Hydrogen bonding. Part 40. Factors that influence the distribution of solutes between water and sodium dodecylsulfate micelles

Michael H. Abraham,[a] Harpreet S. Chadha,[a] Julian P. Dixon,[a] Clara Rafols[a] and Claude Treiner[b]

[a] *Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ*

[b] *Laboratoire d'Electrochimie, Universite Pierre et Marie Curie, 4 place Jussieu, 75230 Paris Cedex 05, France*

The partition of 132 assorted compounds between water and sodium dodecyl sulfate (SDS) micelles at 298 K has been correlated through eqn. (i). The mol fraction water–SDS micelle partition coefficient is denoted as K_x, and the solute explanatory variables, or descriptors, are R_2 the excess molar refraction, π_2^H the dipolarity/polarizability, $\Sigma\alpha_2^H$ and $\Sigma\beta_2^O$ the hydrogen-bond acidity and basicity, and V_x the McGowan characteristic volume. The number of solutes is denoted as n, the correlation coefficient as ρ, the standard deviation as sd, and the F-statistic as F.

$$\log K_x = 1.201 + 0.542\,R_2 - 0.400\,\pi_2^H - 0.133\,\Sigma\alpha_2^H - 1.580\,\Sigma\beta_2^O + 2.793\,V_x \qquad \text{(i)}$$

$$n = 132, \rho = 0.9849, \text{sd} = 0.171, F = 817$$

The two main factors that influence partition are solute hydrogen-bond basicity that reduces partition into micelles, and solute volume that increases partition. It may be deduced from eqn. (i) that SDS micelles behave as though they are highly polar, of quite high hydrogen-bond acidity (although not as high as water) and of about the same hydrogen-bond basicity as water. Comparison with water–alcohol partitions indicates that SDS micelles are as hydrophobic as water-saturated isobutanol. It is also shown that water–octanol partition coefficients, as $\log K_{oct}$, do not correlate well with $\log K_x$ for the 132 varied solutes, but that a double regression in $\log K_{oct}$ and V_x is a useful equation for the estimation of $\log K_x$ values.

$$\log K_x = 1.129 + 0.504\log K_{oct} + 1.216\,V_x \qquad \text{(ii)}$$

$$n = 132, \rho = 0.9755, \text{sd} = 0.215, F = 1269$$

A knowledge of water–micelle partition coefficients is of considerable importance in many areas of chemistry. In separation science, the technique of micellar-enhanced ultrafiltration is an effective method for the removal of organic compounds from aqueous solution,[1] and in biological chemistry the use of micelles to facilitate intermolecular hydrogen-bonding is a recent important advance.[2] Nowick *et al.*[2] have shown that adenine–thymine derivatives can base-pair in sodium dodecyl sulfate (SDS) micelles. The measured association constant, K_{obs}, is the product of the intramicellar base-pair association constant, K_{ass}, and the water–micelle partition constant, K_x, defined through eqn. (1). If the latter constant can be found, then the key association constant can be obtained. Unfortunately, K_x has been too difficult to measure for the compounds studied by Nowick *et al.*,[2] and some method of estimation is thus needed.

$$K_x = \frac{[\text{mol fraction solute in micelle}]}{[\text{mol fraction solute in water}]} \qquad (1)$$

It has been known for some time[3] that $\log K_x$ for a series of solutes in the same water–micelle system can be correlated with their water–octanol partition coefficients, as $\log K_{oct}$, but also that the correlation holds only for certain families of solute.[4] Treiner and Mannebach[4] showed that there was a reasonable connection between $\log K_x$ for water–SDS partitions, and $\log K_{oct}$ for 14 varied solutes, after omitting solutes such as haloalkanes, and aliphatic and aromatic hydrocarbons. Attempts have been made to construct group contribution schemes for the prediction of $\log K_x$ values, but such schemes have usually been restricted to only a few groups or atoms.[5,6] Valsaraj and Thibodeaux[7] investigated a number of different procedures for the correlation of water–SDS partition coefficients and found that there was a good general correlation between $\log P_m$ for water–SDS and $\log K_{oct}$ provided that aliphatic amides and lactams were excluded: P_m is the water–SDS partition coefficient on the molar scale, but the statistics are the same as for K_x except for the numerical value of the intercept. Note also that K_{oct} is always expressed on the molar concentration scale. Unfortunately, Valsaraj and Thibodeaux[7] gave no standard deviation in eqn. (2), and so we recalculated the expression using exactly the reported data. For all the solutes listed,[7] we found eqn. (3) and if aliphatic amides and

$$\log P_m = 0.32 + 0.827\log K_{oct} \qquad (2)$$
$$n = 57, \rho = 0.9924$$

$$\log P_m = 0.740 + 0.693\log K_{oct} \qquad (3)$$
$$n = 63, \rho = 0.9224, \text{sd} = 0.38, F = 348$$

