

Hydrogen bonding. Part 41.¹ Factors that influence the distribution of solutes between water and hexadecylpyridinium chloride micelles



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The partition of 46 compounds between water and hexadecylpyridinium chloride (CPC) micelles at 298 K has been correlated through eqn. (i), using the water–CPC partition coefficients of Christian and co-workers. These 46 compounds include cyclohexane, pentan-1-ol and 44 varied aromatic compounds.

$$\log K(\text{CPC}) = -0.437 + 0.973 R_2 - 0.736 \pi_2^{\text{H}} + 0.769 \Sigma a_2^{\text{H}} - 2.840 \Sigma \beta_2^{\text{O}} + 3.386 V_x \quad (\text{i})$$

$n = 46$, $r = 0.9737$, $\text{sd} = 0.147$, $F = 146$

The water–CPC micelle partition coefficient is denoted as $K(\text{CPC})$, and the solute explanatory variables, or descriptors, are R_2 the excess molar refraction, π_2^{H} the dipolarity/polarizability, Σa_2^{H} and $\Sigma \beta_2^{\text{O}}$ the hydrogen-bond acidity and basicity, and V_x the McGowan characteristic volume in units of ($\text{cm}^3 \text{mol}^{-1}$)/100. The number of solutes is n , the correlation coefficient is r , the standard deviation is sd , and the F -statistic is F . The main factors that influence partition are solute hydrogen-bond basicity that reduces partition into the CPC micelles, and solute volume that increases partition. It can be deduced from eqn. (i) that CPC micelles behave as though they are highly polar, of very high hydrogen-bond basicity and of moderate hydrogen-bond acidity and hydrophobicity. Comparison with water–alcohol partitions indicates that CPC micelles are as hydrophobic as water-saturated pentanol. Analysis of $\log K$ values for water to CPC and to sodium dodecyl sulfate (SDS) micelles, using scaled particle theory, shows that the main factor leading to larger $\log K$ values in the CPC system is an increase in dispersion interactions between solute and the CPC pseudophase.

The coefficients in eqn. (i) are the same in sign and similar in magnitude to those previously reported by Quina and co-workers for partition between water and hexadecyltrimethylammonium bromide micelles and for partition between water and dodecyltrimethylammonium bromide micelles.

The use of micellar systems in separation science is of increasing importance, for example in micellar-enhanced ultrafiltration,² micellar liquid chromatography³ and micellar electrokinetic capillary chromatography.³ In order to understand these systems, a knowledge of the factors involved in the solubilization of solutes by micelles would be helpful, and methods of prediction of water–micelle partition coefficients would be particularly useful. One micellar system that has been intensively investigated is hexadecylpyridinium chloride (CPC) for which Christian and co-workers^{2,4–9} have determined numerous water–CPC partition coefficients, defined using eqn. (1). In an

$$K(\text{CPC}) = \frac{[\text{Concentration of solute in micelle/mol fraction}]}{[\text{Concentration of solute in water/mol dm}^{-3}]} \quad (1)$$

early paper, Christian and co-workers⁴ converted values of $K(\text{CPC})$ to the corresponding gas–CPC partition coefficients, $K'(\text{CPC})$ through use of the limiting gas–water partition coefficient for the solutes concerned. They then analysed the $\log K'(\text{CPC})$ values for nine solutes by a group contribution scheme, but have not subsequently extended the scheme to the large number of other solutes examined.^{4–9} Treiner¹⁰ has set out a group contribution scheme for the partition of aliphatic com-

pounds between water and dodecyltrimethylammonium bromide micelles, but the scheme of Christian and co-workers⁴ suffers from the disadvantage that conversion to $K'(\text{CPC})$ values restricts application of the method to solutes for which gas–water partition coefficients are available. There have also been correlations of various water–micelle partition coefficients with water–octanol partition coefficients, as $\log P_{\text{oct}}$, with moderate success,^{1,11,12} although not for the water–CPC system.

Our aim is to set up an equation that will relate the water–CPC partition coefficients of Christian and co-workers to solute descriptors, and hence to obtain information on the solute factors that influence partition, and to be able to estimate further partition coefficients.

