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Estimation of Water Solubility and Octanol/Water Partition Coefficient of Hydrophobic Dyes. Part II: Reverse-Phase High Performance Liquid Chromatography

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ABSTRACT

Capacity factors were determined for 20 disperse and solvent dyes by a high performance liquid chromatographic method using methanol/water and a C-18 reverse-phase column. Regression equations are given that establish relationships among capacity factors, water solubilities and octanol/water partition coefficients. The method is easy to apply to commercial dyes with resulting estimations that are accurate to better than one order of magnitude. Possible sources of error are discussed and suggested as implicit in the method when applied to dyes. The regressions are also used to estimate the octanol/water partition coefficients and solubilities for 14 other disperse dyes and for indigo, none of which have been previously measured. The estimated values for all of the dyes correspond to calculated sediment/water partition coefficients and bioconcentration factors, ranging from about 2·3 to 8·5 and from 2 to 7 log units, respectively.

1 INTRODUCTION

Water solubility (S) and/or octanol/water partition coefficient (K_{ow}) are widely used to estimate sediment/water and biota–water partition coefficients. Unfortunately few S or K_{ow} values are available for dyes[1,2] and

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they are often extremely difficult to measure. The fact that reliable estimates are frequently adequate for environmental purposes has prompted development of estimation methods. Such methods usually require the molecular structure[3,4] or suitable regression equations.[5,6] Even if the methods are assumed reliable the structure of many industrial dyes have not been published, and suitable data are not available for use in the regression equations. This situation has prompted application of chromatography to the problem.

Although chromatographic methods do not provide direct measurement of either S or K_{ow}, both reverse-phase thin-layer chromatography[7] and reverse-phase HPLC (high performance liquid chromatography)[8-11] have been applied to their estimation. This approach has the advantage of high sensitivity, and high purity and known structures are not required.

Recently an OECD test guideline based on HPLC was subjected to an interlaboratory comparison.[12] Although the HPLC method was viewed as acceptable, estimated K_{ow} values for three out of five dyestuffs included in the study were found to be insufficiently accurate. Because S and K_{ow} were recently measured for 20 dyes[6] the application of the HPLC method to these compounds was decided upon.

2 EXPERIMENTAL

In most respects the methodology is similar to that of an OECD method tested recently.[12] The liquid chromatographic system comprised a Perkin–Elmer Series 2000 pump, a Varian Vari-Chrom absorbance detector and an Alltech Econosil C-18 (10 μm) column (4·6 mm × 25 cm with guard column). The mobile phase, HPLC-grade methanol and deionized water (75/25 vol.%), was filtered for use at a flow rate of 1·3 ml/min. Detection was at the wavelength of maximum absorbance in the visible.

Capacity factors, K' ($K' = (t_r - t_0)/t_0$), were initially determined by measuring K' over a range (5% intervals) of four to five mobile-phase compositions. Time for an unretained component to move through the system (t_0) was identified by injection of water and measured by strip chart recorder, as was retention time (t_r). The data then were interpolated (occasionally extrapolated) by linear regression to 0% (K'_0) or 75% (K'_{75}) MeOH. It was found, however, that the dyes could usually be measured more easily and accurately with the 75/25 MeOH/H_2O. These conditions sometimes necessitated long retention times (up to 90 min) but extrapolation was necessary only for Solvent Green 3 and Disperse Blue 354. All values are reported as the mean of triplicate determinations, for which the variability was about 6%. Capacity factors for commercial dyes and Indigo were obtained in the same manner as with other dyes but without purification. Dye sources, property measurement methods and purification techniques have been reported,[2,6] except for Indigo. Indigo was purchased from EM Science (Cherry Hill, NJ, USA).

3 RESULTS AND DISCUSSION

Properties of the 20 dyes used for this study are given in Table 1. Solubilities and partition coefficients for dyes below Disperse Yellow 42 in the table were determined for this work. Linear regression analysis provided the three equations shown below:

$$\log K_{ow} = 2{\cdot}95 + 2{\cdot}31 \log K'_{75} \qquad \begin{matrix} R^2 = 0{\cdot}791 \\ \sigma = 0{\cdot}659 \end{matrix} \tag{1}$$

$$\log S_l = -3{\cdot}09 - 2{\cdot}68 \log K'_{75} \qquad \begin{matrix} R^2 = 0{\cdot}862 \\ \sigma = 0{\cdot}594 \end{matrix} \tag{2}$$

$$\log S_c = -5{\cdot}39 - 2{\cdot}70 \log K'_{75} \qquad \begin{matrix} R^2 = 0{\cdot}839 \\ \sigma = 0{\cdot}634 \end{matrix} \tag{3}$$

