ΔS°_{tr} for the water–hexadecane partition, mole fraction scale at 298 K.[a]

Parameter	c	d	s	a	b	v	n	r	sd
ΔG°_{tr}	-1.90 ± 0.11	-0.69 ± 0.12	1.63 ± 0.23	5.44 ± 0.23	7.06 ± 0.25	-5.78 ± 0.15	86	0.9896	0.35
ΔH°_{tr}	2.81 ± 0.30	-1.73 ± 0.33	-2.08 ± 0.60	8.11 ± 0.62	10.05 ± 0.67	-2.43 ± 0.41	86	0.9451	0.94
ΔS°_{tr}	15.80 ± 0.88	-3.55 ± 0.95	-12.84 ± 1.74	9.23 ± 1.80	10.34 ± 1.95	11.28 ± 1.19	86	0.8766	2.73
$-T\Delta S^\circ_{tr}$[b]	-4.71	1.06	3.83	-2.75	-3.08	-3.36			

[a] Values from Tables 1 and 3, ΔG°_{tr} and ΔH°_{tr} in kcal mol^{-1}; ΔS°_{tr} in cal K^{-1} mol^{-1}. [b] Calculated from the constants in the ΔS°_{tr} regression. The values do not quite yield the $\Delta H^\circ_{tr} - \Delta G^\circ_{tr}$ constants due to rounding-off errors.

as follows. Hydrogen-bonding from the solute acid to water base will be exothermic, and hence ΔH°_{tr} will be positive (as observed). But the creation of hydrogen bonds will be somewhat disfavoured in terms of entropy, leading to a positive ΔS°_{tr} value and to a ΔG°_{tr} value that is still positive, but less so than ΔH°_{tr}. An exactly similar argument can account for the positive b-constants in ΔG°_{tr}, ΔH°_{tr}, and ΔS°_{tr}. The breakdown of the vV_x 'cavity' term into enthalpic and entropic contributions is especially interesting in that any so-called 'hydrophobic effect' must reside in this vV_x term. Now on the scaled particle theory (SPT),[34] the free energy of cavity formation in water, G^{W}_{cav}, is much more positive than the corresponding value in a solvent such as hexadecane, G^{H}_{cav}. Hence $G^{H}_{cav} - G^{W}_{cav}$ is negative and will correspondingly contribute a negative quantity to ΔG°_{tr}. But the enthalpy of cavity formation in water is smaller than in solvents such as hexadecane, so that $H^{H}_{cav} - H^{W}_{cav}$ is actually positive.[35] We suggest that the vV_2 term in equation (2) and the vV_x term in equation (4) include not only cavity effects, but general dispersion interactions as well. These will always be more exoergic and exothermic in hexadecane than in water (note that water has a particularly low refractive index and molar refraction). Hence a combination of an exoergic interaction transfer with an exoergic cavity transfer will lead to a very negative vV_x term in ΔG°_{tr}. But combination of an exothermic interaction transfer with an endothermic cavity transfer can result in a vV_x term that is still negative, but not greatly so. This is exactly as observed, Table 6.

Our thermodynamic analysis thus reveals that the $s\pi_2^*$ term in equation (2) and equation (4) cannot easily be interpreted on its own, not even in conjunction with the correction term $d\delta_2$. The hydrogen-bond terms, however, seem to be quite straightforward, but the so-called cavity term vV_x (or vV_2) must include not only cavity effects but also general dispersion interactions as well. Our analysis also shows that because of the rather complicated interplay of the coefficients in the Gibbs energy and enthalpy of transfer, no simple relationship between ΔG°_{tr} and ΔH°_{tr} across families of solutes is expected. This is in agreement with the findings of Tomlinson *et al.*[12] and also our own observations.

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