Research Article

Journal of Physical Organic Chemistry

Received: 1 February 2008, Revised: 14 March 2008, Accepted: 18 March 2008,

(www.interscience.wiley.com) DOI 10.1002/poc.1374

Comparison of solubility of gases and vapours in wet and dry alcohols, especially octan-1-ol

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Equations for the solubility of gases and vapours into dry alcohols from methanol to decan-1-ol and into water-saturated alcohols from butan-1-ol to decan-1-ol have been compared through the use of the Abraham solvation equation. It is shown that there are noticeable differences in solvation into the dry and wet alcohols, and that these differences become larger as the alcohols become smaller and take up more water. The two main factors that lead to the differences in solvation are the solute hydrogen-bond basicity, *B*, and solute size, *L*. Increase in solute hydrogen-bond basicity favours the wet alcohols and increase in solute size favours the dry alcohols. Solute hydrogen-bond acidity plays no part, because the hydrogen-bond basicity of water, wet alcohols and dry alcohols is almost the same. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: solvation; alcohols; gas–solvent partition; hydrogen-bond acidity; hydrogen-bond basicity; solute size

INTRODUCTION

There has been considerable discussion over the relative solubility of compounds in dry octan-1-ol (octanol) and in water-saturated octan-1-ol (wet octanol), and the relative partition coefficients from water or octanol-saturated water to dry octanol or wet octanol. Chiou and Freed[1] seem to be the first to point out that not only could solubility in wet octanol be different to that in dry octanol, but solubility in octanol-saturated water could be different to that in water itself. The latter, especially, makes analysis of experimental data rather difficult. The key observations are the water to octanol partition coefficient, P_{OCT}(wet), which is the transfer from octanol-saturated water to water-saturated octanol, and the gas to dry octanol partition coefficient, K_{OCT}(dry), defined through Eqn (1). If concentrations in the gas phase and the solution phase are in the same units, then K is a dimensionless quantity

$$K_{SOLN} = \text{solute concentration in solution} / \text{solute concentration in the gas phase} \quad (1)$$

Values of K_{OCT}(dry) may be transformed into the hypothetical water to dry octanol partition coefficient, P_{OCT}(dry), through Eqn (2) where K_W is the gas to water partition coefficient

$$P_{OCT}(\text{dry}) = K_{OCT}(\text{dry})/K_W \text{ or } \log P_{OCT}(\text{dry}) = \log K_{OCT}(\text{dry}) - \log K_W \quad (2)$$

Similarly, P_{OCT}(wet) can be transformed into the gas to wet octanol partition coefficient through Eqn (3), where K'_W is now the partition coefficient from the gas phase to octanol-saturated water

$$P_{OCT}(\text{wet}) = K_{OCT}(\text{wet})/K'_W \text{ or } \log P_{OCT}(\text{wet}) = \log K_{OCT}(\text{wet}) - \log K'_W \quad (3)$$

If P_{OCT}(wet) and P_{OCT}(dry) are used to compare solubilities in wet and dry octanol, it must be noted that the former refers to transfer from octanol-saturated water and the latter to transfer from water. Similarly, if K_{OCT}(wet) and K_{OCT}(dry) are used, with the former obtained through Eqn (3), the comparison will still include the difference between K'_W and K_W. Only direct measurements of gas to wet octanol and gas to dry octanol partitions will lead to an exact comparison of solubilities in dry and wet octanol.

Fortunately, there have been a number of experiments in which solubilities in water and octanol-saturated water have been determined,[2–5] the ratio of solubilities being the ratio K'_W/K_W. Details are in Table 1; ACV is acyclovir and DCV is deoxyacyclovir. For all 28 compounds, the mean of K'_W/K_W is 0.971(0.011) and if *O*-acetyl-ACV is excluded the mean is 0.980(0.006). These ratios correspond to only −0.01 log units, and so in any comparison of log *P* or of log *K* will be negligible. It is therefore possible to compare log P_{OCT}(wet) and log P_{OCT}(dry) and to compare log K_{OCT}(wet) and log K_{OCT}(dry) with an estimated error of only 0.01 log units, if K'_W/K_W is taken as unity.