The method we use is based on the general solvation eqn. (2).

$$\log \text{SP} = c + rR_2 + s\pi_2^{\text{H}} + a\Sigma a_2^{\text{H}} + b\Sigma \beta_2 + vV_x \quad (2)$$

In eqn. (2),^{13,14} $\log \text{SP}$ is the dependent variable, which we shall take as $\log K$ for the water–CPC partition. The independent variables are solute properties or descriptors as follows:^{13,14} R_2 is an excess molar refraction; π_2^{H} is the solute dipolarity/polarizability; Σa_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,¹⁵ cal-

Table 1 Coefficients in eqn. (2) for some water-phase partitions^{1,17,19,20}

Phase	<i>c</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i> ^a	<i>v</i>	mass% ^b
Isobutyl alcohol	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	0.008	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
SDS ^c	0.060	0.542	-0.400	-0.133	-1.580	2.793	
CPC ^c	-0.011	0.963	-0.722	0.761	-2.857	3.391	

^a The *b*-coefficient 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 Mass% water in the organic phase. ^c The *c*-constant refers to the molar concentration scale in both water and the micelle pseudophase.

culated from molecular structure, with units of (cm³ mol⁻¹)/100. Use of the basicity parameter, $\Sigma\beta_2$, is not quite straightforward, because the relative hydrogen-bond basicity of solutes can alter with the solvent system.¹⁶⁻¹⁸ However, since the solubilizing environment in a micellar pseudo phase is rather aqueous, we expect our $\Sigma\beta_2^O$ descriptor to be the appropriate one to use in eqn. (2).

The coefficients in eqn. (2) convey information about the system under investigation. In Table 1 are collected the coefficients for a number of partitions from water to various phases,^{1,17,19,20} together with the mass% water in the water-saturated phases. The coefficients will relate to the difference in particular properties between water and the phase in question. The *r*-coefficient gives the relative ability of the phase to interact with π - and *n*-electron pairs, the *s*-coefficient is a measure of the difference in dipolarity/polarizability of the phase and water, the *a*-coefficient measures the difference in hydrogen-bond basicity, the *b*-coefficient measures the difference in hydrogen-bond acidity, and the *v*-coefficient is a measure of the phase hydrophobicity. The *c*-coefficient relates to the value of log SP for a solute with zero values for all the descriptors, but also contains a contribution for the particular standard state used in the definition of SP. In the present work, the standard states used for log *K*(CPC) are as in eqn. (1).

We have recently applied eqn. (2) to partition between water and sodium dodecylsulfate (SDS),¹ and find eqn. (3). In eqn.

$$\log K_x = 1.201 + 0.542 R_2 - 0.058 \pi_2^H - 0.057 \Sigma a_2^H - 0.133 \Sigma \beta_2^O + 2.793 V_x \quad (3)$$

$$0.400 \pi_2^H - 0.133 \Sigma a_2^H - 1.580 \Sigma \beta_2^O + 2.793 V_x$$

$$0.071 \quad 0.060 \quad 0.082 \quad 0.073$$

$$n = 132, r = 0.9849, sd = 0.171, F = 817$$

3, *K_x* is the water-SDS mol fraction partition coefficient (mol fraction standard states in both water and the micelle), but this affects only the constant term. The standard deviations of the coefficients are under the coefficients, *n* is the number of solutes, *r* is the correlation coefficient, *sd* is the regression standard deviation, and *F* is the *F*-statistic. The two main factors that influence water-SDS partition coefficients are thus solute hydrogen-bond basicity that decreases log *K_x*, and solute volume that increases log *K_x*.

Results and discussion

The water-CPC partition coefficients obtained by Christian and co-workers are given in Table 2. For a number of solutes, more than one value has been recorded, and we give the values that we have used; usually, we selected the most recent value. We did not use the log *K* values that we have deduced from the given log *K'* values for gas-CPC partition, because we do not know the exact gas-water partition coefficients used⁴ by Chris-

tian and co-workers. We are left with log *K* values for 48 varied solutes, covering a wide range of functionality. The necessary descriptors for these compounds are given in Table 3. When we applied eqn. (2) to the 48 log *K* values, we found that 3-phenylpropanoic acid and 2-chlorophenol were considerable outliers. We have no explanation for this, but for the remaining 46 solutes we deduced eqn. (4). The statistics in eqn. (4) are

$$\log K(\text{CPC}) = -0.437 + 0.973 R_2 - 0.198 \pi_2^H + 0.150 \Sigma a_2^H - 0.736 \Sigma \beta_2^O + 3.386 V_x \quad (4)$$

$$0.107 \quad + 0.088 \quad - 0.166 \quad + 0.210$$

$$n = 46, r = 0.9737, sd = 0.147, F = 146$$

reasonable, bearing in mind that for the solutes in Table 2 for which repeated log *K*(CPC) values are reported, there is some variation. For example, log *K*(CPC) for pentan-1-ol is 1.18² or 1.31,⁹ and log *K*(CPC) for phenol is 1.79² or 1.91,^{7,8} so that an *sd* value of 0.147 log units is not out of line with experimental error. We checked any cross-correlations between descriptors; the strongest are between *R*₂ and π_2^H (*r* = 0.658) and between $\Sigma\beta_2^O$ and *V_x* (*r* = 0.396), which can be tolerated.

