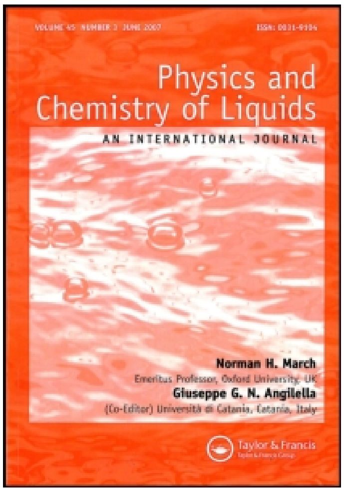

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Mathematical correlation of 1-chloroanthraquinone solubilities in organic solvents with the Abraham solvation parameter model

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The Abraham solvation parameter model is used to calculate the numerical values of the solute descriptors for 1-chloroanthraquinone from experimental solubilities in organic solvents. The mathematical correlations take the form of

$$\log\left(\frac{C_S}{C_W}\right) = c + e\cdot\mathbf{E} + s\cdot\mathbf{S} + a\cdot\mathbf{A} + b\cdot\mathbf{B} + v\cdot\mathbf{V}$$

$$\log\left(\frac{C_S}{C_G}\right) = c + e\cdot\mathbf{E} + s\cdot\mathbf{S} + a\cdot\mathbf{A} + b\cdot\mathbf{B} + l\cdot\mathbf{L}$$

where C_S and C_W refer to the solute solubility in the organic solvent and water, respectively, C_G is a gas phase concentration, **E** is the solute excess molar refraction, **V** is McGowan volume of the solute, **A** and **B** are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity, **S** denotes the solute dipolarity/polarizability descriptor, and **L** is the logarithm of the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The remaining symbols in the above expressions are known solvent coefficients, which have been determined previously for a large number of gas/solvent and water/solvent systems. The Abraham solvation parameter model was found to describe the experimental solubility data of 1-chloroanthraquinone to within an overall standard deviation of 0.126 log units.

Keywords: 1-Chloroanthraquinone solubilities; Organic solvents; Partition coefficients; Molecular solute descriptors; Solubility predictions

1. Introduction

Free energy of partition is an important thermodynamic variable that quantifies the Gibbs energy difference between a molecule in a given phase and the molecule dissolved

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in a second phase. Free energies of partition provide valuable information regarding molecular interactions between dissolved solute and surrounding solvent molecules, and can be used to calculate the numerical values of partition coefficients that describe the equilibrium of a solute between two immiscible liquid phases. The partitioning process plays an important role in determining whether or not a given chemical is able to cross biological membranes. Mathematical correlations have been derived to describe the partitioning behavior of various chemicals between specific animal tissues and air (i.e., liver/air, kidney/air partition coefficients, etc.) based upon the known organic solvent/air partition coefficients of the substance. Expressions can also be found in the environmental literature relating the partitioning behavior of known organic pollutants between the gas phase and a variety of natural substrates in soil, atmosphere and foliage to the pollutant's measured organic solvent/air partition coefficient. Experimental studies have further shown that the mass transfer coefficient of a solute across the interface of two immiscible liquid phases depends both upon the solute concentration in each phase and the partition coefficient.

The general solvation parameter model of Abraham [1–8] is one of the most useful approaches for the analysis and prediction of free energies of partition in chemical and biochemical systems. The method relies on two linear free energy relationships, one for processes within condensed phases

$$\log \mathrm{SP} = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + v \cdot \mathbf{V} \tag{1}$$

and one for processes involving gas to condensed phase transfer

$$\log \mathrm{SP} = c + e \cdot \mathbf{E} + s \cdot \mathbf{S} + a \cdot \mathbf{A} + b \cdot \mathbf{B} + l \cdot \mathbf{L} \tag{2}$$

The dependent variable, log SP, is some property of a series of solutes in a fixed phase. The independent variables, or descriptors, are solute properties as follows: **E** and **S** refer to the excess molar refraction and dipolarity/polarity descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and hydrogen-bond basicity, **V** is the McGowan volume of the solute and **L** is the logarithm of the solute gas phase dimensionless Ostwald partition coefficient into hexadecane at 298 K. The first four descriptors can be regarded as measures of the tendency of the given solute to undergo various solute–solvent interactions. The latter two descriptors, **V** and **L**, are both measures of solute size, and so will be measures of the solvent cavity term that will accommodate the dissolved solute. General dispersion interactions are also related to solute size, hence, both **V** and **L** will also describe the general solute–solvent interactions. The regression coefficients and constants (c, e, s, a, b, v and l) are obtained by regression analysis of experimental data for a specific process (i.e., a given partitioning process, a given stationary phase and mobile phase combination, etc.). In the case of partition coefficients, where two solvent phases are involved, the c, e, s, a, b, v and l coefficients represent differences in the solvent phase properties.

