PERKIN 2

Correlation and prediction of the solubility of Buckminsterfullerene in organic solvents; estimation of some physicochemical properties

Michael H. Abraham,[a] **Caroline E. Green**[a] **and William E. Acree, Jr.**[b]

[a] *Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ*
[b] *Department of Chemistry, University of North Texas, Denton, Texas 76203-0068, USA*

Received (in Cambridge, UK) 14th September 1999, Accepted 17th November 1999

The solubilities of Buckminsterfullerene, C_{60}, in 20 organic solvents have been transformed into water–solvent partition coefficients and the latter, as log *P* values, analysed by the Abraham solvation equation. Our analysis indicates that a water solubility of 10^{-18} mol dm^{-3} is the optimum value. The solubilities can be transformed into air–solvent partitions, *L*, using optimum values of the saturated vapour concentration, 10^{-24} mol dm^{-3}, and the air–water partition coefficient, 10^{-6}. A total of 41 log *P* and log *L* values were thus processed to obtain the Abraham solvation descriptors for C_{60}. It is shown that C_{60} is dipolar/polarisable, has no hydrogen bond acidity, but is a slightly stronger hydrogen bond base than compounds such as acetophenone. The descriptors indicate that C_{60} behaves rather like a polyalkene rather than an aromatic system. Various properties of C_{60} can be predicted from the solvation descriptors; C_{60} is very lipophilic, is distributed between blood and brain largely into the brain, and is taken up by plant matrices from the air or from water almost quantitatively.

Although Buckminsterfullerene, C_{60}, has been extensively studied, there has been comparatively little work on physicochemical properties. Various calculations have been made on properties such as polarisability,[1] the partial molar volume of C_{60} has been determined in a number of organic solvents,[2,3] and the solubility in organic solvents has been measured by various groups of workers.[4–14] Li and Swanson[15] used multilayer films of C_{60} in chemical sensors; they suggested that the sensitivity of such chemical sensors towards vapours could be correlated with the solubility of C_{60} in the corresponding solvents. Grate *et al.*,[16] however, showed that this was not a general effect. One of the few experimental observations of physicochemical properties of C_{60} was that of Golovna *et al.*[17] who used C_{60} as a gas chromatographic stationary phase. They showed that for the retention of alkanes, C_{60} was comparable to nonpolar stationary phases such as squalane. Abraham *et al.*[18] measured gas–solid partition coefficients of a series of nonpolar and polar solute gases on C_{60} and found that C_{60} is only weakly polarisable, has no hydrogen-bond acidity but some hydrogen-bond basicity. They concluded that C_{60} did not behave as a highly aromatic molecule, but, following Taylor and Walton,[19] behaved rather as a giant closed-cage alkene.

Makitra and Pyrih[20] used literature data to correlate the solubility of C_{60} in organic solvents with various solvent properties. They found that solvent dipolarity, hydrogen-bond acidity and hydrogen-bond basicity were not statistically significant, and that the only descriptors required were the solvent refractive index function, $f(\eta) = (\eta^2 - 1)/(\eta^2 + 2)$, and the solvent cohesive energy density, δ^2, through eqn. (1), where *S* is the solubility in mol dm^{-3}.

$$\log S = -11.81 + 33.8\,(\eta^2 - 1)/(\eta^2 + 2) - 5.1\delta^2 \quad (1)$$

Heymann[5] correlated the solubility of C_{60} (and C_{70}) in a number of alcohols at 298 K with δ. He extrapolated results to water as solvent, and calculated that the solubility of C_{60} was 1.3×10^{-11} ng ml^{-1} with an uncertainty of one order of magnitude. This corresponds to $\log S = -19.7\ (\pm 1)$ with the solubility in mol dm^{-3}. However, Heymann[5] noted that if the Flory–Huggins size-effect was introduced, the calculated solubility in water was even smaller.

Methodology

Our method for the correlation of solubilities starts with the set of equations we have constructed[21] for the partition of solutes between water and a given solvent, using our general solvation equation [eqn. (2)].

$$\log P = c + rR_2 + s\pi_2^{\mathrm{H}} + a\Sigma\alpha_2^{\mathrm{H}} + b\Sigma\beta_2^{\mathrm{H}} + vV_x \quad (2)$$

In eqn. (2), the dependent variable in the present work is log *P*, the partition coefficient of a series of solutes between water and a given solvent. The independent variables are solute descriptors as follows:[21] R_2 is the solute excess molar refractivity, π_2^{H} is the solute dipolarity/polarisability, $\Sigma\alpha_2^{\mathrm{H}}$ and $\Sigma\beta_2^{\mathrm{H}}$ are the overall or summation hydrogen-bond acidity and basicity, and V_x is the McGowan characteristic volume[22] in units of (cm^3 mol^{-1})/100.

