Critical Concentration for Micelle Formation and its Aggregation Number in Aqueous Solutions of Paraffin Chain Salts

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1. Introduction

The abrupt change in many physico-chemical properties (refractive index, freezing point, conductivity, osmotic pressure, viscosity, surface tension, absorption spectrum of dye etc.) and the appearance of colloidal properties have been attributed to the aggregation of paraffin chain salts into micelles and the concentration at which such change occurs has been termed the critical concentration for the formation of micelles.

With respect to the aggregation number of paraffin chain salts in aqueous solutions, it has become clear that the aggregation number is represented by a counter balance between the electrical work due to the aggregation of charges in the " heads " of paraffin chain ions and the decrease of the short-range non-electrical energy due to the aggregation of hydrocarbon portion[1,2], i.e., the decrease of oil-water interface. The electrical work which will be compeled at the micelle formation of paraffin chain salts (ions) increases much more rapidly than the aggregation number, while the decrease of the cohesive energy at the micelle formation is approximately proportional to the aggregation number. Hence, the energy decrease of the short-range force accompanied by the increase of one paraffin chain ion in the micelle becomes definite, while the energy increase of electrical force becomes greater with the increasing number of aggregations.

The increase of aggregation number, therefore, must be stopped, when the micelle is enlarged to the right size. If the aggregation number increases more than this, the energy depression per paraffin chain ion passing from the bulk of the solution into the micelle begins to decrease and the micelle of such an aggregation number can not exist. This is the reason why a paraffin chain salt shows a definite number of aggregation and a distinct critical micelle concentration at a given temperature. Thus the critical micelle concentration of a paraffin chain salt in equilibrium with its micelle is analogous to the solubility of ordinary substances in equilibrium with a separate phase. As the micelle formation is a reversible process, a paraffin chain salt in the bulk of the solution must be in equilibrium with the salt in the micelle. The critical micelle concentration can be calculated by equating the partial potential of a paraffin chain ion in the bulk of the solution and that in the micelle.[3]

2. Energy Change at the Micelle Formation

In the present paper, a cylindrical double layer model has been adopted as the micelle shape, its thickness is just twice the length of the long-chain salts molecule. We may express the total energy change at the micelle formation, E, in terms of electrical energy, E_e, and the short range cohesive energy, E_m.

A paraffin chain salt consists of the non-polar portion of hydrocarbon chain and the polar ionic group. If it is assumed that the former is a cylinder of radius r_0 and length l, the following values are given using surface-chemical data.

$$\begin{gathered} l=1.3\times m\text{Å} \\ s_0=\pi r_0^2=20.5\text{Å}^2 \\ r_0=2.56\text{Å} \end{gathered} \tag{3.1}$$

where m is the number of carbon atoms which construct a hydrocarbon chain, s_0 is the cross-sectional area of a hydrocarbon chain, and r_0 is its radius. Above the critical micelle concentration scores of these detergent molecules are aggregated to the micelle. If the micelle consists of n molecules of paraffin chain salts, the area of the cross section of this cylindrical micelle is $ns_0/2$, and the radius becomes

$$R=(ns_0/2\pi)^{1/2} \tag{3.2}$$

Although the edge of an actual micelle may probably be more circular than this model, calculation will be made according to this cylindrical double layer model. The side area of this cylindrical micelle is

$$S=4\pi(ns_0/2\pi)^{1/2}\times 1.3m\text{Å}. \tag{3.3}$$

The total inter-facial energy at the side of a cylindrical micelle is

$$\frac{4\pi(ns_0/2\pi)^{1/2}\times 1.3m\omega}{1.3\times 2\pi r_0}=(2n)^{1/2}m\omega \tag{3.4}$$

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[1] P. Debye: *J. Phys. & Colloid Chem*, **53**, 1 (1949).

[2] M. Nakagaki: *J. Chem. Soc. Japan.*, **72**, 113 (1950); **73**, 802 (1951).

