On the Critical Concentration of n-Aliphatic Acid Salts and Similar Compounds

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I. Introduction

It has been widely accepted that molecules of the soap dissolved in water are associated into grand molecules or micelles, owing to the cohesive interaction between their aliphatic long chain groups. However, properties of the micelle have little been studied theoretically, for examples, the form, dimension or electrolytic behaviour. Therefore, we can hardly explain the experimental facts and are troubled with complicated behaviours.

The aqueous solution of long chain fatty acid salts and the similar compounds (alkylsulfonic, alkylsulfuric, alkylpyridium, alkyltrimethyl-ammonium salts, etc.) changes their properties complicately with increasing concentration and there appear some nick points on the curve of the properties against the concentration. The nick point which appears in the most dilute region among these nick points is understood tacitly as the formation of cmparatively small micelles from the monomolecularly dissolved systems. This concentration is called the critical concentration, which can be determined from this nick point.

In actual case, the critical concentration can be obtained from the observation of the nick point in the density, electric conductivity, viscosity, refractive index, optical absorption, and surface tension against the concentration of a salt. When these experimentally observed values are compared quantitatively with the theoretical ones and the reasonable coincidences are obtained, the circumstances of this micelle formation can be more discretely explained. Therefore, it is valuable to discuss the critical concentration theoretically.

II. Electric Energy of a Monomolecular and an Associated Ion of Soap

A soap molecule is considered to be consisted of three parts, R, $-COO^-$, and M^+. R is an aliphatic long chain group which is strongly hydrophobe, so that in aqueous solution they are apt to associate with each other. On the other hand, carboxyl radical, as well as, metal ion M^+ are hydrophile and they disperse in water. The net work of these associating and dispersing forces induces the formation of the stable micelle.

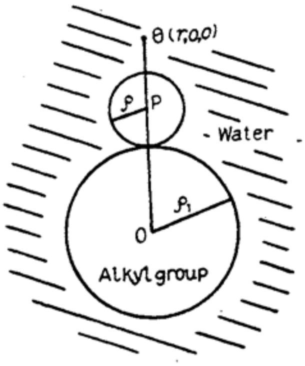

Fig. 1.

In water, the hydrophile property of carboxyl radical prevents itself from emboding in the alkyl group R, therefore it exists contacting directly with the water molecule (Fig. 1). Now the electrostatic energy of a spherical ion (radius ρ) charged with $\mathcal{E}$ in water (dielectric constant $\mu = 80$ at 20°), is

$$\epsilon_0 = \frac{\mathcal{E}^2}{2\mu\rho}$$

If we assign the analogous energy to a carboxyl radical ion, the electrostatic energy of a fatty acid ion is expressed as follows:

$$\epsilon_1 = \epsilon_0 + \epsilon_1(A) \tag{1}$$

where $\epsilon_1(A)$ is the extra electrostatic energy caused by the alkyl group (C_nH_{2n+1}) with low dielectric constant ($\mu_3 = 2.30$). First, we must estimate this extra energy. When the point charge exists on a point P, as shown in Fig. 1, the potential at a point excluding the point P is obtained by the expansion of the spherical harmonics (Appendix (I)). For example, the potential energy at Q in Fig. 1 is

$$\Psi = \frac{\mathcal{E}}{\mu(\rho+\rho_1)}\left\{\frac{\rho+\rho_1}{r-(\rho+\rho_1)} + \sum_0^\infty \frac{\nu(\mu-\mu_3)}{\nu(\mu+\mu_3)+\mu}\,\frac{{\rho_1}^{2\nu+1}}{(\rho+\rho_1)^\nu r^{\nu+1}}\right\} \tag{2}$$

The first term of this equation becomes infinite as $r \to (\rho + \rho_1)$, and if $r = \rho_1 + 2\rho$, it becomes $\mathcal{E}/\mu\rho$. Therefore we should consider that the first term is concerned of the self electrostatic energy ϵ_0 and the other terms represent extra $\epsilon_1(A)$ due to alkyl group. That is,

$$\epsilon_1(A) = \frac{\mathcal{E}^2}{2\mu(\rho + \rho_1)} \times \sum_0^\infty \frac{\nu(\mu-\mu_3)}{\nu(\mu+\mu_3)+\mu}\,\frac{{\rho_1}^{2\nu+1}}{(\rho+\rho_1)^{2\nu+1}} \tag{3}$$

