Determination of Olive Oil–Gas and Hexadecane–Gas Partition Coefficients, and Calculation of the Corresponding Olive Oil–Water and Hexadecane–Water Partition Coefficients

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Olive oil–gas partition coefficients, L_{oil}, have been determined for 80 solutes at 310 K using a gas chromatographic method in which olive oil is used as the stationary phase. Combination with other literature values has enabled a list of 140 log L_{oil} values at 310 K to be constructed. Hexadecane–gas partition coefficients, L_{hex}, have similarly been determined for 140 solutes at 298 K, and used to obtain a reasonably comprehensive list of log L_{hex} values for *ca.* 240 solutes at 298 K. It is shown that olive oil–water partition coefficients, P_{oil}, calculated indirectly from L_{oil} and L_{water} partition coefficients agree quite well with directly determined P_{oil} values. Similarly, hexadecane–water partition coefficients, P_{hex}, obtained from L_{hex} and L_{water} agree with directly determined values. It is suggested that in the case of the two particular solvents, olive oil and hexadecane, mutual miscibility of the two phases is of little consequence, and that P_{oil} and P_{hex} values can conveniently be obtained by combining the respective solvent–gas and water–gas partition coefficients.

Partition coefficients for solutes between oil and the gas phase have proved useful in the correlation of blood–gas partitions, and there have been several attempts to calculate blood–gas partitions from corresponding oil–gas and water–gas values.[1–5] Recently, we have shown[6] that excellent correlations of not only blood–gas partitions but of a range of tissue–gas partitions may be achieved through the regression equation, equation (1), in

$$\log L_{tissue} = c + w \log L_{water} + l \log L_{oil} \qquad (1)$$

which L is the Ostwald coefficient defined by equation (2) and c,

$$L = \frac{\text{concentration of solute in solution}}{\text{concentration of solute in the gas phase}} \qquad (2)$$

w, and l are constants for the particular tissue–gas partitions considered. Because of the use of oil–gas partition coefficients, there have been numerous determinations of L_{oil} values, especially for olive oil, and comprehensive summaries have been published by Weathersby and Homer,[7] and by Fiserova-Bergerova.[8] Unfortunately, there are still numerous series of compounds for which L_{oil} values are not known; even for those compounds listed,[7,8] the L_{oil} values may not be known very accurately (thus Weathersby and Homer[7] give four values for cyclopropane ranging from 7.0 to 12.0).

Related to the determination of L_{oil} values is that of the determination of olive oil–water partition coefficients, P_{oil}.

$$P_{oil} = L_{oil}/L_{water} \qquad (3)$$

Since a knowledge of L_{oil} combined with known L_{water} values will yield P_{oil} for the transfer of solutes from pure water to pure olive oil it would be of interest to compare P_{oil} values obtained indirectly through equation (3) with those obtained by direct partition between olive oil-saturated water and water-saturated olive oil.

Hexadecane–water partition coefficients, P_{hex}, have been used[9] as a comparative standard partition between water and a completely non-polar solvent, and a potentially very convenient method of obtaining P_{hex} values would be to combine hexadecane–gas partition coefficients, L_{hex}, with L_{water} values, as in equation (3). Additionally, we have recently found[10] that L_{hex} values themselves are inherently very valuable in the correlation of many solvent–gas processes.

We therefore set out to determine L values for olive oil at 310 K, the usual temperature at which these values have been obtained before, and L values for hexadecane at 298 K. By far the most convenient method of obtaining solvent–gas partition coefficients, in cases where the solvent is comparatively involatile, is through the measurement of retention volumes of solutes by gas–liquid chromatography with the solvent as the stationary phase. Most of the L values reported in this work were thus obtained, but a number were also measured by the simple, although less convenient, method of head-space analysis.

Experimental

Materials.—All the solutes were commercially available materials used as such, since the g.l.c. method does not require highly purified compounds. Olive oil (Sigma) and n-hexadecane (Sigma) were subjected to rotary evaporation to remove any volatile impurities and used as such.

Gas–Liquid Chromatography.—Absolute L values were measured using a Pye-Unicam 104 chromatograph equipped with a katharometer detector. The instrument was modified by replacing the original flow controllers with high precision Negretti and Zambra flow controllers to ensure reproducible and steady gas flow rates, and the original air thermostat was replaced by a liquid bath thermostat enabling the column to be thermostatted to within 0.05 K. Exit gas flow rates were measured with a soap-bubble meter and were corrected both for the vapour pressure of water and the temperature difference between the soap-bubble meter and the column. Inlet and exit gas pressures were measured with mercury-in-glass U-tubes, and corrections for the pressure drop across the column were also applied (see Theory section). The amount of stationary phase on the support was determined by careful weighing before and after coating the support. Hexadecane was applied as a solution in n-pentane and olive oil as a solution in dichloromethane. The added solvents were removed by rotary evaporation under vacuum, and the coated support was weighed from time to time until constant weight was obtained. All joints were sealed with PTFE tape to avoid errors if greased joints were used. Throughout the experiments, the packed columns were reweighed to check for any loss of stationary phase. The solid support was acid-washed, silanised Celite Chromosorb G.AW.DMCS, of mesh size 45—60, and columns with loadings of 6—8% were used.