[3] K. Shinoda: This Bulletin, **26**, 101 (1953).

where ω is the non-electrical work required to take one methylene radical from the micelle to the bulk of the solution, the denominator of the left-hand side of (3.4) being equal to the area per methylene radical.

As to the estimation of ω we have given attention to the fact that the solubility ratio of homologous aliphatic compounds into water diminishes to about 1/3 with the increase of each methylene radical.³⁾

That is $\omega \fallingdotseq 1.08kT$.

The total energy decrease due to the short-range force is given as follows, considering that the short-range energy depression per paraffin chain molecule is $m\omega$ and using (3.4),

$$E_{nm}=nm\omega-(2n)^{1/2}m\omega \tag{3.5}$$

Here E_{nm} is the short-range energy decrease at the micelle formation when the aggregation number is n.

In estimating the electrical work due to the micelle formation we have neglected the interaction between the two end discs, because there is an experimental fact that a non-polar oil such as benzene or hexane which is solubilized between the monolayer of the micelle shows an increase of x-ray spacing, but shows only a slight effect on the critical micelle concentration.[4,5]

Let us now calculate the electrical energy due to one disc, assuming that the disc has a uniform charge density, σ. Consider a surface element P on the end of a small disc, at a distance x from the center of the disc, as shown in Fig. 1.

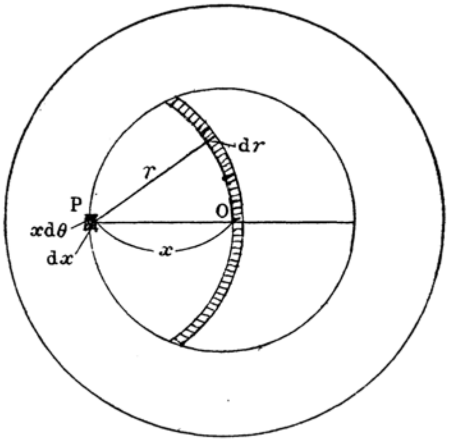

Fig. 1. disc

The area, at the distance of $r\sim r+dr$ from P on this small disc is

$$2\cos^{-1}(r/2x)r\,dr$$

and if we assume the surface charge density of this disc to be σ, the potential at the surface element P due to this portion is

$$\frac{2\cos^{-1}(r/2x)r\sigma^2 dr x d\theta dx}{Dr} \tag{3.6}$$

Integrating all over the small disc, and then integrating all over the disc, we obtain

$$\int_0^{(ns_0/2\pi)^{1/2}}\int_0^{2\pi}\int_0^{2x}\frac{2\cos^{-1}(r/2x)r\sigma^2 dr x d\theta dx}{Dr}$$

$$=\int_0^{(ns_0/2\pi)^{1/2}}\int_0^{2\pi}\frac{4\sigma^2x^2}{D}d\theta dx$$

$$=\int_0^{(ns_0/2\pi)^{1/2}}\frac{8\sigma^2x^2\pi}{D}dx=\frac{(2ns_0)^{3/2}\sigma^2}{3D\pi^{1/2}} \tag{3.7}$$

This is the electrical energy for the formation of one disc, which is composed of $n/2$ molecules. The total electrical energy for the formation of micelle, E_{ne}, is twice this.

Then we must consider the effect of an ion atmosphere. The correct treatment of the ion atmosphere is, however, not yet achieved and we have adopted an experimental parameter to express the effect of the ion atmosphere. That is to say, a reasonable constant must be multiplied to the electrical energy term at the micelle formation. Experimental constants given by Corrin and Harkins[6] for the effect of added salts on the critical micelle concentration are adopted as the parameter, considering that each long-chain ion instead of contributing a charge e to the micelle, would contribute less charge than this because of the adsorbed gegenions:[3]

Thus the total energy change at the micelle formation is

$$\begin{aligned}E_n=E_{nm}+E_{ne}&=nm\omega-(2n)^{1/2}m\omega\\&-\sqrt[4]{2}\,\sigma^2K^2n^{3/2}s_0^{3/2}/3D\pi^{1/2}+ne^2\kappa/3D\end{aligned} \tag{3.8}$$

With respect to the value of K reference may be made later, (4.7). The electrical energy of the long-chain ion in the bulk of the solution is expressed by $e^2\kappa/3D$.