The estimated values are almost trivial (Table 1). The form of associated molecule is also considered to be spherical at the first approximation. The energy ϵ_n can be written,

$$\epsilon_n = n\epsilon_0 + \epsilon_n(A) \tag{4}$$

where $\epsilon_n(A)$ is the extra energy relating to the centrally associated alkyl groups. Hereupon,

$$\epsilon_n(A) = \frac{1}{2}\, n\mathcal{E}\sum_1^n \psi_n + n\epsilon_1(A, \rho_n) \tag{5}$$

in which ψ_n is the electrostatic potential at point P, due to the n-th $-COO^-$ radical and $\epsilon_1(A, \rho_n)$ is the value of Eq. (3) in which ρ_1 is replaced with ρ_n.

$\epsilon_n(A)$ approaches rapidly to the value of

$$\frac{n^2\mathcal{E}^2}{2\mu(\rho + \rho_n)} \tag{6}$$

in the larger degree of association (Appendix (II)).

III. The Association of n-Fatty Acid Ions

The energy of a n-fatty acid ion in aqueous solution depends mainly on the interfacial energy between aliphatic group and water and on the electrostatic energy. Therefore fatty acid ions should be associated into a grand ion with appropriate degree of association owing to the counterbalancing action of the interfacial and electric energy in water. If we assume that the grand ion with n degrees of association is formed spherically, then the radius of this sphere, ρ_n, is

$$\frac{4\pi}{3}\rho_n{}^3 = nv, \quad \frac{4\pi}{3}\rho_1{}^3 = v \tag{7}$$

where v is the volume of an alkyl group. The interfacial energies are

$$\epsilon_1{}' = 4\pi\rho_1{}^2\sigma^* - \varDelta \qquad \text{for an ion,} \tag{8}$$

$$\epsilon_n{}' = 4\pi\rho_n{}^2\sigma^* - n\varDelta \qquad \text{for an associated ion,} \tag{9}$$

where σ^* is the microscopic interfacial free energy between alkyl group and water, and $\varDelta$ is the contribution due to the connection part of alkyl group to $-\mathrm{COO}^-$ radical.

The total energies are

$$\sum\epsilon_1 = \epsilon_0 + \epsilon_1(\mathrm{A}) + 4\pi\rho_1{}^2\sigma^* - \varDelta \qquad \text{for an ion,} \tag{10}$$

$$\sum\epsilon_n = n\epsilon_0 + \epsilon_n(\mathrm{A}) + 4\pi\rho_n{}^2\sigma^* - n\varDelta \qquad \text{for an associated,} \tag{11}$$

and the energy difference per molecule is

$$\begin{aligned}\varDelta\epsilon &= \sum\epsilon_1 - \left(\sum\epsilon_n/n\right)\\ &= 4\pi\rho_1{}^2\sigma^* - 4\pi\rho_n{}^2\sigma^*/n + \epsilon_1(\mathrm{A})\\ &\quad - n\mathcal{E}^2/2\mu(\rho+\rho_n)\end{aligned} \tag{12}$$

The most probable degree of association is defined by

$$\partial(\varDelta\epsilon)/\partial n = 0 \tag{13}$$

and is reduced to

$$\frac{4\pi}{3}\left(\frac{3}{4\pi}v\right)^{\frac{2}{3}}\sigma^* = \frac{\mathcal{E}^2}{2\mu}\frac{n}{\left(\frac{3v}{4\pi}\right)^{\frac{1}{3}}+\frac{\rho}{n^{\frac{1}{3}}}}\times$$

$$\left\{1-\frac{1}{3}\frac{\left(\frac{3}{4\pi}v\right)^{\frac{1}{3}}}{\left(\frac{3v}{4\pi}\right)^{\frac{1}{3}}+\frac{\rho}{n^{\frac{1}{3}}}}\right\} \tag{14}$$

From this condition, $n(\rho_n)$ is determined for the appropriate σ^*, and $\varDelta\epsilon$ can be calculated with Eq. (12).