Relative L values were measured using a Perkin-Elmer F11 gas chromatograph, modified by incorporation of high-precision flow controllers and by replacement of the air thermostat with a liquid bath thermostat, as above.

In order to convert weight of solvent on the column to the required volume of solvent on the column, the density of olive oil at 310 K was measured, and found to be 0.9013 g cm^{-3}.

Head-space Analysis.—Very dilute solutions of solutes in hexadecane (at 298 K) or in olive oil (at 310 K) were prepared and thermostatted. Samples of the head-space above the solutions were taken using gas-syringes and analysed (by analytical gas chromatography), exactly as described in detail before[11,12] except that we used a reference solute (cyclohexane) together with the solute to be investigated. This procedure removes any error due to the volume of gas samples, since both the solute and the reference solute are together in the head-space. Additionally, if corrected L° values for the reference solute are used, then the L values for the investigated solute can be taken as corrected values.

Theory

The basic relationship between the Ostwald coefficient [equation (2)] and the retention volume V_N is given in equation (4). The volume of moving gaseous phase required to elute the solute is V_N, and the volume of solvent present as the stationary phase is V_L. The following equations are well known, and we use

$$L = V_N/V_L \qquad (4)$$

those given by Conder and Young,[13] with occasional differences in symbols. If V_R is the measured retention volume, and V_M the gas hold-up volume, then we have equation (5) where J_3^2 is given by equation (6); P_i and P_o are the inlet and outlet pressures

$$L = J_3^2\,(V_R - V_M)/V_L \qquad (5)$$

$$J_n^m = \frac{n}{m}\cdot\left[\frac{(P_i/P_o)^m - 1}{(P_i/P_o)^n - 1}\right] \qquad (6)$$

across the column containing the stationary phase. If it is necessary to take into account gas imperfections, equation (5) may be replaced by (7), in which B_{23} is the cross second virial coefficient between solute vapour and carrier gas, and $\bar{V}_2$ is the solute molar volume (the correction term actually contains V_2^{∞}, the partial molal volume of the solute in the stationary phase, but $\bar{V}_2$ is nearly always used as an approximation to V_2^{∞}).

$$\ln L^{\circ} = \ln(V_N/V_L) - (2B_{23} - \bar{V}_2)P_oJ_3^4/RT \qquad (7)$$

Values of B_{23} when the carrier gas is helium, as used in this work, are not known for most of the solutes studied. The few measured values of B_{23} are all positive, however, so that there is a cancellation of effects in the term $(2B_{23} - \bar{V}_2)$. We calculated B_{23} using one of the suggested formulae [equation (8)] which

$$\frac{B_{23}}{V_{23}^{c}} = 0.461 - 1.158\left(\frac{T_{23}^{c}}{T}\right) - 0.503\left(\frac{T_{23}^{c}}{T}\right)^3 \qquad (8)$$

requires a knowledge of the 'cross' critical temperature and critical volume of the gas–solute pair. These were in turn calculated using the combining rules in equations (9) and (10).[13]

$$T_{23}^{c} = (T_{22}^{c}\cdot T_{33}^{c})^{\frac{1}{2}} \qquad (9)$$

$$V_{23}^{c} = {}^{1}/_{8}\,[(V_{22}^{c})^{1/3} + (V_{33}^{c})^{1/3}]^3 \qquad (10)$$

The values of T_{33}^{c} and V_{33}^{c} for helium were taken as 5.19 K and 58.0 cm^3 mol^{-1} respectively, and those for other solutes from Kudchadker *et al.*[14] Values of B_{23} calculated *via* equations (8)—(10) agreed reasonably well with observed values when the latter were known: thus for helium–pentane we calculated 29 cm^3 mol^{-1} at 310 K as compared with 28 cm^3 mol^{-1} at 298 K,[15] and for helium–benzene we calculated 36 cm^3 mol^{-1} at 310 K as compared with a value of 49 cm^3 mol^{-1} at 323 K.[16] In any case, since P_i and P_o were quite close to atmospheric pressure (typical values being 1.31 atm for P_i and 1.00 atm for P_o), the term $P_o\cdot J_3^4$ in equation (7) is not far from unity, and the entire correction term amounts to −0.004 in a typical case, corresponding to only −0.002 in log L. Absolute L values for n-alkanes on olive oil at 310 K are in Table 1, together with the corrected L° values *via* equation (7).