lactams were excluded,† eqn. (4). We denote the number of data

$$\log P_m = 0.326 + 0.826 \log K_{oct} \quad (4)$$
$$n = 59, \rho = 0.9571, \text{sd} = 0.29, F = 622$$

points as n, the correlation coefficient as ρ, the standard deviation as sd, and the F-statistic as F. Although eqn. (4) is quite good, it is nowhere near as good as the reported eqn. (2). We cannot explain the difference, but we note that for a similar correlation of log P_m for hexadecyltrimethylammonium bromide micelles, Valsaraj and Thibodeaux report $\rho = 0.9917$ for 26 solutes, whereas we find $\rho = 0.9152$ for the same 26 solutes, using the same listed data. Garrone *et al.*[8] studied a number of monosubstituted benzoic acids and obtained eqn. (5) for SDS micelles, after exclusion of the 4-hydroxy compound.

$$\log P_m = 1.40 + 0.484 \log K_{oct} \quad (5)$$
$$n = 20, \rho = 0.910, \text{sd} = 0.12, F = 87$$

Not only is the correlation not very good for a related series of compounds, but the slope is completely different to that found for the varied set of solutes in eqn. (2) or eqn. (4). It seems that any correlation between log P_m (or log K_x) and log K_{oct} is unlikely to be general. It is of interest that Garrone *et al.*[8] markedly improved eqn. (5) by incorporation of the solute molar refraction, R, as a descriptor, eqn. (6).

$$\log P_m = 1.35 + 0.405 \log K_{oct} + 0.306\, R \quad (6)$$
$$n = 20, \rho = 0.984, \text{sd} = 0.05, F = 256$$

Valsaraj and Thibodeaux[7] also set up a bond contribution scheme, and a group contribution scheme for the prediction of water–SDS partition coefficients, using much more data than hitherto[5,6] but as they do not give any measure of the deviation of calculated and observed values, it is difficult to assess the usefulness of the schemes. In any case, neither bond or group contribution schemes nor correlations with log P_{oct} lead to any understanding of the factors involved in water–micelle partition, and workers have had to rely on what are no more than rules of thumb in any discussion of solute effects on partition.[9]

The aim of the present work is to apply our general solvation equation, eqn. (7)[10,11] to log K_x values for water–SDS micelle partitions in order to understand and to quantify the various solute factors involved, and in order to be able to predict further log K_x values. In eqn. (7) the dependent variable in the present

$$\log \text{SP} = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2 + vV_x \quad (7)$$

work will be log K_x for water–SDS partition, and the independent variables are solute properties or descriptors as follows:[10,11] R_2 is an excess molar refraction that can be determined simply from a knowledge of the compound refractive index or can be easily estimated; π_2^H is the solute dipolarity/polarizability, it being not possible to devise descriptors for these separately; $\Sigma\alpha_2^H$ is the solute overall or effective hydrogen-bond acidity; $\Sigma\beta_2$ is the solute overall or effective hydrogen-bond basicity; V_x is the McGowan characteristic volume,[12] calculated from molecular structure. Use of the basicity parameter, $\Sigma\beta_2$, is not quite straightforward. Taylor *et al.*,[13] and later Abraham[14] showed that for a number of solutes the relative basicity was not constant but varied with the solvent system. The solutes concerned included sulfoxides, anilines and alkylpyridines. For partitions between water and solvents in which water is sparingly soluble (such as hydrocarbons, chloroform, *etc.*) a general basicity parameter, $\Sigma\beta_2^H$, can be used for all solutes. For partitions between water and organic solvents in which water is quite soluble (such as octanol), the same basicity parameter $\Sigma\beta_2^H$ is used, except for the particular solutes mentioned above, when $\Sigma\beta_2^H$ is replaced by the alternative descriptor $\Sigma\beta_2^O$. Although both Abraham[14] and more recently Taylor *et al.*[15] have commented on this phenomenon of variable relative basicity, the origin of the effect is still not clear. However, in practical terms, since the solubilizing environment in a micellar pseudo phase is certainly rather aqueous, we expect the $\Sigma\beta_2^O$ descriptor to be the appropriate one to use in eqn. (7).