From eqn. (4), it can be seen that solute excess molar refraction (weakly), solute hydrogen-bond acidity (weakly) and solute volume (strongly) all increase log *K*(CPC), whereas solute dipolarity/polarizability (weakly) and solute hydrogen-bond basicity decrease log *K*(CPC). The volume term is very important, as can be seen from the log *K*(CPC) values for 4-isopropylbenzaldehyde/benzaldehyde, 4-isopropylaniline/aniline and 4-isopropylphenol/phenol. The effect of the introduction of the isopropyl group is to increase log *K*(CPC) by 1.30, 0.91 and 1.11 units, respectively. This is largely due to a change in volume, which would increase log *K*(CPC) by 1.34 units. Other minor factors account for the difference. We can show exactly the solute effect on the log *K*(CPC) values, through a term-by-term analysis of eqn. (4). This is given in Table 4, for three representative solutes; benzene, *p*-toluidine (a base) and *m*-cresol (an acid). Among these aromatic compounds, the *rR*₂ and *sπ*₂^H terms do not vary very much; indeed the sum of these two terms is almost constant. The effect of the *aΣa*₂^H term is quite small; even for the quite strong hydrogen-bond acid, *m*-cresol, this term amounts to only -0.44 log units. The *bΣβ*₂^O term is more significant, and for the hydrogen-bond base, *p*-toluidine, reduces log *K* by 1.48 units. Eqn. (4) is therefore not merely a correlation equation, but it enables solute effects on log *K*(CPC) values for water-CPC micelle partitions to be analysed in a chemically interpretable way.

It is of considerable interest to compare solute effects on the water-CPC system, with those on the water-SDS system. The main differences between eqn. (4) and eqn. (3) are that (*i*) hydrogen-bond acidity increases the log *K*(CPC) value, but

Table 2 Values of log K (CPC) for water–CPC partition

Solute	Ref.	log K	Taken
Pentane	4	2.86	
Hexane	4	3.64	
Cyclohexane	4	3.06	
Cyclohexane	2	2.63	2.63
Butan-1-ol	4	1.32	
Pentan-1-ol	4	1.71	
Pentan-1-ol	2	1.18	
Pentan-1-ol	9	1.31	1.31
Benzene	4	2.04	
Benzene	2	1.60	1.60
Toluene	4	2.42	
Chlorobenzene	2	2.21	2.21
Benzaldehyde	8	1.38	1.38
4-Methylbenzaldehyde	8	1.83	1.83
4-Ethylbenzaldehyde	8	2.35	2.35
4-Isopropylbenzaldehyde	8	2.68	2.68
4-Fluorobenzaldehyde	8	1.53	1.53
4-Chlorobenzaldehyde	8	2.03	2.03
4-Bromobenzaldehyde	8	2.19	2.19
4-Methoxybenzaldehyde	8	1.74	1.74
4-Nitrobenzaldehyde	8	1.70	1.70
4-Cyanobenzaldehyde	8	1.28	1.28
4-Trifluoromethylbenzaldehyde	8	2.17	2.17
Aniline	8	1.53	1.53
4-Methylaniline	8	1.72	1.72
4-Ethylaniline	8	2.13	2.13
4-Isopropylaniline	8	2.44	2.44
4-Fluoroaniline	8	1.53	1.53
4-Chloroaniline	8	2.25	2.25
4-Bromoaniline	8	2.48	2.48
4-Cyanoaniline	8	1.65	1.65
4-Methoxyaniline	8	1.20	1.20
4-Trifluoromethylaniline	8	2.70	2.70
Benzoic acid	6	1.86	1.86
Phenylacetic acid	6	1.81	1.81
3-Phenylpropanoic acid	6	1.82	1.82
Phenol	4	1.73	
Phenol	2	1.79	
Phenol	7, 8	1.91	1.91
<i>o</i> -Cresol	5	2.27	2.27
<i>m</i> -Cresol	5	2.28	2.28
<i>p</i> -Cresol	4	2.53	
<i>p</i> -Cresol	2, 5	2.29	
<i>p</i> -Cresol	8	2.35	2.35
4-Ethylphenol	8	2.73	2.73
4-Isopropylphenol	8	3.02	3.02
4-Fluorophenol	8	2.10	2.10
2-Chlorophenol	7	2.67	2.67
3-Chlorophenol	7	2.73	2.73
4-Chlorophenol	7, 8	2.90	2.90
4-Bromophenol	8	2.92	2.92
2,3-Dichlorophenol	7	3.35	3.35
2,4-Dichlorophenol	7	3.48	3.48
2,5-Dichlorophenol	7	3.28	3.28
2,6-Dichlorophenol	7	2.86	2.86
3,4-Dichlorophenol	7	3.52	3.52
4-Trifluoromethylphenol	8	2.96	2.96
4-Methoxyphenol	8	1.85	1.85
4-Cyanophenol	8	1.96	1.96
4-Nitrophenol	8	2.37	2.37