For polar solutes, use of a gas chromatograph with katharometer detector is not very satisfactory, because of the comparatively large quantities of solute needed, and so for the remaining solutes we transferred to the flame ionisation detector. Although absolute values cannot now be obtained easily, due to the difficulty of measuring flow rates, relative values are easily measured. Then by use of the absolute values for the n-alkanes (Table 1) chromatography of mixtures

Table 1. Absolute L values for n-alkanes in olive oil at 310 K

	n-Pentane (C_5)		n-Hexane (C_6)		n-Heptane (C_7)		n-Octane (C_8)		n-Nonane (C_9)		n-Decane (C_{10})	
Run no.	L	log L	L	log L	L	log L	L	log L	L	log L	L	log L
1	46.84	1.670	135.2	2.131								
2	48.69	1.687	131.9	2.121			1 115	3.047				
3	46.31	1.666	129.8	2.113	377.1	2.577	1 058	3.025				
4	43.72	1.641			392.1	2.593	1 104	3.043	3 038	3.483		
5	46.93	1.671	137.8	2.131	392.7	2.594	1 131	3.053	3 041	3.483	8 242	3.916
6	46.80	1.670	138.1	2.140	390.3	2.591	1 104	3.043	3 050	3.484	8 289	3.918
7	48.62	1.687	137.7	2.139	386.6	2.587	1 087	3.036	3 009	3.478	8 209	3.914
8	48.23	1.683	138.0	2.140	389.5	2.590	1 097	3.040	3 033	3.482		
Mean	47.02	1.672	135.5	2.131	388.1	2.589	1 100	3.041	3 034	3.482	8 247	3.916
Standard deviation	(1.55)	(.015)	(3.20)	(.010)	(5.5)	(.006)	(22)	(.009)	(14)	(.002)	(40)	(.002)
log L^0		1.673		2.132		2.590		3.042		3.484		3.918

Table 2. Comparison of log L values obtained by the g.l.c. and head-space analysis methods

	Hexadecane at 298 K		Olive oil at 310 K	
Solute	G.l.c.	Head-space	G.l.c.	Head-space
n-Octane	3.68	3.78		
n-Nonane	4.18	4.33		
Benzene	2.80	2.80	2.60	2.68
Toluene	3.34	3.38	3.08	3.30
Ethanol	1.49	1.60	1.96	2.07
Propan-1-ol	2.10	2.14		
Propan-2-ol	1.82	1.87		
Butan-1-ol	2.60	2.68		
t-Butyl alcohol	2.02	2.05	2.27	2.27
Propanone	1.76	1.72	1.92	1.88
Butanone	2.29	2.31	2.36	2.33
Ethyl acetate	2.38	2.36	2.36	2.38
Ethyl propanoate	2.88	2.91	2.71	2.84
CH_2Cl_2	2.02	2.00	2.14	2.16
$CHCl_3$	2.48	2.46	2.58	2.59
CCl_4	2.82	2.83	2.53	2.57
CCl_3CH_3	2.69	2.69	2.47	2.47
n-C_4H_9Cl	2.72	2.73	2.46	2.55
1,2-Dimethoxyethane	2.66	2.70	2.55	2.60

containing the n-alkanes and other solutes will lead to absolute L values for these other solutes. Note that although this procedure implies that the correction term in equation (7) is the same for the other solutes as for the reference alkanes, almost no error is introduced by this assumption. With helium, the correction term is always very small, and in any case there is almost complete cancellation of correction terms between the other solutes and the n-alkanes. All the L values for solutes on olive oil at 310 K determined by the 'g.l.c. method' have been obtained by this reference n-alkane procedure.

In the case of solvent n-hexadecane, there have been numerous determinations[17-21] of absolute L° values for solutes at 298 K, and we therefore measured relative values using the flame ionisation detector, as described above for olive oil.

Results and Discussion

Solvent–Gas Partition Coefficients.—Values obtained by the g.l.c. method and by the head-space analysis method are compared in Table 2. There is generally good agreement between the two sets of values: in hexadecane, the head-space analysis values on average are higher by 0.03 units than the g.l.c. values, and higher by 0.04 units in olive oil. This might possibly be due to corrections for the non-ideality not being completely cancelled in the case of the head-space analysis method. Note that although these corrections are small for helium as the supporting gas, they are not small for air (or nitrogen) as the supporting gas in head-space analysis.

We also compare our g.l.c. olive oil–gas partition coefficients with literature values (Table 3). Although there is fair agreement between our values and those of Sato and Nakajima,[4,5] the latter are systematically higher by *ca.* 0.06 units. Sato and Nakajima[4,5] used an automated head-space analysis method, as did also Perbellini *et al.*[22] However, log L values for alkanes found by the latter workers are in good agreement with our values. Stern and Shiah[23] determined L values by a classical method; their results for five solutes show no systematic deviations from ours, the average difference between the two sets of values being 0.00 log units. Other literature values are also in good agreement with our values.[7,24] Quite recently, Lebert and Richon[25] obtained activity coefficients of n-alkanes and alkan-1-ols in olive oil between 298 and 328 K using a novel head-space stripping method. Unlike the determination of L values, calculation of γ^∞ requires a knowledge of solvent molecular weight. From the olive oil composition given by Lebert and Richon[25] we calculated M_1 as 867.9 and converted interpolated γ^∞ values into log L values at 310 K. These log L values are systematically lower than our values and (for the n-alkanes) lower than those of Perbellini *et al.*[22] However, since our g.l.c.-determined log L values generally agree very well with all other previous results, we are satisfied by the reproducibility and accuracy of the g.l.c. method.