We have also used[21] another solvation equation [eqn. (3)]

$$\log L = c + R_2 + s\pi_2^{\mathrm{H}} + a\Sigma\alpha_2^{\mathrm{H}} + b\Sigma\beta_2^{\mathrm{H}} + l\log L^{16} \quad (3)$$

for partition of solutes between the gas phase and solvents. The dependent variable is now log *L*, where *L* is the gas–solvent partition coefficient, or Ostwald solubility coefficient, for a series of solutes in a given solvent; *L* is defined through eqn. (4).

$$L = \text{[conc. in solvent]}/\text{[conc. in gas phase]} \quad (4)$$

The descriptors in eqn. (3) are exactly the same as those in eqn. (2), except that V_x is replaced by $\log L^{16}$, where L^{16} is the gas–liquid partition coefficient on hexadecane at 298 K.[23] The determination of the solute descriptors used in eqn. (2) and eqn. (3) from experimental data has been described in detail.[24,25]

Table 1 Coefficients in eqn. (2) for partition between water and solvents

Solvent[a]	c	r	s	a	b	v
n-Pentane	0.369	0.386	−1.568	−3.535	−5.215	4.514
n-Hexane	0.361	0.579	−1.723	−3.599	−4.764	4.344
n-Decane	0.160	0.585	−1.734	−3.435	−5.078	4.582
Isooctane	0.288	0.382	−1.668	−3.639	−5.000	4.561
Cyclohexane	0.159	0.784	−1.678	−3.740	−4.929	4.577
Dichloromethane	0.314	0.001	0.022	−3.238	−4.137	4.259
Trichloromethane[b]	0.327	0.157	−0.391	−3.191	−3.437	4.191
Tetrachloromethane	0.260	0.573	−1.254	−3.558	−4.588	4.589
1,2-Dichloroethane	0.227	0.278	−0.167	−2.816	−4.324	4.205
Benzene	0.142	0.464	−0.588	−3.099	−4.625	4.491
Toluene	0.143	0.527	−0.720	−3.010	−4.824	4.545
Chlorobenzene	0.040	0.246	−0.462	−3.038	−4.769	4.640
Bromobenzene	−0.130	0.394	−0.280	−3.331	−4.640	4.583
Iodobenzene	−0.181	0.410	−0.334	−3.300	−4.595	4.549
Nitrobenzene	−0.181	0.576	0.003	−2.356	−4.420	4.263
Dimethylformamide, dry	0.105	0.317	0.462	1.154	−4.843	3.757
Methanol, dry[b]	0.329	0.299	−0.671	0.080	−3.389	3.512
Ethanol, dry[b]	0.208	0.409	−0.959	0.186	−3.645	3.928
Propan-1-ol, dry	0.148	0.436	−1.098	0.389	−3.893	4.036
Butan-1-ol, dry	0.153	0.438	−1.177	0.096	−3.919	4.122
Pentan-1-ol, dry	0.080	0.521	−1.294	0.208	−3.908	4.208
Hexan-1-ol, dry	0.044	0.470	−1.153	0.083	−4.057	4.249
Octan-1-ol, dry	−0.034	0.490	−1.048	−0.028	−4.229	4.219

[a] The solvents denoted as 'dry' are those for which partitions refer to transfer from water to the pure dry solvent. The other partitions are from water (more correctly water saturated with solvent) to the solvent saturated with water; see also the text. [b] Not used in the analysis.

Table 2 Coefficients in eqn. (3) for partition between the gas phase and solvents

Solvent	c	r	s	a	b	l
n-Pentane	0.335	−0.276	0.000	0.000	0.000	0.968
n-Hexane	0.292	−0.169	0.000	0.000	0.000	0.979
n-Decane	0.156	−0.143	0.000	0.000	0.000	0.989
Isooctane	0.275	−0.244	0.000	0.000	0.000	0.972
Cyclohexane	0.163	−0.110	0.000	0.000	0.000	1.013
Dichloromethane	0.121	−0.450	1.677	0.404	0.786	0.940
Trichloromethane	0.116	−0.467	1.203	0.138	1.432	0.994
Tetrachloromethane	0.282	−0.303	0.460	0.000	0.000	1.047
1,2-Dichloroethane	0.011	−0.150	1.436	0.649	0.736	0.936
Benzene	0.107	−0.313	1.053	0.457	0.169	1.020
Toluene	0.121	−0.222	0.938	0.467	0.099	1.012
Chlorobenzene	0.053	−0.553	1.254	0.364	0.000	1.041
Nitrobenzene	−0.273	0.039	1.803	1.231	0.000	0.929
Dimethylformamide, dry	−0.161	−0.181	2.327	4.756	0.000	0.808
Methanol, dry	−0.004	−0.215	1.173	3.701	1.432	0.769
Ethanol, dry	0.012	−0.206	0.789	3.635	1.311	0.853
Propan-1-ol, dry	−0.028	−0.185	0.648	4.022	1.043	0.869
Butan-1-ol, dry	−0.039	−0.276	0.539	3.781	0.995	0.934
Pentan-1-ol, dry	−0.042	−0.277	0.526	3.779	0.983	0.932
Hexan-1-ol, dry	−0.035	−0.298	0.626	3.726	0.729	0.936
Octan-1-ol, dry	−0.120	−0.203	0.560	3.576	0.702	0.939

The coefficients in eqn. (2) for partitions between water and a number of solvents are given in Table 1, and the coefficients for partition between the gas phase and solvents are in Table 2. The solvent systems we consider in the present work fall into two classes, (1) solvents such as alkanes, chloroalkanes and most aromatic solvents that are so immiscible with water that partitions between the mutually saturated solvents can be taken as the same as partitions between pure solvents, and (2) solvents such as alcohols in which the partitions refer to transfer from water or the gas phase to the pure dry solvent.