There are many molecules with various dergees of association in an aqueous solution of fatty acid salt, and the equilibrium schemes are

$$\mathrm{A}_n \rightleftarrows \mathrm{A}_{n-1} + \mathrm{A}_1,\ \mathrm{A}_{n-1} \rightleftarrows \mathrm{A}_{n-2} + \mathrm{A}_1,\ \text{etc.,}$$

where A_n is the molecule with n-degree of association. If the partition functions of these molecules write Z_n, the equilibrium conditions are given as follows according to the statistical thermodynamic way to the dilute solution,

$$\frac{Z_{n-1}Z_1}{Z_n} = \frac{N_{n-1}N_1}{N_0N_n}, \quad \frac{Z_{n-2}Z_1}{Z_{n-1}} = \frac{N_{n-2}N_1}{N_0N_{n-1}}$$

$$\therefore \quad \frac{Z_1{}^n}{Z_n} = \frac{N_1{}^n}{N_0{}^{n-1}N_n} \tag{15}$$

in which N_0 is the number of the water molecules in the system and N_n is the number of the associated molecule A_n.

When the concentration C is expressed in mol/l., N_n is C_nN and N_0 is $1000\times N/18$, in which N is the Avogadro's number, Eq. (15) is reduced to

$$\frac{C_n}{C_1} = \left(\frac{C_1}{\frac{1000}{18}\left(\frac{Z_1{}^n}{Z_n}\right)^{\frac{1}{n-1}}}\right)^{n-1} = \left(\frac{C_1}{C_0}\right)^{n-1},$$

$$\text{where} \qquad C_0 = \frac{1000}{18}\left(\frac{Z_1{}^n}{Z_n}\right)^{\frac{1}{n-1}}. \tag{16}$$

We define the critical concentration C_c for the most probable degree of association as the apparent concentration at $C_n = C_1$ $(C_1 = C_0)$,

$$C_c = (n+1)C_0 = (n+1)\frac{1000}{18}\left(\frac{Z_1{}^n}{Z_n}\right)^{\frac{1}{n-1}} \tag{17}$$

Then, the behaviour of C_n/C_1 versus $C(=C_1+nC_n)$ is very characteristic. In the case of $C_1 < C_0$ $(C < C_c)$, C_n/C_1 is far smaller than unity, but in the case of $C_1 > C_0$ $(C > C_c)$, C_n/C_1 is far larger than unity, since n is usually far larger than unity. The property which depended mainly on the associated molecule is not distinguishable until C reaches to C_c but predominant beyond C_c. It is the nick point on the curve of property against concentration as shown in Fig. 3.

Rewriting the partition function Z as below

$$Z = Z_0 e^{-\Sigma\epsilon/kT} \qquad \text{etc.,} \tag{18}$$

$\exp(-\sum\epsilon/kT)$ is the part owing to the energy of electrostatic and interfacial free energies, and Z_0 is the other part which is not mainly depended on the degree of association. C_c is expressed as

$$C_c = \frac{1000}{18}(n+1)e^{-\frac{n}{n-1}\frac{\Delta\epsilon}{kT}} \tag{19}$$

where $\Delta\epsilon$ is the value for the most probable degree of association.

IV. Calculated and Observed Values

Critical Concentration.—The values dotted in Fig. 4 are the experimental results which have been proceeded at various temperatures (18°—60°)(1). Fortunately, the critical con-

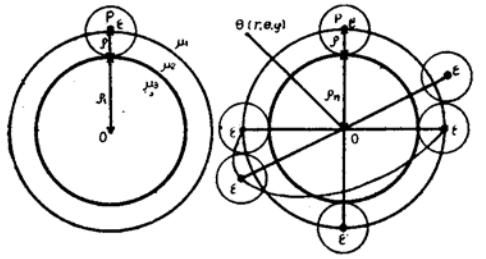

Fig. 2.

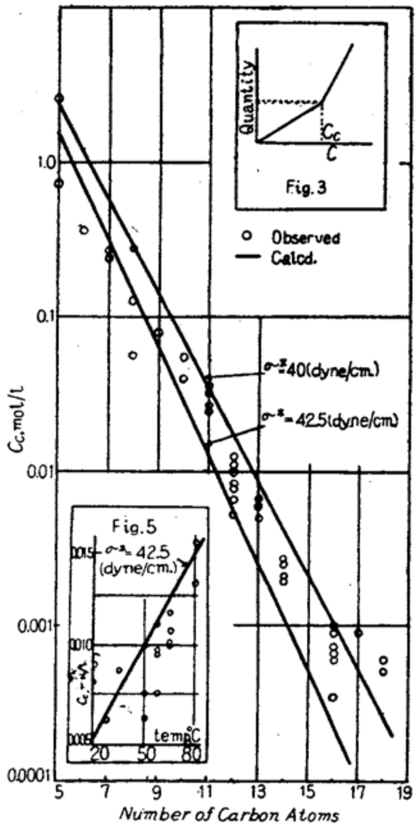

Fig. 4.