The coefficients in eqn. (7) are not simply fitting constants, but convey information about the system under investigation. In Table 1 are collected the coefficients, or 'characteristic constants' for a number of partitions from water to various phases,[14,16,17] together with the weight % water in the water-saturated phases. The constants will relate to the difference in particular properties between water and the phase in question. The r-constant gives the relative ability of the phase to interact with π- and n-electron pairs, the s-constant is a measure of the difference in dipolarity/polarizability of the phase and water, the a-constant measures the difference in hydrogen-bond basicity, the b-constant measures the difference in hydrogen-bond acidity, and the v-constant is a measure of the phase hydrophobicity. The c-constant notionally relates to the value of log SP for a solute with zero values for all the descriptors, but contains also a contribution for the particular standard state used in the definition of SP. In the present work, we use mol fraction standard states to define K_x, eqn. (1), but if we had used molar standard states, as with P_m, the c-constant would alter, but all the other constants would remain the same.

It can be seen from Table 1 that in general as the water content of the organic phase decreases, the phase becomes markedly less acidic (the b-constant varying from -2.26 to -4.87) and markedly more hydrophobic (the v-constant now varying from 2.78 to 4.43). Except for the water–hexadecane partition, the other constants do not alter very much. We have suggested before,[16,17] that this is due to water and wet alcohols having much the same dipolarity/polarizability and hydrogen-bond basicity.‡ We shall use Table 1 to interpret the characteristic constants for the water–SDS system later.

Results and discussion

Water–micelle partition coefficients have been determined by many groups of workers, using different methods and under various conditions. It is not easy to obtain a coherent set of results, and we have relied extensively on the reviews of Sepulveda, Lissi and Quina,[18] Treiner and Mannebach[4,19] and Valsaraj and Thibodeaux.[7] In addition, we used the results of Garrone *et al.*[8] on the benzoic acids, and data by Causi *et al.*,[20] by Manabe *et al.*,[21] by Stilbs,[22] and by a number of other workers as shown in Table 2. We have in Table 2, values of log K_x for 140 solutes for which we have the necessary descriptors, and we include for completeness a number of other solutes for which the descriptors are missing. In general we have simply averaged the various values of log K_x for any solute, since we have no reason for omitting any particular value. However, for the benzoic acids we used only the results of Garrone *et al.*,[8] as these formed a self-consistent set. Descriptors for most of the

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† Valsaraj and Thibodeaux[7] list 63 pairs of log P_m/log K_{oct} values. Four of these refer to aliphatic amides and lactams, and if these are left out we have 59 data points. Which 57 data points Valsaraj and Thibodeaux used is not clear.

‡ But note that there is a difficulty over the hydrogen-bond basicity of bulk water;[16,17] the solvatochromic β-parameter for water is less than that for alcohols, although the equations in Table 1 suggest that bulk water and bulk alcohols have the same hydrogen-bond basicity.

Table 1 Characteristic constants in eqn. (7) for some water–phase partitions[14,16,17]

Phase	c	r	s	a	b[a]	v	wt %[b]
Isobutanol	0.227	0.514	−0.693	0.020	−2.258	2.776	17.0
Pentanol	0.175	0.575	−0.787	0.020	−2.837	3.249	9.0
Hexanol	0.143	0.718	−0.980	0.145	−3.214	3.403	7.0
Octanol	0.088	0.562	−1.054	0.034	−3.460	3.814	4.6
Decanol	0.088	0.485	−0.974	0.015	−3.798	3.945	3.6
Oleyl alcohol	−0.359	−0.270	−0.528	−0.035	−4.042	4.204	1.5
Hexadecane	0.087	0.667	−1.617	−3.587	−4.869	4.433	0.005

[a] The b-constant is for the $\Sigma\beta_2^O$ descriptor, except for octanol and decanol where no 'variable basicity' solutes were included, and oleyl alcohol and hexadecane where the $\Sigma\beta_2^H$ descriptor was used. [b] Weight % water in the organic phase.

solutes have been given before,[10,12,14,17] and so are not listed in Table 2.

On application of eqn. (7) to the 140 solutes, we found that propionamide and 4-hydroxybenzoic acid (see above) were marked outliers; for the remaining 138 solutes we obtained eqn. (8). In these equations the $\Sigma\beta_2^O$ descriptor was employed, although use of the $\Sigma\beta_2^H$ descriptor would make rather little difference. The sd values for the individual coefficients are given below each coefficient. This is the first equation that provides

$$\log K_x = \underset{0.060}{1.280} + \underset{0.063}{0.484}R_2 - \underset{0.079}{0.431}\pi_2^H - \underset{0.067}{0.183}\Sigma\alpha_2^H - \underset{0.088}{1.721}\Sigma\beta_2^O + \underset{0.079}{2.878}V_x \quad (8)$$

$$n = 138, \rho = 0.9808, \text{sd} = 0.192, F = 668$$

any detailed information as to the factors that influence water–SDS log K_x values. Solute excess molar refraction (weakly) and solute volume (greatly) promote an increase in log K_x, whereas solute dipolarity/polarisability (weakly), solute hydrogen-bond acidity (weakly) and solute hydrogen-bond basicity (strongly) lead to a decrease in log K_x. Somewhat surprisingly, the alkanes fit eqn. (8) quite well, even though it has been suggested that they behave differently to other solutes in that they are sorbed by the hydrophobic chain part of the micelle.[4] We therefore repeated the correlation after leaving out the six alkanes, and obtained eqn. (9). There is not a great deal of difference between