Presently, we are in the process of developing/updating correlation equations for additional/existing solvent systems [7–9] and for several biological processes [10,11], and in developing new computational methodologies for calculating solute descriptors from available experimental data and/or structural information [12–16]. The existing values that we have for the molecular descriptors of several crystalline organic compounds were derived almost entirely from 'practical' partitioning data. For some solutes, there was only very limited experimental data of marginal quality, and one or two incorrect data points could lead to the calculation of incorrect values for the molecular descriptors. For other crystalline solutes there is not sufficient experimental data to even calculate the solute descriptor values. Of particular interest are those solutes for which published biological and environmental data exists, but not calculated descriptors. For such solutes, we need to calculate the solute descriptors so that we can use the biological data in developing predictive correlations. In the present study, solubilities of 1-chloroanthraquinone were measured in several alkane, alcohol, ether, ester, ketone and alkanenitrile solvents of varying polarity and hydrogen-bonding characteristics. Results of these measurements were interpreted using the Abraham solvation parameter model.

2. Materials and methods

1-Chloroanthraquinone (Aldrich, 98%) was recrystallized several times from anhydrous methanol. Hexane (Aldrich, 99%), heptane (Aldrich, 99%, anhydrous), octane (Aldrich, 99+%, anhydrous), decane (TCI, 99+%), hexadecane (Aldrich, 99%), cyclohexane (Aldrich, HPLC, 99.9+%), methylcyclohexane (Aldrich, 99+%, anhydrous), isooctane (Aldrich, HPLC, 99.7%), benzene (Aldrich, HPLC, 99.9+%), toluene (Aldrich, 99.8%, anhydrous), chlorobenzene (Aldrich, HPLC, 99.9%), 1-chlorobutane (Aldrich, HPLC, 99.5%), chlorocyclohexane (Aldrich, 99%), ethanol (Aaper Alcohol and Chemical Company, absolute), methanol (Aldrich, 99.8%, anhydrous), 1-propanol (Aldrich, 99+%, anhydrous), 1-butanol (Aldrich, HPLC, 99.8+%), 1-pentanol (Aldrich, 99+%), 1-hexanol (Alfa Aesar, 99+%), 1-heptanol (Alfa Aesar, 99+%), 1-octanol (Aldrich, 99+%, anhydrous), 2-propanol (Aldrich, 99+%, anhydrous), 2-butanol (Aldrich, 99+%, anhydrous), 2-methyl-1-propanol (Aldrich, 99+%, anhydrous), 2-methyl-2-propanol (Arco Chemical Company, 99+%), 3-methyl-1-butanol (Aldrich, 99%, anhydrous), 1-decanol (Alfa Aesar, 99+%), 2-pentanol (Acros, 99+%), 2-ethyl-1-hexanol (Aldrich, 99%), 2-methyl-2-butanol (Aldrich, 99+%), 2-methyl-1-pentanol (Aldrich, 99%), 4-methyl-2-pentanol (Acros, 99+%), diethyl ether (Aldrich, 99+%, anhydrous), diisopropyl ether (Aldrich, 99%, anhydrous), dibutyl ether (Aldrich, 99.3%, anhydrous), methyl *tert*-butyl ether (Arco, 99.9+%), tetrahydrofuran (Aldrich, 99.9%, anhydrous), acetone (Aldrich, 99.9%), 2-butanone (Aldrich, 99+%), cyclohexanone (Aldrich, 99.8%), methyl acetate (Aldrich, 99.5%, anhydrous), ethyl acetate (Aldrich, HPLC, 99.9%), propyl acetate (Aldrich, 99.5%), butyl acetate (Aldrich, HPLC, 99.7%), pentyl acetate (Aldrich, 99%), acetonitrile (Aldrich, 99.8%, anhydrous), propionitrile (Aldrich, 99%) and butyronitrile (Aldrich, 99.7%, anhydrous) were stored over molecular sieves and distilled shortly before use. Gas chromatographic analysis showed solvent purities to be 99.7 mole percent or better.