Table 1

No. of C atoms in alkyl radical R		5	6	8	10	12	14	16	18
Density of hydrocarbon HR at 20°C.		0.621	0.655	0.694	0.723	0.752	0.765	0.775	0.777
$\rho_1\times10^8$, cm.		3.58	3.73	4.02	4.26	4.47	4.67	4.86	5.05
$\epsilon_1(A)\times10^{14}$, erg		0.7		0.9		1.0			1.1
$4\pi\sigma^*\rho_1^2\times10^{14}$, erg	$\sigma^*=40$, dyne/cm.	64.3	69.8	81.0	91.2	101	110	119	128
	$=42.5$	67.3	74.2	86.1	97.0	107	117	126	136
Degree of Association n	$=40$	9.0	10	12.5	15	17	19	21.5	24
	$=42.5$	9.5	11	13	15.5	18	20.5	23	25.5
$\rho_n\times10^8$, cm.	$=40$	7.5	8.0	9.3	10.3	11.4	12.5	13.5	14.5
	$=42.5$	7.7	8.2	9.5	10.6	11.6	12.7	13.8	14.8
$\dfrac{4\pi\sigma^*\rho_n^2}{n}\times10^{14}$, erg	$=40$	30.9	32.2	34.9	37.2	39.5	41.1	42.5	44.5
	$=42.5$	31.4	33.7	36.3	38.9	40.9	42.8	44.5	46.4
$\dfrac{n\epsilon^2}{2\mu(\rho+\rho_n)}\times10^{14}$, erg	$=40$	14.1	14.7	16.3	17.3	18.3	19.3	20.2	21.0
	$=42.5$	14.7	15.4	16.9	18.0	19.0	20.1	21.0	22.0
$\Delta\epsilon\times10^{14}$, erg	$=40$	20.0	23.5	30.5	37.5	44.0	50.5	57.0	63.5
	$=42.5$	22.0	26.0	33.5	41.0	48.0	55.0	61.5	69.0
Crit. conc. C_c, equiv./l.	$=40$	2.5	1.0	0.25	6×10^{-2}	1.3×10^{-2}	3×10^{-3}	7×10^{-4}	1.7×10^{-4}
	$=42.5$	1.5	0.9	0.10	2.5×10^{-2}	5×10^{-3}	1.3×10^{-3}	2.0×10^{-4}	5×10^{-5}

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(1) K. Hess, *Kolloid Z.*, **88**, 40 (1939); *J. Am. Chem. Soc.*, **61**, 322, 539, 544, 549 (1939); Jander and Weitendorf, *Z. anorg. Chem.*, **41**, 197 (1934); Bury and Parry, *J. Chem. Soc.*, 629 (1935); Howell, *Proc. Roy. Soc.*, **A 115**, 386 (1936); Lottermoser, *Kolloid Z.*, **63**, 175 (1935); Hartley, *Trans. Faraday Soc.*, **34**, 799, 1296, 2348 (1938); Ekwell, *Z. physik. Chem.*, **A 161**, 195 (1932); Ulmann, *Z. physik. Chem.*, **A 182**, 18 (1938).

Table 2

Temp. °C	Density of HR	μ	C_c, equiv./l. calc.
20	0.752	80.0	0.005
40	0.738	73.0	0.008
60	0.722	66.8	0.011
80	0.708	61.8	0.015

($\sigma^* = 42.5$ dyne/cm.)

centrations are not so greatly changed in these temperature intervals, that we can plot these observed values without serious consideration about temperature at which the experiments were proceeded.

