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Discussion

Relationship between liquid–liquid distribution and liquid–micelle distribution systems

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Micellar electrokinetic chromatography (MEKC) has quickly established itself as a common tool in separation science. Now that the initial evaluation phase of its development is nearing completion attention has turned to gaining an understanding of fundamental characteristics, especially an understanding of retention and its relationship to systematic method development. The separation buffer in MEKC contains an homogeneous dispersion of molecular aggregates (micelles) distributed throughout the solution. These micelles are composed of surfactant monomers with their hydrocarbon chains packed into a central core surrounded by the polar head groups. They differ from bulk solvents in several respects: they are spatially heterogeneous (the core region is hydrocarbon like and nearly anhydrous and the surface region is polar and highly solvated by water); on account of their small size and shape they have a high surface-to-volume ratio (interfacial solvents); and their size, shape, aggregation number, and other characteristic properties depend on their external environment (ionic strength, buffer ion, pH, etc.) The spatial heterogeneity of micelles is the reason for the speculation that solutes of different polarity are localized in different regions of the micelle: nonpolar solutes in the hydrocarbon core and polar solutes in the surrounding palisade layer. Under conditions of high external concentration penetration of the hydrocarbon core region of the micelles seems to be the only practical explanation of a large number of spectroscopic experiments and practical applications of micelles in detergency and synthetic chemistry. These results may not be helpful in interpreting retention data in MEKC in which the analyte concentration is much less than the micelle concentration, and solute distribution between the micelles and buffer solution occurs within the Henry's law region. Our opinion has been in favor of a single or average solvation environment for conditions germane to MEKC, and is reflected in recent mechanistic papers from this laboratory [1–5]. In a recent issue of this journal Katsuta and Saitoh [6] offered experimental evidence in support of a two-site sorption model for polar and nonpolar solutes in sodium dodecyl sulfate (SDS) micelles. We would like to present a different interpretation of their data in general agreement with our previous studies.

Katsuta and Saitoh [6] determined the distribution constants of 26 aromatic compounds and four inert metal acetylacetonates between SDS micelles and buffer (using MEKC) and compared these values to the liquid–liquid distribution constant for the same solutes between heptane and water, adopting the hydrocarbon solvent as a model for the hydrocarbon core of the micelles. A reasonably good correlation

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coefficient for the plot of the heptane–water distribution constants against the SDS micelle–buffer distribution constants for nine methyl- and chlorobenzene compounds and naphthalene was taken as evidence that these compounds were distributed to the hydrocarbon core of the micelle. The micelle–buffer distribution constants of phenols (without ortho substituents) and 2-naphthol were also reasonably well correlated with the heptane–water distribution constants but the difference in values between the distribution constants were large at 2.22 to 2.61 log units. This was interpreted as indicating much stronger interactions for polar solutes with hydrophilic (hydrogen-bond acid or hydrogen-bond donor) functional groups with the micelles than could be accounted for by the heptane–water distribution model resulting from their localization in the Stern layer surrounding the hydrocarbon core. Interactions with water contained in the Stern layer were identified as the likely reason for the difference in selectivity between the core and peripheral regions of the micelle. Thus, according to Katsuta and Saitoh the distribution of solutes of low polarity and those containing hydrogen-bond forming functional groups is explained by their localization in different regions of the micelle were the capacity of the micelle for specified intermolecular interactions is different.

Our approach to the interpretation of the sorption of organic compounds by micelles has been to construct a solvation parameter model for the distribution process as indicated below

$$\mathrm{SP} = c + mV_X + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^0 \qquad (1)$$

where SP is some experimentally observed retention property, in this case the distribution constant for the 26 aromatic compounds between the SDS micelles and buffer as published by Katsuta and Saitoh [6]. The solute descriptors (V_X, R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^0$) characterize the ability of the solute to participate in defined intermolecular interactions, as described elsewhere [1–5], and the system constants the complementary properties of the distribution system. The *r* constant determines the difference in capacity of the micelles and mobile phase (separation buffer and additives) to interact with solute n- or π-electrons; the *s* constant to the difference in capacity of the micelles and mobile phase to take part in dipole–dipole and dipole-induced dipole interactions; the *a* constant is a measure of the difference in hydrogen-bond basicity of the micelles and the mobile phase; the *b* constant is a measure of the difference in hydrogen-bond acidity of the micelles and mobile phase and the *m* constant is a measure of the relative ease of cavity formation for the solute in the micelles and mobile phase. From the data of Katsuta and Saitoh we obtained the following model

