Hemimicelle shape and size

T. Gu[1]) and H. Rupprecht

Institut für Pharmazie, Universität Regensburg, FRG
[1]) On leave from Department of Chemistry, Peking University, Beijing, China

Abstract: Based on the assumption of spherical hemimicelle with a hydrophobic core of diameter of maximum hydrocarbon chain length of surfactant, the aggregation numbers of hemimicelles have been calculated for several values of n, the carbon atoms of surfactant alkyl chain. The results are in reasonable good agreement with the hemimicelle aggregation number from experimental data for several corresponding systems. The other possibilities of the hemimicelle shape which allow to incorporate a larger number of hydrocarbon chains in a hemimicelle have also been discussed.

Key words: Hemimicelle shape; hemicelle size; hemimicelle aggregation number; spherical hemimicelle; elliptical hemimicelle.

The adsorption of surfactants onto solids from solutions has received considerable attention because of its importance in fields as diverse as froth flotation, detergency, enhanced oil recovery, drug preparations, etc. It is generally accepted that the adsorption of surfactants at solid/liquid interfaces may involve hydrophobic aggregation or hemimicelle formation through hydrophobic interactions between hydrocarbon chains of the surfactant molecules [1–4]. However, little is known about the detailed structure of adsorbates due to the phenomena of surface aggregation. In particular, the interpretation of experimental data based on the suggested coadsorption models [1–3] is not convincing concerning the influences of different counterions or very low saturation values of adsorption on several oxidic adsorbents.

Recently, a two-step adsorption model was established [4, 5]. It is characterized by a first step of adsorption where the surfactant ions or molecules are adsorbed by electrostatic attraction to oppositely charged surface sites and/or by strong specific interactions. In the second step further surfactant species are adsorbed by their hydrocarbon chains through hydrophobic interactions with the primarily adsorbed species. As a consequence, an empirical approach was proposed which allows the calculation of the aggregation number of hemimicelle (n_{hm}) from the adsorption isotherm. Thereafter, based on the mass-action model of surfactant adsorption, the theoretical approaches were developed to also allow the calculation of the hemimicelle aggregation number [6–8]. The results show that the n_{hm} values obtained by the mass-action model are in good agreement with those obtained by the empirical approach proposed earlier [6]. Very recently, based on the two-step adsorption mechanism and the mass-action treatment, a general surfactant adsorption isotherm equation has been derived which can interpret the various types of surfactant adsorption isotherms published in the literature [9, 10]. In addition, the general equation also includes the constant n_{hm} which can be evaluated by trial and error from experimental adsorption data. The n_{hm} values thus obtained are also in good agreement with those obtained by previous approaches [10]. All these results lead us to accept the proposed adsorption pictures and the mass-action treatment with confidence. However, the details of structure, shape, and properties of the hemimicelles still remain open. In this short communication (based on the simple model calculation)

some suggestions on the structure, shape and properties of the hemimicelle are proposed which can interpret the experimental results reasonably well.

The calculations are based on the following assumptions:

a) The hemimicelle contains a hydrophobic core consisting entirely of the hydrocarbon chains. It is assumed that no solvent enters the core.

b) According to Tanford, near room temperature the volume occupied by an alkyl chain of n carbon atoms embedded in the hydrocarbon core, v in nm^3/chain, can be represented by [11]

$$v = 0.0274 + 0.0269n, \tag{1}$$

and the maximum length (L) for a chain with n carbon atoms is (in nm) [11]

$$L = 0.15 + 0.1265n. \tag{2}$$

c) Globular hemimicelles with the diameter of a hydrophobic core correspond to the L of the amphiphile, and the number of hydrocarbon chains per hemimicelle n_{hm} is, thus, uniquely determined for each value of n by combination of Eqs. (1) and (2).