In order to calculate the critical concentration with Eq. (17), we are to assign the appropriate value for the volume of an alkyl-group. This is done by the calculation of molecular volume of the corresponding n-hydrocarbon at 20°. In Table 1, the calculated values are listed and the critical concentration at 20° for $\sigma^* = 40$ dyne/cm. and 42.5 dyne/cm. are shown by straight lines in Fig. 4.

Dependence on Temperature.—Since observed interfacial tension between water and hydrocarbon scarcely varies with temperature, we assume that the microscopic interfacial tension is also constant with temperature. Now dependence on temperature of critical concentration can be calculated easily, on which dielectric constant of water and temperature are mainly effecting. Observed and calculated values for dodecyl $C_{12}H_{26}$-group derivatives are shown in Table 2 and Fig. 5.

Generally, the coincidences between observed and calculated values are satisfactory. The slope of the curve for calculated values is steeper than the observed. This would be caused from the fact that the observations for higher homologues ($C_{15}H_{31}-$, $C_{16}H_{33}-$, $C_{17}H_{35}-$, $C_{18}H_{38}-$, etc.) were done at higher temperature (~60°) than the culculation (20°), so that the observed critical concentrations are larger. It can be very easily accepted also that the microscopic interfacial tension between n-octane and water is as large as 42 dyne/cm., because the interfacial tension between n-octane and water is as large as 50 dyne/cm. at 20°.

I think that the procedure mentioned above is valuable for the estimation of microscopic interfacial free energy between water and aliphatic groups.

Appendix

(I) There is an electric system as shown in Fig. 2, in which the point charge exists at a outer point P. The potential at the point (r, θ, φ) excluding P, is the solution of Laplacian equation $\nabla^2\phi = 0$. Namely,

$$\phi = \sum_{\nu}\left(A_\nu r^\nu + \frac{B_\nu}{r^{\nu+1}}\right)S_\nu \tag{20}$$

where A_ν and B_ν are coefficients and S_ν is spherical harmonics.

When we divide the space into three parts; outer $(r \geqq \rho + \rho_1)$, mediate $(\rho + \rho_1 \geqq r \geqq \rho)$ and inner $(r \leqq \rho_1)$, the potential in these regions are respectively

$$\left.\begin{aligned}\phi_1 &= \sum_{\nu} \frac{{}_1B_\nu}{r^{\nu+1}} P_\nu(\cos\theta)\\ \phi_2 &= \sum_{\nu}\left({}_2A_\nu r^\nu + \frac{{}_2B_\nu}{r^{\nu+1}}\right)P_\nu(\cos\theta)\\ \phi_3 &= \sum_{\nu}({}_3A_\nu r^\nu P_\nu(\cos\theta)\end{aligned}\right\} \tag{21}$$

where S_ν is replaced by P_ν, because the potential is completely symmetrical about Z axis. Of course, the electric charge should be considered as distributed on the sphere surface with radius $\rho + \rho_1$, which is expanded with spherical harmonics. Therefore, the surface charge at $(\rho + \rho_1, \theta, \varphi)$ is expressed as

$$\sigma = \sum_{\nu} \frac{(2\nu + 1)\varepsilon}{4\pi(\rho + \rho_1)} P_\nu(\cos\theta) \tag{22}$$

The boundary conditions are

$$\left.\begin{aligned}&\phi_1 = \phi_2, \quad -\mu_1\frac{\partial\phi_1}{\partial r} + \mu_2\frac{\partial\phi_2}{\partial r} = -4\pi\sigma\\ &\qquad \text{at } r = \rho + \rho_1\\ &\phi_2 = \phi_3, \quad -\mu_2\frac{\partial\phi_2}{\partial r} + \mu_3\frac{\partial\phi_3}{\partial r} = 0\\ &\qquad \text{at } r = \rho_1\end{aligned}\right\} \tag{23}$$