Now the partition coefficient of a solid between water and a solvent phase can be obtained from the solubility of the solid in water, S_w, and the solvent, S, as in eqn. (5), provided that

$$\log P = \log S - \log S_w \tag{5}$$

certain conditions are fulfilled.[26] The major condition is that the same solid phase must be in equilibrium with the saturated solutions in water and in the given solvent.

Values of log S for C_{60} are available in most of the solvents for which we have coefficients. The latter are given in Tables 1 and 2, and the values of log S, where S is in mol dm^{-3}, are listed in Table 3. In many cases, different solubilities have been recorded, and we have generally taken the average of the recorded solubilities. In order to obtain a value for log S_w, we start with the suggested value[5] of −20, and then calculate the corresponding log P values through eqn. (5). In this way we obtain 23 log P values for which we have all the coefficients for eqn. (2) in Table 1. It is then possible to assign descriptors in eqn. (2) to C_{60} that will best reproduce the 23 log P values. Before doing this, we can effect some simplification by calculating V_x using McGowan's method.[22] We find that V_x is 390.6 cm^3 mol^{-1}, in reasonable accord with the partial molar volumes in nonpolar solvents determined by Ruelle *et al.*,[2] noting that the characteristic volume of McGowan is always smaller than the partial molar volume in nonpolar solvents. Then with V_x = 3.906 (cm^3 mol^{-1})/100, only four descriptors in eqn. (2) need to be assigned. In the event, $\Sigma\alpha_2^H$ was zero, as expected for a

Table 3 Solubility of C_{60} in dry solvents, as log S in mol dm^{-3}

Solvent	log S (obs)	Ref.
n-Pentane	−5.25	3,7,14
n-Hexane	−4.23	3,7,8,14
n-Heptane	−4.17	14
n-Octane	−4.66[a,b]	14
Isooctane	−4.44	7
n-Nonane	−4.06[c]	14
n-Decane	−4.01	3,7
n-Dodecane	−2.90[b,c]	7
n-Tetradecane	−3.76	7
Cyclopentane	−5.55[b,c]	3
Cyclohexane	−4.26	3,7,9
Dichloromethane	−3.46	3,7,9
Trichloromethane	−3.64	3,10
Tetrachloromethane	−3.28	3,7
1,2-Dichloroethane	−3.96	9
Benzene	−2.75	3,7,10,11,12
Toluene	−2.43[d]	3,7,11,13
Chlorobenzene	−2.06	3,11
Bromobenzene	−2.37	3,11
Iodobenzene	−2.54	11
Nitrobenzene	−2.96	3
Dimethylformamide	−4.43	9
Methanol	−7.31	5,14
Ethanol	−5.92	5,3,14
Propan-1-ol	−5.24	5,14
Butan-1-ol	−4.89	5,14
Pentan-1-ol	−4.38	5,14
Hexan-1-ol	−4.23	5,14
Octan-1-ol	−4.19	5,14
Propanone[c]	−5.85	3
Dioxane[c]	−4.24	7
Propan-2-ol[c]	−5.54	14
Butan-2-ol[c]	−5.30	14
Ethane-1,2-diol	Not measurable	14

[a] Value of −4.46 from ref. 7 not used. [b] Not used, because value seems in error. [c] No solvation equation for this solvent. [d] Value of −3.12 from ref. 12 not used.

Table 4 Correlation of 20 log P values through eqn. (2).[a] S_w in mol dm^{-3}

log S_w	R_2/((cm^3 mol^{-1})/10)	π_2^H	$\Sigma\beta_2^H$	sd
−14	1.745	1.473	1.409	0.490
−15	1.822	1.497	1.194	0.433
−16	1.900	1.514	0.979	0.389
−17	1.977	1.535	0.764	0.361
−17.5	2.016	1.545	0.657	0.354
−18	2.054	1.555	0.549	0.353
−18.5	2.093	1.565	0.441	0.358
−19	2.132	1.576	0.334	0.367
−20	2.209	1.596	0.119	0.401
−21	2.287	1.617	−0.096	0.450

[a] V_x was taken as 3.906 (cm^3 mol^{-1})/100, and $\Sigma\alpha_2^H$ was always zero.

Table 5 Correlation of 20 log P and 21 log L values through eqn. (2) and eqn. (3)[a]

log L_w	R_2/((cm^3 mol^{-1})/10)	π_2^H	$\Sigma\beta_2^H$	log L^{16}	sd
3.0	1.392	1.374	0.510	16.661	0.455
4.0	1.553	1.409	0.520	17.720	0.442
5.0	1.713	1.443	0.530	18.779	0.434
6.0	1.873	1.477	0.541	19.838	0.432
7.0	2.034	1.512	0.550	20.897	0.434
8.0	2.194	1.546	0.560	21.956	0.442
9.0	2.355	1.581	0.570	23.045	0.454

[a] V_x was taken as 3.906 (cm^3 mol^{-1})/100 mol^{-1}, and $\Sigma\alpha_2^H$ was always zero. Log S_w was taken as −18, see Table 4.