Unlike solubilities in water and octanol-saturated water, solubilities in dry octanol and wet octanol may show considerable differences. Dallas and Carr[2] suggested that the differences were rather small, but the 14 compounds studied were not very polar. For the ACV and DCV compounds studied by Kristl and Vesnaver[3] the average difference is no less than 0.67 log unit. As can be seen by the summary in Table 2[2–8], nonpolar compounds seem more soluble in dry octanol, and polar compounds more soluble in wet octanol. Pinsuwan *et al.*[9] listed the ratio of solubilities in water and wet octanol, corresponding to log P_{OCT}(wet), and compared them to values of log P_{OCT}(dry) for no less than 84 compounds. Although the obtained Eqn (4) shows the two to be highly correlated, the slope is not unity. The equation shows that for highly hydrophilic

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Table 1. Solubilities in water and in octanol-saturated water, in mol dm^{-3} at 298 K

Compound	Water	Octanol-sat water	Ratio	References
Methanol	1.580	1.582	0.999	2[a]
Ethanol	3.744	3.757	0.997	2[a]
Propan-1-ol	13.36	13.36	1.000	2[a]
Butan-1-ol	50.19	49.47	1.014	2[a]
Pentan-1-ol	198.0	192.4	1.029	2[a]
Hexan-1-ol	798.8	783.8	1.019	2[a]
Propan-2-ol	7.595	7.610	0.998	2[a]
2-Methylpropan-2-ol	11.91	11.87	0.935	2[a]
2-Methylpropan-1-ol	48.86	48.55	1.006	2[a]
3-Methylbutan-1-ol	208.0	206.6	1.007	2[a]
Cyclohexanol	157.0	157.3	0.998	2[a]
Acyclovir (ACV)	7.15×10^{-3}	6.98×10^{-3}	0.976	3
N-Acetyl-ACV	11.95×10^{-3}	11.68×10^{-3}	0.977	3
O-Acetyl-ACV	1.996×10^{-3}	1.450×10^{-3}	0.726	3
Diacetyl-ACV	7.200×10^{-3}	7.030×10^{-3}	0.976	3
Deoxyacyclovir (DCV)	83.50×10^{-3}	82.78×10^{-3}	0.991	3
N-Acetyl-DCV	137.1×10^{-3}	132.2×10^{-3}	0.965	3
O-Acetyl-DCV	107.9×10^{-3}	103.1×10^{-3}	0.956	3
Diacetyl-DCV	187.2×10^{-3}	180.2×10^{-3}	0.963	3
Sulfanilamide	42.7×10^{-3}	40.5×10^{-3}	0.948	4
Sulfacetamide	38.7×10^{-3}	36.2×10^{-3}	0.935	4
Sulfapyridine	1.05×10^{-3}	0.976×10^{-3}	0.930	4
Sulfadiazine	0.269×10^{-3}	0.246×10^{-3}	0.914	4
Sulfamerazine	0.801×10^{-3}	0.750×10^{-3}	0.936	4
Sulfamethazine	1.60×10^{-3}	1.57×10^{-3}	0.981	4
Sulfathiazole	1.80×10^{-3}	1.74×10^{-3}	0.967	4
Sulfamethoxazole	1.47×10^{-3}	1.52×10^{-3}	1.034	4
Benzocaine	5.80×10^{-3}	5.93×10^{-3}	1.022	5

[a] Values given are of activity coefficients.

Table 2. Values of $\log K_{OCT}(\text{wet}) - \log K_{OCT}(\text{dry}) = \Delta$

Compounds	Number	Δ	References
Alcohols, aromatics	14	0.069	2
ACV and DCV compounds	8	0.667	3
Sulfonamides	8	0.287	4
Benzocaine	1	0.166	5
Alkanes	4	−0.250	6,7
Alcohols, ketones	10	0.190	6,7
Amines	2	0.600	6,7
Naproxen	1	0.122	8

compounds with low values of log *P*, log P_{OCT}(wet) will be larger than log P_{OCT}(dry), on the lines of the data in Table 2.

$$\log P_{OCT}(\text{wet}) = 0.41 + 0.88 \log P_{OCT}(\text{dry}) \qquad (4)$$

The structures of wet octanol and dry octanol have been studied several times. An X-ray diffraction analysis by Franks *et al.*[10] showed little structural difference although aggregation into spherical micelles was more pronounced in wet octanol. Chen and Siepmann[11] have carried out Monte Carlo simulations of wet and dry octanol, and of solvation of nonpolar and polar molecules by the two solvent systems. They suggest that nonpolar solutes partition into the nonpolar regions of the solvents; this slightly favours partition into dry octanol. When the polar solutes, methanol and butanol, dissolve in the two solvents, there is an increase in the average coordination numbers for the hydroxyl oxygen atoms in the solutes on going from the dry to the wet octanol. The increase is larger for methanol solute than for butanol solute which was attributed to preferential partition of methanol solute into the core of water-rich aggregates. Although Chen and Siepmann[11] focussed on the hydrogen-bond environment of solutes in wet and dry octanol, no distinction was made between the solutes as hydrogen-bond acids or as hydrogen-bond bases (and conversely for the solvents). Our method of analysis of solvation and solubility leads directly to quantitative estimates of the two hydrogen-bond motifs, and so complements the simulations of Chen and Siepmann. We review our method as applied to solvation in wet and dry alcohols, and we set out improved equations that yield better comparisons between wet and dry octanol.