Table 3. Comparison of log L values on olive oil at 310 K with literature values

Solute	This work (g.l.c.)	Literature
Benzene	2.60	2.69[5]
Toluene	3.08	3.17[5]
Ethylbenzene	3.49	3.58[5]
o-Xylene	3.64	3.64[5]
p-Xylene	3.52	3.57[5]
Propanone	1.92	1.93[5]
Butanone	2.32	2.42[5]
Pentan-2-one	2.70	2.80[5]
CH_2Cl_2	2.14	2.18[4]
$CHCl_3$	2.58	2.56[22] 2.60[4] 2.59[23]
CCl_4	2.53	2.56[4] 2.60[24]
CH_2ClCH_2Cl	2.61	2.65[4]
CCl_3CH_3	2.47	2.55[4]
$CHCl_2CHCl_2$	4.12	4.12[4]
Bu^nCl	2.46	2.54[4]
Chlorobenzene	3.46	3.57[4]
o-Dichlorobenzene	4.60	4.60[4]
$CHCl{:}CCl_2$	2.79	2.86[4]
$CCl_2{:}CCl_2$	3.22	3.28[4]
Diethyl ether	1.81	1.84[24] 1.81[7] 1.84[23]
CHF_2OCF_2CHFCl	2.02	1.99[7]
$CHF_2OCHClCF_3$	1.98	1.99[7] 1.94[23]
$CH_3OCF_2CHCl_2$	2.93	2.97[23]
$CF_3CHClBr$	2.29	2.29[23]
Propan-1-ol	2.50	2.32[25]
Butan-1-ol	2.94	2.79[25]
Pentan-1-ol	3.38	3.26[25]
Hexan-1-ol	3.82	3.73[25]
Pentane	1.67	1.59[25] 1.67[22]
Hexane	2.13	2.04[25] 2.16[22]
Heptane	2.59	2.50[25] 2.65[22]
Octane	3.04	2.96[25]
Cyclohexane	2.44	2.47[22]

A complete list of our log L values for solutes on olive oil at 310 K is in Table 4, together with other values from Sato and Nakajima,[4,5] literature reviews,[7,8] and some results for a number of permanent gases from the Solubility Data Project Series.[26] Our determined log L values on hexadecane are also in Table 4, together with as many other reliable values that we have been able to collect from the literature. Martire and his co-workers[27] have used n-heptadecane or n-octadecane, rather than n-hexadecane, as a g.l.c. solvent stationary phase for a number of alcohol and amine solutes. We find an excellent correlation between log L on n-heptadecane or on n-octadecane and log L on n-hexadecane, and we have included a number of log L values calculated in this way. Given log L_{oil} or log L_{hex} for a few members of an homologous series, it is easy to estimate log L values for other members through plots of log L against solute carbon number; a number of useful log L values estimated in this way are included in Table 4.

We have not included in Table 4 any values of log L for water, although this is an important compound, because of the diffi-

Table 4. Ostwald coefficients for solutes on hexadecane and olive oil (as log *L*)