slightly decreases the SDS log K_x value, (ii) the b -coefficient is much larger in eqn. (4) than in eqn. (3), and (iii) the ν -coefficient is also much larger in eqn. (4) than in eqn. (3). On the general eqn. (2), effect (i) means that the CPC micellar pseudophase is a stronger hydrogen-bond base than water or the SDS micellar phase. Now quaternary ammonium ions, or quaternary pyridinium ions, would not be expected to act as hydrogen-bond bases, so our interpretation is that the chloride counter-ion in CPC acts as a stronger hydrogen-bond base than does the dodecylsulfate ion in SDS. This seems reasonable, because the negative charge in the dodecylsulfate ion will be considerably dispersed. Effect (ii) implies that the CPC micelle is a weaker hydrogen-bond acid than is the SDS micelle, which in turn is a weaker hydrogen-

Table 3 The solute descriptors used in the calculations

Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^O$	V_x
Cyclohexane	0.305	0.10	0.00	0.00	0.845
Pentan-1-ol	0.219	0.42	0.37	0.48	0.872
Benzene	0.610	0.52	0.00	0.14	0.716
Chlorobenzene	0.718	0.65	0.00	0.07	0.839
Benzaldehyde	0.820	1.00	0.00	0.39	0.873
4-Methylbenzaldehyde	0.862	1.00	0.00	0.42	1.014
4-Ethylbenzaldehyde	0.873	0.99	0.00	0.41	1.155
4-Isopropylbenzaldehyde	0.859	0.97	0.00	0.45	1.296
4-Fluorobenzaldehyde	0.711	1.01	0.00	0.39	0.891
4-Chlorobenzaldehyde	0.930	1.08	0.00	0.36	0.995
4-Bromobenzaldehyde	1.090	1.16	0.00	0.37	1.048
4-Methoxybenzaldehyde	0.920	0.96	0.00	0.61	1.073
4-Nitrobenzaldehyde	1.080	1.53	0.00	0.51	1.047
4-Cyanobenzaldehyde	0.950	1.53	0.00	0.50	1.028
4-Trifluoromethylbenzaldehyde	0.443	0.93	0.00	0.32	1.067
Aniline	0.955	0.96	0.26	0.50	0.816
<i>p</i> -Toluidine	0.923	0.95	0.23	0.52	0.957
4-Ethylaniline	0.942	0.91	0.23	0.56	1.098
4-Isopropylaniline	0.922	0.87	0.23	0.60	1.239
4-Fluoroaniline	0.760	1.09	0.28	0.41	0.834
4-Chloroaniline	1.060	1.13	0.30	0.35	0.939
4-Bromoaniline	1.190	1.19	0.31	0.35	0.991
4-Cyanoaniline	1.087	1.78	0.40	0.50	0.971
4-Methoxyaniline	1.050	1.10	0.23	0.72	1.016
4-Trifluoromethylaniline	0.555	0.94	0.37	0.25	1.010
Benzoic acid	0.730	0.90	0.59	0.40	0.932
Phenylacetic acid	0.730	0.95	0.60	0.63	1.073
3-Phenylpropanoic acid	0.730	1.20	0.60	0.58	1.214
Phenol	0.805	0.89	0.60	0.30	0.775
<i>o</i> -Cresol	0.840	0.86	0.52	0.30	0.916
<i>m</i> -Cresol	0.822	0.88	0.57	0.34	0.916
<i>p</i> -Cresol	0.820	0.87	0.57	0.31	0.916
4-Ethylphenol	0.800	0.90	0.55	0.36	1.057
4-Isopropylphenol	0.791	0.89	0.55	0.38	1.198
4-Fluorophenol	0.670	0.97	0.63	0.23	0.793
2-Chlorophenol	0.853	0.88	0.32	0.31	0.898
3-Chlorophenol	0.909	1.06	0.69	0.15	0.898
4-Chlorophenol	0.915	1.08	0.67	0.20	0.898
4-Bromophenol	1.080	1.17	0.67	0.20	0.950
2,3-Dichlorophenol	0.960	0.94	0.48	0.20	1.020
2,4-Dichlorophenol	0.960	0.84	0.53	0.19	1.020
2,5-Dichlorophenol	0.960	0.88	0.56	0.18	1.020
2,6-Dichlorophenol	0.900	0.90	0.38	0.24	1.020
3,4-Dichlorophenol	1.020	1.14	0.85	0.03	1.020
4-Trifluoromethylphenol	0.420	0.90	0.72	0.07	0.969
4-Methoxyphenol	0.900	1.17	0.57	0.48	0.975
4-Cyanophenol	0.940	1.63	0.79	0.29	0.930
4-Nitrophenol	1.070	1.72	0.82	0.26	0.949