$$\begin{aligned}\log K_X = {} & 3.13(\pm 0.23)V_X + 0.34(\pm 0.12)R_2 \\ & - 0.53(\pm 0.10)\pi_2^H - 0.12(\pm 0.07)\Sigma\alpha_2^H \\ & - 2.06(\pm 0.13)\Sigma\beta_2^0 + 0.19(\pm 0.18) \qquad (2)\end{aligned}$$

with a multiple correlation coefficient $\rho = 0.984$, standard error (S_E) = 0.087, and Fischer *F*-statistic = 123. Statistically the fit is reasonable and the system constants make chemical sense. A plot of the experimental distribution constants and those predicted by the model, Fig. 1, does not indicate any difference in the accuracy of the prediction for the ten nonpolar compounds or for the phenols. Thus, the solvation environment of all solutes must be similar, since it is unlikely that a single model could be obtained for a chemically diverse group of compounds in distinctly different solvation environments. A similar model can be obtained for the heptane–water distribution system

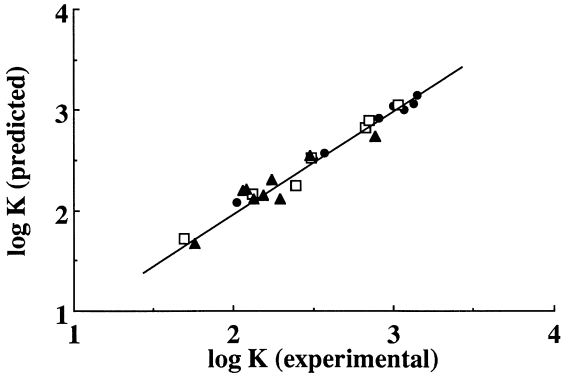

Fig. 1. Plot of predicted values for the solute distribution constants between buffer and SDS micelles, obtained from the solvation parameter model Eq. (2), and the experimental values given in [6]. ●=Alkyl- and chlorobenzene compounds (see Table 1); □=phenols (without ortho substituents identified in [6]) and 1-naphthol and 2-naphthol; and ▲=miscellaneous polar aromatic compound identified in [6].

$$\log K_D = 4.42(\pm 0.35)V_X + 0.63(\pm 0.18)R_2 - 1.87(\pm 0.15)\pi_2^H - 3.45(\pm 0.10)\Sigma_2^H\alpha - 4.79(\pm 0.20)\Sigma\beta_2^0 + 0.34(\pm 0.28) \quad (3)$$

with $\rho = 0.997$, $S_E = 0.132$ and F-statistic = 658. Clearly the system constants for the micellar system, Eq. (2), and those for heptane–water, Eq. (3), are very different in magnitude, and if it is assumed that the heptane–water system is a reasonable model for sorption interactions at the micelle core, then the typical environment for solute sorption in the micelle is significantly more polar than that of the core region.

The above results are in no sense anomalous. For example, in a recent study of the retention characteristics of 40 varied aromatic compounds in MEKC [2] (SDS concentration = 50 m*M*, pH 8, 20 m*M* sodium phosphate–borate buffer) the following system constants were obtained $m = 2.99$, $r = 0.46$, $s = -0.44$, $a = -0.30$, $b = -1.88$; and by headspace gas chromatography for the sorption of aromatic and aliphatic compounds to SDS micelles from water [5,7,8] $m = 3.02$, $r = 0$, $s = -0.58$, $a = -0.37$, $b = -1.65$. There is good agreement between the models in terms of the description of the solute sorption environment and the data presented by Katsuta and Saitoh given the anticipated differences resulting from the influence of the buffer type and concentration on the properties of the micelles. Abraham and Chadha [9] have provided reference values for alkane–water distribution systems ($m = 4.28$, $r = 0.65$, $s = -1.66$, $a = -3.52$, $b = -4.82$) that are in good agreement with the results of Katsuta and Saitoh. Abraham and Chadha have also summarized distribution constants for a further 21 water–solvent distribution systems, from which we can state that none of these water–solvent distribution systems can successfully imitate the solvation environment of SDS micelles. The solvents closest in properties to the micelle are water saturated alcohols (e.g., isobutanol and octanol), which have a similar capacity for dipole-type and hydrogen-bond base interactions, but are significantly weaker hydrogen-bond acids than the SDS micelles.