Solute	Hexadecane at 298.15 K^{a}	Olive oil at 310.1 K^{a}
Helium	-1.741^{b}	-1.756^{26}
Neon	-1.575^{26}	-1.663^{26}
Argon	-0.688^{26}	-0.824^{26}
Krypton	$-0.211^{26,c}$	-0.346^{26}
Xenon	$0.378^{26,b}$	0.237^{26}
Radon	0.877^{d}	0.566^{d}
Hydrogen	-1.200^{b}	-1.305^{26}
Deuterium		
Nitrogen	-0.978^{b}	-1.134^{26}
Oxygen	-0.723^{26}	-0.936^{26}
Carbon monoxide	-0.812^{e}	-1.011^{6}
Carbon dioxide	0.057^{e}	0.130^{6}
Ammonia	0.269^{e}	
Hydrogen sulphide	0.529^{e}	
Hydrogen chloride	0.277^{20}	
Sulphur dioxide	0.756^{e}	
Nitrous oxide	0.164^{e}	0.146^{26}
SF_6	-0.450^{d}	-0.583^{6}
Carbon disulphide	2.353	2.178^{24}
Methane	$-0.323^{20,b}$	-0.510^{6}
Ethane	$0.492^{18,20,b,c}$	0.279^{d}
Propane	$1.050^{18-20,b,f}$	0.742^{d}
n-Butane	$1.615^{18,20}$	1.267
2-Methylpropane	1.409^{18}	1.050^{d}
n-Pentane	2.162	1.673
2-Methylbutane	2.013^{17}	
n-Hexane	2.668	2.132
2-Methylpentane	2.549^{17}	
3-Methylpentane	2.602^{27}	
2,3-Dimethylbutane	2.510^{27}	
2,2-Dimethylbutane	2.323^{17}	
n-Heptane	3.173	2.590
2-Methylhexane	3.001^{d}	
3-Methylhexane	3.044^{27}	
2,2-Dimethylpentane	2.791^{d}	
2,4-Dimethylpentane	2.841^{27}	
2,3-Dimethylpentane	3.016^{d}	
3,3-Dimethylpentane	2.946^{d}	
2,2,3-Trimethylbutane	2.849^{d}	
3-Ethylpentane	3.091^{d}	
n-Octane	3.677	3.042
2,2,4-Trimethylpentane	3.120^{19}	
n-Nonane	4.182	3.484
n-Decane	4.686	3.918
n-Undecane	5.191^{g}	4.361^{g}
n-Dodecane	5.696^{g}	4.803^{g}
n-Tridecane	6.200^{g}	5.245^{g}
n-Tetradecane	6.705^{g}	5.687^{g}
n-Pentadecane	7.209^{g}	6.129^{g}
n-Hexadecane	7.714^{g}	6.572^{g}
Cyclopropane	1.314^{d}	1.068^{6}
Cyclopentane	2.447^{17}	1.995^{d}
Cyclohexane	2.913	2.439
Cycloheptane	3.526	
Cyclo-octane	4.119	
Methylcyclopentane	2.771^{17}	
Methylcyclohexane	3.252	
Adamantane	4.768	
Ethene	0.289^{18}	0.100^{6}
Propene	0.946^{c}	
But-1-ene	1.491^{g}	
Pent-1-ene	2.013^{h}	
Hex-1-ene	2.547^{h}	
Hept-1-ene	3.063^{h}	
Oct-1-ene	3.591^{g}	
Buta-1,3-diene	1.543^{18}	
Cyclopentadiene	2.222	
Ethyne	0.150^{i}	0.243^{6}
Propyne	1.025^{18}	
Benzene	2.803	2.598
Toluene	3.344	3.075
Ethylbenzene	3.765^{h}	3.493
n-Propylbenzene	4.221	3.990^{5}
n-Butylbenzene	4.686^{g}	4.462
o-Xylene	3.937	3.639^{5}
m-Xylene	3.864	3.522
p-Xylene	3.858	3.531
Cumene	4.105^{g}	3.793^{5}
Styrene	3.908^{g}	3.677
Allylbenzene	4.227^{g}	3.906^{5}
Methanol	$0.922^{27,j}$	1.468^{k}
Ethanol	1.485^{27}	1.961^{k}
Propan-1-ol	2.097	2.497
Propan-2-ol	1.821	2.160
Butan-1-ol	2.601	2.938
t-Butyl alcohol	2.018	2.267
Isobutyl alcohol	2.399^{27}	
s-Butyl alcohol	2.338^{27}	
Pentan-1-ol	3.106	3.380
Pentan-2-ol	2.840	
Hexan-1-ol	3.610	3.822
Hexan-2-ol	3.340	
Heptan-1-ol	4.115	4.263
Heptan-2-ol	3.842	
Octan-1-ol	4.619	4.705^{g}
Octan-2-ol	4.343^{g}	
Nonan-1-ol	5.124^{g}	5.146^{g}
Decan-1-ol	5.628^{g}	5.588^{g}
Decan-2-ol	5.356^{g}	
Allyl alcohol	1.996	
Cyclohexanol	3.671	
Benzyl alcohol	4.443	4.733
CF_3CH_2OH	1.224	
$(CF_3)_2CHOH$	1.392	
Phenol	3.856	4.290
o-Cresol	4.242	
m-Cresol	4.329	
p-Cresol	4.307	
2-Isopropylphenol	4.921	
3-Fluorophenol	3.844	
2-Nitrophenol	4.684	
2,6-Difluorophenol	3.693	
Methanal		1.415
Ethanal	1.230	
Propanal	1.815	
Butanal	2.270	
Pentanal	2.770^{g}	
Hexanal	3.370^{g}	
Propanone	1.760	1.921
Butanone	2.287	2.358
Pentan-2-one	2.755	2.696
Pentan-3-one	2.811	2.717
Hexan-2-one	3.262^{g}	$3.214^{5,6}$
Hexan-3-one	3.310^{g}	
MeCOBu^{i}	3.050	2.967^{5}
Heptan-2-one	3.760	3.832^{5}
Heptan-3-one	3.812	
Heptan-4-one	3.820	
MeCOBu^{t}	2.887^{42}	
Octan-2-one	4.257	
Octan-3-one	4.308^{g}	
Nonan-2-one	4.755^{g}	
Cyclopentanone	3.120	3.205
Cyclohexanone	3.616	
Acetophenone	4.483	
Diethyl ether	2.061	1.813
Di-n-propyl ether	2.989^{42}	
Di-isopropyl ether	2.559	2.151^{a*}
Di-n-butyl ether	4.001^{42}	3.417
Dimethoxymethane (methylal)		1.957^{24}