bond acid than bulk water. Again, this may have little to do with the acidity of the respective head-groups, and more to do with the hydrogen-bond acidity of the hydrated counter-ions that will form part of the micelle palisade layer or micelle surface, where solubilization of solutes takes place. The hydrated sodium ion will be a stronger hydrogen-bond acid than will the chloride ion, and this may be the reason why SDS is a more acidic pseudophase than is CPC. Of course, in both cases, water molecules near or just inside the surface will contribute to the phase hydrogen-bond acidity. Effect (iii) shows that the CPC pseudophase is more hydrophobic than is the SDS pseudophase. This is unlikely to be due to the 16 carbon atom chain, as compared to the 12 carbon atom chain, and a more plausible explanation possibly rests with head group effects. A number of workers have suggested^{21,22} that neutral (*i.e.* unsubstituted) aromatic compounds undergo weak but specific interactions with quaternary ammonium head groups in cationic micelles, although Viaene and co-workers²³ suggest that differences in interphase water penetration, micellar structure, and chain packing and folding are more important. If this weak but specific interaction does exist it seems to be limited to unsubstituted aromatic compounds, according to results obtained by Treiner and co-workers.²⁴ The r - and s -coefficients

Table 4 A term-by-term analysis of solubilization by CPC and SDS micelles through eqns. (4)–(6)^a

Solute	rR_2	$s\pi_2^H$	$a\Sigma a_2^H$	$b\Sigma\beta_2^O$	vV_x	Calc.	Obs.
CPC system ^a							
Benzene	0.59	-0.38	0.00	-0.40	2.43	1.79	1.60
<i>p</i> -Toluidine	0.90	-0.70	0.18	-1.48	3.24	1.69	1.72
<i>m</i> -Cresol	0.80	-0.65	0.44	-0.96	3.10	2.28	2.28
CPC system ^b							
Benzene	0.59	-0.38	0.00	-0.40	2.43	2.23	2.04
<i>p</i> -Toluidine	0.90	-0.70	0.18	-1.48	3.24	2.13	2.16
<i>m</i> -Cresol	0.80	-0.65	0.44	-0.96	3.10	2.72	2.72
SDS system ^c							
Benzene	0.33	-0.21	0.00	-0.22	2.00	1.96	1.81
<i>p</i> -Toluidine	0.50	-0.38	-0.03	-0.82	2.67	2.00	1.90
<i>m</i> -Cresol	0.45	-0.35	-0.08	-0.54	2.56	2.10	2.00

^a Calculated values from eqn. (4), with the descriptors in Table 2; observed values from Table 1. The constant term is -0.44 in all cases.

^b Calculated values from eqn. (6); the constant term is now -0.01.

^c Calculated values from eqn. (5); the constant term is 0.06.

do not differ very much in the SDS and CPC systems, and a closer analysis is necessary to probe exactly the differences in solubilization by SDS and CPC micelles.

First of all, the $\log K$ values for the water-CPC and water-SDS systems must be re-calculated using the same standard states. We choose the standard state of unit molar concentration in water and unit molar concentration in the micelle. Then with molar volumes of $0.375 \text{ dm}^3 \text{ mol}^{-1}$ for CPC and $0.250 \text{ dm}^3 \text{ mol}^{-1}$ for SDS, the constant term in eqn. (3) and eqn. (4) will alter, to yield eqns. (5) and (6). Note that change in standard

$$\log K^C(\text{SDS}) = 0.060 + 0.542 R_2 - 0.400 \pi_2^H - 0.133 \Sigma a_2^H - 1.580 \Sigma \beta_2^O + 2.793 V_x \quad (5)$$

$$\log K^C(\text{CPC}) = -0.011 + 0.973 R_2 - 0.736 \pi_2^H + 0.769 \Sigma a_2^H - 2.840 \Sigma \beta_2^O + 3.386 V_x \quad (6)$$

states affects only the constant term in eqn. (3) and eqn. (4); all the other coefficients remain unchanged.