$$\log K_x = \underset{0.058}{1.201} + \underset{0.057}{0.542}R_2 - \underset{0.071}{0.400}\pi_2^H - \underset{0.060}{0.133}\Sigma\alpha_2^H - \underset{0.082}{1.580}\Sigma\beta_2^O + \underset{0.073}{2.793}V_x \quad (9)$$

$$n = 132, \rho = 0.9849, \text{sd} = 0.171, F = 817$$

eqn. (8) and eqn. (9) but we prefer the latter as the best representation of the water–SDS log K_x values. The regression equation is not as good as those for *e.g.* water–solvent regressions, but there are very considerable differences between the log K_x values determined by various workers, see Table 2. We have tried to mitigate this by not using any K_x values obtained by micellar liquid chromatography, where adsorption on the support may affect the results, but even so it is doubtful if the average error in the taken set of log K_x values in Table 2 is less than 0.1 log unit. We checked also for any cross-correlations in the descriptors used in eqn. (9). The maximum degree of cross-correlation is between R_2 and π_2^H ($\rho = 0.730$ and $\rho^2 = 0.533$) and between R_2 and V_x ($\rho = 0.604$ and $\rho^2 = 0.365$), which is acceptable.

The solute effect on log K_x can be further investigated through a term-by-term analysis of eqn. (9). This is illustrated for some representative solutes in Table 3. The rather large effect of the $v \times V_x$ term is shown by the comparison between methanol and pentan-1-ol, where the volume term alters by 1.58 log units. The other significant effect, that of solute basicity is illustrated by decane-1,10-diol which has a very large value of $\Sigma\beta_2^O$ (0.92); here the $b\Sigma\beta_2^O$ term makes a contribution of −1.46 log units. On the other hand, solute acidity plays a very small part. Even for pentachlorophenol with $\Sigma\alpha_2^H = 0.96$, the $a\Sigma\alpha_2^H$ term is but −0.13 log units.

We can compare the water–SDS regression equation with those for various water–alcohol partitions,[14,16,17] noting that in the water–alcohol work, the organic phase is saturated with water. The interior of an SDS micelle has repeatedly been shown to be water-free, but water molecules solvate the surfactant ionic group, and some water molecules may penetrate as far as the second methylene group of the hydrocarbon chain. Most of the solute molecules used in the present analysis, Table 2, are to a greater-or-lesser extent polar, and so they should be solubilized either in the micelle palissade layer or at the micelle surface. Hence the portion of the micelle pseudo phase that undergoes interactions with the solubilized molecules will be to some extent aqueous, and comparison of the micelle pseudo phase with various water-saturated alcohols seems reasonable.

The regression coefficients for the water–alcohol partitions are in Table 1, together with the wt% water in the organic alcoholic solvent. The v-constant is probably the best indicator of how hydrophobic is the organic phase, and inspection of Table 1 suggests that the SDS pseudo phase is comparable in hydrophobicity to water-saturated isobutanol, which contains 17 wt% water. A number of other SDS properties have been deduced through various methods. Handa *et al.*[23] have measured the Kamlet-Taft solvatochromic parameters, $\pi^* = 1.10$ and $\alpha = 0.65$, as well as the effective relative permittivity (dielectric constant), $\varepsilon = 51$, and Reichardt's E_T parameter (57.5). Drummond *et al.*[24] find ε to be 56, and Varadaraj *et al.*[25] give E_T as 57.3 units. These values may be compared with those for wet alcohols given by Marcus[26] and other workers,[27,28] as shown in Table 4. If wet alcohols are a reasonable model for SDS micelles, then we can deduce values for some of these parameters for SDS micelles from the characteristic constants in the regression equations. The s-constant in eqn. (7) reflects the difference in the π^* values between water and the organic phase. From a plot of the s-constant for the various water–alcohol partitions *vs.* π^* for the wet alcohols, the SDS s-constant of 0.40 leads to a π^* value of 0.80, lower than the value of 1.10 given by Handa *et al.*[23] Similarly, the b-constant in eqn. (7) will be due to the difference in the solvatochromic α parameter of water and the wet alcohol. There is only a rough connection between the b-constant and the α parameter for the water–alcohol systems, from which we deduce a value of about 1.0 for the α parameter for SDS, appreciably more than the value of 0.65 of Handa *et al.*[23] We cannot do much with a comparison of the a-constants with the solvatochromic parameter β, except to say that from the regression equations the SDS pseudo phase and all the wet alcohols seem to have the same β value as apparently does water.