METHODS AND RESULTS

Our methods are based on the two linear free energy relationships, Eqn (5) and Eqn (6)[12,13]

$$\mathrm{SP} = c + e\,E + s\,S + a\,A + b\,B + v\,V \qquad (5)$$

$$\mathrm{SP} = c + e\,E + s\,S + a\,A + b\,B + l\,L \qquad (6)$$

In Eqn (5) and Eqn (6), the independent variables are solute descriptors as follows. E is the solute excess molar refractivity in units of $(\mathrm{cm^3\,mol^{-1}})/10$, S is the solute dipolarity/polarizability, A and B are the overall or summation hydrogen-bond acidity and basicity, V is the McGowan characteristic volume in units of $(\mathrm{cm^3\,mol^{-1}})/100$ and L is the logarithm of the gas to hexadecane partition coefficient at 298K. Eqn (5) is used for transfer of solutes from one condensed phase to another, and Eqn (6) is used for processes that involve the transfer of solutes from the gas phase to a solvent phase. The dependent variable, SP, is a set of solute properties in a given system. For example SP in Eqn (5) could be the water to wet octanol partition coefficient, as log P_{OCT}(wet), and SP in Eqn (6) could be the gas to wet octanol partition coefficient, as log K_{OCT}(wet).

With the present systems, the coefficients in Eqn (5) refer to differences in properties of the solvents water and alcohols, whereas those in Eqn (6) refer to differences in properties of the gas phase and alcohols (effectively properties of the alcohols themselves) and are easier to interpret. Thus although we have reported on the application of Eqn (5) to partitions between water and wet and dry alcohols,[14–16] we concentrate on Eqn (6) and on partitions from the gas phase to wet and dry alcohols. Coefficients in Eqn (6) are shown in Table 3; N is the number of solutes used in the regression equations, SD is the regression standard deviation, R is the correlation coefficient and F is the F-statistic.

There were not enough data to obtain an equation for solubility in dry nonanol through the usual regression analysis. However, data are available for solubility of a few compounds,[17–19] and so we have used these data to obtain coefficients for Eqn (6) that fit the data and conform to the general trend shown for solubility in the other alcohols. The obtained coefficients for dry nonanol are in Table 3; we give no values for R^2 and F because they have no meaning on our fitting procedure. Also in Table 3, for comparison are coefficients for the solubility of gaseous compounds in water itself.[20]

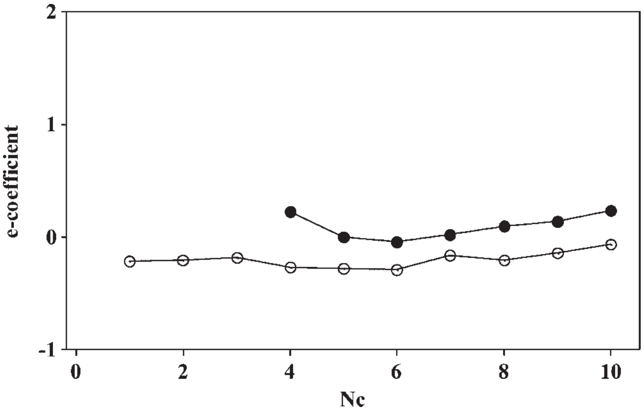

Figure 1. Plots of the e-coefficient against the number of carbon atoms in the alcohol for dry alcohols ○ and wet alcohols ●

There has been considerable work on the solubility of gases and vapours in wet and dry alcohols.[14–16] Data for the dry alcohols were invariably obtained by direct measurements of log K(dry), and data for the wet alcohols were obtained from log P(wet) through Eqn (3), on the assumption that K'_{W} is equivalent K_{W}.[14–16] Application of Eqn (6) leads to the coefficients in Table 3; these coefficients reflect the chemical properties of the solvents that influence solubility. In Figs 1–5 are given plots of the coefficients against the number of carbon atoms in the alcohols, N_{c}. The scale of the Figures is the same, except for the plot

Table 3. Coefficients in Eqn (6) for partition between the gas phase and wet and dry alcohols

