The Effect of Chain Length, Salts and Alcohols on the Critical Micelle Concentration

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Introduction

The effect of chain length and salts on the critical micelle concentration of colloidal electrolytes was measured by several authors,(1)~(6) and discussed by Corrin(7) and Hobbs.(8) The effect of alcohols and of alcohols and salts on the critical micelle concentration was measured by Corrin, Harkins and Herzfeld.(9)(10) However, the theoretical treatment was not completely done. In the present paper, the model of large flat micelle is adopted and the following experimental facts are explained theoretically:

1) The effect of chain length on the critical micelle concentration of paraffin chain salts follows the equation.(1)~(6)

$$\log_{10} C = -K_0 m + K_1 \qquad (1.1)$$

2) The decrease of critical micelle concentration by the addition of salts follows the equation.(6)

$$\log_{10} C = -K_2 \log_{10}(C + C_s) + K_3 \qquad (1.2)$$

3) The effect of alcohol chain length on the critical micelle concentration follows the equation.(9)

$$\log_{10}(\mathrm{d}C/\mathrm{d}C_a) = K_4 m' + K_5 \qquad (1.3)$$

4) The critical micelle concentration is a linear function of the alcohol concentration.(9)

$$C' = -(\mathrm{d}C/\mathrm{d}C_a)C_a + C \qquad (1.4)$$

where C: critical micelle concentration mole per liter

C_s: concentration of added salts in equivalents of effective ion per liter.

C_a: concentration of added alcohols mole per liter.

$K_0, K_1, K_2, K_3, K_4, K_5$: constant and K_0 is nearly equal to 0.3 and K_4 is nearly equal to 0.47 according to the experimental results.

m: number of carbon atoms of the soap molecule.

m': number of carbon atoms of alcohol molecule.

$\mathrm{d}C/\mathrm{d}C_a$: rate of change of critical micelle concentration with alcohol concentration in mole units.

Basic Assumption of the Theory

1) Due to the fact that a nonpolar oil such as benzene or hexane is solubilized between the monolayers of the soap micelle increasing X-ray spacing but showing only a slight effect on the critical concentration,(11)(12) we have ignored interaction of the two end discs.

2) In the light of the basic assumption of the Debye theory of the micelle, we may express the total energy change in the micelle formation in terms of the electrical energy and the cohesive energy, and the change of cohesive energy per one molecule by the formation of a micelle is assumed to be proportional to the number of carbon atoms. We express this in term of $m\omega$.

3) With respect to the value of ω, Debye(1) has adopted the heat of vaporization of the hydrocarbon, and he assumed $\omega \approx 2.0\,kT$. But Hobbs,(8) referring to the heat of vaporization, adopted $\omega = 1.0\,kT$ to explain the empirical results. Cassie and Palmer(14) assumed $\omega \approx 0.85\,kT$ or $1.2\,kT$ on the basis of adsorption data of Powney and Addison(15) at the water-xylene interface. We have calculated an approximate

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(1) G. S. Hartley, *Kolloid-Z*, **88**, 22 (1939).

(2) K. Hess, W. Philippoff and H. Kiessig, *Kolloid-Z*, 88, 40 (1939).

(3) A. B. Scott and H. V. Tartar, *J. Am. Chem. Soc.*, **65**, 692 (1943).

(4) J. Stauff, *Z. Physik. Chem*, **183** A, 55 (1938).

(5) W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).

(6) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).

(7) M. L. Corrin, *J. Colloid Sci.*, **3**, 333 (1948).

(8) M. E. Hobbs, *J, Phys. and Colloid Chem.* **55**, 675 (1951).

(9) S. H. Herzfeld, M. L. Corrin and W. D. Harkins *J. Phys. & Coll. Chem.* **54**, 271 (1950).

(10) M. L. Corrin and W. D. Harkins, *J. Chem. Fhys.* **14**, 640 (1946).

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

(12) R. W. Mattoon, R. S. Stearns and W, D. Harkins, *J, Chem. Phys.* **16**, 644 (1948).

(13) P. Debye, *J. Colloid Sci.*, **4**, 407 (1949).

(14) A. B. D. Cassie and R. C. Palmer, *Trans. Farad. Soc.*, **37**, 156 (1941).

