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Estimation of Water Solubility and Octanol/Water Partition Coefficient of Hydrophobic Dyes. Part I: Relationship between Solubility and Partition Coefficient*

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ABSTRACT

*Three regression approaches are examined for use in estimating water solubilities and octanol/water partition coefficients, two fundamental equilibrium constants that are widely used in predicting the fate of organic chemicals in aquatic systems. Approaches examined are regression of solubility against partition coefficient, determination of the product of solubility and partition coefficient, and application of an equation from Yalkowsky and Valvani (*J. Pharm. Sci., ***69*** *(1980) 912). The regressions are based on data for water solubility, octanol/water partition coefficient, entropy of fusion, and melting point of 20 disperse and solvent dyes.*

In the study all three methods produced more reliable data on dyes than other equations available in the literature. Root-mean-square deviations are on the order of a factor of four to six for all three methods. Factors such as purity, polymorphism, tautomerization, polarization and hydrogen bonding are suggested as factors precluding the development of highly reliable prediction relationships between solubility and partition coefficient of dyes. Sources of error in both the data and methodologies are discussed.

The study also provided information on entropies of fusion, which ranged from 50·7 to 136 and averaged 78·8 J/mol K. Anthraquinone dyes exhibited much lower entropies of fusion than did many azo dyes. Thus use of an average entropy in estimation is inappropriate for dyes and leads to more error than neglecting the change in heat capacity.

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* Note: Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the US Environmental Protection Agency.

1 INTRODUCTION

Water solubility and the *n*-octan-1-ol/water partition coefficient (K_{ow}) are fundamental equilibrium constants that can be used to predict other partition equilibria, e.g. the affinity of disperse dyes. Among the more widespread uses of these constants is the prediction of the bioconcentration and environmental distribution of uncharged organic compounds in aquatic systems. These two uses have prompted the measurement of solubility and partitioning[1,2] for some disperse dyes. By 1987 about 15 dye K_{ow} values had been published, but most of those values were not credible because structures, names and/or methodological detail were not reported. The same lack of valid data holds for the water solubility of disperse dyes. A recent review[3] concluded that reliable solubility values are available for perhaps 30 older dyes and that no data are available for modern dyes.

Both parameters are extremely difficult to measure accurately when the values are extreme for a particular chemical, i.e. if K_{ow} is greater than about 10^4 or if solubility is less than 0·1 mg/liter. Nevertheless, under the current approach to environmental pollutant assessment and regulation, the efficient evaluation of chemicals by both industry and government agencies requires these equilibrium constants. Fortunately, in many cases, a reliable approximation is sufficient and painstakingly measured values are not needed.

The above circumstances have created interest in predicting these parameters by a-priori computational methods,[4,5] regressions of solubility against K_{ow} (see Isnard & Lambert[6] for a survey) or chromatographic methods.[7-9] There have also been attempts,[9-13] which are not discussed in this paper, to provide a theoretical basis for most of these computational methods.

Baughman and Perenich[3] have suggested that methods of predicting K_{ow} were unsatisfactory when applied to disperse dyes. They concluded that both the widely used computer program CLOGP[4] and the frequently applied equation of Yalkowsky and Valvani[13] gave low values of log K_{ow} for these materials. Recently published K_{ow} and solubility data[14] confirm that both methods can yield significant under-estimates.

In view of the above it was decided to determine whether 'calibration' of earlier approaches would permit improved predictions. Three methods that have been used to relate K_{ow} and water solubility (S) were selected: regression of log K_{ow} against log S, determination of the product of K_{ow} and S, and application of the equation of Yalkowsky and Valvani[13] relating to log K_{ow}, log S, entropy of fusion (ΔS_f) and melting point (mp). Estimation of K_{ow} and S by reverse-phase high performance liquid chromatography is presented in a companion article.[15]

2 EXPERIMENTAL

Purification of dyes and measurement of solubility were performed as described previously,[14,16] except for Solvent Green 3; for this dye the solubility was estimated by the approach of Morris *et al.*[17] Specifically, in two different experiments, the solubility of Solvent Green 3 was measured at three different compositions of $MeOH/H_2O$. The combined solubilities, as $\log S$, were extrapolated to zero volume percent MeOH to give the estimated solubility in water. The regression R^2 was 0·987. Partition coefficients were measured by the batch method or estimated as the ratio of measured octanol and water solubilities.[14]

Melting points and enthalpies were obtained by differential scanning calorimetry (DSC) using a Mettler TA 4000 microprocessor-controlled DSC 20 furnace. The instrument was calibrated against melting point standards from the National Bureau of Standards and against high purity indium, tin, benzoic acid and biphenyl. Onset of melting (the intercept, on the temperature axis, of a line tangent to the low temperature side and through the inflection point of the melting endotherm) is reported as the melting point. Heating rates were usually 2 or 5°C/min but were varied as necessary. Calibration consistently showed that calorimetric accuracy was better than 5% and melting points are believed to be accurate within 1°C.