We can now make an exact comparison of the two systems, and use the same three compounds that were analysed above. Details are given in Table 4. For any compound, the vV_x term will be larger in the CPC system and will result in $\log K^C$ being larger than in the SDS system. This can be shown both in Fig. 1, and by subtracting eqn. (5) from eqn. (6) to obtain eqn. (7).

$$\log K^C(\text{CPC}) - \log K^C(\text{SDS}) = -0.071 + 0.431 R_2 - 0.336 \pi_2^H + 0.902 \Sigma a_2^H - 1.260 \Sigma \beta_2^O + 0.593 V_x \quad (7)$$

In addition, an increase in solute excess molar refraction favours CPC over SDS, and an increase in solute dipolarity/polarizability favours SDS. However, these effects are not large, and for aromatic solutes with moderate values of R_2 and π_2^H , will largely cancel out, see Table 4. The effect of solute hydrogen-bond acidity does not cancel out, see Fig. 1 and eqn. (7), and any increase in Σa_2^H will favour CPC, as shown in Table 4 for *m*-cresol. Apart from the volume term, the largest effect is due to solute hydrogen-bond basicity. Both $\log K^C(\text{SDS})$ and $\log K^C(\text{CPC})$ are greatly reduced by an increase in solute $\Sigma \beta_2^O$ value, but the effect on the CPC system is much the larger, as can be seen in Fig. 1, from eqn. (7), and from the values for *p*-toluidine in Table 4. In our analysis, there is no particular specific interaction of benzene (or unsubstituted aromatics) with the pyridinium head group, and we tend to agree with the conclusions of Viaene and co-workers,²³ above.

There remains the problem of why the volume term is larger in the CPC system than in the SDS system. The volume term, as

Table 5 Calculation of gas-micelle partition coefficients

	He	Ne	Ar	Kr	Xe
CPC system					
$\log K^C$	0.22	0.28	0.64	0.83	1.11
$\log L_w$	-2.02	-1.96	-1.47	-1.21	-0.97
$\log L_{\text{CPC}}^a$	-1.80	-1.68	-0.83	-0.38	0.14
$\log L_{\text{CPC}}^b$	-2.03	-1.33	-0.60	-0.39	-0.20
SDS system					
$\log K^C$	0.25	0.30	0.59	0.75	0.98
$\log L_w$	-2.02	-1.96	-1.47	-1.21	-0.97
$\log L_{\text{SDS}}^a$	-1.77	-1.66	-0.88	-0.46	0.01
$\log L_{\text{SDS}}^b$	-1.97	-1.33	-0.67	-0.48	-0.31

^a From $\log K^C$ and $\log L_w$. ^b Calculated using scaled particle theory (SPT).

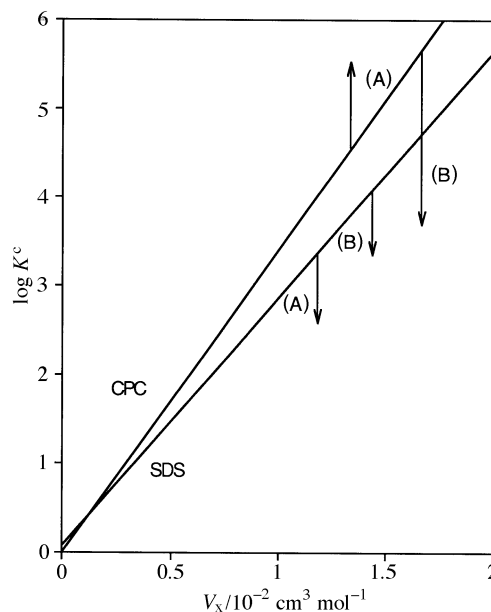


Fig. 1 Plots of $\log K^C$ for CPC (above) and SDS (below) against V_x , showing (A) the effect of an increase in solute Σa_2^H value by 1 unit in increasing $\log K(\text{CPC})$ and in decreasing $\log K(\text{SDS})$ and (B) the effect of an increase in solute $\Sigma \beta_2^O$ value by 1 unit in greatly decreasing $\log K(\text{CPC})$ and in decreasing $\log K(\text{SDS})$