(15) J. Powney and C. C. Addison, *Trans. Farad. Soc.* **33**, 1243 (1937).

value of ω from the fact that the solubility in water of aliphatic homologous compounds diminishes about 1/3 with the increase of one carbon atom. That is, the following equation is obtained for the homologous aliphatic compounds, since the solubility is thought to be proportional to the exponential of energy change per one molecule when it dissolves:

$$C_n/C_{n-1}\exp(-\omega/kT)=1/3 \qquad (2.1)$$

Where C_n/C_{n-1} is solubility ratio of the homologous aliphatic compounds of n carbon compound to $n-1$ carbon compound.

Calculating (2.1), we obtain

$$\omega=1.08\,kT \qquad (2.2)$$

This value will be referred to later.

The Electrical Potential at the Charged Surface of Lamellar Micelle

If long chain electrolytes are aggregated to the micelle, they will give effectively a plane charge at the micelle surface. The ordinary Debye-Hückel approximation $e\phi/kT \ll 1$ can not be used, because the contribution of electrical energy is too large to assume the above condition.(8)(14)(16) However, for a uniformly charged plane surface the Poisson-Boltzmann equation can be integrated without making this approximation.

$$\frac{d^2\phi}{dx^2}=-\frac{4\pi}{D}\sum z_i n_i e^{-z_i\varepsilon\phi/kT}$$

Where ϕ: electrical potential
x: the direction normal to the surface
D: the dielectric constant of the solution
Z: the valency of ion
n: number of ions per c.c. in the bulk of the solution

Giving the boundary condition and neglecting the contribution of the same ion in the bulk, Hobbs(8) obtained the equation for a uni-univalent electrolyte:

$$\phi=\frac{kT}{e}\log\left\{\frac{1000\,\pi\sigma^2}{2DRT}-\log C_i\right\} \qquad (3.1)$$

Where C_i: total concentration of gegen ion in mole per liter
σ: charge density at the micelle surface
e: electric elementary quantum

The integral work of introducing another charge of e into the surface of the micelle is given by ϕe. However, the alternative is to assume that each molecule contributes less than this because of the adsorbed gegen ions and the electrical potential due to the ion atmosphere in the solution. Accordingly, a factor K_6 should be introduced in this equation.

Then, $$(\phi-\phi')e=K_6kT\left\{\log\frac{1000\,\pi\sigma^2}{2DRT}-\log C_i\right\} \qquad (3.2)$$

Where ϕ': the electrical potential in the solution

Statistical Treatment of Critical Micelle Concentration

According to the analogy of the equilibrium condition between vapor and liquid we assumed the equilibrium condition between solute and pure liquid might be given, equating the partial potential of solute and that of liquid (micelle). The partial potential of a soap ion in the micelle is assumed to be.(17)

$$\mu^L=-\chi-kT\log(2\pi mkT)^{3/2}v/h^3-kT$$
$$-kT\log j(T)+pv^L \qquad (4.1)$$

and the partial potential of a soap ion in the solution may be given by the equation

$$\mu^S=-\chi'+kT\log CNkT/1000$$
$$-kT\log(2\pi m)^{3/2}(kT)^{5/2}/h^3-kT\log j'(T) \qquad (4.2)$$

Where v: free volume per one molecule
$j(T)$: partition function for the internal degrees of freedom, to be equal in the two phases
$-\chi$: uniform potential of liquid which is a smoothed value for all relative configurations of the given molecule (ion) and its neighbours, in this time χ contains electrical energy.
C: molar concentration of soap in molecular dispersion

As they are in equilibrium, equations (4.1) and (4.2) are equated, and the following equation is obtained:

$$\log C=\log 1000/Nv-(\chi-\chi')/kT-1$$
$$+pv^L/kT \qquad (4.3)$$

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(16) D. Edelson and R. M. Fuoss, *J. Am. Chem. Soc.*, **70**, 2832 (1948).

(17) R. H. Fowler and Guggenheim, E. A. "Statistical, Thermodynamics", Cambridge. 1939, p. 329.

Where
$\chi-\chi'$: energy difference between micellar state and solute state, and equal to the summation of cohesive energy change $m\omega$ and the electrical energy change $e(\phi-\phi')$ per one molecule.

At ordinary pressure (concentration), pv^L is negligibly small compared with kT, and might be omitted without loss of accuracy.