Entropies of fusion were obtained as the ratio of the melting point to the absolute temperature with entropy units (eu) in J/mol K. Purities also were obtained by DSC using the TA 4000 algorithm based on the Van't Hoff equation for melting point depression.

3 RESULTS AND DISCUSSION

The partition coefficient and the water solubility of a crystalline dye (S_c) can be correlated as shown in eqns (1) through (4) using data from Table 1. Here S_c is in mol/m^3, mp is in °C, R is the correlation coefficient, and σ is the root-mean-square deviation between measured and calculated values:

$$\log K_{ow} = 1{\cdot}32 - 0{\cdot}77 \log S_c \qquad \begin{array}{c} R^2 = 0{\cdot}785 \\ \sigma = 0{\cdot}67 \end{array} \qquad (1)$$

$$\log K_{ow} = 2{\cdot}16 - 0{\cdot}77 \log S_c - 0{\cdot}0049(\mathrm{mp}\ 25) \qquad \begin{array}{c} R^2 = 0{\cdot}800 \\ \sigma = 0{\cdot}64 \end{array} \qquad (2)$$

$$\log S_c = 0{\cdot}34 - 1{\cdot}02 \log K_{ow} \qquad \begin{array}{c} R^2 = 0{\cdot}785 \\ \sigma = 0{\cdot}76 \end{array} \qquad (3)$$

$$\log S_c = 1{\cdot}27 - 1{\cdot}03 \log K_{ow} - 0{\cdot}0050(\mathrm{mp}\ 25) \qquad \begin{array}{c} R^2 = 0{\cdot}797 \\ \sigma = 0{\cdot}74 \end{array} \qquad (4)$$

TABLE 1

Water Solubilities and Partition Coefficients of Dyes

Dye name (Color Index Number)	*Molecular weight*	*Solubility*		log K_{ow}	
		(mol/liter)	*(%CV)/N*	*(measured)*	*(%CV)/N*
N1[a]	546	1·3E−09		5·4	
N2[a]	362	2·0E−07		3·4	
N3[a,b]	363	2·8E−10		5·8	
N5[a]	449	1·3E−09		5·5	
N7[a]	427	3·7E−08		5·4	
N9[a]	374	7·4E−07		4·0	
Ra[a]	438	1·8E−08		3·0	
Disperse Blue 79 (11345)[a]	625	8·3E−09		4·8	
Disperse Yellow 54 (47020)[a]	289	2·6E−09		5·0	
Disperse Red 60 (60756)[a,b]	331	1·9E−09		6·2	
Disperse Red 1 (11110)[c]	314	5·1E−07		4·3	
Disperse Yellow 42 (10338)[d]	369	5·4E−07		4·6	
Disperse Red 274	501	9·0E−09	(14)/19	3·8	(32)/9
Disperse Red 5 (11215)	378	2·7E−07	(10)/26	4·3	(19)/5
Disperse Violet 1 (61100)	238	1·4E−06	(19)/22	3·0	(9)/10
Disperse Red 11 (62015)	268	1·8E−06	(17)/18	3·5	(6)/5
Disperse Red 9 (60505)	237	5·1E−07	(12)/20	4·1	(15)/5
Solvent Yellow 33 (47000)[e]	273	6·2E−07		4·1	
Solvent Red 1 (12150)[a,b]	278	1·2E−09	(18)/16	7·5	
Solvent Green 3 (61565)[b]	418	2·2E−13		9·3	

[a] Solubility and K_{ow} from Ref. 3.
[b] Underlined values are estimated—see text.
[c] Solubility from Ref. 16.
[d] Solubility from Ref. 18; log K_{ow} from Ref. 18 is 4·3.
[e] Solubility from Ref. 19.

The root-mean-square deviations for these equations are clearly greater than desirable (about a factor of four to six). However, their comparison with other available equations is instructive.

Isnard and Lambert[6] reported regression equations that had been developed for other compounds by a number of authors. For those in the form of eqns (1), (3) and (4) they compiled three different regression equations each. For the eqn (2) form they compiled five regressions. In the case of eqn (1) the three equations have root-mean-square deviations in log K_{ow} of 1·6–3·3 for data in Table 1. The six regressions in the form of eqns (3) and (4) produce root-mean-square deviations for data that range from 1·3 to 3·3. The five equations like eqn (2) have root-mean-square deviations of 0·75, 0·77, 1·0, 1·1 and 1·4.