System	c	e	s	a	b	l	N	SD	R^2	F	References
Butanol, wet	−0.123	0.220	1.414	3.430	2.600	0.523	78	0.24	0.954	298	16
Pentanol, wet	−0.107	−0.001	1.188	3.614	1.671	0.721	106	0.20	0.998	13 149	16
Hexanol, wet	−0.302	−0.046	0.880	3.609	1.785	0.824	105	0.23	0.991	6387	16
Heptanol, wet	−0.159	0.018	0.825	3.539	1.425	0.830	78	0.17	0.998	6387	16
Octanol, wet	−0.222	0.088	0.701	3.473	1.477	0.851	395	0.21	0.988	6363	16
Nonanol, wet	−0.197	0.141	0.694	3.616	1.299	0.827	82	0.17	0.998	6261	16
Decanol, wet	−0.302	0.233	0.741	3.531	1.177	0.835	54	0.18	0.994	1699	16
Methanol, dry	−0.004	−0.215	1.173	3.701	1.432	0.769	93	0.13	0.995	3681	14
Ethanol, dry	0.012	−0.206	0.789	3.635	1.311	0.853	68	0.14	0.997	3534	14
Propanol, dry	−0.028	−0.185	0.648	4.022	1.043	0.869	77	0.12	0.997	6073	14
Butanol, dry	−0.039	−0.276	0.539	3.781	0.995	0.934	92	0.16	0.997	5099	14
Pentanol, dry	−0.042	−0.277	0.526	3.779	0.983	0.932	61	0.08	0.999	19 143	14
Hexanol, dry	−0.035	−0.298	0.626	3.726	0.729	0.936	46	0.09	0.999	18 181	14
Heptanol, dry	−0.062	−0.168	0.429	3.541	1.181	0.927	38	0.07	0.999	23 045	14
Octanol, dry	−0.120	−0.203	0.560	3.576	0.702	0.939	156	0.12	0.997	10 573	15
Nonanol, dry	−0.105	−0.140	0.440	3.625	0.730	0.943	14	0.06			[a]
Decanol, dry	−0.136	−0.068	0.325	3.674	0.767	0.947	45	0.09	0.999	15 984	14
Gas to water	−1.271	0.822	2.743	3.904	4.814	−0.213	392	0.18	0.992	10 229	20

[a] This work, see text. Values of R^2 and F are not given because they have no meaning.

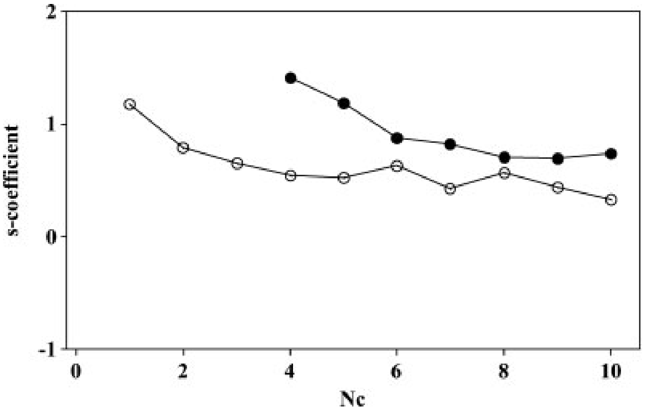

Figure 2. Plots of the *s*-coefficient against the number of carbon atoms in the alcohol for dry alcohols ○ and wet alcohols ●

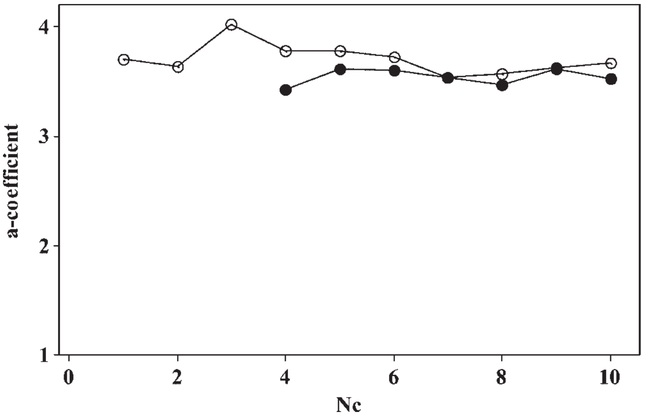

Figure 3. Plots of the *a*-coefficient against the number of carbon atoms in the alcohol for dry alcohols ○ and wet alcohols ●

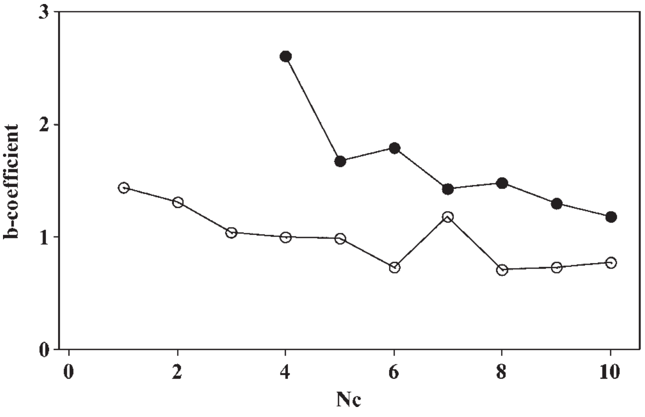

Figure 4. Plots of the *b*-coefficient against the number of carbon atoms in the alcohol for dry alcohols ○ and wet alcohols ●

of the *l*-coefficient, to indicate the relative importance of the coefficients. The *e*- and *s*-coefficients for the wet alcohols are always larger than for the corresponding dry alcohols, showing that the wet alcohols are slightly more dipolar and polarizable than the dry alcohols, with the effect getting larger as the alcohols become smaller and take up more water.