explained previously,^{13,14} is made up of a cavity term plus a general (London) dispersion interaction term. We can make some headway through the calculation of the cavity term, using scaled particle theory, SPT, as set out by Pierotti²⁵ and by Wilhelm and Battino.²⁶ First, we calculate values of $\log K^C$ for the rare gases *via* eqn. (5) and eqn. (6), and combine these with values of $\log L_w$, where L_w is the gas-water partition coefficient²⁷ of the rare gases, to obtain $\log L_{\text{CPC}}$ and $\log L_{\text{SDS}}$, where L_{CPC} and L_{SDS} are the gas-micelle partition coefficients. The method is that used by Christian and co-workers;⁴ details are in Table 5. Knowing $\log L$ for the rare gases, and the micellar pseudophase molar volume, it is possible to obtain σ_1 and ε_1 for the micellar pseudophase through SPT, as outlined by Wilhelm and Battino;²⁶ here σ_1 is the pseudophase hard sphere diameter and ε_1 is the pseudophase energy parameter. For CPC, we take a monomer molar volume of $0.375 \text{ dm}^3 \text{ mol}^{-1}$ and an aggregation number of 84 (by comparison with that for hexadecyltrimethylammonium bromide,²⁸ and that for CPC itself²⁹ in $0.0175 \text{ mol dm}^{-3}$ NaCl) leading to a pseudophase molar volume of $31.500 \text{ dm}^3 \text{ mol}^{-1}$. In the case of SDS we use a monomer molar volume of $0.250 \text{ dm}^3 \text{ mol}^{-1}$ and an aggregation number of 64, leading to a pseudophase molar volume of $16.000 \text{ dm}^3 \text{ mol}^{-1}$. We then determined σ_1 and ε_1 for CPC as the values that lead to the best agreement of calculated and

Table 6 Contribution of dispersion interaction and cavity effects to the νV_x term in water–SDS and water–CPC partitions

System	log K_{cav}		$\Delta(\nu V_x)_{cav}^a$	$\Delta(\nu V_x)_{disp}^a$	νV_x
	Water	Micelle			
Argon–CPC	–3.32	–3.37	–0.05	0.68	0.63
Argon–SDS	–3.32	–3.25	0.07	0.52	0.59
Benzene–CPC	–6.92	–5.70	1.22	1.21	2.43
Benzene–SDS	–6.92	–5.59	1.33	0.67	2.00
6.5 Å–CPC ^b	–9.97	–7.69	2.28	1.91	4.19
6.5 Å–SDS ^b	–9.97	–7.57	2.40	1.05	3.45

^a Contribution to the νV_x term for transfer from water to the CPC or SDS micelle. ^b Calculations for a solute of $\sigma_2 = 6.5$ Å.

observed log L (CPC) values. A range of values from $\sigma_1 = 44.99$ Å and $\varepsilon_1 = 3000$ K to $\sigma_1 = 45.03$ Å and $\varepsilon_1 = 3400$ K gave the same agreement, and so we chose an average set of values, $\sigma_1 = 45.00$ Å and $\varepsilon_1 = 3150$ K, leading to the calculated log L (CPC) values in Table 5. Similarly, for SDS, a range of values from $\sigma_1 = 35.55$ Å and $\varepsilon_1 = 2200$ K to $\sigma_1 = 35.68$ Å and $\varepsilon_1 = 3000$ K gave the same agreement and we chose the average set of values $\sigma_1 = 35.62$ Å and $\varepsilon_1 = 2590$ K; the calculated log L (SDS) values are also given in Table 5. In all these calculations we used the σ_2 and ε_2 values for the rare gases of Wilhelm and Battino.²⁶

Then knowing σ_1 for the micelle pseudophase, as above, we can calculate the SPT cavity term in the pseudophase for any solute of known σ_2 value. A corresponding cavity term in water can be similarly calculated using²⁵ $\sigma_1 = 2.77$ Å and a molar volume of 0.1807 dm³ mol^{–1}. The cavity contribution to the νV_x term can be subtracted from the total νV_x term to give the contribution of the solute–micelle general (London) dispersion interaction. Results are in Table 6 for the case of the solutes argon ($\sigma_2 = 3.40$ Å), benzene ($\sigma_2 = 5.26$ Å), and a solute with $\sigma_2 = 6.50$ Å, corresponding to 4-isopropylphenol, the largest solute listed in Tables 2 and 3. In all three cases, it is evident that the cavity term itself would make the νV_x term slightly more negative in the water–CPC system than in the water–SDS system. The reason for the larger νV_x term in the CPC system is that there is a larger contribution from general (London) dispersion forces in CPC than in SDS. We conclude that a major factor in the larger values of log K^C for solutes in the water–CPC system over the water–SDS system is preferential solute–micelle general dispersion interactions in CPC over SDS. We note also that the same conclusion is obtained no matter what σ_1 and ε_1 combinations, above, for the pseudophases are used.

