FREE ENERGY OF SYMMETRIC CATANIONIC
SURFACTANTS IN MICELLIZATION
AND SURFACE ADSORPTION

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The catanionic (cationic-anionic) surfactant is a special kind of surfactant, the two ions of which are both organic. In the case of that the hydrophobic hydrocarbon chains of the two organic ions are of the same length (strictly speaking, the two organic ions should be of the same surface activity), the catanionic surfactant is said to be symmetric.

The micellization and surface adsorption processes of the catanionic surfactants may be schematically illustrated in Fig. 1. In the aqueous solution, the two surface active ions are self-coiled[1], and in the micelle and adsorption layer they are of nearly equal number, i. e. the mole fraction of each ion is 0.5.[2,3] The surface tension changes from γ_0 to γ before and after adsorption. Then, according to the mass action model or charged pseudo-phase separation model[2], the

Fig.1 Micellization(M) and adsorption(S) of catanionic surfactant

standard free energy of micellization for the symmetric catanionic surfactant may be written as

$$\Delta G_m^0 = 2RT \ln \text{cmc} \tag{1}$$

where cmc is the critical micelle concentration(in terms of mole fraction). In the adsorption process (at cmc), besides the ln cmc term, the free energy change should contain the surface free energy change term, $(\gamma_0-\gamma)A_s$, (A_s: average surface molecular area of the oriented hydrophobic chain), due to adsorption. Thus

$$\Delta G_s^0 = 2RT \ln \text{cmc} - 2\pi A_s N_0 \tag{2}$$

where $\pi = \gamma_0 - \gamma$.

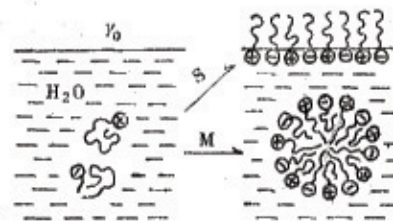The hydrophobic free energy of transfer of 1 mole catanionic surfactant from the

aqueous solution to the micelle "phase" would be [1]

$$\Delta G_m^0(HC) = 2\gamma_{HC-H_2O}(A_m - A_w)N_0$$
$$= 100(A_m - A_w)N_0 \tag{3}$$

where γ_{HC-H_2O} is the interfacial tension of hydrocarbon/water interface and which is assummed to be a value of $\sim 50 \text{mN} \cdot \text{m}^{-1}$; A_m is the average area occupied by a surfactant molecule at the surface of the micelle and A_w is the molecular area of the surfactant hydrocarbon chain in contact with water in the aqueous solution, and they may be calculated by assuming a liquid like spherical micelle and a self-coiled hydrocarbon chain of spherical form in the aqueous phase [1]; N_0 is the Avogadro number.

In the case of adsorption, the molar hydrophobic free energy of transfer at cmc comprises two parts, (1) due to the decrease in area of the hydrocarbon/water interface, (2) due to the vanishing of a water surface and simultaneous formation of a hydrocarbon surface, thus

$$\Delta G_s^0(HC) = 2[\gamma_{HC-H_2O}(A_s - A_w) - (\gamma_0 - \gamma)A_s]N_0 \tag{4}$$

where A_s is the average molecular area of the surface active ion at the surface, which can be obtained experimentally from the surface tension – log concentration curve by applying the Gibbs adsorption equation. [3] The $(\gamma_0 - \gamma)$ value at cmc for the common catanionic surfactant is in effect nearly equal to γ_{CH-H_2O} ($\sim 50 \text{mN} \cdot \text{m}^{-1}$) [3,4,5] and then Eqn (4) may be simplified,

$$\Delta G_s^0(HC) = -2\gamma_{HC-H_2O}A_wN_0 = -100A_wN_0 \tag{5}$$

ΔG_m^0 may be divided into $\Delta G_m^0(HC)$ and $\Delta G_m^0(W)$ for hydrocarbon chain and hydrophilic head respectively. Then, from equation (1)

$$2RT \ln \text{cmc} = \Delta G_m^0(HC) + \Delta G_m^0(W) \tag{6}$$

combining Eqns. (6) and (3)

