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Discussion

Reply to “Relationship between liquid–liquid distribution and liquid–micelle distribution systems”: the solvation environment in micelles evaluated by the linear solvation energy relationship method

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Sir,

The structural future of surfactant micelles, compared with homogeneous solvent, is the existence of two or more divided parts with different properties, e.g., for the ionic micelles, the hydrocarbon core and the surface layer composed of water, counterions and a part of hydrocarbon chains [1,2]. It is a general view deduced from a lot of experimental data that solutes of different polarity are located in different regions of the micelles [3], and such a multi-site model for solubilization is also supported by the theoretical model [4]. In the earlier paper, we compared the distribution constants of various aromatic compounds between sodium dodecyl sulfate (SDS) micelles and water with those between heptane and water and concluded that the hydrogen-bonding solutes (hydrogen-bond donors and acceptors) and the non-hydrogen-bonding solutes are located in the different solvation environments in the micelles [5]. On the other hand, Poole and Poole [6] quantitatively expressed the retention factor in micellar electrokinetic chromatography (MEKC) based on the linear solvation energy relationships (LSERs) of Abraham [7] without considering different solubilization sites in the micelles. The success of the LSER

method for the distribution in the micelle–water systems led to their claim that all the solutes should be in a similar solvation environment, since it is unlikely that the single-site model for micelles could be obtained for a group of chemically diverse compounds in different solvation environments. This threw us the question whether the results obtained by the LSER method deny the multi-site model or not.

Now we suppose a micelle-like heterogeneous model composed of the core and the surface layer which are equivalent in the solvation environment to heptane and 1-octanol, respectively. As a matter of convenience, the volumes of these regions are assumed to be equal. Neglecting the adsorption on the interfaces, the distribution constant in molarity scale between this imaginary micelles and water ($K_{d,imc/w}$) is calculated from the liquid–liquid distribution constants in the heptane–water ($K_{d,hep/w}$) and in the octanol–water ($K_{d,oct/w}$) systems, i.e., $K_{d,imc/w} = (K_{d,hep/w} + K_{d,oct/w})/2$. The logarithmic values of $K_{d,hep/w}$ and $K_{d,oct/w}$ of 22 neutral aromatic compounds are shown in Table 1. As seen from these values, heptane and 1-octanol are obviously different in the solvation environment, especially for the hydrogen-bonding solutes. The amount ratio of the

Table 1
Distribution constants in heptane–water and 1-octanol–water systems

Solute	Log $K_{d,hep/w}^a$	Log $K_{d,oct/w}^b$
Benzene	2.29	2.13
Toluene	2.85	2.69
<i>o</i> -Xylene	3.39	2.80
<i>m</i> -Xylene	3.54	3.20
<i>p</i> -Xylene	3.45	3.15
Chlorobenzene	2.92	2.84
1,2-Dichlorobenzene	3.37	3.38
1,3-Dichlorobenzene	3.53	3.38
1,4-Dichlorobenzene	3.53	3.39
Naphthalene	3.38	3.37
Phenol	−0.90	1.46
<i>o</i> -Cresol	−0.05	2.04
<i>p</i> -Cresol	−0.35	1.94
3,5-Dimethylphenol	0.27	2.31
2-Chlorophenol	0.79	2.17
4-Chlorophenol	−0.11	2.35
1-Naphthol	0.55	2.98
2-Naphthol	0.30	2.84
Benzyl alcohol	−0.70	1.10
Anisole	2.10	2.11
Acetophenone	1.08	1.58
Nitrobenzene	1.43	1.85

^a Ref. [5].

^b Ref. [12].

solute located in the heptane-like core to that in the octanol-like surface layer, which is evaluated by the $K_{d,hep/w}/K_{d,oct/w}$ ratio, shows that the hydrogen-bonding solutes (except for anisole) are primarily located in the surface layer and that a half or more part of the non-hydrogen-bonding solutes are in the core region. The LSER method was applied to this multi-site model: the $K_{d,imc/w}$ values of all the solutes were treated by the multiple linear regression analysis based on Abraham's equation, $\log K_{d,imc/w} = c + mV_x/100 + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H$, where the solute descriptors (V_x , R_2 , π_2^H , $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$) were cited from the literature [8]. The results obtained are as follows: $c = 0.35 \pm 0.26$, $m = 3.79 \pm 0.31$, $r = 0.74 \pm 0.17$, $s = -1.35 \pm 0.21$, $a = -0.30 \pm 0.11$, $b = -4.19 \pm 0.21$; a multiple correlation coefficient $R = 0.994$, standard error $S_E = 0.104$, and F -statistic = 262. Such a good correlation proves that the success of the LSER method does not conflict with the multi-site model. The coefficients (c , m , r , s , a , b) express an overall environment of the imaginary micelles including two divided regions with

different properties, and all the solutes are not in the identical solvation environment.

Although it is commonly accepted that amphiphiles such as phenols are mostly located in the surface layer of the micelles, there is still no agreement upon the solubilization site of non-hydrogen-bonding aromatic compounds such as benzene [3]. However, in the SDS micelles the thermodynamic and spectroscopic studies [9,10] supported that a considerable part of the aromatic hydrocarbons are located in the core region. We have recently observed quite different patterns of the solubilization isotherms of benzene and phenol in the SDS solution, indicating that these solutes are obviously different in solubilization mechanism even in the low concentration region of the solutes [11]. The location of the solutes in the micelles is an important factor concerning the effect of additives on the retention factor in MEKC [5] and the dependence of the distribution constant on the solute concentration [11].

The LSER method would be useful to characterize the overall solvation property of the micelles. However, we should recognize the limitations of this method as a tool for studying the mechanism of solubilization in heterogeneous systems such as micelles.

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