Then (4.3) can be written

$$\log C=\log 1000/Nv-m\omega/kT+e(\phi-\phi')/kT-1 \qquad (4.4).$$

This gives critical micelle concentration in unit of mole per liter.

The effect of Salts and chain Length on the Critical Micelle Concentration

Substituting (3.2) into (4.4), we obtain

$$\log C=\log\frac{1000}{Nv}+K_6\left\{\log\frac{1000\,\pi\sigma^2}{2DRT}-\log C_i\right\}-\frac{m\omega}{kT}-1 \qquad (5.1)$$

Introducing the values $\sigma=e/20.5$ A.^{2}, $D=80.8$, $T=291$°K., and $\omega=1.08\,kT$ and assuming $Nv=10$ cc., equation (5.1) becomes

$$\log_{10} C=-K_6\log_{10}(C+C_S)-0.47\,m+1.565+1.686\,K_6 \qquad (5.2).$$

Where C_S: the concentration of added salts and $C+C_S$ is equal to C_i

Comparing this to the experimental equation of Corrin and Harkins⁽¹⁸⁾ for Potassium Laurate:

$$\log_{10} C=-0.5696\log_{10}(C+C_S)-2.6172 \qquad (5.3).$$

We obtain

$$K_6=0.57 \qquad (5.4).$$

It is thus shown that the effect of added salts on the critical micelle concentration is given by the equation (1.2). When no salts was added we obtain from (5.2) and (5.4):

$$\log_{10} C=-0.57\log_{10} C-0.47\,m+1.565+0.96 \qquad (5.5).$$

Then $$\log_{10}C=-0.3\,m+1.61 \qquad (5.6).$$

Where m is the number of carbon atoms constituting a hydrocarbon chain, and for fatty acid soap one carbon atom which organizes carboxyl radical must be excluded. Thus the effect of chain length on the critical micelle concentration, equation (1.1), is explained. However, we must consider work of hydration to represents the experimental results for different head group.

The Effect of Alcohols on the Critical Micelle Concentration

The effect of alcohols upon the critical micelle concentration is a matter of some dispute. Herzfeld, Corrin, and Harkins measured the critical concentration of dodecylammonium chrolide in the presence of ethanol, 1-propanol, 1-buthanol, 1-hexanol, 1-heptanol, 1-decanol, 1-undecanol, 2-propanol, and trimethyl-carbinol.⁽⁹⁾ We have measured the critical micelle concentration of potassium laurate in the presence of ethanol, 1-buthanol, isoamylalcohol, 1-hexanol, 1-octanol, 1-decanol, and 2-ethylhexanol by the dye titration method. Many other authors have measured the effect of alcohols on the critical micelle concentration.⁽¹⁹⁾ ⁽²⁰⁾

However, the mechanism by which long chain alcohols depress the critical concentration was unknown. It has been definitely established that the long chain alcohols penetrate into the oriented structure of the micelle.⁽²¹⁾ An attempt is made in this paper to explain the effect of alcohols based on the concept of a decreased charge density at the micelle surface neglecting the interaction of the two end discs.

We denote the concentration of soap ion in the solution equilibrium with the soap micelle at the given temperature and pressure by $C_S°$, and the concentration of alcohol molecule in the solution equilibrium with the imaginary alcohol micelle at the given temperature and pressure by $C_A°$, and the concentrations of soap ion and alcohol in the solution equilibrium with the mixed micelle by C_S and C_A respectively. Assuming that the alcohol molecule and the soap ion in the micelle dissolve each other in the state of regular solution. We obtain:

$$C_S\doteqdot C_S°N_S/(N_S+N_A)\dots\dots N_S/(N_S+N_A)\approx 1 \qquad (6.1).$$

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(18) M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 683 (1947).

(19) G. L. Brown, P. F. Grieger and C. A. Kraus, *J. Am. Chem. Soc.*, **71**, 95 (1949).

(20) A. W. Ralston and D. N. Eggenberger, *J. Am. Chem. Soc.*, **70**, 783 (1948).