$$\Delta G_m^0(W) = 2RT \ln \text{cmc} - 100(A_m - A_w)N_0 \tag{6a}$$

Similarly,

$$\Delta G_s^0(W) = 2[RT \ln \text{cmc} - \pi A_s N_0[- 100A_wN_0 \tag{6b}$$

For the homologous series of cationic and anionic surfactants, there should be

$$\Delta G_m^0(CH_2) = ([\Delta G_m^0]_2 - [\Delta G_m^0]_1)/(n_2 - n_1)$$
$$= [2/(n_1 - n_2)]RT \ln(\text{cmc}_1/\text{cmc}_2) \tag{7a}$$

$$\Delta G_m^0(CH_2) = ([\Delta G_m^0(HC)]_2 - [\Delta G_m^0(HC)]_1)/(n_2 - n_1)$$
$$= 100N_0[(A_{m2} - A_{w2}) - (A_{m1} - A_{w1})] \tag{7b}$$

$$\Delta G_s^0(CH_2) = ([\Delta G_s^0]_2 - [\Delta G_s^0]_1)/(n_2 - n_1)$$
$$= [2/(n_1 - n_2)]RT \ln(\text{cmc}_1/\text{cmc}_2)$$

$$-2N_0(\pi_2 A_{s2} - \pi_1 A_{s1})$$
$$\Delta G_s^0(CH_2) = ([\Delta G_s^0(HC)]_2 - [\Delta G_s^0(HC)]_1)/(n_2 - n_1) \qquad (8a)$$
$$= (100N_0[(A_{s2} - A_{w2}) - (A_{s1} - A_{w1})])/(n_2 - n_1)$$
$$- (2N_0(\pi_2 A_{s2} - \pi_1 A_{s1}))/(n_2 - n_1) \qquad (8b)$$

where the subscripts 1 and 2 are for the two surfactants with different n. (–number of HC –Chain) Eqn. (8b) would become

$$\Delta G_s^0(CH_2) = 100N_0(A_{w1} - A_{w2}) \qquad (9)$$

if $\pi_1 \approx \pi_2 \approx 50 mN \cdot m^{-1}$ (for the common catanionics).

The free energy of transfer in micellization and surface adsorption for the catanionic surfactants are calculated by the above mentioned equations and listed in table 1 and table 2.

The results show that (1) the $\Delta G_m^0(CH_2)$ values deduced from the mass action (or charged phase–separation) model and the hydrocarbon/water interfacial free energy model are fairly in accord with each other, being in a very reasonable value—— $\sim -3 KJ \cdot mol^{-1}$, [7] and this is also just the case for $\Delta G_s^0(CH_2)$; (2) from ΔG_m^0 (or ΔG_s^0) and $\Delta G_m^0(HC)$ (or $\Delta G_s^0(HC)$), a well constant value of $\Delta G_m^0(W)$ (or $\Delta G_s^0(W)$) for the homologous catanionic surfactant is obtained. Therefore, the reasonableness of the proposed models of micellization and adsorption for the catanionic surfactants and the correctness of the equations for calculating various standard free energies are obviously demonstrated, and also is the self–coiling of surfactant hydrocarbon chain in aqueous solution further evidenced. If the HC–chain is assumed to be of fully extended conformation in the aqueous solution, the A_w value would be much larger than that for the self–coiling conformation and the $\Delta G_m^0(CH_2)$ or $\Delta G_s^0(CH_2)$ value obtained from Eqn. (7b) or Eqn. (8b) is not $\sim -3 kT mol^{-1}$ but about $-6.5 kT mol^{-1}$ instead, which is obviously unreasonable, showing the improbability of the allstaggered conformation of the HC–chain.

Table 1 Standard free energy values of surfactants in micellization (kJ·mol⁻¹, 25°C)

Surfactant	ΔG_m^0	$\Delta G_m^0(HC)$		$\Delta G_m^0(W)$	$\Delta G_m^0(CH_2)$ Epn. (7a)	Eqn. (7b)
1 [3] $C_8 NM^+$-$C_8 S^-$	-44.2	-57.2		13.0	-3.45	-3.25
2 [4] $C_{10} NM^+$-$C_{10} S$	-58.0	-70.7		12.6	-2.89	-3.15
3 [5] $C_{12} NM^+$-$C_{12} S^+$	-69.4	-83.2		13.8		
4 [6] $C_8 NE^+$-$C_8 S^-$			Av.	13.1	-3.15	-3.25
	-43.7	-57.2	Av.	14.0	-3.13 Av.	-3.20
5 [6] $C_{10} NE^+$-$C_{10} S^-$	-56.2	-70.6				