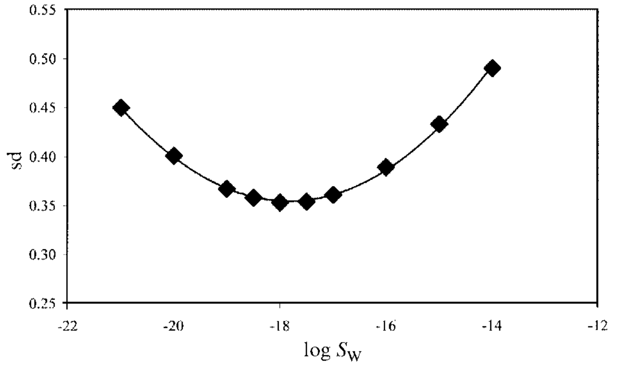

Fig. 1 A plot of the obtained sd value *vs.* the assumed value of log S_w; from Table 4.

solute with no acidic hydrogen atom, and so only three descriptors are missing, *viz.*: R_2, π_2^H, and $\Sigma\beta_2^H$. Now it must be noted that many of the correlation equations summarised in Table 1 have been constructed with solutes much smaller than C_{60}, so that considerable extrapolation to the volume of C_{60} is often needed. There are two main consequences: firstly the error in correlating the log P values for C_{60} will be much larger than the correlation error (usually a standard deviation of around 0.15 log units is obtained for the correlations), and secondly there will be some correlation equations that will extrapolate to unreasonable values. In the event, with log S_w taken as an initial value of −20, we found that 20 solvent systems were in good agreement and could correlate the 20 log P values with a standard deviation, sd, of 0.40 log units (see Table 4). By trial-and-error we deduced the log S_w value (−18) that led to the smallest sd value of 0.35 log units in the observed and calculated log P values (Table 4). A plot of the sd value *vs.* the assumed value of log S_w is shown in Fig. 1. There is but a shallow minimum so that a log S_w value between −17 and −19 yields essentially the same sd value. Our calculations are thus in good agreement with the log S_w value of −20 ± 1 suggested by Heymann.[5]

We can proceed further, by making use of eqn. (3) that uses log L as the dependent variable. Values of log L for C_{60} in various solvents can be obtained from eqn. (6).[26] We take the

$$\log L = \log L_w + \log P \tag{6}$$

various log P values that correspond to log $S_w = -18$, and if we assume a given value for the gas–water partition coefficient, as log L_w, we can deduce values of log L for C_{60}. From the set of equations in log P and log L we can assign values of the four unknown descriptors, R_2, π_2^H, and $\Sigma\beta_2^H$ as above, together with the additional descriptor in eqn. (3), log L^{16}.

We now have a total of 23 equations in log P and 21 equations in log L, but three of the log P equations were not used, see above. This left 41 equations in total. Results are summarised in Table 5 and show that if log L_w is taken as 6.0 then all 41 values of (log P plus log L) can be calculated with a sd value of only 0.43 log units. A plot of sd *vs.* log L_w is a rather shallow curve, so that log L_w values between 4 and 8 give essentially the same sd value.

It is very reassuring that the descriptors for C_{60} obtained from the total log P and log L equation sets are very close to those obtained from just the log P sets. The descriptors calculated with log $L_w = 6.0$ are close to those in Table 4 calculated with log $S_w = -18$, and these are the descriptors that we select. From log L_w and log S_w it is possible to calculate the saturated vapour concentration at 298 K of C_{60}, using log L_w = log S_w − log C_g, whence log $C_g = -24$ with the vapour concentration in mol dm^{-3}; this corresponds to log VP = −22.6 with the saturated vapour pressure, VP, in atmospheres. Since log L_w can range from 4 to 8 with almost no change in the sd value, the error in log C_g and log VP must be at least 2 log units.

Table 6 Comparison of solvation descriptors[a]

Compound	R_2/((cm^3 mol^{-1})/10)	π_2^H	$\Sigma\beta_2^H$	log L^{16}	V_x/((cm^3 mol^{-1})/100)
C_{60}	1.873	1.477	0.540	19.84	3.906
Octacosane	0.000	0.00	0.00	13.78	4.054
Dodecylbenzene	0.571	0.47	0.15	8.60	2.407
Pyrene	2.808	1.71	0.28	8.83	1.585
Chrysene	3.027	1.73	0.36	10.33	1.823
Picene	4.000	2.04	0.44	13.07	2.192
Cyclohexa-1,3-diene	0.515	0.30	0.14	2.92	0.759
Cyclohepta-1,3,5-triene	0.764	0.46	0.20	3.44	0.853
Cycloocta-1,3,5,7-tetraene	0.800	0.52	0.25	3.88	0.955

[a] Values of $\Sigma\alpha_2^H$ are zero for all compounds in Table 6.