Since the solvatochromic parameters for SDS (and for other

Table 2 Values of log K_x for water–SDS partition

Solute	Ref.					Taken
	18	19	7	20, 21	22	
Argon					1.64^a	1.64
Oxygen					1.64^a	1.64
Methane			1.76		1.87^a	1.82
Ethane	2.52		2.53			2.52
Propane	3.11		3.10			3.10
Butane	3.78		3.79			3.78
Pentane	4.21		4.22			4.22
Hexane		4.51	4.26			4.38
Cyclohexane		3.62	3.49			3.55
Tetrafluoromethane					2.12^a	2.12
Dichloromethane			2.28		2.30^b	2.29
Trichloromethane		2.72	2.84		2.83^b	2.80
Tetrachloromethane		2.90	2.45		3.44^b	3.44
Dioxane					1.74	1.74
Propanone					1.53	1.53
Butanone					2.11	2.11
Pentan-2-one					2.43	2.43
Pentan-3-one					2.43	2.43
4-Methylpentan-2-one					2.85	2.85
Heptan-2-one					3.46	3.46
Butanonitrile		2.38				2.38
Propionamide			2.24			2.24
Butanamide		2.07	2.43			2.25
Pentanamide			2.74			2.74
Methanol		1.27				1.27
Ethanol		1.71				1.71
Propan-1-ol		2.02			2.07	2.04
Propan-2-ol		1.86			1.92	1.89
Butan-1-ol	2.48	2.44	2.47	2.54	2.29	2.44
2-Methylpropan-1-ol				2.65	2.42	2.53
Butan-2-ol				2.56	2.26	2.41
tert-Butanol		2.41		2.40	1.87	2.23
Pentan-1-ol	2.86	2.89	2.86	3.01	2.95	2.91
Pentan-2-ol				2.89	2.50	2.69
Pentan-3-ol					2.43	2.43
3-Methylbutan-1-ol					2.88	2.88
2-Methylbutan-2-ol					2.38	2.59
2,2-Dimethylpropan-1-ol					2.63	2.63
Hexan-1-ol	3.35	3.39	3.36	3.38	3.46	3.39
Hexan-2-ol					3.33^c	3.33
Heptan-1-ol	3.79	3.64	3.79	3.69	3.78	3.74
Heptan-2-ol					3.70^c	3.70
Octan-1-ol					4.22	4.22
Decan-1-ol			4.41			4.41
2-Ethoxyethanol					1.74	1.74
2-Butoxyethanol				3.04		3.04
Propane-1,3-diol		1.45				1.45
Butane-1,4-diol		1.62			1.68	1.65
Hexane-1,6-diol		2.38				2.38
Decane-1,10-diol		3.96				3.96
Tributylphosphine oxide				3.75		3.75
Benzene		2.60	3.05	3.00	3.15	2.95
Toluene			3.23		3.68	3.45
p-Xylene			4.17			4.17
Biphenyl			4.83			4.83
Naphthalene			3.81			3.81
1-Methylnaphthalene			4.82			4.82
Anthracene			5.57			5.57
Phenanthrene			5.60			5.60
Pyrene			6.20			6.20
Perylene			7.20			7.20
1,2-Dichlorobenzene			3.89			3.89
1-Bromonaphthalene			5.29			5.29
Acetophenone					3.34^d	3.34
p-Methoxyacetophenone					3.50^d	3.50
Propriophenone					3.70^d	3.70
Isobutyrophenone					3.90^d	3.90
Benzophenone					4.46^d	4.46
Aniline	3.66		2.61			2.92
4-Methylaniline			3.04			3.04
Ethyl 4-aminobenzoate			3.84			3.84
Benzidine	4.09					4.09

Table 2 (*cont.*)