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

$$C_A \doteqdot K C_A{}^{\circ} N_A/(N_S+N_A) \ldots\ldots N_A/(N_S+N_A) \ll 1 \qquad (6.2).$$

Where $N_S/(N_S+N_A)$, $N_A/(N_S+N_A)$ is the molar fraction of soap and alcohol in the micelle. The molar fraction of soap is nearly equal to 1, and K is the constant. As there exists the equilibrium between the alcohol molecule in the water and that in the micelle, the concentration of alcohol equilibrium with mixed micelle is expressed as follows, using (6.2) and according to the analogy of equation (4.3):

$$C_A \propto N_A/(N_S+N_A)\exp\{-(\chi-\chi')/kT\} \qquad (6.3).$$

Where $\chi-\chi'=m'\omega$: cohesive energy change per one alcohol molecule.

If we denote molar fraction of alcohol in the micelle by x, we obtain

$$x \propto C_A \exp\{m'\omega/kT\} \qquad (6.4).$$

Thus the molar fraction of alcohol in the micelle increases proportionally as the bulk concentration increases. And the concentration of alcohol in the bulk equilibrium with the micelle of given molar concentration decreases about $1/3=\exp(-\omega/kT)$ with the increase of one hydrocarbon chain in the alcohol molecule. As the effect of solubilization on the alcohol concentration in the bulk must be negligibly small at the critical point, the concentration of added alcohol is equal to the concentration of alcohol in the bulk.

On the other hand the equilibrium concentration of soap ion in the bulk decreases, depending on the molar fraction of the soap ion in the micelle and on the decrease of the charge density. When the molar fraction of alcohol becomes x, the molar fraction of soap in the micelle becomes $1-x$, and the charge density decreases from σ to $(1-x)\sigma$.

Thus the critical concentration at the presence of alcohol is expressed using (6.1) and substituting $(1-x)\sigma$ into (5.1). Then we obtain:

$$(1+K_6)\log C'=(1+K_6)\log C+\log(1-x) + K_6\log(1-x)^2 \qquad (6.5).$$

Where C': critical micelle concentration of soap-alcohol mixed micelle, when the molar fraction of alcohol is x.

C: critical micelle concentration of soap micelle in the absence of alcohol

From (6.5) we deduce:

$$C'/C=(1-x)^{1+2K_6/1+K_6} \qquad (6.6).$$

When $K_6=0.57$, and the molar fraction x is small compared with unity, we obtain:

$$C'/C \doteqdot 1-1.36x \qquad (6.7).$$

Then using the equation (6.4), we obtain:

$$(C-C')/C \propto x \propto C_A\exp\{m'\omega/kT\} \qquad (6.8).$$

Thus for a given alcohol we obtain the relation:

$$C'=K_7C_A+C \qquad (6.9).$$

Where K_7: always negative

This equation expresses the fact that the critical concentration is a linear function of alcohol concentration, and corresponds to (1.4).

For various alcohol we obtain:

$$\log_{10}(C-C')/C_A=0.47\,m'+K_5 \qquad (6.10).$$

This equation expresses the effect of alcohol chain length on the critical concentration, and corresponds to (1.3). And the decreasing effect by the addition of alcohol is similar with any soap.

Comparison of the Effect of Alcohols with the Experimental Results

According to the data given by Herzfeld, Corrin, and Harkins$^{(9)}$ for dodecylammonium-chloride at 25°C. and those given by the author for potassium laurate at 10°C the rate of change of critical concentration with alcohol concentration is constant for a given alcohol but varies with the kind of alcohol employed.

Table 1 shows the comparison with the experimental data and the calculated values, assuming the rate of change of critical concentration by hexanol is 0.213 molar concentration per mole of alcohol.

Table 1

The Rate of Change of Critical Micelle Concentration in Molar Concentration per Mole of Alcohol

Alcohol	Dodecylammonium-chloride at 25°C.	Potassium-Laurate at 10°C.	Calculated C. M. C.
Ethanol	0.00145	0.00252	0.0026
Fropanol	0.00624	—	0.0079
1-Buthanol	0.0192	0.0258	0.0237
Isoamylalcohol	—	0.070	0.071
1-Hexanol	0.213	0.23	(0.213)
1-Heptanol	0.623	—	0.639
1-Octanol	—	1.87	1.92
1-Decanol	20.2	(8.64)	17.28
1-Undecanol	44.5	—	51.8

Thus the change of the effect of alcohols on the critical concentration has explained based on the solubility ratio of alcohols.

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