Table 4 (*continued*)

Solute	Hexadecane at 298.15 K[a]	Olive oil at 310.1 K[a]
1,2-Dimethoxyethane	2.655	2.550
Divinyl ether		1.778[8]
$CH_3OCF_2CHCl_2$(methoxyflurane)	2.864	2.927
$CHF_2OCHClCF_3$ (isoflurane)	1.576	1.980
CHF_2OCF_2CHFCl (enflurane)	1.653[d]	2.019
$CF_3CH_2OCH{:}CH_2$ (fluroxene)		1.681[7]
THF	2.534	2.389
1,4-Dioxane	2.797	2.830
Propylene oxide	1.775[42]	
Anisole	3.926	
o-Dimethoxybenzene	4.967	
m-Dimethoxybenzene	5.022	
p-Dimethoxybenzene	5.044	
1-Chloro-2-methoxy-1,2,3,3-tetrafluorocyclopropane		2.093[8]
Methyl formate	1.459	1.561
Ethyl formate	1.901	1.962
n-Propyl formate		2.421[g]
n-Butyl formate	2.925	2.865
Methyl acetate	1.960	2.017
Ethyl acetate	2.376	2.360
n-Propyl acetate	2.878	2.777
n-Butyl acetate	3.379	3.196
n-Pentyl acetate	3.881[g]	3.482
n-Hexyl acetate	4.382[g]	
Isopropyl acetate	2.633	2.790
Methyl propanoate	2.459[1]	
Ethyl propanoate	2.881	2.707
Butyl propanoate	3.860	3.668
Methyl butanoate	2.943[1]	
Ethyl butanoate	3.379[1]	
Methyl pentanoate	3.442[1]	
Methyl hexanoate	3.984[1]	
Ethyl chloroacetate	2.559	
CH_3F		0.057[6]
C_2H_5F		0.578[6]
n-C_3H_7F		0.924[6]
i-C_3H_7F		1.090[6]
Perfluoropentane	0.690[m]	
Perfluoroheptane	1.121[m]	
Perfluorononane	1.771[m]	
CH_3Cl	1.163[g]	
CH_2Cl_2	2.019	2.136
$CHCl_3$	2.480	2.582
CCl_4	2.823	2.527
C_2H_5Cl	1.678[g]	1.548[24]
CH_2ClCH_2Cl	2.573	2.614
$CHCl_2CH_3$	2.350	2.272[4]
$CHCl_2CH_2Cl$		3.357[4]
CCl_3CH_3	2.690	2.471
$CHCl_2CHCl_2$	3.826	4.121
CCl_3CH_2Cl		3.634[4]
n-C_3H_7Cl	1.997	2.076[4]
$(CH_3)_3CCl$	2.217	
$CH_3CHClCH_3$	1.970	
$CH_3CHClCH_2Cl$		2.873[4]
n-C_4H_9Cl	2.722	2.464
n-$C_5H_{11}Cl$	3.223[h]	2.990[4]
C_2H_5Br	2.020	
n-C_4H_9Br	3.105	
CH_3I	2.106	
C_2H_5I	2.573	2.159[6]
CH_2I_2	3.853	
CH_2BrCl	2.440[25]	
CH_2Br_2	2.849	
$CHBrCl_2$	2.927[25]	
$CHBr_2Cl$	3.341[25]	
$CHBr_3$	3.747	
$CBrCl_3$	3.269[27]	
CH_2BrCH_2Br	3.399	3.556
CF_3CH_2Cl		1.380[8]
$CHClF_2$		0.644[7]
CF_3CHFBr (teflurane)		1.462[7]
$CF_3CHClBr$ (halothane)	2.177	2.293
CCl_2FCF_2Cl	2.123	
$CHF_2CF_2CH_2Br$		2.509[6]
$CFBr_3$	3.206	
$CCl_2{:}CH_2$	2.110	
cis-$CHCl{:}CHCl$	2.450	2.431[4]
trans-$CHCl{:}CHCl$	2.350	2.277[4]
$CHCl{:}CCl_2$	2.997	2.790
$CHCl{:}CF_2$		1.146[8]
$CCl_2{:}CCl_2$	3.584	3.219
Allyl chloride	2.109	
Allyl bromide	2.510	
Benzyl chloride	4.290	
Hexafluorobenzene	2.528	
p-Difluorobenzene	2.766	
Chlorobenzene	3.640	3.455
o-Dichlorobenzene	4.405	4.601[4]
m-Dichlorobenzene		4.433[4]
Bromobenzene	4.035	4.141
Ethylamine	1.677	
n-Propylamine	2.141	
n-Butylamine	2.618	
t-Butylamine	2.493	
n-Pentylamine	3.086[g]	
n-Hexylamine	3.557[g]	
Methyl-n-propylamine	2.487[27]	
Methylisopropylamine	2.293[27]	
Methyl-n-butylamine	3.049[27]	
Diethylamine	2.395[27]	
Di-n-propylamine	3.372[27]	
Di-isopropylamine	2.893[27]	
Trimethylamine	1.620	
Triethylamine	3.077	2.834
N-Methylimidazole	3.805	4.839
NN-Dimethylaniline	4.754	4.661
Aniline	3.993	
Piperidine		3.913[a*]
Pyridine	3.003	3.196
2-Methylpyridine	3.437	3.536
3-Methylpyridine	3.603	3.735
4-Methylpyridine	3.593	3.749
DMF	3.173	3.458
DMA	3.717	3.896
Nitromethane	1.892	2.445
Nitroethane	2.367	2.750
1-Nitropropane	2.710	
2-Nitropropane	2.550	
Nitrobenzene	4.460	
Formic acid		3.234
Acetic acid	3.290	3.642
Propanoic acid		3.942
DMSO	3.437	4.379
Acetonitrile	1.560	
Propiononitrile	1.940	
Dimethyl methanephosphonate	3.977	