Table 7 Calculations of some log L and log P values for C_{60}

System	log L^a	log $P^{a,b}$	log L^c	log $P^{c,d}$	log P^e
Gas to water	2.7		6.0		
Water to dry octan-1-ol	22.6	19.9	19.8	13.5	
Water to cyclohexane	13.8	11.1	19.7	14.4	
Water to trichloromethane	18.1	15.4	20.4	14.6	
Cyclohexane to dry octan-1-ol		8.8		−0.9	0.1
Cyclohexane to trichloromethane		4.4		0.2	0.6
Chloroform to dry octan-1-ol		4.4		−0.9	−0.5

[a] Ref. 27. [b] From the log L values. [c] This work. [d] These are from equations for log P, and not from log L values. [e] Ratios of solubilities, Table 3.

Discussion

The present work represents the first attempt to derive physicochemical descriptors for C_{60}. Hence we cannot compare our descriptors with any obtained previously. Comparisons can be made with other hydrophobic compounds, as shown in Table 6, however. Values of R_2 and π_2^H are appreciably smaller than expected for a polyaromatic hydrocarbon (PAH) with a V_x of 3.906 units, but are probably in the right range for a cyclic polyene. Not much can be deduced from the $\Sigma\beta_2^H$ values, because there is little variation between the different types of compound. The log L^{16} descriptor for C_{60} is certainly much larger than that of an alkane of the same volume, but smaller than that of a PAH of the same volume, as judged from data on PAHs. Again, this is the behaviour of a cyclic polyene, and is in accord with the suggestion of Taylor and Walton,[19] and with experimental results using C_{60} as a chromatographic stationary phase.[16,18] The solubility defined in eqn. (1) by Flunt *et al.*[20] implies that C_{60} behaves as a quite nonpolar compound, with neither polarisability nor hydrogen bond basicity. Our results indicate that C_{60} is not completely nonpolar; indeed, the hydrogen bond basicity of C_{60} lies between that for acetophenone (0.48) or ethyl benzoate (0.46) and that for the quite strong hydrogen bond base, benzamide (0.67).

There has only been one other attempt to calculate physicochemical properties of C_{60}; Torrens *et al.*[27] used their 'universal model' to calculate solvation Gibbs free energies and then log P values for C_{60}. Their results are in Table 7; differences of up to 7 log units in log L and up to 6 log units in log P for gas–solvent and water–solvent partitions are observed between values calculated by Torrens *et al.*[27] and our values. Since there are no experimental values for any of the above log L or log P values, no conclusions can immediately be drawn. However, it is possible to deduce log P values for transfer from one organic phase to another, as shown in Table 7. These log P values can then be compared with those obtained from the ratio of experimental solubilities given in Table 3. The three calculated log P values of Torrens *et al.*[27] are in error by 4.9, 3.8 and 8.7 log units whereas our three calculated log P values differ from the experimental ratios by −0.4, 0.4 and 1.0 log units. Thus the calculations in the present work are certainly much more consistent with known solubilities of C_{60}.

Table 8 Observed and calculated log S values for C_{60}, with S in mol dm^{-3}

Solvent	log S (obs)	log S (calc)
n-Pentane	−5.25	−4.41
n-Hexane	−4.23	−4.71
n-Decane	−4.01	−4.16
Isooctane	−4.44	−4.35
Cyclohexane	−4.26	−3.64
Dichloromethane	−3.46	−3.25
Tetrachloromethane	−3.28	−3.08
1,2-Dichloroethane	−3.96	−3.41
Benzene	−2.75	−2.82
Toluene	−2.43	−2.79
Chlorobenzene	−2.06	−2.64
Bromobenzene	−2.37	−2.42
Iodobenzene	−2.54	−2.62
Nitrobenzene	−2.96	−2.84
Dimethylformamide, dry	−4.43	−4.56
Propan-1-ol, dry	−5.24	−5.00
Butan-1-ol, dry	−4.89	−4.79
Pentan-1-ol, dry	−4.38	−4.53
Hexan-1-ol, dry	−4.23	−4.38
Octan-1-ol, dry	−4.19	−4.47

We can check our results by using our calculated values of log P for water–solvent partitions, together with our suggested value of −18 for log S_w, to deduce solubilities, as log S, in the 20 nonaqueous solvents we have used. These are given in Table 8. The sd value between the observed and calculated log S values is 0.36 log units, the average absolute deviation is 0.27 log units, and the average deviation is −0.02 log units, so that our indirect method can correlate solubilities of C_{60} reasonably well.

The vapour pressure of a solid solution of C_{60} and C_{70} has been determined between 772 and 929 K by Pan *et al.*[28] who fitted the experimental data to eqn. (7).

$$\ln \mathrm{VP/atm} = 15.202 - 23160/T \qquad (7)$$

A very long extrapolation to 298 K yields a value of −27.1 for log VP of the solid solution. Since C_{60} is known[28] to be more volatile than C_{70}, log VP for C_{60} is likely to be appreciably larger than that for the solid solution, and our value of −22.6 (± 2) for log VP at 298 K is thus consistent with the high temperature data of Pan *et al.*[28]

Although there have been no direct measurements of the solubility of C_{60} in water, numerous equations have been put forward for the estimation of log S_w values.[29] Our equation [eqn. (11), ref. 29] using only solvation descriptors gives a value of −13.5, but the corresponding equation with a melting point correction gives −18.1 for log S_w, if the melting point is taken as 800 K.[30] A similar result of −18.4 is obtained from Yalkowsky's equation[31] that also has a melting point correction [eqn. (3), ref. 29], but the agreement of the two latter values with our suggested value of −18.0, must be rather fortuitous.