* $C_n = C_n H_{2n+1}$, NM·N(CH₃)₃, NE·N(C₂H₅)₃. S·SO₄
cmc(mol·kg⁻¹): 1. 7.5×10^{-3}; 2. 4.5×10^{-4}; 3. 4.6×10^{-5}; 4. 8.2×10^{-3}; 5. 6.5×10^{-4}
(divided by 55.5 to give the mole fraction unit)

387

It is worth noting that the $-\Delta G_s^0(W)$ value is much larger than $-\Delta G_m^0(W)$. This may be due to the very close packing and hence the much more dehydration of the ionic head at the solution surface during the adsorption. (e. g. for $C_8NM^+-C_8S^-$, A_s is ~ 29 Å² whereas A_m, ~ 69 Å²)

The aqueous solutions of $C_nNM^+-C_nS^-$ become turbid beyond cmc and phase separation occurs[8]. It is often considered that this is not the real cmc but the solubility point and/or there is so giant a micelle that it separates as a new concentrated surfactant phase. However, the above mentioned results interestingly show that the cmc is real and the micelles are of sphericial shape, at least at cmc——The fact that $C_8NE^+C_8S^-$ can form a clear micellar solution and also have the standard free energy values similar to $C_nNM^+-C_nS^-$ may be taken as a collateral evidence.

Table 2. Standard free energy values of surfactants in
adsorption (kJ·mol⁻¹, 25°C)

Surfactant	ΔG_s^0	ΔG_s^0 (HC)	ΔG_s^0 (W)	ΔG_s^0 (CH₂) Eqn. (8a)		Eqn. (8b)
1. $C_8NM^+-C_8S^-$	-61.6	-93.8	37.7	-3.47		-3.18
2. $C_{10}NM^+-C_{10}S^-$	-75.5	-112.0	36.5	-2.83		-3.05
3. $C_{12}NM^+-C_{12}S^-$	-86.8	-124.2	37.4			
			Av. 37.2	-3.15		-3.12
4. C_8NE-C_8S	-62.6	-97.5	Av. 35.9	-2.80	Av.	-3.42
5. $C_{10}NE-C_{10}S$	-73.8	-110.9				

* * γ_{cmc} (mNm⁻¹): 1, 2 and 3, ~50; 4, ~45; 5, 47.
A_s(Å): 1, 2 and 3, ~29; 4, 35; 5, 31.

REFERENCES

[1] Zhao, Guoxi, Zhu Buyao, 物理化学学报, 1990, 6, 513
[2] Zhao, Guoxi, Zhu, Buyao, in "Phenomena in Mixed Surfactant Systems", J. F. Scamehorn, ed., ACS Symp. Ser. No. 311, ACS, Washington, D.C.(1986), p.184
[3] 赵国玺, 程玉珍, 欧进国, 田丙申, 黄智民, 化学学报, 1980, 38, 409
[4] Corkill, J. M., Goodman, J. F., Ogden, C. R., Tate, J. R., *Proc. Roy. Soc.*, 1963, 273, 84
[5] Rosen, M. J., "Surfactant and Interfacial Phenomena", 2nd ed., John-Wiley & Sons, New York, (1989), p.223
[6] 俞致健, 北京大学化学系博士研究生学位论文, 1987
[7] Tadros, Th. F., ed., "Surfactants", Ch. 2, Academic Press, London, 1984
[8] Yu. Z.-J., Zhao, G.-X., *J. Colloid Interface Sci.*, 1989, 130, 414, 421

对称正-负离子表面活性剂的胶团化和
表面吸附自由能

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摘　　要

根据所建议的表面活性剂疏水碳氢基在水溶液中自卷曲的分子构型和碳氢链/水界 面自由能降低模型导出了对称正-负离子表面活性剂胶团化和表面吸附自由能及疏水自由能公式，计算结果支持上述理论模型。

关键词：正-负离子表面活性剂　　自由能　　吸附　　胶团化作用