TABLE 2

Product (Q) of K_{ow} and S

	Q^a	$Q_m{}^b$	$Q_t{}^c$
Geometric mean (mol/m^3)	1·8	91	310
σ^d	0·76	0·77	0·66
Range	0·06–39	2·8–1 500	8·8–5 500

[a] Based on solubility of crystal (S_c).

[b] Based on solubility of sub-cooled liquid assuming $\Delta S_f/R = 6{\cdot}8$ (see Ref. 10).

[c] Based on solubility of sub-cooled liquid using measured ΔS_f and mp.

[d] Root-mean-square deviation in $\log Q$.

The two investigators also reported R^2 for five of eight regressions in the form of eqns (1) and (2). Of these, one was 0·66 but the other four were greater than 0·88.

In the same study Isnard and Lambert developed equations, of the same form as (1) through (4), from a database of 300 compounds. In this case R^2 was 0·93 and σ was 0·47 and 0·44 for the equations analogous to (1) and (2), respectively. Analogs to eqns (3) and (4) had R^2 of 0·93 with σ of 0·66 and 0·58. Nevertheless, if their equations are used to calculate $\log K_{ow}$ or $\log S_c$ from data in Table 1, the resulting root-mean-square deviations are greater than 1·5 log units. This may result from the fact that the compounds previously studied as a basis for such relationships are very different in structure from the dyes and, on average, have much lower melting points.

Inclusion of a term for the melting point (eqns (2) and (4)) makes only a slight improvement in the regressions. This result is consistent with the observation of Isnard and Lambert.[6]

Miller *et al.*[10] have noted that the product of S and K_{ow} is a 'pseudooctanolsolubility' (Q) and discussed factors leading to its variability. Table 2 shows the values when Q is calculated using actual and sub-cooled liquid solubilities (S_L). The geometric mean value for Q_t (Table 2) is about 20 times greater than the value reported previously,[3] which is consistent with the previous conclusion that the CLOGP predictions of $\log K_{ow}$ were much too low. This mean value is also more in line with the higher values reported by Miller *et al.*[10] This result may be compared with the data in Table 3.

Equation (5), from Yalkowsky and Valvani,[13] provides a third approach relating to K_{ow} and S_c (mol/liter):

$$\log K_{ow} \approx \log S_c - 0{\cdot}000\,194\,\Delta S_f(\text{mp } 25) + 0{\cdot}54 \tag{5}$$

This equation includes terms for mp (°C) and ΔS_f.

Usually ΔS_f is approximated by the value of 56·5 eu (i.e. $\Delta S_{f/r} = 6{\cdot}8$), but

TABLE 3
Measured Dye Solubilities in Octanol and Water

Dye	*Octanol/water*[a]				*Water/octanol*[b]		
	(M)	%*CV*	*N*	*Lit.* (M)[c]	(M)	%*CV*	*N*
N1	1·6E−4	7	5	1·5E−4[d]	7·5E−10	49	4
	3·1E−4[d]						
N2	3·1E−4	8	4	2·8E−4[d]	1·6E−7	4	4
N3	1·9E−4[d]	10	3	3·3E−4[d]			
N5	3·9E−4	3	4	9·1E−4[d]	1·2E−9	13	8
N7				2·2E−3[d]			
N9	1·7E−4	12	5	5·6E−3[d]	1·7E−7	14	3
Ra	1·3E−4	3	7		5·4E−9	29	4
	1·0E−4[d]	23	3				
Disperse Blue 79	2·6E−4	3	3		3·7E−9	26	4
Disperse Yellow 54	7·6E−4	3	4		7·8E−9	60	3
Disperse Red 60	3·2E−3	10	4				
Disperse Red 1	8·4E−3	8	4		7·0E−7	4	4
Disperse Yellow 42	4·6E−3	9	3		9·9E−8	32	5
Disperse Red 274	1·7E−4	16	10		2·6E−8	27	9
Disperse Red 5	5·9E−3	6	5		3·4E−7	29	5
Disperse Violet 1	7·6E−3	8	4		6·7E−6	25	10
Disperse Red 11	3·2E−3	5	5		1·1E−6	10	5
Disperse Red 9	1·8E−3	16	4				
Solvent Yellow 33	2·4E−3	24	5		1·7E−7	21	5
Solvent Red 1	3·9E−2	5	3				
Solvent Green 3	4·0E−3	8	4				

[a] Solubility in octanol saturated with water.
[b] Solubility in water saturated with octanol.
[c] From Ref. 2.
[d] Solubility in dry octanol.

this has been shown to be too low for disperse dyes. Instead a value of 66 eu has been suggested.[3] If the latter value for entropy is used, all but two of the K_{ow} values in Table 1 are over-estimated and the root-mean-square deviation is 1·34 log units. Use of the measured values of ΔS_f and mp still produces over-estimates of all but four K_{ow} values, and the root-mean-square deviation only decreases to 1·02.