Heymann[5] used the solubility of C_{60} in water, log $S_w = -20$, to calculate that 10^{25} metric tons of water would be required to dissolve all the C_{60} contained in clays at the Cretaceous–Tertiary boundary, estimated[32] to be 6×10^{10} g. Since the oceans contain only (!) 1.4×10^{18} tons of water, Heymann[5] concluded that the C_{60} could not have been leached out. Although the solubility we obtain, log $S_w = -18$, is less than that of Heymann, the required mass of water to dissolve the C_{60} in the clay layer, 10^{23} metric tons, is still much larger than the mass of water in the oceans, and so the conclusion of Heymann[5] remains valid. But now that we have an estimate of the saturated vapour concentration of C_{60}, log $C_g = -24$, we are in a position to calculate whether or not C_{60} could have been lost from the Cretaceous–Tertiary clay boundary by sublimation into the atmosphere. The weight of the atmosphere[33] is 5.1×10^{18} kg which corresponds to 4.3×10^{21} litres. Even if this were saturated by C_{60}, there would only be 3 g of C_{60} in the atmosphere.

Recently, derivatives of C_{60} have been used in a number of biological applications (see ref. 34) including *in vivo* studies on mice. It would therefore be of some importance to be able to predict the passive distribution of C_{60} between blood and biological phases. We have constructed equations of the type of eqn. (2) for distribution of nonelectrolytes between blood and a number of biological phases, such as heart, lung, kidney, *etc.*,[35] but the spread of V_x in these equations is too small to allow estimation of the distribution of C_{60}. However, our equation[36] for blood–brain distribution with the latter defined as eqn. (8),

$$\text{BB} = [\text{conc of solute in brain}]/[\text{conc of solute in blood}] \quad (8)$$

covers a range of V_x values from 0.085 to 3.447, and so extrapolation to V_x for C_{60} is not too hazardous. We calculate that log BB is 2.83 for C_{60}, which would make Buckminsterfullerene one of the most brain-penetrating compounds by passive transport. We can also calculate the lipophilicity of C_{60}, using the standard water–wet octanol partitioning system,[37–42] through our known equation,[43] and calculate that log *P*(water–wet octanol) = 12.6 indicating a very high lipophilicity. An important environmental process is the uptake of compounds by vegetation. We have recently obtained[44] an equation of the type of eqn. (2) for water–plant cuticular matrix, covering a range of V_x from 0.31 to 2.674; for C_{60} the very large value of 13.1 for log *P*(water–matrix) can be estimated. Eqn. (3) was applied[44] to the corresponding air–matrix partition for compounds with log L^{16} values from 0.97 to 12.88; our calculated value for log *L*(air–matrix) is no less than 18.9 log units.

A referee has commented that the McGowan volume of C_{60}, and hence the calculated value of log *P*(oct), is surprisingly low. We therefore sought to compare our calculated value of V_x (391 cm^3 mol^{-1}) with other measures of volume. In Fig. 2 are plotted values of V_x against liquid molar volumes, V_{liq} in cm^3 mol^{-1}, for a series of cyclic compounds: **1** C_{60} (480),[2] **2** cryptand 222 (345),[2] **3** cryptand 211 (263),[45] **4** 1-bromo-3,5-dimethyladamantane (199),[45] **5** 1,3-dimethyladamantane (185),[45] **6** cyclododecatriene (182),[45] **7** α-pinene (159),[45] **8** adamantane (145),[2] **9** 5-ethylidene-2-norbornene (135),[45] **10** dicyclopentadiene (134),[45] **11** 2-bromonorbornane (128),[45] **12** cyclohexane (109),[45] and **13** cyclopentane (93).[45] The solid line represents the points for the *n*-alkanes,[45] as a base line. Although the values of V_{liq} for C_{60} and cryptand 222 were estimated,[2] the plot does indicate that our McGowan volume for C_{60} is reasonable. Another measure of volume is the partial molar volume of a solute at infinite dilution in an inert solvent, V^o in cm^3 mol^{-1}. Fortunately, values are known[2] for C_{60} in several inert solvents including hexadecane (438), benzene (358), carbon disulfide (351) and decahydronaphthalene (403). Values are available also for cryptand 222 in decane (353) and benzene (344),[46] **14** diadamantane in hexane (161) and benzene (178),[2] adamantane in dodecane (143) and tetrachloromethane (140),[2] **15** 2-bromotriadamantane in tetrachloromethane (219),[47] and **16** 4-bromodiadamantane in tetrachloromethane (189).[47] The corresponding values of V_x are plotted against V^o in Fig. 3, where the full line represents data for the *n*-alkanes in tetrachloromethane.[48] Note that V^o values for the *n*-alkanes in *n*-alkane solvents[49] are almost the same as those in tetrachloromethane solvent. Judging from the plot in Fig. 3, our value of V_x for C_{60} is certainly not too small; compared to the value of V^o in hexadecane it is about right, and compared to values in other relatively nonpolar solvents it is actually too large. Taking Fig. 2 and Fig. 3 together, our calculated value of V_x for C_{60} does seem quite reasonable.