The volume and area per hydrophobic core of hemimicelle are

$$V_{hm} \text{ (in nm}^3) = \frac{4}{3} \pi (L/2)^3, \tag{3}$$

and

$$A_{hm} \text{ (in nm}^2) = 4\pi (L/2)^2, \tag{4}$$

respectively. If one assumes that all the hydrocarbon tails of the amphiphiles which form hemimicelle are located in the hydrophobic core, then the aggregation number of hemimicelle can be calculated from

$$n_{hm} = V_{hm}/v . \tag{5}$$

In Table 1 values of n_{hm} calculated for several values of n are compared to the experimental values of n_{hm} for several systems. For comparison, Table 1 also includes the aggregation numbers of spherical micelles with diameter of $2L$.

The results show that most of the calculated values of n_{hm} are in a correct order of magnitude with the experimental results derived by the two-step adsorption model. The large A_m/n_m and A_{hm}/n_{hm} values

suggest that only a small portion of the surfaces of micelle and hemimicelle are occupied by polar groups of the surfactant molecules. This favors that the adsorbed counterions on the micelle and/or hemimicelle surface be located between the polar head groups, not only because of electrostatic attraction, but also as a result of minimizing the area of hydrocarbon/water interface. In addition, A_{hm}/n_{hm} (1.25 nm^2/molecule) is about two times that of A_m/n_m (0.63 nm^2/molecule). This means that more counterions might be adsorbed per unit surface area of hemimicelles than on that of micelles.

Many experiments show that in the presence of electrolyte the n_{hm} values are generally somewhat higher than those in the absence of added electrolyte for the same amphiphiles [4, 5, 12]. To incorporate a larger number of hydrocarbon chains in a hemimicelle, there are several possibilities:

1) The diameter of the hydrophobic core of a spherical hemimicelle may be increased to a certain degree, if the mean distance between the closest neighboring adsorption sites on the solid adsorbent is larger than the aggregates.

2) The other possibilities may involve a distortion in the hemimicelle shape, i.e., ellipsoids of revolution. Both the prolate and oblate ellipsoids are possible, if the mean distance between the closest neighboring adsorption sites on the solid adsorbent is larger than the major axis a_0. However, if the mean distance between those adsorption sites is larger than the minor axis b_0, but smaller than the major axis a_0, only prolate ellipsoids are possible.

It should be noted that formation of an ellipsoid (b_0) from a sphere ($r = b_0$) is accompanied by an increase in total surface area (A_{hm}), but the increase is less than the increase in volume. The surface area per hydrocarbon chain is thus diminished. For amphiphiles with a single hydrocarbon chain this is equivalent to the surface area per molecule (A_{hm}/n_{hm}) and this is an important quantity because it is a measure of the separation between amphiphile head groups [11].

It should be noted that any actual system that forms hemimicelles will undoubtedly consist of a distribution of sizes and corresponding shapes about an optimal value of A_{hm}/n_{hm}. At a given total amphiphile concentration, this optimal value will be determined by the opposing influences of repulsion between head groups, and the tendency to avoid contact between the surface of the hydrophobic core and the solvent. Repulsion between head groups will

Table 1. Comparison of the calculated aggregation numbers of hemicelles and the experimental n_{hm} for several systems

n	L, nm	V nm³	For micelle[1]				For hemimicelle				n_{hm} (exp.) [2]
			$\overline{V}_m$ nm³	A_m nm²	n_m	A_m/n_m nm². mole-cule⁻¹	$\overline{V}_{hm}$	A_{hm}	n_{hm}	A_{hm}/n_{hm} nm². mole-cule⁻¹	
8	1.16	0.243	6.54	16.91	27	0.629	0.82	4.23	3-4	1.24	OMS-SiO$_2$ 5.7[8]; TX 100-SiO$_2$ 3.9– 4.0[8];
10	1.42	0.296	11.99	25.34	41	0.626	1.50	6.33	5	1.24	DEMS-SiO$_2$ 7.5–11.8[8]; DEMS-CB 11.6–13.3[10]; C$_{10}$PyCl-Aerosil 4.5[12];
12	1.67	0.350	19.51	35.05	56	0.629	2.11	8.76	7	1.25	SDS-PS (10^{-3}NaBr) 4.5[10]; C$_{12}$PyCl-Aerosil 6[12];
14	1.92	0.404	29.65	46.32	73	0.631	3.71	11.58	9	1.26	TPB-SiO$_2$ 12.7[6]; C$_{14}$PyCl-Aerosil 7.2[12];
16	2.17	0.458	42.80	59.17	93	0.634	5.35	14.79	12	1.26	CTAB-SiO$_2$ 9.0[7]; C$_{16}$PyCl-Aerosil 7[12];
18	2.43	0.512	60.10	74.20	117	0.632	7.51	18.55	15	1.26	
						av. 0.630				av. 1.25	