	Ref.					
Solute	18	19	7	20, 21	22	Taken
Acetanilide		3.11				3.11
Benzoic acid	4.03				3.23^e	3.23
3-Methylbenzoic acid					3.66^e	3.66
4-Methylbenzoic acid	4.10				3.64^e	3.64
4-Ethylbenzoic acid	4.40					4.40
3-Fluorobenzoic acid					3.41^e	3.41
4-Fluorobenzoic acid					3.49^e	3.49
3-Chlorobenzoic acid					3.84^e	3.84
4-Chlorobenzoic acid					3.84^e	3.84
3-Bromobenzoic acid					3.96^e	3.96
4-Bromobenzoic acid					3.98^e	3.98
3-Iodobenzoic acid					4.13^e	4.13
4-Iodobenzoic acid					4.17^e	4.17
3-Hydroxybenzoic acid					3.22^e	3.22
4-Hydroxybenzoic acid					2.54^e	2.54
3-Methoxybenzoic acid					3.51^e	3.51
4-Methoxybenzoic acid					3.49^e	3.49
3-Cyanobenzoic acid					3.31^e	3.31
4-Cyanobenzoic acid					3.40^e	3.40
3-Nitrobenzoic acid					3.45^e	3.45
4-Nitrobenzoic acid					3.49^e	3.49
3-Acetylbenzoic acid					3.52^e	3.52
4-Acetylbenzoic acid					3.49^e	3.49
Phenol	3.44	2.79	2.76	2.91		2.96
2-Methylphenol			3.08			3.08
3-Methylphenol			3.14			3.14
4-Methylphenol	3.66		3.14			3.14
2,3-Dimethylphenol			3.52			3.52
2,4-Dimethylphenol			3.56			3.56
2,5-Dimethylphenol			3.56			3.56
2,6-Dimethylphenol			3.52			3.52
3,5-Dimethylphenol			3.56			3.56
2,4,5-Trimethylphenol			3.85			3.85
2,3,5,6-Tetramethylphenol			4.19			4.19
4-Ethylphenol	3.95	3.39	3.47			3.60
4-Propylphenol	4.18					4.18
4-*tert*-Butylphenol	4.32					4.32
4-*tert*-Pentylphenol	4.76					4.76
4-Fluorophenol			2.99			2.99
4-Chlorophenol			3.24			3.24
4-Bromophenol			3.54			3.54
4-Iodophenol			3.91			3.91
3,5-Dichlorophenol			3.72			3.72
2,3,5-Tricholorophenol			4.20			4.20
2,3,4,5-Tetrachlorophenol			4.68			4.68
Pentachlorophenol			5.13			5.13
3-Trifluoromethylphenol			3.87			3.87
4-Methoxyphenol			2.93			2.93
4-Ethoxyphenol			3.20			3.20
4-Formylphenol			2.85			2.85
4-Cyanophenol			2.93			2.93
4-Nitrophenol			2.96			2.96
Catechol			2.56			2.56
Methyl 4-hydroxybenzoate			3.33			3.33
Ethyl 4-hydroxybenzoate			3.60			3.60
Propyl 4-hydroxybenzoate			3.99			3.99
1-Naphthol			4.01			4.01
4-Chloronaphthol			5.00			5.00
6-Bromonaphthol			4.80			4.80
Benzyl alcohol		2.71		3.09	2.77	2.86
2-Phenylethanol		2.98		3.26		3.12
3-Phenylpropanol		3.28		3.53		3.40
4-Phenylbutanol		3.63		3.91		3.77
5-Phenylpentanol		4.02		4.37		4.19
6-Phenylhexanol		4.39		4.78		4.58
2-Phenoxyethanol		3.11				3.11
δ-Valerolactam		2.45	2.43			2.44
ε-Caprolactam		2.50	2.73			2.61
18-Crown-6					3.91	3.91
15-Crown-5					3.19	3.19
12-Crown-4					2.42	2.42
Butylurea		2.51				2.51

Table 2 (*cont.*)

Solute	Ref. 18	19	7	20, 21	22	Taken
Perfluoro-*tert*-butanol	2.98					2.98
Hexane-2,5-diol	2.21					2.21
p-*tert*-Butoxybenzoic acid	4.65					4.65
Pentafluorophenol			3.92			3.92
Allylthiourea		2.11				2.11
Octyldimethylamine oxide				3.14		3.14
Dodecyldimethylamine oxide				3.16		3.16
Octyldimethylphosphine oxide				2.59		2.59
2,4-Dinitrochlorobenzene	2.89					2.89
4-Bromo-*p*-terphenyl			6.74			6.74
3-Phenoxypropan-1-ol		3.38				3.38
2-*N*-Phenylcarboxamidophenol			4.15			4.15
2,3,5,6-Tetrafluorophenol			3.69			3.69
2,4,6-Tribromophenol			5.07			5.07
2,4,6-Triiodophenol			6.11			6.11
2-Carboxamidophenol			2.54			2.54
Xanthone					3.83[d]	3.83
N-Trifluoroacetylindole	4.37					4.37
Ferrocene	4.28					4.28

[a] W. Prapaitrakul and A. D. King, Jr., *J. Colloid Interfac. Sci.*, 1985, **106**, 186, using the mol fraction solubility in water at 298 K given by E. Wilhelm, R. Battino and R. J. Wilcock, *Chem. Rev.*, 1977, **77**, 219. [b] K. T. Valsaraj, A. Gupta, L. J. Thibodeaux and D. P. Harrison, *Water Res.*, 1988, **22**, 1173. [c] R. De Lisi and S. Milioto, *J. Solution Chem.*, 1988, **17**, 245. [d] J. C. Scaiano and J. C. Selwyn, *Can. J. Chem.*, 1981, **59**, 2368. [e] Ref. 8.