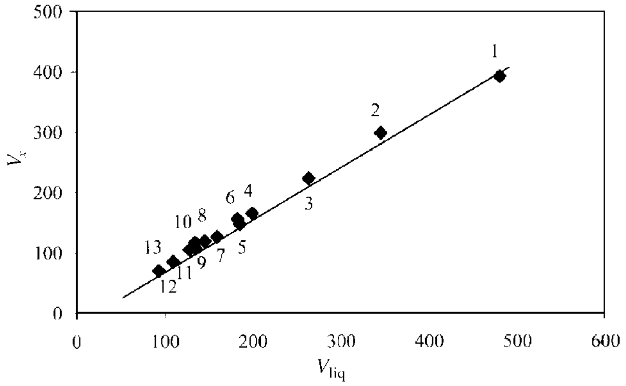

Fig. 2 A plot of values of V_x *vs.* values of V_{liq} (both in cm^3 mol^{-1}). Compounds are numbered as in the text, and the solid line represents data for the *n*-alkanes.

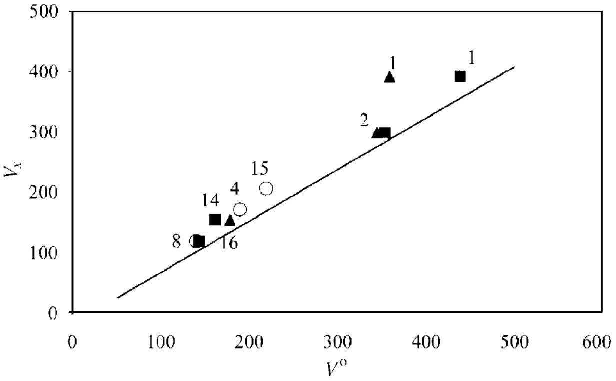

Fig. 3 A plot of values of V_x *vs.* values of V^o (both in cm^3 mol^{-1}). Compounds are numbered as in the text, and the solid line shows data for the *n*-alkanes in tetrachloromethane. ■ solutes in alkane solvents, ▲ solutes in benzene, ○ solutes in tetrachloromethane.

In conclusion, we can correlate the solubility of C_{60} in organic solvents, and in so doing we derive our solvation descriptors as well as the aqueous solubility, the gas–water partition, and the saturated vapour pressure. The solvation descriptors describe some general chemical properties, such as dipolarity/polarisability and hydrogen bond propensity, of C_{60}. With these solvation descriptors, together with the solvation equations, eqn. (2) and eqn. (3), it is possible to

Table 9 Some calculated properties of C_{60} at 298 K

Property	Symbol	Value
Excess molar refraction	R_2	1.873
Dipolarity/polarisability	π_2^H	1.477
Overall hydrogen bond acidity	$\Sigma\alpha_2^H$	0.000
Overall hydrogen bond basicity	$\Sigma\beta_2^H$	0.541
Gas–hexadecane partition	$\log L^{16}$	19.838
McGowan volume/cm^3 mol^{-1}	V_x	3.906×10^2
Solubility in water/mol dm^{-3}	$\log S_w$	−18.0
Air–water partition	$\log L_w$	−6.0
Gas phase concentration/mol dm^{-3}	$\log C_g$	−24.0
Saturated vapour pressure/atm	log VP	−22.6
Lipophilicity (water–wet octan-1-ol)	$\log P$(oct)	12.6
Blood–brain distribution	log BB	2.8
Air–plant distribution	$\log P_{\text{A-Mx}}$	18.9
Water–plant distribution	$\log P_{\text{W-Mx}}$	13.1

estimate a number of properties of C_{60}; these are collected in Table 9.

Acknowledgements

We thank the European Commission for a studentship (to C. E. G.); contract number SMT4-CT96-2144 (DG12-RSMT).