[1]) $\overline{V}_m$ and A_m are the volume and area per hydrophobic core of micelle, and n_m is the micelle aggregation number
[2]) SiO$_2$: porous silica $\overline{d}_{pore}$ = 9 nm
    CB: carbon black; this adsorbent is quite different from oxides PS: polystyrene

OMS: octhylmethylsuphoxide	TPB: tetradecylpyridinium bromide	C$_{10}$PyCl: dedylpyridinium chloride
DEMS: decylmethylsulphoxide	CTAB: cethyltrimethylammonium	C$_{12}$PyCl: Dodecylpyridiuniumchloride
SDS: sodium dodecylsulfate	CTAB: cethyltrimethylammonium chloride	C$_{14}$PyCl: tetradecylpyridinium chloride
		C$_{16}$PyCl: hexadecylpyridinium chloride

tend to increase A_{hm}/n_{hm}, but will become unimportant when A_{hm}/n_{hm} becomes sufficiently large. When A_{hm}/n_{hm} becomes large there will necessarily be contact between the core surface and water molecules, and forces arising to reduce A_{hm}/n_{hm}. The optimal value of A_{hm}/n_{hm} will be determined by proper balance between these factors [11]. In addition, the n_{hm} for a certain amphiphile increases with the concentration of added electrolyte, corresponding to a decrease in A_{hm}/n_{hm}. The decrease in A_{hm}/n_{hm} with added electrolyte is, of course, to be expected as a result of the decrease in the effect of electrostatic repulsion. For ionic amphiphiles, the counterions are attracted into the Stern layer formed by the amphiphile head groups of the hemimicelles; they reduce the repulsion between the amphiphile head groups by charge compensation. In this way, they favor the input of more amphiphile ions into the hemimicelle and, thus, also decrease A_{hm}/n_{hm}.

References

1. Fuerstenau DW, Wakamatsu T (1975) Faraday Discuss Chem Soc 59:157
2. Harwell JH, Hoskins JC, Schechter RS, Wade WH (1985) Langmuir 1:251
3. Koopal KL, Keltjens L (1986) Colloids and Surfaces 17:371
4. Gao Y, DU J, Gu T (1987) J Chem Soc Faraday Trans I 83:2671
5. Huang Z, Ma C, Gu T (1989) Acta Chim Sinica (Eng Ed) 2:105
6. Gu T, Gao Y, He L (1988) J Chem Soc, Faraday Trans I, 84:4471
7. Gu T, Huang Z (1989) Colloids Surfaces 40:71
8. Gu T, Zhu BY (1990) Colloids Surfaces 46:339
9. Zhu BY, Gu T (1989) J Chem Soc, Faraday Trans I, 85:3813
10. Zhu BY, Gu T, Zhao X (1989), J Chem Soc., Faraday Trans I, 85:3819
11. Tanford C (1972) J Phys Chem 76:3020
12. Ullmann E, Thoma K, Rupprecht H (1968) Arch Pharmaz 301:357

Authors' address:

T. Gu and H. Rupprecht
Institut für Pharmazie
Universität Regensburg
Universitätsstr. 31
8400 Regensburg, FRG