TABLE 1
Dye Properties

Dyes	*Molecular weight*	*Melting point* (°C)	$\log K_{ow}$	$\log S_c$ (M)	$\log K'_{75}$
N1	546·4	192	5·4	−8·90	0·967
N2	361·8	227	3·4	−6·69	0·554
N3	363·4	217	5·8	−9·56	1·651
N5	449·5	151	5·5	−8·88	1·017
N7	426·3	198	5·4	−7·43	1·161
N9	373·8	155	4·0	−6·13	0·462
Disperse Red 60	438·5	185	6·2	−8·71	1·176
Disperse Blue 79	625·4	148	4·8	−8·08	0·964
Disperse Yellow 54	289·3	266	5·0	−8·59	1·083
Disperse Red 274	331·3	196	3·8	−8·05	0·834
Ra	314·4	171	4·6	−7·74	0·525
Disperse Red 1	369·4	167	4·3	−6·29	0·650
Disperse Yellow 42	501·5	159	4·6	−6·27	0·262
Disperse Red 5	378·8	192	4·3	−6·57	0·688
Disperse Violet 1	238·3	268	3·0	−5·85	−0·076
Disperse Red 11	268·3	237	3·5	−5·76	0·097
Disperse Red 9	237·3	170	4·1	−6·30	0·774
Solvent Yellow 33	273·3	241	4·1	−6·21	0·598
Solvent Red 1	278·3	183	7·5	−8·90	1·236
Solvent Green 3	418·5	218	9·3	−12·65	2·519

In these equations S_c and S_l are the molar solubilities of the crystalline dye and the sub-cooled liquid dye, respectively, at 25°C, and K'_{75} is the capacity factor for 75% volume $MeOH/H_2O$. S_l is defined as $S_c/\exp\{\Delta S_f(1-\mathrm{mp}/T)/R\}$,[13] where ΔS_f is the entropy of fusion, mp is the melting point, T is the temperature in Kelvins and R is the gas constant.

The regression coefficients for these equations are relatively low. Nevertheless, they are regarded as reasonable given that four K_{ow} and one S value in Table 1 are experimental estimates, and all of the compounds have high melting points. Significantly, the equations have deviations and regression coefficients similar to regressions of $\log K_{ow}$ against $\log S$ for the same data set.[6] This is expected since the K' measurements are considerably more precise than those of S and K_{ow}.

Tomlinson and Hafkenscheid[9] discussed the theoretical basis for relationships among solubility, partition coefficient and capacity factor. They used an equation similar to eqn (1) but linear in K', and, after rejecting outliers, obtained an R^2 of 0·96 for 79 compounds using 75/25 $MeOH/H_2O$. If the data in Table 1 are fitted to their log-linear relationship, R^2 is only 0·56.

The same authors also used equations of the form

$$\log X = a + bK'_{75} + c(f_{(T)}) \qquad (4)$$

where $f_{(T)}$ is $(\mathrm{mp}/T) - 1$ or $\log(\mathrm{mp}/T)$, T being the temperature of interest, and X is the mole fraction solubility. In those cases their R^2 values were 0·93 and 0·94, but the data in Table 2 result in an R^2 that is considerably lower, i.e. 0·58.

Similarly, Whitehouse and Cook[11] obtained an R^2 of 0·97 for an equation in the form of eqn (5). This equation fits the data in Table 1 with $R^2 = 0{\cdot}855$:

$$\log S_c = -4{\cdot}95 - 2{\cdot}76 \log K'_{75} - 0{\cdot}001\,80[\mathrm{mp}(^\circ\mathrm{C})] \qquad (5)$$

Thus, as in the case of regressions of $\log S_c$ against $\log K_{ow}$, inclusion of a melting point term results in only a small improvement in regression coefficient.[6,14] For eqn (5) the standard error of the prediction actually increases slightly.

Sources of error in the measured solubilities and partition coefficients were discussed in Part I of this study[6] and are not discussed further. However, the chromatographic method can be strongly affected by some of the same sources of error, e.g. those due to solvent interactions. Some factors which are especially likely to be important for dyes include hydrogen bonding, polarization and tautomerization. These factors mitigate strongly against extrapolations in solvent composition to obtain K', even at the expense of long retention times.