[a] This work, using the g.l.c. method, unless otherwise shown. Values marked with an asterisk are by the head-space analysis method, this work. [b] M. H. Abraham and E. Matteoli, survey of results. [c] P. J. Lin and J. F. Parcher, *J. Chromatogr. Sci.*, 1982, **20**, 33. [d] Estimated value using Abraham's R_G parameter. [e] K. K. Tremper and J. M. Prausnitz, *J. Chem. Eng. Data*, 1976, **21**, 295. [f] W. Hayduk and R. Castaneda, *Can. J. Chem. Eng.*, 1973, **51**, 353; W. Hayduk, E. B. Walter, and P. Simpson, *J. Chem. Eng. Data*, 1972, 17, 59. [g] Estimated from a correlation of log *L* with carbon number for the homologous series. [h] P. Alessi, I. Kikic, A. Alessandrini, and M. Fermeglia, *J. Chem. Eng. Data*, 1982, **24**, 445, 448. [i] Y. Miyano and W. Hayduk, *Can. J. Chem. Engl.*, 1981, **59**, 746. [j] E. E. Tucker, S. B. Farnham, and S. D. Christian, *J. Phys. Chem.*, 1969, **73**, 3820. [k] Estimated from a correlation of log L_{hex} with log L_{oil} for alkan-1-ols. [l] M. P. Barral, M.-I. P. Andrade, R. Guieu, and J.-P. E. Grolier, *Fluid Phase Equilib.*, 1984, 17, 187. [m] T. M. Reed, III, *Anal. Chem.*, 1958, **30**, 221.

Table 5. Comparison of direct and indirect olive oil–water partition coefficients at 310 K

Solute	log L_{oil}[a]	log L_{water}[b]	log P_{oil} (calc)	log P_{oil} (obs)
Ethanol	1.961	3.329	−1.37	−1.268[31] −1.337[32]
Propanol	2.497	3.185	−0.69	−0.863[33]
Butanol	2.938	3.060	−0.12	−0.201[33]
Acetone	1.921	2.536	−0.61	−0.582[31]
Hexane	2.130	−2.073	4.20	4.04 ± 0.1[35]
Benzene	2.598	0.447	2.15	2.52 ± 0.2[35]
Tetrachloromethane	2.527	−0.602[6]	3.13	3.18 ± 0.2[35]

[a] Table 4. [b] Calculated from results in ref. 34.

Table 6. Comparison of direct and indirect hexadecane–water partition coefficients at 298 K

Solute	log L_{hex}[a]	log L_{water}[b]	log P_{hex} (calc)	log P_{hex} (obs)
Methanol	0.922	3.740	−2.82	−2.42[38]
Ethanol	1.485	3.667	−2.18	−2.24[38]
Propan-1-ol	2.097	3.557	−1.46	−1.48[38]
Butan-1-ol	2.601	3.461	−0.86	−1.08[39]
Pentan-1-ol	3.106	3.352	−0.25	−0.39[39]
Hexan-1-ol	3.610	3.234	0.38	0.11[39]
Heptan-1-ol	4.115	3.088	1.03	0.77[39]
Propanone	1.760	2.794	−1.03	−1.09[b] −1.54[38]
Butanone	2.287	2.721	−0.51	−0.27[38]
Diethyl ether	2.061	1.283[6]	0.78	0.66[38]
Trichloromethane	2.480	0.75[6]	1.73	1.74[38]

[a] Table 4. [b] At 293 K, W. Kemula, H. Buchowski, and R. Lewandowski, *Bull. Acad. Sci. Polon. Sci.*, 1964, **12**, 267.

culty in obtaining accurate values. Schatzberg[28] measured the solubility of water in n-hexadecane as 6.8 × 10^{-4} mol fraction at 298 K, from which a log L_{hex} value of 0.258 may be deduced, as compared with a value of 0.330 calculated from Christian's[29] direct determination of the Gibbs energy of solution of water vapour in n-hexadecane. In the case of olive oil, the only available result is a partition coefficient for D_2O between water and olive oil at 295 K of 7 × 10^{-4} due to Collander.[30] Assuming a factor *ca.* 1.4 between P_{oil} at 295 K and at 310 K, this corresponds to a log L_{oil} value of roughly 1.35 at 310 K.