Table 3 An analysis of eqn. (9) for some solutes[a]

Solute	rR_2	$s\pi_2^H$	$a\Sigma\alpha_2^H$	$b\Sigma\beta_2^O$	vV_x	$\log K_x$ Calc.	Obs.
Cyclohexane	0.16	−0.04	0.00	0.00	2.37	3.69	3.55
Pentan-2-one	0.08	−0.28	0.00	−0.81	2.32	2.51	2.54
Methanol	0.15	−0.18	−0.06	−0.74	0.86	1.23	1.27
Pentan-1-ol	0.12	−0.17	−0.05	−0.76	2.44	2.78	2.91
Benzene	0.33	−0.21	0.00	−0.22	2.00	3.10	2.88
Pentachlorophenol	0.66	−0.35	−0.13	−0.01	3.88	5.25	5.13
Decan-1,10-diol	0.20	−0.38	−0.10	−1.46	4.58	4.04	3.96

[a] In all cases the *c*-constant is 1.20 log units.

micelles) determined by Handa *et al.*[23] are the only ones recorded, and since they are of particular interest, we consider their determination in detail. The method used involved measurement of the solvent dependent absorption maxima of Reichardt's betaine dye, to obtain E_T, and of the cationic dye, methylene blue (MB), in the visible region of the spectrum. The values of λ_{max} for MB were correlated with π^* and α for seven solvents, including water and four alcohols, and the resulting equation was used with a corresponding equation[29] for E_T to arrive at the simultaneous equation, eqn. (10). This was solved,[23] using the measured E_T value of 57.5 and the measured value of 666.5 nm for λ_{max}, to obtain π^* and α as 1.10 and 0.65, respectively. Our fit for λ_{max} using the more recent

$$\begin{aligned} E_T &= 29.35 + 16.3\pi^* + 15.8\alpha \\ \lambda_{max}(\text{MB}) &= 650 + 17\pi^* - 5\alpha \end{aligned} \tag{10}$$

data in Table 5 is a little different, but this is no matter. What does affect the calculation is the E_T correlation equation that is used. The equation given by Kamlet,[30] together with our recalculated equation for λ_{max}, leads to the simultaneous eqn. (11), from which we obtain values of 1.16 and 0.73 for π^* and α. The recent E_T equation of Marcus[26] is very close to that of Kamlet, and leads to essentially the same values. However, we note the error in equations such as eqn. (10) for the calculation of α is around $\sigma = 0.07$, so we would not expect the simultaneous eqn. (11) to yield π^* and α to better than 0.1 units. The π^* and α values from eqn. (11) of 1.16 and 0.73 may be compared to our deduced values of 0.80 and 1.0 for π^* and α for the SDS pseudo phase from the regression equations. The two sets are not in very good agreement; that from the regression equations shows that SDS behaves as a solubilizing agent as though it were quite dipolar ($\pi^* = 0.80$) and strong hydrogen-bond acid ($\alpha = 1.0$), though not as strong as water ($\alpha = 1.16$). In addition, it seems as though the pseudo phase has about the same hydrogen-bond basicity as water and alcohol solvents, as judged from the regression equations.

$$\begin{aligned} E_T &= 31.00 + 13.43\pi^* + 15.06\alpha \\ \lambda_{max}(\text{MB}) &= 651.1 + 17.14\pi^* - 6.05\alpha \end{aligned} \tag{11}$$

The effective relative permittivity of 51–56 for SDS micelles is much larger than that for wet isobutanol, the latter being only about 22, as we estimate from the measurements of Akerlof[31] on several water–alcohol mixtures. Likewise, the Reichardt E_T value of 57.5 is higher than the value we estimate for wet isobutanol (51), so that although wet isobutanol may be a good model as regards hydrophobicity, it is not so good with respect to other properties. Plieninger and Baumgartel,[32] on the basis of NMR studies, have suggested that the betaine dye used in the E_T determination is solubilized at the water–micelle interface, with the positive pole of the betaine dipole close to the

Table 4 Some parameters for SDS and for wet alcohols[a]

	π^*	β	α	E_T	ε
SDS[b]	1.10	—	0.65	57.5	51–56
SDS[c]	1.16	—	0.73		
SDS[d]	0.80	0.8	1.0		
Water[a]	1.09	0.47	1.17		
Water[e]	1.33	0.43	1.16	63.1	78.3
Water[e]	1.08	0.58	1.16		
Isobutanol	0.69	0.82	0.80	51 (est)	22.0
Pentanol	0.63	0.78	0.80		
Hexanol	0.59	0.78	0.80		
Octanol[a]	0.52	0.77	0.81		8.5[f]
Octanol[g]	0.58	0.79	0.71		
Octanol[g]	0.48	0.95	0.82		
Decanol	0.50	0.75	0.77		