As a consequence of the above factors, it is likely that statistical reliability of the chromatographic method will be primarily limited by availability of

TABLE 2

K_{ow} Values and Solubilities Predicted from Measured K'_{75}

Disperse dye	K'_{75}	$\log K_{ow}$[a]	*Solubility* (M)	
			Calculated[b]	*Literature*[c]
Orange 25	3·8	4·3		
Orange 30	4·0	4·3		
Brown 1	3·5	4·5		
Orange 29	9·3	5·2		
Blue 14	4·5	4·4	7·1*E*−8	(1·4, 2·8)*E*−7, 4·1*E*−6
Blue 56	7·6	5·0		
Blue 7	1·1	3·0		
Yellow 64	27·3	6·3		
Blue 3	1·4	3·3	1·6*E*−6	1·2*E*−7, 4·7*E*−5
Yellow 23	17·8	5·8		
Violet 8	0·50	2·2		
Blue 165	10·4	5·3		
Yellow 3	3·9	4·3	1·0*E*−7	1·2*E*−7, 4·4*E*−6
Blue 354	120	7·8		
Indigo	2·1	3·6		

[a] Calculated from eqn (1).
[b] Calculated from eqn (3).
[c] From Ref. 1.

accurate dye solubilities and K_{ow} values. This should not obscure the fact that speciation changes can and, for dyes, probably do result in data that are 'chemically' accurate but which may not give desirable statistical (i.e. predicted) results. Whether the estimates are adequate must be determined by the use of the data and, as noted earlier, for environmental purposes the demands on precision are often not great. In the present case root-mean-square deviations from the reference values in Table 1 are on the order of a factor of four to five.

To illustrate the utility of the method, K'_{75} was measured for some commercially formulated dyes, and eqns (1) and (3) were used to estimate the solubilities and K_{ow} values (Table 2). Few of these dye solubilities and none of the K_{ow} values have been previously reported. It is noteworthy that the absence of melting points, for substances like Indigo that decompose before melting, does not prevent estimation.

Measured (Table 1) and predicted values (Table 2) were used to calculate the sediment/water partition coefficient (K_{oc}) and potential bioconcentration factor (BCF) for all dyes used in this work (Table 3). The data clearly show that some of the dyes have a large potential to partition to sediments and biota. In many cases this conclusion would not change even if there were

TABLE 3
Sediment–Water and Biota–Water Partition Coefficients

Dyes	*Calculated*		
	$\log K_{oc}$[a]	$\log$ BCF[b] (K_{ow})	$\log$ BCF[c] (S)
Reference			
N1	5·5	3·9	4·8
N2	3·8	2·4	3·8
N3	5·9	4·2	5·1
N5	5·7	4·0	4·8
N7	5·0	3·9	4·1
N9	4·0	2·8	3·5
Disperse Red 60	5·8	4·5	4·7
Disperse Blue 79	5·1	3·4	4·4
Disperse Yellow 54	5·1	3·6	4·6
Disperse Red 274	4·6	2·7	4·4
Ra	4·8	3·3	4·2
Disperse Red 1	4·2	3·0	3·6
Disperse Yellow 42	4·2	3·0	3·6
Disperse Red 5	4·2	3·0	3·7
Disperse Violet 1	3·3	2·1	3·4
Disperse Red 11	3·5	2·4	3·3
Disperse Red 9	4·1	2·9	3·6
Solvent Yellow 33	3·9	2·9	3·5
Solvent Red 1	6·4	5·5	4·8
Solvent Green 3	8·5	6·8	6·6
Commercial			
Disperse Orange 25	4·3	3·0	3·9
Disperse Orange 30	4·3	3·1	3·9
Disperse Brown 1	4·4	3·0	3·8
Disperse Orange 29	5·0	3·7	4·4
Disperse Blue 14	4·4	3·2	4·0
Disperse Blue 56	4·9	3·6	4·3
Disperse Blue 7	3·3	2·1	3·2
Disperse Yellow 64	5·9	4·5	5·0
Disperse Blue 3	3·5	2·3	3·3
Disperse Yellow 23	5·5	4·2	4·7
Disperse Violet 8	2·6	1·5	2·8
Disperse Blue 165	5·1	3·8	4·4
Disperse Yellow 3	4·3	3·0	3·9
Disperse Blue 354	7·2	5·7	5·8
Indigo	3·8	2·6	3·6

[a] Average of value from eqns (4-5), (4-7) and (4-9) of Ref. 5, and eqns (15) and (22) of Ref. 15.

[b] Based on K_{ow} from eqn (1) and eqn (5-1) of Ref. 5.

[c] Calculated from S_c using eqn (5-3) of Ref. 5.

rather large errors in the data. For example, data in Table 3 also show that the solubility equations return values of log BCF that are on average about 0·7 log units larger than those from K_{ow}.

4 CONCLUSIONS

The empirical reverse-phase HPLC method can provide useful estimates of the octanol/water partition coefficient and water solubility of hydrophobic dyes. Reasonable accuracy requires calibration against a series of dyes having known values. It is probable that accuracy of the method for dyes is limited by accuracy of the calibration data. It is also probable that some of the error is due to chemical processes that are inherent in the measurements. For these regressions melting point correction provides no improvement in $\log S_c$ estimation.

Calculated sediment/water sorption coefficients ($\log K_{oc}$) and potential bioconcentration factors (log BCF) for the dyes in this study are in the range 2–8 and 2–7, respectively.

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