We can compare the SDS and CPC micellar phases with various wet alcohols through the coefficients listed in Table 1. The SDS micellar pseudophase is more comparable to water-saturated isobutyl alcohol, and the CPC micellar pseudophase to water-saturated pentanol (except for the difference in the a -coefficient). Again, this shows the more dipolar and more acidic character of the SDS phase, as compared to the more hydrophobic nature of the CPC phase.

For the SDS log K_x values, we showed¹ that there was only a moderate connection with log K_{oct} , where K_{oct} is the water–octanol partition coefficient, eqn. (8). However, comparison of

$$\log K_x = 2.01 + 0.693 \log K_{oct} \quad (8)$$

$n = 132$, $r = 0.9345$, $sd = 0.346$, $F = 896$

the SDS eqn. (3) with that for water–octanol partition, Table 1, showed that the relative effect of solute volume on log K_{oct} values was much less than on log K_x for the SDS system, and suggested incorporation of V_x as a descriptor. This yielded a reasonable predictive equation, especially since both log K_{oct}

Table 7 Comparison of coefficients in eqn. (2) for partition between water and various micelles

Micelle	r	s	a	b	ν	Ref.
SDS	0.54	–0.40	–0.13	–1.58	2.79	1
SDS	0.32	–0.57	–0.08	–1.84	3.25	31
CPC	0.97	–0.74	0.77	–2.84	3.39	This work
DTAB	0.57	–0.40	0.28	–1.82	2.98	31
CTAB	0.76	–0.32	1.02	–3.78	3.57	31

and V_x can be calculated from structure,^{15,30} eqn. (9). For the

$$\log K_x = 1.13 + 0.504 \log K_{oct} + 1.216 V_x \quad (9)$$

$n = 132$, $r = 0.9755$, $sd = 0.215$, $F = 1269$

CPC system only a poor relationship with log K_{oct} was obtained, for the same 46 solutes as in eqn. (4), eqn. (10). But

$$\log K(\text{CPC}) = 0.554 + 0.807 \log K_{oct} \quad (10)$$

$n = 46$, $r = 0.8751$, $sd = 0.298$, $F = 144$

now, the relative effect of volume on log K and log K_{oct} is quite close, and incorporation of V_x as a descriptor leads to no improvement over eqn. (10). The terms that alter relatively in the CPC and the log K_{oct} equations are those in R_2 and Σa_2^H ; incorporation of these as descriptors leads to eqn. (11), again for the 46 compounds in eqn. (4). This might have some

$$\log K(\text{CPC}) = -0.152 + 0.569 R_2 + 0.739 \Sigma a_2^H + 0.791 \log K_{oct} \quad (11)$$

$n = 46$, $r = 0.9651$, $sd = 0.165$, $F = 190$

advantage over eqn. (4), for the prediction of further log K (CPC) values, because both R_2 and log K_{oct} can be calculated from structure, and only the descriptor Σa_2^H needs to be known, or estimated. However, we should point out that the sd values in eqn. (4) and eqn. (11), 0.147 and 0.165 log units, mean that in practice only rather rough estimates of log K (CPC) can be made.

Finally, we compare our results on water–SDS and water–CPC partitions with those of Quina and co-workers,³¹ who used exactly the same general eqn. (2) to analyse water–micelle partition coefficients in four systems. Their equation for partition between water and Brij-35 was based on only 19 solutes, but equations for water–SDS, water–DTAB and water–CTAB were set up for 66, 39 and 42 solutes respectively; DTAB is dodecyltrimethylammonium bromide and CTAB is hexadecyltrimethylammonium bromide. In Table 7 we compare the coefficients in eqn. (2) reported by Quina and co-workers with those we have obtained. There is good agreement between the two sets of coefficients for water–SDS partitions, except for the magnitude of the ν -coefficient (2.79 or 3.25). More relevant are the coefficients for the three cationic micellar systems, CPC, DTAB and CTAB. We should not expect any exact agreement between an alkylpyridinium chloride micelle (CPC) and the alkyltrimethylammonium bromide micelles (DTAB and CTAB), but it is remarkable that the signs and general magnitude of the coefficients are the same for the three water–micelle partition systems. In all three systems, solute excess molar refraction (weakly), solute hydrogen-bond acidity (weakly) and solute volume (strongly) all increase partition into the cationic micelles, whereas solute dipolarity/polarizability (weakly) and solute hydrogen-bond basicity (strongly) decrease partition. If this were general for partitions between water and cationic micelles, it would greatly simplify

the selection of cationic micelles for particular separation purposes.

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