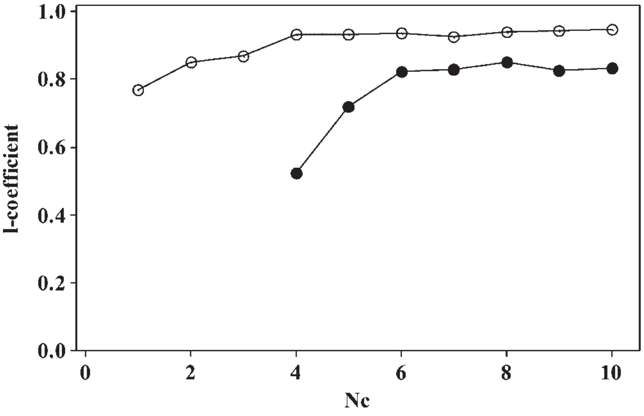

Figure 5. Plots of the *l*-coefficient against the number of carbon atoms in the alcohol for dry alcohols ○ and wet alcohols ●

The behaviour of the *a*-coefficient is, at first sight, surprising, as shown in Fig. 3. The wet and dry alcohols have almost the same hydrogen-bond basicity, except perhaps for butanol where the wet alcohol is less basic than the dry alcohol. Previous studies of the effect of solute hydrogen bonding on log P_{OCT}(wet) have led to the conclusion that wet octanol and water have about the same hydrogen-bond basicity,[21–24] and comparison of the *a*-coefficients in Table 3 shows quite conclusively that water, wet alcohols and dry alcohols have nearly the same hydrogen-bond basicity. Dallas and Carr[2] measured solvatochromic parameters of wet and dry octanol and showed that the β-basicity parameter was almost the same. Rosés *et al.*[25] measured β for methanol–water and ethanol–water mixtures and observed that β did not alter on addition of substantial quantities of water to the alcohols. Of course, these measurements are based on spectroscopic energies, unlike the *a*-coefficient which is free energy related, but they still suggest that wet alcohols have a similar hydrogen-bond basicity to dry alcohols.

On the other hand, the *b*-coefficient is always much larger for the wet alcohols than for the dry alcohols, and increases with the water content of the wet alcohol, as shown in Table 3 and Fig. 4. Water itself has a much larger *b*-coefficient than even wet butanol. Previous work has shown that water is a much stronger hydrogen-bond acid than wet octanol,[21–24] and the data in Table 3 now indicate that it is much stronger than wet butanol. These results are contrary to solvatochromic measurements of the hydrogen-bond solvent acidity parameter α. Dallas and Carr[2] found that α was almost the same for wet and dry octanol, and Rosés *et al.*[25] observed that addition of water to methanol and ethanol actually resulted in a decrease in α. As noted above, the solvatochromic measurements refer to spectroscopic energies. There is no logical connection between spectroscopic energies and thermodynamic free energies, and so it is not entirely surprising that different conclusions may be drawn.

The *l*-coefficient also differs as between wet and dry alcohols, but is now larger for the dry alcohols than the corresponding wet alcohols. The result of this is that hydrophobic solutes are more soluble in the dry alcohols, as expected.

In summary, the two terms that have the most influence on whether a solute is more soluble in a wet or in a dry alcohol are *bB* and *lL* in Eqn (6). This is illustrated in Fig. 6, which shows how log *K*(wet) − log *K*(dry) changes across the range of alcohols, just due to the effect of the *bB* terms for a solute with $B = 1$. As N_c becomes larger, the effect of *B* becomes smaller and the partition

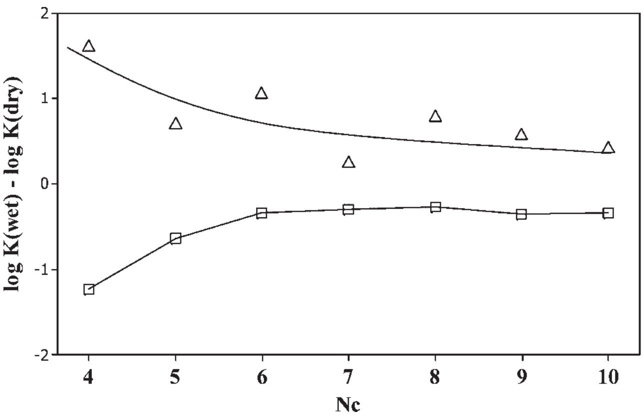

Figure 6. The separate effect of B and of L values on log K for partition into wet and dry alcohols: Δ the effect on log K of a solute with $B = 1$, □ the effect on log K of a solute with $L = 3$. N_c is the number of carbon atoms in the alcohol