Excess solute and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature water bath at $25.0 \pm 0.1^{\circ}C$ for at least 24 h (often longer) with periodic agitation. After equilibration, the samples stood unagitated for several hours in the constant temperature bath to allow any finely dispersed solid particles to settle. Attainment of equilibrium was verified both by repetitive measurements the following day (or sometimes after two days) and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a slightly higher temperature. Aliquots of saturated 1-chloroanthraquinone solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol (or with 2-propanol for decane and hexadecane solutions) for spectrophotometric analysis at 335 nm on a Bausch and Lomb Spectronic 2000. Concentrations of the dilute solutions were determined from a Beer–Lambert law absorbance *versus* concentration working curve for nine standard solutions. The calculated molar absorptivity varied systematically with concentration, and ranged from approximately $\varepsilon \approx 5060$ to $\varepsilon \approx 4800\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ for 1-chloroanthraquinone concentrations from 6.10×10^{-5} to 3.05×10^{-4} Molar. Identical molar absorptivities were obtained for select 1-chloroanthraquinone solutions that contained up to 4 vol% of the neat alkane, alcohol, ester, ether, ketone and alkanenitrile solvents.

Experimental molar concentrations were converted to (mass/mass) solubility fractions by multiplying by the molar mass of 1-chloroanthraquinone, volume(s) of volumetric flask(s) used and any dilutions required to place the measured absorbances on the Beer-Lambert law absorbance *versus* concentration working curve, and then dividing by the mass of the saturated solution analyzed. Mole fraction solubilities were computed from solubility mass fractions using the molar masses of the solute and solvent. Experimental 1-chloroanthraquinone solubilities, X_S, in the 48 organic solvents studied are listed in table 1. Numerical values represent the average of between four and eight independent determinations, and were reproducible to within ±1.5%.

3. Results and discussion

Equation (1) predicts partition coefficients, and for select solvents both 'dry' and 'wet' equation coefficients have been reported. For solvents that are partially miscible with water, such as 1-butanol and ethyl acetate, partition coefficients calculated as the ratio of the molar solute solubilities in the organic solvent and water are not the same as those obtained from direct partition between water (saturated with the organic solvent) and organic solvent (saturated with water). Care must be taken not to confuse the two sets of partitions. In the case of solvents that are fully miscible with water, such as methanol, no confusion is possible. Only one set of equation coefficients has been reported, and the calculated $\log P$ value must refer to the hypothetical partition between the two pure solvents. And for solvents that are 'almost' completely immiscible with water, such as alkanes, cyclohexane, dichloromethane, trichloromethane, tetrachloromethane and most aromatic solvents, there should be no confusion because indirect partition (see equation (3)) will be nearly identical to direct partition.

The predictive applicability of the Abraham solvation parameter model is relatively straightforward. We start with the set of equations that we have constructed for the partition of solutes between water and a given solvent. Table 2 gives the coefficients in equation (1) for the water–solvent partitions we shall consider. The actual numerical values may differ slightly from values reported in earlier publications. Coefficients are periodically revised when additional experimental data becomes available. Table 2 includes our recently derived correlations for 3-methyl-1-butanol and 2-pentanol. Note that many of these are 'hypothetical partitions' between pure water and the pure dry solvent; these are shown as 'dry' in table 2. Although 'hypothetical', these partitions

Table 1. Experimental 1-chloroanthraquinone mole fraction solubilities, X_S, in select organic solvents at 25°C.

Organic solvent	X_S
Hexane	0.000303
Heptane	0.000405
Octane	0.000480
Decane	0.000667
Hexadecane	0.001131
Cyclohexane	0.000381
Methylcyclohexane	0.000467
Isooctane	0.000292
Methanol	0.000237
Ethanol	0.000364
1-Propanol	0.000480
1-Butanol	0.000607
1-Pentanol	0.000880
1-Hexanol	0.001222
1-Heptanol	0.001446
1-Octanol	0.001700
1-Decanol	0.002185
2-Propanol	0.000328
2-Butanol	0.000510
2-Methyl-1-propanol	0.000404
2-Methyl-2-propanol	0.000453
2-Methyl-2-butanol	0.000793
3-Methyl-1-butanol	0.000603
2-Pentanol	0.000667
2-Methyl-1-pentanol	0.000782
4-Methyl-2-pentanol	0.000691
2-Ethyl-1-hexanol	0.001211
Diethyl ether	0.002016
Diisopropyl ether	0.001019
Dibutyl ether	0.001692
Methyl *tert*-butyl ether	0.002155
Tetrahydrofuran	0.01926
Benzene	0.01223
Toluene	0.01483
Chlorobenzene	0.01956
Acetonitrile	0.001745
Propionitrile	0.003515
Butyronitrile	0.005182
Methyl acetate	0.006787
Ethyl acetate	0.006876
Propyl acetate	0.006754
Butyl acetate	0.006977
Pentyl acetate	0.006435
Acetone	0.005380
2-Butanone	0.006736
Cyclohexanone	0.01373
1-Chlorobutane	0.003870
Chlorocyclohexane	0.004882