3. Aggregation Number and the Critical Micelle Concentration

The aggregation number might be explained by the counter balance between the short-range energy and the electrical long-range energy. From this point of view it may be said that the micelle which requires maximum energy to take out one paraffin chain salt molecule must be the most stable, and the aggregation number is calculated by differentiating the energy for the micelle formation with respect to the aggregation number as follows.[7]

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[4] E. C. Lingafelter, O. L. Wheeler, and H. V. Tartar: *J. Am. Chem. Soc.*, **68**, 1940 (1946).

[5] R. W. Mattoon, R. S. Stearns, and W. D. Harkins: *J. Chem. Phys.*, **16**, 644 (1948).

[6] M. L. Corrin and W. D. Harkins: *J. Am. Chem. Soc.*, **69**, 683 (1947). cf. S. H. Herzfeld: *J. Phys. Chem.*, **56**, 959 (1952).

[7] Y. Ooshika: *Butseiron-Kenkyu* **44**, 30 (1951).

$$\frac{\partial E_n}{\partial n}=m\omega-m\omega/(2n_0)^{1/2}$$
$$-2\sqrt{2}\,\sigma^2K^2n_0^{1/2}s_0^{3/2}/D\pi^{1/2}+e^2\kappa/3D$$
$$=max \tag{4.1}$$

and

$$\frac{\partial^2 E_n}{\partial n^2}=m\omega/\sqrt{2}\,n_0^{3/2}-2\sqrt{2}\,\sigma^2K^2s_0^{3/2}/D\pi^{1/2}n_0^{1/2}$$
$$=0 \tag{4.2}$$

Calculating (4.2) we obtain the aggregation number of the micelle,

$$n_0=m\omega D\pi^{1/2}/4\sigma^2K^2s_0^{3/2} \tag{4.3}$$

Substituting n_0 (4.3) into the equation (4.1), we obtain

$$\frac{\partial E_{n0}}{\partial n}=m\omega-\sqrt{2}\,m\omega/n_0^{1/2}+e^2\kappa/3D \tag{4.4}$$

This is the maximum energy difference between the paraffin chain salt in micellar state and in non-aggregated state. Those micelles which would require maximum energy are certainly most stable, and other micelles which are smaller or larger will tend to increase or decrease their aggregation number until they assume the right size. This condition is given in (4.3), and the critical micelle concentration will be given by using (4.4).

As the micelle formation is a reversible process, paraffin chain salts in the bulk of the solution are in statistical equilibrium with those in the micelle. The critical micelle concentration can be obtained by equating the partial potential of each state. The relation has been derived already in the previous paper.3) That is

$$log\,C=log\,1000/v-(\chi-\chi')/kT-1 \tag{4.5}$$

Where $\chi-\chi'$ is the energy difference between the paraffin chain ion in the micellar state and that in the solute state; v is free volume per molecule; C is the critical micelle concentration in moles per liter.

Substituting the relation (4.4) into the equation (4.5), we obtain

$$log\,C=log\,1000/Nv-m\omega/kT+\sqrt{2}\,m\omega/n_0^{1/2}kT$$
$$-e^2\kappa/3DkT-1 \tag{4.6}$$

Introducing $\omega=1.08\,kT$, $D=80.8$ $\sigma=e/20.5\text{Å}^{-2}$, $e=4.8\times10^{-10}$ *esu*, and $s_0=20.5\text{Å}^2$ into (4.3) we obtain n_0, and then introducing n_0 into (4.6) and assuming $Nv=10$ *c.c.*, we obtain

$$log\,C=3.60-1.08m+2.77m^{1/2}K-0.77C^{1/2}-1 \tag{4.7}$$

where K is 0.57 for fatty acid soaps and 0.46 for sodium alkyl sulfate. Critical micelle concentrations of common soaps are calculatd using these values.