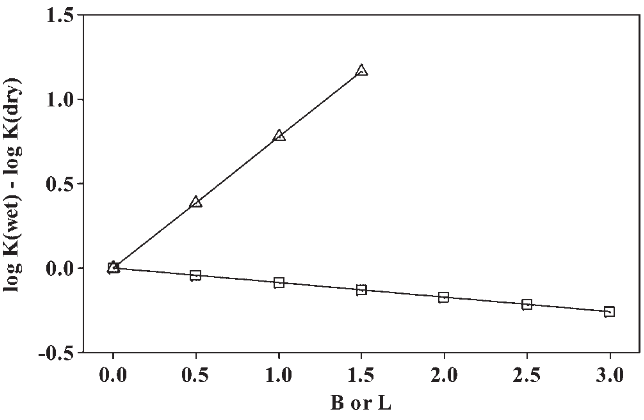

Figure 7. Effect of B and L values on log K for partition into wet and dry octanol: Δ the effect on log K(wet) − log K(dry) of change in B, □ the effect on log K(wet) − log K(dry) of change in L

coefficients into the wet and dry alcohols become closer. Similarly, the effect of just the lL terms for a solute with $L = 3$ (an average value) also becomes smaller as N_c becomes larger. Hence for a solute with reasonably large values of B and L, there will be a large difference between log K(wet) and log K(dry) for the smaller alcohols, but a much smaller difference between log K(wet) and log K(dry) for the larger alcohols.

We can focus on octanol, and show the effect of change in B or L on solubility in wet and dry octanol in Fig. 7. If a solute has a moderate hydrogen-bond basicity, of around 0.5, and is rather small so that L is about 1.0 units, there will be little difference between log K_{OCT}(wet) and log K_{OCT}(dry), because the effects of the terms in bB and lL tend to cancel out. However for solutes with large values of B and small values of L or with small values of B and very large values of L, there will be significant differences. This is the reason why Cabani *et al.*[6] and Dallas and Carr[2] observed rather small differences in solubility in wet and dry octanol. Our observation that increase in L leads to preferential solubility in dry octanol over wet octanol is in agreement with the conclusions of Chen and Siepmann.[11] However, the finding that hydrogen-bond effects relate only to the difference in hydrogen-bond acidity of wet and dry octanol cannot be deduced from the results of Chen and Siepmann.[11]

Since the equation for dry octanol was constructed (in 2001), a number of extra values of log K_{OCT}(dry) have been determined by the direct method. Li *et al.*[26] have carried out a very though investigation into 16 polychlorobiphenyls, PCBs, including an analysis of log K_{OCT}(dry) values. They first selected a literature derived value (LDV), and then adjusted the value, where necessary, to achieve internal consistency over a number of physicochemical properties. Li *et al.* denoted the final adjusted value as FAV. We use only the recommended FAV values of Li *et al.*[26] for the PCBs; these are in Table 4, together with the original data used by Abraham *et al.*[15] Other directly determined

Table 4. Recent values of log K_{OCT}(dry), both directly determined, and from values of log S_{OCT} and log C_G

Compound	log K_{OCT}	log S_{OCT}	log C_G	References
Helium	−1.72			15
Neon	−1.57			15
Argon	−0.71			15
Krypton	−0.24			15
Xenon	0.38			15
Hydrogen	−1.29			15
Oxygen	−0.76			15
Nitrogen	−1.02			15
Nitrous oxide	0.33			15
Carbon monoxide	−0.88			15
Carbon dioxide	0.16			15
Methane	−0.38			15
Ethane	0.42			15
Propane	0.97			15
n-Butane	1.53			15
n-Pentane	1.95			15
n-Hexane	2.44			15

(*Continues*)

Table 4. (*Continued*)

Compound	log K_{OCT}	log S_{OCT}	log C_G	References
n-Heptane	2.95			15
n-Octane	3.30			15
Cyclohexane	2.71			15
Methylcyclohexane	3.05			15
Ethene	0.28			15
Pent-1-ene	1.93			15
Hex-1-ene	2.41			15
Oct-1-ene	3.35			15
Non-1-ene	3.83			15
2-Methylbuta-1,3-diene	2.06			15
Cyclohexene	2.83			15
Tetrafluoromethane	−0.95			15
Chloromethane	1.39			15
Dichloromethane	2.27			15
Trichloromethane	2.80			15
Tetrachloromethane	2.79			15
1,1-Dichloroethane	2.41			15
1,2-Dichloroethane	2.78			15
1,1,1-Trichloroethane	2.70			15
1,1,2-Trichloroethane	3.40			15
Hexachloroethane	4.47			15
1-Chloropropane	2.24			15
1,2-Dichloropropane	2.96			15
1-Chlorobutane	2.72			15
cis-1,2-Dichloroethene	2.56			15
Trichloroethene	2.99			15
Tetrachloroethene	3.48			15
Dibromomethane	3.07			15
Bromoethane	2.11			15
Iodomethane	2.16			15
Iodoethane	2.59			15
Dibromochloromethane	3.59			15
Dimethylether	1.37			15
Diethylether	2.19			15
Di-*n*-propylether	2.97			15
Diisopropylether	2.66			15
Di-*n*-butylether	3.89			15
Diisobutylether	3.40			15
Di-*n*-pentylether	4.80			15
tert-Butylmethylether	2.58			15
Tetrahydrofuran	2.86			15
Tetrahydropyran	3.22			15
1,4-Dioxane	3.17			15
Propanone	2.31			15
Butanone	2.77			15
Pentan-2-one	3.19			15
Pentan-3-one	3.20			15
3-Methylbutan-2-one	3.04			15
Hexan-2-one	3.68			15
Heptan-2-one	4.15			15
Cyclopentanone	3.67			15
Methyl formate	1.75			15
Ethyl formate	2.19			15
n-Propyl formate	2.66			15
Methyl acetate	2.31			15