are very useful; as we show later, they can be used to predict solubilities (and activity coefficients) in the pure dry solvent. The partition coefficient of a solid between water and a solvent phase, P, is related to

$$\mathrm{SP} = P = C_S/C_W \quad \text{or} \quad \log \mathrm{SP} = \log P = \log C_S - \log C_W \tag{3}$$

Table 2. Coefficients in equations (1) and (2) for various processes.[a]

Process/solvent	*c*	*e*	*s*	*a*	*b*	*v*/*l*
A. Water to solvent: equation (1)						
Hexane	0.361	0.579	−1.723	−3.599	−4.764	4.344
Heptane	0.325	0.670	−2.061	−3.317	−4.733	4.543
Octane	0.223	0.642	−1.647	−3.480	−5.067	4.526
Decane	0.160	0.585	−1.734	−3.435	−5.078	4.582
Hexadecane	0.087	0.667	−1.617	−3.587	−4.869	4.433
Methylcyclohexane	0.246	0.782	−1.982	−3.517	−4.293	4.528
Isooctane	0.288	0.382	−1.668	−3.639	−5.000	4.461
Diethyl ether (dry)	0.330	0.401	−0.814	−0.457	−4.959	4.320
Dibutyl ether (dry)	0.203	0.369	−0.954	−1.488	−5.426	4.508
Methyl *tert*-butyl ether (dry)	0.376	0.264	−0.788	−1.078	−5.030	4.410
Tetrahydrofuran (dry)	0.207	0.372	−0.392	−0.236	−4.934	4.447
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
Methanol (dry)	0.329	0.299	−0.671	0.080	−3.389	3.512
1-Propanol (dry)	0.147	0.494	−1.195	0.495	−3.907	4.048
2-Propanol (dry)	0.063	0.320	−1.024	0.445	−3.824	4.067
1-Butanol (dry)	0.152	0.437	−1.175	0.098	−3.914	4.119
1-Pentanol (dry)	0.080	0.521	−1.294	0.208	−3.908	4.208
1-Hexanol (dry)	0.044	0.470	−1.153	0.083	−4.057	4.249
1-Heptanol (dry)	−0.026	0.491	−1.258	0.035	−4.155	4.415
1-Octanol (dry)	−0.034	0.490	−1.048	−0.028	−4.229	4.219
1-Decanol (dry)	−0.062	0.754	−1.461	0.063	−4.053	4.293
2-Butanol (dry)	0.106	0.272	−0.988	0.196	−3.805	4.110
2-Methyl-1-propanol (dry)	0.177	0.355	−1.099	0.069	−3.570	3.990
2-Methyl-2-propanol (dry)	0.197	0.136	−0.916	0.318	−4.031	4.113
3-Methyl-1-butanol (dry)	0.123	0.370	−1.243	0.074	−3.781	4.208
2-Pentanol (dry)	0.115	0.455	−1.331	0.206	−3.745	4.201
Ethyl acetate (dry)	0.358	0.362	−0.449	−0.668	−5.016	4.155
Acetone (dry)	0.335	0.349	−0.231	−0.411	−4.793	3.963
Acetonitrile (dry)	0.413	0.077	0.326	−1.566	−4.391	3.364
(Gas to water)	−0.994	0.577	2.549	3.813	4.841	−0.869
B. Gas to solvent: equation (2)						
Hexane	0.292	−0.169	0.000	0.000	0.000	0.979
Heptane	0.275	−0.162	0.000	0.000	0.000	0.983
Octane	0.215	−0.049	0.000	0.000	0.000	0.967
Decane	0.156	−0.143	0.000	0.000	0.000	0.989
Hexadecane	0.000	0.000	0.000	0.000	0.000	1.000
Methylcyclohexane	0.318	−0.215	0.000	0.000	0.000	1.012
Isooctane	0.275	−0.244	0.000	0.000	0.000	0.972
Diethyl ether (dry)	0.288	−0.347	0.775	2.985	0.000	0.973
Dibutyl ether (dry)	0.165	−0.421	0.760	2.102	−0.664	1.002
Methyl *tert*-butyl ether (dry)	0.278	−0.489	0.801	2.495	0.000	0.993
Tetrahydrofuran (dry)	0.189	−0.347	1.238	3.289	0.000	0.982
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
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
1-Propanol (dry)	−0.028	−0.185	0.648	4.022	1.043	0.869
2-Propanol (dry)	−0.060	−0.335	0.702	4.017	1.040	0.893
1-Butanol (dry)	−0.039	−0.276	0.539	3.781	0.995	0.934
1-Pentanol (dry)	−0.042	−0.277	0.526	3.779	0.983	0.932
1-Hexanol (dry)	−0.035	−0.298	0.626	3.726	0.729	0.936
1-Heptanol (dry)	−0.062	−0.168	0.429	3.541	1.181	0.927