4. Qualitative Discussion of the Effect of Added Salts, Polar Oil and Non-polar Oil

1) The paraffin chain ions aggregated into the micelle attract the gegenions to positions near the micelle surface. But the gegenions, which tend to move away by thermal agitation, also attract the paraffin chain ions and tend to take them away from the micelle. This is one of the reasons why the ionic detergents are much more soluble into water than non-electrolyte of the same hydrocarbon chain length. As the adsorption of gegenions to the micelle increases with the increasing concentration of added gegenions, the aggregation number of long-chain ions in the micelle increases according to (4.3), and the critical micelle concentration decreases with the increase of the aggregation number according to (4.6). In other words the decrease of the critical micelle concentration in the presence of added salts is due to the decrease in the repulsive forces between the polar head groups of the molecules (ions) in the micelle. As the same ions are apart from the micelle due to the Coulombic repulsive force, the effect of salts is independent of the kind or valency of the ions of the same sign and only depends on the concentration and valency of gegenions.

2) Solubilization of polar compounds such as alcohols, fatty acids, etc. can be considered to involve penetration into the palisade layer of the micelle rather than incorporation into the micelle center.8,9) Thus the effective charge density on the micelle surface decreases with the increase of the penetration of the polar-nonpolar molecules into the micelle. If the mole fraction of alcohols penetrated into the micelle is x, the charge density will become from σ to $(1-x)\sigma$, and the aggregation number of paraffin chain salts increases according to (4.3), and the critical micelle concentration decreases according to (4.3), (4.6) and the free energy of mixing.3)

3) The extensive x-ray work of many investigators10-14) shows that the nonpolar oil enters the hydrocarbon center of the micelle. Thus the solubilization of nonpolar molecules does not affect the charge density, but only affects the interaction between discs. Since the thickness of the micelle is just twice the length, of the paraffin chain salts, the repul-

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8) W. D. Harkins, R. W. Mattoon, and R. Mittelmann: *J. Chem. Phys.*, **15**, 763 (1947).

9) J. H. Schulmann, and A. H. Hughes: *Biochem. J.*, **29**, 1243 (1935).

10) K. Hess, and J. Gundermann: *Ber.*, **70**B, 1800 (1937).

11) H. Kiessig, and W. Philippoff: *Naturwissenschaften*, **27**, 593 (1939).

12) J. Stauff: *Kolloid-Z.*, **89**, 224 (1939): **96**, 244 (1942).

13) E. W. Hughes, W. M. Sawyer, and J. R. Vinograd: *J. Chem. Phys.*, **13**, 131 (1945).

14) W. D. Harkins, R. W. Mattoon, and M. L. Corrin: *J. Colloid Sci.*, **1**, 105 (1946).

sion due to the same ions between discs and the attraction due to the gegenions around the micelle may be ignored, and the interaction between discs is supposed to be small. This anticipation coincides with the experimental results that the critical micelle concentration decreases slightly with the added hydrocarbons.[4,5,15]

Summary

The cylindrical double layer model for the micelle was adopted and the aggregation number was calculated by the condition that $\partial^2 E_n/\partial n^2=0$, and by using the aggregation number given by the above condition, an equation for the critical micelle concentration was derived. This equation shows that the critical micelle concentrations depend on the number of carbon atoms in the hydrocarbon chains and not on the kind of gegenions of the same valency. Moreover, the effect of added salts, polar oil and nonpolar oil on the aggregation number and on the critical micelle concentration in aqueous solution of paraffin chain salts was discussed qualitatively.

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[15] H. B. Klevens: *J. Phys. & Colloid Chem.*, **54**, 1012 (1950).