The log L_{hex} values for a series of solutes should be related to fundamental solute properties. At the moment, we are working with Professor R. Fuchs on the correlation of log L_{hex} (and of log L_{oil}) values with solute properties, in order to understand the underlying physicochemical basis of these gas–liquid partition coefficients.

Solvent–Water Partition Coefficients.—A large number of oil–water partition coefficients have been reported, usually with an unspecified oil and at an unspecified temperature. Only a few log P_{oil} values refer definitely to olive oil, and fewer still to coefficients for olive oil at 310 K. Some of these[31–35] are in Table 5, together with log P_{oil} values calculated from log L_{oil} and log L_{water}. The latter values are taken from ref. 34, and have been corrected to 310 K. There is generally quite good agreement between calculated and observed log P_{oil} values, so that it seems permissible to use log L values that refer to water and olive oil in order to calculate log P_{oil} values for partition between the mutually saturated solvents. Also in Table 5 are similar results for partition at 293—310 K between water and glyceryl trioleate obtained by Platford.[35] Given the rather large quoted errors in the observed log P_{oil} values, there is again reasonable agreement. Since we now have to hand log L_{oil} values at 310 K for *ca.* 140 solutes, and the methodology to determine further values for not-too-involatile solutes, it is now possible to generate a comprehensive set of log P_{oil} values that refer to olive oil at 310 K. We hope to enlarge on this point in a future publication.

In a similar way, log P_{hex} values at 298 K can be calculated from our log L_{hex} values in Table 3 and compilations[34,36,37] of log L_{water} values. A number of comparisons of calculated and observed log P_{hex} values are in Table 6, with the observed values mostly taken from the work of Franks and Lieb,[38] or of Aveyard and Mitchell.[39] Once again, there is reasonable agreement between the indirect calculated values and the direct observed values. Hence our compilation of log L_{hex} values in Table 3 can now lead to a comprehensive set of indirect log P_{hex} values. Of course, the reverse calculations are always possible. Thus Finkelstein[40] has measured log P_{hex} for water and for acetamide as −4.38 and −4.67 respectively; knowing log L_{water} as 4.64 (from the saturated vapour pressure) and 7.12,[41] values of log L_{hex} may then be deduced as 0.26 and 2.45 for water and for acetamide. This seems to be a useful method of obtaining log L_{hex}, and log L_{oil}, when direct determinations are difficult. On the other hand, Aarna *et al.*[42] have used experimental values of log L_{hex} and log P_{hex} to deduce log L_{water}, at 293 K.

It should be noted that the relationship between L values in the pure solvents and the partition coefficient for the mutually saturated phases [see equation (3)] will only apply in general when the solvent mutual solubilities are very small. The molar solubility of water in various solvents commonly used in partition work is: hexadecane (0.002), olive oil (0.038), diethyl ether (0.58), ethyl acetate (1.45), and octan-1-ol (1.48), and the corresponding molar solubility of the solvents in water is: hexadecane (4 × 10^{-9}), olive oil (-), diethyl ether (0.5), ethyl acetate (0.74), and octan-1-ol (4.4 × 10^{-3}).[28,30,34,43] The mutual solubility of hexadecane–water, and probably also olive oil–water, is orders of magnitude less than that of the systems diethyl ether–water, ethyl acetate–water, and octan-1-ol–water. Hence although equation (3) has been shown to apply to hexadecane–water and olive oil–water partitions, it would not be expected to apply in general to the other three solvent–water systems, above.

Conclusions.—Provided that due care is taken over experimental details, the g.l.c. procedure is a rapid, convenient, and accurate method of obtaining solvent–gas partition coefficients for an extended series of solutes on not-too-volatile solvent stationary phases. The method has the advantage that the partition coefficients refer to very low solute concentration in the solvent phase, and that the solutes need not be purified at all. However, if the solutes are rather involatile or the solvent phase rather volatile, the method, although feasible, is much less convenient.

For the two particular solvent phases olive oil and hexadecane, it is shown that solvent–water partition coefficients calculated from a knowledge of solvent–gas and water–gas partition coefficients agree well with directly determined solvent–water coefficients. Thus even for the distribution of solutes such as alkan-1-ols, factors such as the mutual miscibility of the two phases seem unimportant. The method of indirect determination of solvent–water partition coefficients can clearly be extended to other solvent pairs that are very immiscible, but would not be expected to apply to solvent pairs such as octanol–water, in which mutual miscibility is quite high.

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