Equation (5) and similar derivations reflect the reasonable assumption that a term containing the change in heat capacity (ΔC_p) is small and is thus omitted. The approach usually taken[20,21] is to use ΔC_p at the melting point rather than at 25°C. Indeed, the former is normally quite small while estimation of the latter requires questionable extrapolation, at best.

To better examine its role, estimates of ΔC_p from literature for nine of the

TABLE 4
Difference in Heat Capacity (ΔC_p) between Sub-cooled Liquid and Solid at 25°C ($C_{pl} - C_{ps}$)

Compound	ΔC_p (*J/mol K*)	*Reference*
Solvent Red 1	$5{\cdot}3 \times 10^2$	22
Disperse Violet 1	$3{\cdot}2 \times 10^2$	22
Disperse Red 9	$6{\cdot}1 \times 10^2$	22
Solvent Yellow 33	1×10^3	22
N3	$5{\cdot}2 \times 10^2$	This work
Disperse Blue 79	$2{\cdot}7 \times 10^2$	This work
N5	$2{\cdot}2 \times 10^2$	This work
Disperse Yellow 3	14	23
Disperse Yellow 42	3	23

dyes in this study were obtained (Table 4). The estimates are probably not very accurate, however, because most involve long extrapolations. We also measured ΔC_p for three of the dyes. In those cases plots of heat capacity versus temperature (between transitions) were smooth, almost linear and easily extrapolated. This is probably not often the case[23] and does not assure accuracy (see below).

Even if errors are large the data in Table 4 readily show that, for the most part, ΔC_p is not small. More importantly, it is in the wrong direction (i.e. positive) to improve the estimates of K_{ow}. This strongly suggests that the ΔC_p values are very much in error. Measured (extrapolated) ΔC_p values are undoubtedly influenced by some of the factors, discussed below, that affect solubility and partition coefficient. This is consistent with the considerable improvement when the data in Tables 1 and 5 are used to obtain eqn (6). Also, in this case, the intercept is not different from zero at the 95% confidence level:

$$\log K_{ow} = -0{\cdot}82 \log S_c - 1{\cdot}05 \times 10^{-4} \Delta S_f(\text{mp } 25) - 0{\cdot}03 \qquad \begin{array}{c} R^2 = 0{\cdot}836 \\ \sigma = 0{\cdot}58 \end{array} \qquad (6)$$

Because eqns (1) through (6) have low regression coefficients it is important to examine data on which they are based and to identify possible sources of error. It is not feasible, however, to determine whether partition coefficients or their related solubilities contribute the most error.

The group of four largest residuals from each regression equation (or calculation of Q) always includes Solvent Red 1. The remaining three usually include N3 and, unless melting point is considered, Disperse Red 274. Unfortunately it was necessary to estimate the K_{ow} values for Solvent Red 1, N3 and two other dyes in Table 1 as the ratio of solubility in water-saturated

TABLE 5
Entropies of Fusion (ΔS_f) of Hydrophobic Dyes

Dye	*Transitions (°C)*		*Purity (mol%)*	ΔS_f	*Reference*[a]
	mp	*Other*		*J/mol K (%CV)*	
N1	192		95	127 (1·3)	
N2	227		>99	70·3 (1·8)	
N3	217	182	>99	50·7 (4·1)	
N5	151		>99	89·3 (3·1)	
N7	198	155, 179, 191	98	82·5 (2·4)	
N9	155	127	99	61·4 (2·2)	
Disperse Red 60	185		>99	67·2 (1·3)	
Disperse Blue 79	148		95	136 (2·0)	
Disperse Yellow 54	266	211	>99	57·3 (2·1)	
Disperse Red 274	196		>99	111 (1·6)	
Ra			97	90·4 (2·0)	
Disperse Red 1	167	140	97	66·0 (1·3)	
				71·5	20
Disperse Yellow 42	159	155	—	82·4 (1·0)	
				86·1	24
Disperse Red 5	192	158, 167	99	69·8 (1·3)	
				65·4	20
Disperse Violet 1	268		98	56·5 (3·0)	
				37·0	22
				51·8	25
				50·0	20
				52·3	24
Disperse Red 11	237	235	—	65·9 (7·0)	
				68·1	20
Disperse Red 9	170	156	96	65·0 (1·0)	
				60·7	22
				66·1	24
Solvent Yellow 33	241		99	56·8 (2·8)	
				21·9	22
Solvent Red 1	183		98	77·3 (2·0)	
				61·9	22
Solvent Green 3	218		99	74·5 (1·7)	