(*Continues*)

Table 4. (*Continued*)

Compound	log K_{OCT}	log S_{OCT}	log C_G	References
Ethyl acetate	2.70			15
n-Propyl acetate	3.17			15
n-Butyl acetate	3.65			15
n-Pentyl acetate	4.12			15
n-Hexyl acetate	4.58			15
Isopropyl acetate	2.93			15
Isobutyl acetate	3.45			15
Isopentyl acetate	3.94			15
Ethyl propanoate	3.15			15
Ethyl butanoate	3.56			15
Acetonitrile	2.31			15
Proprionitrile	2.69			15
1-Cyanopropane	3.12			15
2-Cyanopropane	2.87			15
1-Cyanobutane	3.60			15
1-Cyanopentane	4.08			15
n-Butylamine	3.61			15
Methylamine	1.90			15
Dimethylamine	2.00			15
Trimethylamine	1.94			15
Di-*n*-propylamine	3.59			15
Nitromethane	2.52			15
Nitroethane	2.88			15
1-Nitropropane	3.25			15
N,*N*-Dimethylformamide	4.38			15
Methanol	2.84			15
Ethanol	3.20			15
Propan-1-ol	3.68			15
Propan-2-ol	3.38			15
Butan-1-ol	4.19			15
2-Methylpropan-1-ol	3.93			15
Butan-2-ol	3.80			15
2-Methylpropan-2-ol	3.50			15
Pentan-1-ol	4.69			15
3-Methylbutan-1-ol	4.52			15
Hexan-1-ol	5.18			15
Octan-1-ol	6.03			15
Hexadecan-1-ol	9.90			15
Octadecan-1-ol	10.93			15
Eicosan-1-ol	12.06			15
2-Chloroethanol	4.30			15
Cyclohexanol	5.18			15
Acetic acid	4.31			15
Dimethylsulfoxide	4.96			15
Sulfur hexafluoride	−0.30			15
Carbon disulphide	2.28			15
Tetramethyltin	2.62			15
Benzene	2.80			15
Toluene	3.31			15
Ethylbenzene	3.72			15
o-Xylene	3.90			15
m-Xylene	3.79			15
p-Xylene	3.79			15
n-Propylbenzene	4.09			15
Isopropylbenzene	3.98			15

(*Continues*)

Table 4. (*Continued*)