References

1 J. Cioslowski, *Electronic Structure Calculations on Fullerenes and Their Derivatives*, Oxford University Press, Oxford, 1995.
2 P. Ruelle, A. Farinda-Cuendet and U. W. Kesselring, *J. Am. Chem. Soc.*, 1996, **118**, 1777.
3 R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379.
4 C. Gripon, L. Legrande, I. Rosenman and F. Boue, *Fullerene Sci. Technol.*, 1996, **4**, 1195.
5 D. Heymann, *Fullerene Sci. Technol.*, 1996, **4**, 509.
6 K. Fujiwara, Y. Murata, T. S. M. Wan and K. Komatsu, *Tetrahedron*, 1998, **54**, 2049.
7 N. Sivaraman, R. Dhamodaran, I. Kaliappan, T. G. Srinivasan, P. R. Vasundeva-Rao and C. K. Mathews, *J. Org. Chem.*, 1992, **57**, 6077.
8 R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *Nature*, 1993, **362**, 140.
9 M. T. Beck, G. Mandi and S. Keki, in *Fullerenes*, vol. 2, eds. R. S. Ruoff and K. S. Kadish, The Electrochemical Society, Pennington, NJ, 1995.
10 M. T. Beck and G. Mandi, in *Fullerenes*, vol. 3, eds. K. S. Kadish and R. S. Ruoff, The Electrochemical Society, Pennington, NJ, 1996.
11 W. A. Scrivens and J. M. Tour, *J. Chem. Soc., Chem. Commun.*, 1993, 1207.
12 T. M. Letcher, P. B. Crosby, U. Domanska, P. W. Fowler and A. C. Legon, *S. Afr. J. Chem.*, 1993, **46**, 41.
13 X. Zhou, J. Liu, Z. Jin, Z. Gu and Y. Sun, *Fullerene Sci. Technol.*, 1997, **5**, 285.
14 D. Heymann, *Carbon*, 1996, **34**, 627.
15 D. Li and B. I. Swanson, *Langmuir*, 1993, **9**, 3341.
16 J. W. Grate, M. H. Abraham, C. M. Du, R. A. McGill and W. J. Shuely, *Langmuir*, 1995, **11**, 2125.
17 R. V. Golovna, M. B. Terenina, E. L. Ruchkina and V. L. Karnatsevich, *Mendeleev Commun.*, 1993, **97**, 3379.
18 M. H. Abraham, C. M. Du, J. W. Grate, R. A. McGill and W. J. Shuely, *J. Chem. Soc., Chem. Commun.*, 1993, 1863.
19 R. Taylor and D. R. M. Walton, *Nature* (*London*), 1993, **363**, 685.
20 R. Flunt, R. Makitra, O. Makohon and J. Pyrih, *Org. React.*, 1997, **31**, 21.
21 M. H. Abraham, *Chem. Soc. Rev.*, 1993, **22**, 73.
22 M. H. Abraham and J. C. McGowan, *Chromatographia*, 1987, **23**, 243.
23 M. H. Abraham, P. L. Grellier and R. A. McGill, *J. Chem. Soc., Perkin Trans. 2*, 1987, 797.
24 M. H. Abraham, K. Takacs-Novak and R. C. Mitchell, *J. Pharm. Sci.*, 1997, **86**, 310.
25 M. H. Abraham, R. Kumarsingh, J. E. Cometto-Muniz, W. S. Cain, M. Roses, E. Bosch and M. L. Diaz, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2405.
26 M. H. Abraham, C. E. Green, W. E. Acree, Jr., C. E. Hernandez and L. E. Roy, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2677.
27 F. Torrens, J. Sanchez-Marin and I. Nebot-Gil, *J. Chromatogr. A*, 1998, **827**, 345.
28 C. Pan, M. S. Chandrasekharaiah, D. Agan, R. H. Hauge and J. L. Margrave, *J. Phys. Chem.*, 1992, **96**, 6752.
29 M. H. Abraham and J. Le, *J. Pharm. Sci.*, 1999, **88**, 868.
30 http://www.carbon60.co.uk
31 S. H. Yalkowsky and S. C. Valvani, *J. Pharm Sci.*, 1980, **69**, 912.
32 D. Heymann, M. A. Nazarov, A. Korochantsev and J. Smit, *Lunar and Planetary Science XXVI* (*Abstracts*), The Lunar and Planetary Institute, Houston, Texas, USA, 1995.
33 J. W. Moore and E. A. Moore, *Environmental Chemistry*, Academic Press, New York, 1976.
34 F. Moussa, S. Roux, C. Pressac, E. Genin, M. Hadchouel, F. Trivin, A. Rassat, R. Ceolin and H. Szwarc, *New J. Chem.*, 1998, 989.
35 M. H. Abraham and P. K. Weathersby, *J. Pharm. Sci.*, 1994, **83**, 1450.
36 M. H. Abraham, H. S. Chadha and R. C. Mitchell, *J. Pharm. Sci.*, 1994, **83**, 1257.
37 C. Hansch, *Acc. Chem. Res.*, 1969, **2**, 232.
38 A. Leo, C. Hansch and D. Elkins, *Chem. Rev.*, 1971, **71**, 525.
39 A. J. Leo, *Chem. Rev.*, 1993, **93**, 1281.
40 R. Mannhold and K. Dross, *Quant. Struct.-Act. Relat.*, 1996, **15**, 403.
41 H. van de Waterbeemd and R. Mannhold, *Quant. Struct.-Act. Relat.*, 1996, **15**, 410.
42 P. Buchwald and N. Bodor, *Curr. Med. Chem.*, 1998, **5**, 353.
43 M. H. Abraham, H. S. Chadha, G. S. Whiting and R. C. Mitchell, *J. Pharm. Sci.*, 1994, **83**, 1085.
44 M. H. Abraham and J. A. Platts, *Environ. Sci. Technol.*, in the press.
45 Calculated from the compound liquid densities.
46 T. M. Letcher and J. D. Mercer-Chalmers, *J. Solution Chem.*, 1993, **22**, 851.
47 J. T. Edward, P. G. Farrell and F. Shahidi, *Can. J. Chem.*, 1979, **57**, 2892.
48 J. T. Edward, P. G. Farrell and F. Shahidi, *J. Phys. Chem.*, 1978, **82**, 2310.
49 H. Itsuki, S. Terasawa, K. Shinohara and H. Ikezawa, *J. Chem. Thermodyn.*, 1987, **19**, 555.

Paper a907461i