[a] This work unless otherwise stated.

octanol to the water solubility. Miller *et al.*[10] pointed out that the partition coefficient should be well approximated by the ratio of octanol and water solubilities, and that the influence of mutual solvent solubilities is not great. This is confirmed by the measured solubilities of dyes in octanol (Table 3). Further, the ΔS_f for dye N3 is smaller than expected, even for such a rigid structure, and this leads to an even larger difference between calculated and measured values of $\log K_{ow}$ or $\log S_L$. Taken by themselves these observations suggest that data for Solvent Red 1 and N3 probably should be rejected on the basis of accuracy.

There are several reasons, however, for retaining all of the data. Dyes have properties that make accurate measurement of water solubility or octanol/water partition coefficients more difficult than for many other compounds. These include purity, polymorphism, tautomerism, hydrogen bonding and polarization. The difficulties in obtaining pure dyes are well known and are not further addressed, except to note that most of the compounds used in this study are purer than usual (Table 5).

Different polymorphic forms of a compound are known to have different solubilities, and this is believed to be important in fabric dyeing with disperse dyes.[26–28] This factor is almost universally ignored in solubility and partitioning studies. As can be seen in Table 5, however, at least 9 of the 20 dyes used in this study probably have more than one crystal form. Unfortunately, as is the case with most other methods, the generator column and the batch technique (as used in this work) implicitly assume that the most stable solid form is in equilibrium with the liquid phase. Fortunately the magnitude of this effect is probably low, i.e. less than an order of magnitude.

Tautomerization, hydrogen bonding, aggregation and polarization are much better known, but perhaps even more difficult to quantify. All are known to be strongly influenced by solvent composition and to be important for many dyes (see Refs 29 and 30 for solvent effects on tautomeric equilibria). Tautomerization also has been suggested to be a factor in solid–solid equilibria of dyes,[31] and hence may in some cases affect ΔS_f or C_p.

ΔS_f and melting points measured for the dyes in this study are given in Table 3. In general, the data are in good agreement with other available values. An exception is the value for Solvent Yellow 33 reported by Krien,[22] who found both a molecular weight and a dehydration (apparently for technical grade dye) that were not seen in this study.

We experienced considerable difficulty with erratic melting behavior of N2 and Disperse Red 11. This may be due to factors noted above or to some liquid or plastic crystal behavior, as has been suggested for Disperse Red 9 by Jones and Flores.[24]

As was anticipated, the average ΔS_f value of 78 J/mol K is significantly greater than the 66 J/mol K value that was based on previously available data.[3] Table 3 shows that the anthraquinone dyes (Disperse Red 60, Disperse Red 9, Disperse Red 11 and Solvent Green 3) have ΔS_f values near 66 J/mol K, as do the other 'rigid' structures (Disperse Yellow 54 and Disperse Yellow 33). However, addition of large flexible chains to the anthraquinone ring system raises the ΔS_f to about 78 J/mol K.[32] The only

ΔS_f that seems unreasonable is the low value of 50·7 J/mol K for the rigid dye, N3. This value is almost certainly too low, but it did not increase with further purification.

It is not surprising that ΔS_f values for the much more flexible azo dye molecules are higher than those of the anthraquinones. Some of the values, however, are about a factor of two greater than the previously used average of 66 J/mol K. Such large differences make it clear that application of a single average value for different structural groups of dyes will give gross errors in prediction.

4 CONCLUSIONS

Presented equations provide the possibility of estimating water solubility from partition coefficient, or vice versa, with reliability on the order of a factor of four to six for dyes. This level of reliability is not likely to improve soon because of both experimental and chemical limitations. The latter include polymorphism, tautomerization, polarization, hydrogen bonding and possibly aggregation.

Similar considerations limit reliability of data on change in heat capacity. Inclusion of melting point considerations makes only a small improvement in the results. This is attributed to the small range in melting points, all of which are rather high.

Neglect of a term for the change in heat capacity is less important than using accurate values for entropy of fusion. The anthraquinone dyes have entropies of fusion on the order of 60–70 eu; values for the azo dyes are often much greater. Thus use of a single value for entropy of fusion leads to large errors.

None of the three methods examined is markedly superior. However, availability of data severely limits the utility of equations dependent on entropies.

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