[a] Solvatochromic parameters from ref. 26, unless shown otherwise. [b] Refs. 23–25. [c] Recalculated from eqn. (11). [d] This work, see text. [e] Solvatochromic parameters from ref. 27; the first line shows π^* and β values from aniline indicators, and the second line from 4-nitroanisole and 4-nitrophenol indicators. [f] B. C. Lippold and M. S. Alder, *Arch. Pharm.*, 1972, **305**, 417. [g] Solvatochromic parameters from ref. 28; the first line shows π^* and β values from aniline indicators, and the second line from 4-nitroanisole and 4-nitrophenol indicators. Recorded α values are 0.71, 0.78, 0.82 and 0.82 from four indicators.

Table 5 Solvatochromic parameters for water and dry solvents[a]

	π^*	β	α
Water	1.13	0.50	1.16
Methanol	0.60	0.73	1.09
Ethanol	0.55	0.80	0.88
Propan-1-ol	0.53	0.85	0.79
Octan-1-ol[b]	0.50	0.86	0.70
Benzene[c]	0.59	0.10	0.00
Me_2SO	1.00	0.76	0.00
Formamide[c]	0.97	0.55	0.71

[a] Average values from ref. 27 unless shown otherwise; note that the values for water are also average values. [b] Ref. 28, selected so as to be in line with values from ref. 27. [c] M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.

anionic head-groups. It would not be surprising, therefore, if the betaine dye 'detected' a quite polar environment.

Our conclusion is that the SDS pseudo phase, in terms of solubilizing a range of solutes, behaves as though it was highly polar, of considerable hydrogen-bond acidity (although less than that of bulk water), and of the same hydrogen-bond basicity as alcohols and probably as bulk water itself. This is in agreement with the general concensus, see above, that the area of the pseudo phase involved in solubilization of solutes is heavily hydrated.

Finally, we explore the connection between log K_x and log K_{oct} for the very general data set used in eqn. (9). A few values of log K_{oct} were missing, and so we calculated these from our descriptors and the coefficients in the water–octanol equation,[17] see. Table 1. The calculated values are in Table 6, and the regression equation for all 132 solutes is given as eqn. (12). The

$$\log K_x = 2.006 + 0.693 \log K_{oct} \qquad (12)$$
$$n = 132, \rho = 0.9345, \text{sd} = 0.346, F = 896$$

rather low correlation coefficient and the high sd value confirm previous conclusions,[4,8] as well as our recalculation of the data

Table 6 Some values of log K_{oct} calculated through eqn. (7) with the regression constants in Table 1

Solute	
Tributylphosphine oxide	1.19
Isobutyrophenone	2.77
4-Ethylbenzoic acid	2.91
2,3-Dimethylphenol	2.52
2,4,5-Trimethylphenol	2.80
2,3,5,6-Tetramethylphenol	3.04
4-Chloro-1-naphthol	3.61
6-Bromo-1-naphthol	3.71
4-Phenylbutan-1-ol	2.30
5-Phenylpentan-1-ol	2.77
6-Phenylhexan-1-ol	3.31
δ-Valerolactam	−0.70

of Valsaraj and Thibodeaux, that log K_{oct} is not a very good general descriptor for the estimation of SDS log K_x values. We can see exactly the reason for this, by comparing the coefficients in eqn. (9) with those for the water–octanol equation in Table 1. For a given water–solvent system to be a good model as a descriptor, it is not necessary for the coefficients to be numerically the same in the water–solvent and the water–SDS equations. What is required is that the *ratio* of the coefficients within each equation should be the same. For the two main terms, the v/b ratio in the SDS eqn. (9) is 1.77, but in the octanol equation it is 1.10 only. Hence the relative effect of volume in the octanol equation is less than required for a good correlation. We can account for this simply by using volume as an addtional descriptor, as shown in eqn. (13). Now eqn. (12) has been

$$\log K_x = 1.129 + 0.504 \log K_{oct} + 1.216\, V_x \qquad (13)$$
$$n = 132, \rho = 0.9755, \text{sd} = 0.215, F = 1269$$

transformed into an equation that could be used as a first estimate of log K_x, with the advantage that both of the descriptors can be calculated from a knowledge of structure. The McGowan volume can easily be obtained using the algorithm of Abraham,[10] and log K_{oct} can be calculated by the CLOGP program of Leo.[33] Our analysis using the general eqn. (7) also explains the success of eqn. (6), above, because it is known[34] that molar refraction is well correlated with volume.

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