(*Continued*)

Table 2. Continued.

Process/solvent	*c*	*e*	*s*	*a*	*b*	*v*/*l*
1-Octanol (dry)	−0.119	−0.203	0.560	3.576	0.702	0.940
1-Decanol (dry)	−0.136	−0.038	0.325	3.674	0.767	0.947
2-Butanol (dry)	−0.013	−0.456	0.780	3.753	1.064	0.906
2-Methyl-1-propanol (dry)	−0.012	−0.407	0.670	3.645	1.283	0.895
2-Methyl-2-propanol (dry)	0.071	−0.538	0.818	3.951	0.823	0.905
3-Methyl-1-butanol (dry)	−0.014	−0.341	0.525	3.666	1.096	0.925
2-Pentanol (dry)	−0.031	−0.325	0.496	3.792	1.024	0.934
Ethyl acetate (dry)	0.203	−0.335	1.251	2.949	0.000	0.917
Acetone (dry)	0.154	−0.277	1.522	3.258	0.078	0.863
Acetonitrile (dry)	−0.007	−0.595	2.461	2.085	0.418	0.738
(Gas to water)	−1.271	0.822	2.743	3.904	4.814	−0.213

[a] The solvents denoted as ‘dry’ are those for which partitions refer to transfer to the pure dry solvent. The other partitions are from water (more correctly water saturated with solvent) to the solvent saturated with water (see text).

the molar solubility of the solid in water, C_W, and in the solvent, C_S. Hence, if C_W is known, predicted $\log P$ values based upon equation (1) will lead to predicted molar solubilities through equation (3). The molar solubility of 1-chloroanthraquinone in water, $\log C_W = -5.54$ was measured as a part of this study. The value is used to calculate the experimental solubility ratios, $\log(C_S/C_W)$, and to convert the predicted solubility ratios back to predicted molar solubilities.

Three specific conditions must be met in order to use the Abraham solvation parameter model to predict saturation solubilities. First, the same solid phase must be in equilibrium with the saturation solutions in the organic solvent and in water (i.e., there should be no solvate or hydrate formation). Second, the secondary medium activity coefficient of the solid in the saturated solutions must be unity (or near unity). This condition generally restricts the method to those solutes that are sparingly soluble in water and nonaqueous solvents. Finally, for solutes that are ionized in aqueous solution, C_W, refers to the solubility of the neutral form.

For partition of solutes between the gas phase and solvents, equation (2) is used. (Equation coefficients are given in table 2 for several organic solvents.) Predicted $\log L$ values can also be converted to saturation molar solubilities, provided that the solid saturated vapor pressure at 298.15 K, $\mathrm{VP^o}$, is available. $\mathrm{VP^o}$ can be transformed into the gas phase concentration, C_G, and the gas–water and gas–solvent partitions, L_W and L_S, can be obtained through

$$\mathrm{SP} = L_W = C_W/C_G \quad \text{or} \quad \log \mathrm{SP} = \log L_W = \log C_W - \log C_G \tag{4}$$

$$\mathrm{SP} = L_S = C_S/C_G \quad \text{or} \quad \log \mathrm{SP} = \log L_S = \log C_S - \log C_G \tag{5}$$

Equations (4) and (5), respectively. As before, the computational method will be valid if conditions discussed above are met. If one cannot find an experimental vapor pressure for the solute at 298.15 K in the published literature, one can assume an estimated value in the preliminary calculations. The value can be adjusted if necessary in order to reduce the $\log L$ deviations, and to make the $\log P$ and $\log L$ predictions internally consistent.