Compound	log K_{OCT}	log S_{OCT}	log C_G	References
Hexamethylbenzene	6.31			15
trans-Stilbene	7.48			15
Biphenyl	6.15			15
Naphthalene	5.19			15
Acenaphthene	6.31			15
Fluorene	6.83			15
Anthracene	7.55			15
Phenanthrene	7.52			15
Fluoranthene	8.61			15
Pyrene	8.75			15
1,2-Dichlorobenzene	4.36			15
1,4-Dichlorobenzene	4.46			15
1,2,3-Trichlorobenzene	5.19			15
1,3,5-Trichlorobenzene	4.85			15
1,2,3,4-Tetrachlorobenzene	5.64			15
1,2,3,5-Tetrachlorobenzene	5.55			15
1,2,4,5-Tetrachlorobenzene	5.62			15
Pentachlorobenzene	6.49			15
Hexachlorobenzene	7.17			15
1,4-Dibromobenzene	5.21			15
Methylphenylether	4.01			15
Benzonitrile	4.46			15
4-Ethoxyacetanilide	9.59			15
2-Hydroxybenzoic acid	7.44			15
4-Hydroxybenzoic acid	8.08			15
Methyl 4-hydroxybenzoate	8.57			15
Piperidine	4.04			15
N-Methylpyrrolidine	3.64			15
Pyrrolidine	4.07			15
4-Chlorobiphenyl	6.78			26
2,4′-Dichlorobiphenyl	7.34			26
4,4′-Dichlorobiphenyl	7.85			26
2,4,4′-Trichlorobiphenyl	7.85			26
2,4,5-Trichlorobiphenyl	7.78			26
2,4′,5-Trichlorobiphenyl	7.94			26
2,2′,5,5′-Tetrachlorobiphenyl	8.22			26
2,3,4,5-Tetrachlorobiphenyl	8.55			26
2,2′,4,5,5′-Pentachlorobiphenyl	8.79			26
2,3,3′,4,4′-Pentachlorobiphenyl	9.45			26
2,3,4,4′,5-Pentachlorobiphenyl	9.36			26
2,2′,3,4,4′,5′-Hexachlorobiphenyl	9.66			26
2,2′,4,4′,5,5′-Hexachlorobiphenyl	9.44			26
2,2′,4,4′,6,6′-Hexachlorobiphenyl	9.14			26
2,2′,3,4,4′,5,5′-Heptachlorobiphenyl	10.16			26
2,2′,3,3′,4,4′,5,5′-Octachlorobiphenyl	11.13			26
1,2-Dichlorobenzene	4.33			27
1,3-Dichlorobenzene	4.13			27
1,4-Dichlorobenzene	4.18			27
1,2,3-Trichlorobenzene	5.16			27
1,2,4-Trichlorobenzene	4.84			27
1,3,5-Trichlorobenzene	4.64			27
1,2,3,4-Tetrachlorobenzene	5.61			27
1,2,3,5-Tetrachlorobenzene	5.53			27
1,2,4,5-Tetrachlorobenzene	5.65			27
Pentachlorobenzene	6.28			27

(*Continues*)

Table 4. (*Continued*)

Compound	log K_{OCT}	log S_{OCT}	log C_G	References
Hexachlorobenzene	6.90			28
p,p-DDT[a]	10.09			28
p,p′-DDE[b]	9.70			29
p,p′-DDD[c]	10.03			29
cis-Chordane	8.83			29
trans-Chlordane	8.83			29
Heptachlor	7.76			29
Heptachlor epoxide	8.59			29
Aldrin	8.26			29
Dieldrin	8.84			29
Endrin	8.32			29
α-Endosulfan (Endosulfan I)	8.43			29
β-Endosulfan (Endosulfan II)	9.53			29
Phenol	5.68	0.94	−4.74	30, 32
Bibenzyl	6.45	−0.35	−6.80	30, 32
Hexachloroethane	4.42	−0.28	−4.70	30, 32
Hexamethylbenzene	6.31	−0.89	−7.20	30, 32
Lindane	7.96	−0.74	−8.70	30, 33

[a] 1,1,1-Trichloro-2,2-(4-chlorophenyl)ethane.
[b] 1,1-Dichloro-2,2-(4-chlorophenyl) ethene.
[c] 1,1-Dichloro-2,2-(4-chlorophenyl)ethane.

values of log K_{OCT}(dry), have been recorded by Wania *et al.*,[27] Chen *et al.*[28] and Shen and Wania;[29] these are also in Table 4. In addition to these directly determined values, it is possible to obtain log K_{OCT}(dry) through measurements of the solubility of solutes in dry octanol, S_{OCT}(dry), together with measurements of the corresponding vapour pressures (equivalent to concentration in the gas phase), both measurements being at 298 K. Pinsuwan *et al.*[30] and Raevsky *et al.*[31] have compiled lists of S_{OCT}(dry) but unfortunately, there are few corresponding values of vapour pressure at 298 K available, and for most of those solutes for which both S_{OCT}(dry) and vapour pressure are known, values of log K_{OCT}(dry) by the direct method are known. However, there are a few additional compounds for which log K_{OCT}(dry) can be obtained by the indirect method, taking solubilities from Pinsuwan *et al.*,[30] and vapour pressures at 298K from the literature.[32,33] Details are given in Table 4.

There are 200 compounds in Table 4; application of Eqn (6) yields

$$\begin{aligned}\text{Log } K_{OCT}(\text{dry}) = &-0.147(0.022) - 0.214(0.034)\,E \\ &+ 0.561(0.042)\,S + 3.507(0.072)\,A \\ &+ 0.749(0.049)\,B + 0.943(0.007)\,L\end{aligned} \tag{7}$$

$ND = 200$, $SD = 0.142$, $R^2 = 0.997$, $F = 15\,405.9$

Here, ND is the number of data points, SD is the standard deviation, *R* is the correlation coefficient and *F* is the *F*-statistic. The coefficients in Eqn (7) are very close to those listed for log K_{OCT}(dry) in Table 3, and so the extra data confirms the original[15] equation.

Finally, we point out that we have carried out the present analysis using Eqn (6) because the coefficients in Eqn (6) are easier to interpret than those in Eqn (5). However, if we had used Eqn (5) as the basis for the analysis, the general interpretation would be unchanged.

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