Now that we have a reasonable model for the sorption properties of the SDS micelle system (Eq. (2)), it is necessary to use the model to explain the original observations of Katsuta and Saitoh described earlier. In the plot of the distribution constants of the alkyl- and chlorobenzene compounds for the micelle system against the distribution constants for the heptane–water system, Fig. 2, six of the ten values are closely grouped on the plot, and the correlation coefficient (r^2) at 0.899 is only modest. The contribution of individual intermolecular interactions to the sorption process by the SDS micelles is given in Table 1. Since none of the solutes are hydrogen-bond acids the contribution of $a\Sigma\alpha_2^H$ is unimportant; the range of solute hydrogen-bond base/system hydrogen bond acid interactions are numerically small and closely grouped; and the contribution from solute lone pair electron interactions and dipole type interactions are numerically small, similar in value for the same compound, and opposite in sign resulting in a significant degree of self-canceling. Thus the dominant term resulting in differences in solvation between the micelle system and the hexane–water system is the relative ease of cavity formation. The slope of the plot in Fig. 2 is 0.815 in good agreement with the ratio of the m system constants for the heptane–water and the sodium dodecyl micelle

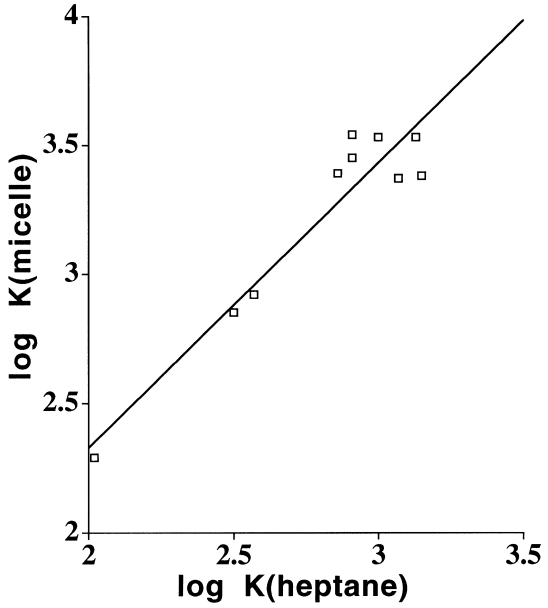

Fig. 2. Plot of the distribution constant for SDS micelle buffer system against the distribution constant for hexane–water for alkyl- and chlorobenzenes identified in Table 1. Data from [6].

Table 1
Contribution of intermolecular interactions to retention in the SDS micelles

Solute	Contribution to retention			
	mV_X	rR_2	$s\pi_2^H$	$b\Sigma\beta_2^0$
Benzene	2.24	0.21	−0.28	−0.29
Toluene	2.68	0.20	−0.28	−0.29
o-Xylene	3.12	0.23	−0.19	−0.33
m-Xylene	3.12	0.21	−0.28	−0.33
p-Xylene	3.12	0.21	−0.28	−0.33
Naphthalene	3.40	0.46	−0.49	−0.41
Chlorobenzene	2.63	0.24	−0.35	−0.14
1,2-Dichlorobenzene	3.01	0.30	−0.41	−0.08
1,3-Dichlorobenzene	3.01	0.29	−0.39	−0.04
1,4-Dichlorobenzene	3.01	0.28	−0.51	−0.04

distribution systems at 0.71. Given the nature of the plot in Fig. 2 better agreement cannot be expected, and small contributions from differences in polar interactions have also to be taken into consideration. Thus the correlation between the distribution constants for heptane–water and the SDS micellar system is due to solute selection (limited capacity for polar interactions) and the dominance of differences in phase cohesion as the solvation mechanism.

We have studied more than ten different surfactant systems and perhaps over 200 varied solutes in MEKC without finding the need to evoke a multisite model to explain their retention [1–5]. One study [10], out of several [11–13], that employed the solvatochromic model, claimed to show evidence for a multisite sorption mechanism related to differences in solute polarity. The solvatochromic model is based on different solute descriptors to those used in the solvation parameter model, not all of which are clearly derived from free energy processes. For this data also, a good fit was obtained using the solvation parameter model [5] without any need to invoke a special mechanism for some solutes based on localization in different micellar microenvironments. The reason for the lack of fit with the solvatochromic model we believe is due to deficiencies in the solute descriptors and from poor solute selection for the property segregated data sets resulting in the construction of local models that inadequately characterize the sorption site for the micelles. Although we would not care to state at this juncture that solutes with different capacities for polar interactions are never located in different regions of a micelle, we have been unable to find any evidence for this under conditions pertinent to MEKC, and in terms of a general model of retention in MEKC multisite models do not seem to be helpful (or necessary) to an understanding of the retention process.

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