To determine the solute descriptors for 1-chloroanthraquinone we first convert the experimental mole fractions in table 1 into molar solubilities by dividing X_S^{exp}, by the ideal molar volume of the saturated solution (i.e., $C_S^{exp} \approx X_S^{exp}/[X_S^{exp} V_{Solute} + (1–X_S^{exp}) V_{Solvent}]$). A value of $V_{Solute} = 165\,cm^3\,mol^{-1}$ was used for the molar volume of the hypothetical subcooled liquid 1-chloroanthraquinone. Any errors resulting from our estimation of the 1-chloroanthraquinone's hyphothetical subcooled liquid molar volume, V_{Solute}, or the ideal molar volume approximation should have a negligible effect of the calculated C_S^{exp} values. 1-Chloroanthraquinone is not very soluble in many of the solvents considered, and the $X_S^{exp} V_{Solute}$ term contributes very little to the molar volumes of the saturated solutions.

The aqueous solubility prediction is included in the solubility computations. The published correlation of Abraham and Le [17]

$$(\log C_W)/5 = 0.104 - 0.2011\mathbf{E} + 0.154\,\mathbf{S} + 0.434\,\mathbf{A} + 0.848\,\mathbf{B} - 0.672\,\mathbf{A}\cdot\mathbf{B} - 0.797\,\mathbf{V} \tag{6}$$

and its updated version (unpublished)

$$(\log C_W)/5 = 0.079 - 0.191\mathbf{E} + 0.064\mathbf{S} + 0.231\mathbf{A} + 0.651\mathbf{B} - 0.157\mathbf{A}\cdot\mathbf{B} - 0.666\mathbf{V} \tag{7}$$

was used for the aqueous predictions. The cross $\mathbf{A}\cdot\mathbf{B}$ term was added to the model to account for hydrogen-bond interactions between the acidic and basic sites in the pure liquid or solid solute. Such interactions are not normally included in solubility ratio and partition coefficient correlations. In practical partitioning studies, the solute is generally at a very low concentration and is surrounded by solvent molecules. In the case of solubility ratios, the same equilibrium solid phase must be present for both C_S and C_W measurements. This allows contributions from breaking of crystal forces to cancel in the calculation of the solubility ratio.

Combining the two sets of linear free-energy relationships, we have a total of 66 equations for which partition data and equation coefficients are available. Not all of the solubility data can be used at the present time because we are missing equation coefficients for several of the organic solvents. The unused solubility data will be used in subsequent studies when we derive equation coefficients for additional solvents. The characteristic McGowan volume of 1-chloroanthraquinone ($\mathbf{V} = 1.6512$) is calculated from the individual atomic sizes and number of bonds in the molecule [18] and $\mathbf{E}$ is estimated as 1.900. The set of 66 equations were then solved using Microsoft 'Solver' to yield the values of the four unknown solute descriptors that best described the equations (1) and (2) experimental partitioning data. The final set of molecular descriptors were: $\mathbf{S} = 1.790$, $\mathbf{A} = 0.000$, $\mathbf{B} = 0.570$ and $\mathbf{L} = 9.1707$; and the vapor phase concentration was log $C_G = -11.574$. The vapor phase concentration corresponds to a gas-to-liquid partition coefficient of log $L = 6.034$, which is in good agreement with the calculated values based upon equations (1) and (2) (the last numerical entry in table 3.)