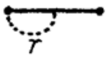
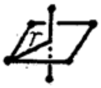
where $\mu_1 = \mu_2 (= \mu)$ and μ_3 are dielectric constants. From these boundary conditions and orthogonality of P_ν, the following equations are obtained:

$$\left.\begin{aligned}&{}_1A_\nu(\rho + \rho_1)^\nu + \frac{{}_2B_\nu}{(\rho + \rho_1)^{\nu+1}} = \frac{{}_2B_\nu}{(\rho + \rho_1)^{\nu+1}}\\ &\frac{(\nu + 1)\,{}_1B_\nu}{(\rho + \rho_1)^{\nu+2}} + \nu\,{}_2A_\nu(\rho + \rho_1)^{\nu-1}\\ &\qquad -\frac{(\nu + 1)\,{}_2B_\nu}{(\rho + \rho_1)^{\nu+2}} = -\frac{(2\nu + 1)\varepsilon}{\mu(\rho_1 + \rho)^2}\\ &\qquad {}_3A_\nu\rho_1{}^\nu = {}_2A_\nu\rho_1{}^\nu + \frac{{}_2B_\nu}{\rho_1{}^{\nu+1}}\\ &\qquad \mu_3\,{}_3A_\nu - \mu\left\{{}_2A_\nu - \frac{(\nu+1)\,{}_2B_\nu}{\rho^{\nu+2}}\right\} = 0\end{aligned}\right\} \tag{24}$$

Solving these simultaneous equations, we get the values for coefficients A and B. Potential at point Q ($r \geq \rho + \rho_1$) is

$$\phi_1 = \frac{\mathcal{E}}{\mu(\rho+\rho_1)} \times \left\{ \frac{\rho+\rho_1}{r\sqrt{1-\frac{2(\rho+\rho_1)}{r}\cos\theta+\left(\frac{\rho+\rho_1}{r}\right)^2}} + \sum_0^\infty \frac{\nu(\mu-\mu_3)}{\nu(\mu+\mu_3)+\mu} \frac{\rho_1^{2\nu+1} P_\nu(\cos\theta)}{(\rho+\rho_1)^\nu r^{\nu+1}} \right\} \quad (25)$$

Table 3

	Point charge system		Surface charge system	Ratio
Charge	Figure	Energy (P)	Energy (S)	(S/P)
2ε		$\frac{1}{2}\frac{\varepsilon^2}{r}$	$2\frac{\varepsilon^2}{r}$	4.00
3ε		$\sqrt{3}\frac{\varepsilon^2}{r}$	$4.5\frac{\varepsilon^2}{r}$	2.60
4ε		$\frac{3\sqrt{3}}{\sqrt{2}}\frac{\varepsilon^2}{r}$	$8\frac{\varepsilon^2}{r}$	2.18
6ε		$(6\sqrt{2}+1.5)\frac{\varepsilon^2}{r}$	$18\frac{\varepsilon^2}{r}$	1.80
8ε		$(6\sqrt{3}+3\sqrt{2}+2)\times\frac{\varepsilon^2}{r}$	$32\frac{\varepsilon^2}{r}$	1.65
12ε		$(6\sqrt{2}+8\sqrt{3}+27)\frac{\varepsilon^2}{r}$	$72\frac{\varepsilon^2}{r}$	1.46

From this equation, (2) can be derived for $\theta = 0$, $\cos\theta = 1$.

(II) We may compare the electrostatic energy of the point charge system with that of the spherical surface charge. The ratio approaches to unity when the number of charges becomes larger, as shown in Table 3. Now let us estimate the electrostatic energy of the system shown in Fig. 2, which is the degree of association 6, $\rho_6 = 6.03$ Å. (for oenanthylic acid ions), and $\rho = 1.80$ Å.

The estimation is easy, because $P_\nu(\cos\theta)$ in Eq. (25) are simple for $\theta = 0$, $\pi/2$ and π. The potential energy at P due to the other five charges is

$$\Psi = 4\phi_6(\cos\theta = 0) + \phi_6(\cos\theta = -1)$$

in which ϕ_6 is the value for $r = \rho + \rho_6$ and $\rho_1 \rightarrow \rho_6$ in Eq. (25) and therefore the electrostatic energy is

$$\frac{1}{2} 6\mathcal{E}\Psi + 6\epsilon_1(A_1\rho_6) = 13.1\frac{\mathcal{E}^2}{\mu(\rho+\rho_6)}$$

for $\mu = 80$ and $\mu_3 = 2.3$.

Comparing it with the case of $\mu_3 = \mu = 1$ (Table 3), this value is more close to the surface charge $6\mathcal{E}$ on the sphere with radius $\rho + \rho_6$, *i. e.*, $18.0\,\mathcal{E}^2/\mu(\rho+\rho_6)$

Therefore, we may safely replace the point charge system with the spherical surface charge for much larger degree of association.

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