Examination of the numerical entries in table 3 reveals that the final set of molecular descriptors reproduce the 66 experimental $\log P$ and $\log L$ values to within an overall standard deviation of 0.126 log units. Individual standard deviations were 0.140 and 0.111 log units for the 34 calculated and observed log P values and 32 calculated and observed $\log L$ values, respectively. The aqueous solubility calculations were included in the $\log P$ statistics. Statistically there is no difference between the set of 34 $\log P$ values and the total set of 66 $\log P$ and $\log L$ values, suggesting that the value of $\log C_G = -11.574$ is a feasible value for 1-chloroanthraquinone. Whether or not the

Table 3. Comparison between observed and back-calculated partitions and molar solubilities of 1-chloroanthraquinone based upon equations (1) and (2) and existing values for molecular solute descriptors.[a]

		Equation (1)			Equation (2)		
Solvent	$\log C_S$	$\log P^{exp}$	$\log P^{calc}$	$\log C_S^{calc}$	$\log L^{exp}$	$\log L^{calc}$	$\log C_S^{calc}$
Hexane	−2.638	2.902	2.834	−2.706	8.936	8.949	−2.625
Heptane	−2.561	2.979	2.712	−2.828	9.013	8.982	−2.592
Octane	−2.534	3.008	3.080	−2.460	9.042	8.990	−2.584
Decane	−2.468	3.072	2.839	−2.701	9.106	8.954	−2.620
Hexadecane	−2.415	3.125	3.004	−2.536	9.159	9.171	−2.403
Methylcyclohexane	−2.439	3.101	3.214	−2.326	9.135	9.190	−2.384
Isooctane	−2.755	2.785	2.709	−2.831	8.819	8.725	−2.849
Diethyl ether (dry)	−1.716	3.824	3.943	−1.597	9.858	9.939	−1.635
Dibutyl ether (dry)	−2.003	3.537	3.547	−1.993	9.571	9.536	−2.038
Methyl *tert*-butyl ether (dry)	−1.742	3.798	3.882	−1.658	9.832	9.889	−1.685
Tetrahydrofuran (dry)	−0.584	4.956	4.743	−0.797	10.990	10.751	−0.823
Benzene	−0.868	4.672	4.750	−0.790	10.706	10.848	−0.726
Toluene	−0.961	4.679	4.611	−0.929	10.713	10.715	−0.859
Chlorobenzene	−0.723	4.817	4.624	−0.916	10.851	10.794	−0.780
Methanol (dry)	−2.235	3.305	3.563	−1.977	9.339	9.556	−2.018
1-Propanol (dry)	−2.194	3.346	3.456	−2.084	9.380	9.344	−2.230
2-Propanol (dry)	−2.370	3.170	3.374	−2.166	9.204	9.342	−2.232
1-Butanol (dry)	−2.181	3.359	3.450	−2.090	9.393	9.538	−2.036
1-Pentanol (dry)	−2.091	3.449	3.474	−2.066	9.483	9.481	−2.093
1-Hexanol (dry)	−2.011	3.529	3.577	−1.963	9.563	9.519	−2.055
1-Heptanol (dry)	−1.992	3.548	3.577	−1.963	9.582	9.561	−2.013
1-Octanol (dry)	−1.969	3.571	3.577	−1.963	9.605	9.508	−2.066
1-Decanol (dry)	−1.948	3.592	3.534	−2.006	9.626	9.495	−2.079
2-Butanol (dry)	−2.258	3.282	3.472	−2.068	9.316	9.432	−2.142
2-Methyl-1-propanol (dry)	−2.361	3.179	3.400	−2.140	9.213	9.377	−2.197
2-Methyl-2-propanol (dry)	−2.319	3.221	3.308	−2.232	9.255	9.282	−2.292
3-Methyl-1-butanol (dry)	−2.261	3.279	3.395	−2.145	9.313	9.383	−2.191
2-Pentanol (dry)	−2.215	3.325	3.399	−2.141	9.359	9.387	−2.187
Ethyl acetate (dry)	−1.156	4.384	4.244	−1.296	10.418	10.215	−1.359
Acetone (dry)	−1.141	4.399	4.396	−1.144	10.433	10.311	−1.263
Acetonitrile (dry)	−1.482	4.058	4.195	−1.345	10.092	10.274	−1.300
Gas-to-Water		6.034	5.989		6.034	5.991	

[a] Numerical values of the descriptors used in these calculations are: $\mathbf{E} = 1.900$, $\mathbf{S} = 1.790$, $\mathbf{A} = 0.000$, $\mathbf{B} = 0.570$, $\mathbf{V} = 1.6512$ and $\mathbf{L} = 9.1707$.

assumed value is in accord with future experimental vapor pressures, we can regard our value of $\log C_G$ simply as a constant that leads to calculations and predictions via equations (2). Based on our past experience using various solution models, we have found that the better predictive equations estimate solubilities to within ±0.2 log units. The Abraham solvation parameter model meets this criterion.

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