THEORETICAL DEVELOPMENT AND EXPERIMENTAL VERIFICATION OF
A PRIMITIVE MODEL FOR THE INTER-MICELLAR INTERACTIONS

by

Eric Yueh-Lang Sheu

B.S., National Tsing-Hua University, Taiwan
(1977)

M.S., University of Florida, Gainesville, Florida
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Departmental Committee on Graduate Students

Signature of Author

Certified by _______ Sow-Hsin Chen
Thesis Supervisor

Department of Nuclear Engineering
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ABSTRACT

A series of ionic micellar solutions, formed respectively by anionic surfactants lithium dodecyl sulfate, sodium dodecyl sulfate, sodium dodecyl orthoxylene sulfonate, and di-2-ethylhexylsulfosuccinate, were investigated using small angle neutron scattering (SANS) technique and analyzed with proper geometric models for micelles along with a statistical mechanical theory for calculation of inter-particle interactions. A contrast variation method at finite scattering vector Q was proposed to determine the molecular parameters such as the dry volume of the hydrophobic tail and that of the hydrophilic head of the surfactant molecule. The theories used for characterizing inter-particle interactions through calculation of inter-particle structures, $S_{ij}(Q)$, are hypernetted chain (HNCA) and mean spherical (MSA) approximations. A rescaling procedure based on the analytical MSA solutions of multi-component Ornstein-Zernike equations was proposed for the computation of $S_{ij}(Q)$ when the system concentration is dilute in order to remedy the defect of MSA in this region. The micellar growth, measured in terms of mean aggregation number $n$, and an apparent charge $Z^*$ were successfully extracted from SANS intensity distribution function through the geometric model of the micelle and $S_{ij}(Q)$. For all the systems investigated the minimum micelles were found to be spherical in shape with volumes equal to compact packing of the surfactant molecules. As surfactant concentration increases the micelle size grows gradually and the micellar shape transform from spherical to prolate/oblate spheroidal depending on the surfactant molecules. The apparent charge of a micelle, $Z^*$, was found to be much less than the bare charge of the micelle suggesting a charge condensation phenomenon occur near the micellar surface.

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CHAPTER I

INTRODUCTION

The amphiphilic molecules (surfactant), which contain a hydrophilic "head" portion on one end and a hydrophobic "tail" part attaching to the head, are known to form aggregates (micelles) in aqueous solution when surfactant concentration exceeds a threshold value called critical micellar concentration (CMC). As surfactant concentration further increases these aggregates may grow and transform into other geometries in shape (see Fig. 1). Due to these unusual phenomena the formation and growth of micelles have received increasing attention from colloidal scientists. Until recently much theoretical work on micellar physics have been devoted to these two issues at the concentrations near CMC [1-3] since conventional spectroscopic techniques such as static and dynamic light scatterings [4-6] are applicable only in this region. For ionic micellar solution, however, the electrostatic interaction between micelles are long ranged and strong even at concentration near CMC. Under such nonideal condition the theoretical approach based on an ideal solution and a single particle picture may not be applicable. Furthermore, interpretation of light scattering experiments becomes more difficult when both the surfactant concentration and micellar charges are high. Thus, a theory, which properly taking into account the electrostatic interactions among particles and an appropriate spectroscopic technique, are needed for characterization of strongly interacting
micellar systems.

In the course of investigating ionic micellar solutions the mean aggregatin number \( \Pi \) (number of surfactant molecules that form a micelle) and the apparent charge (or effective charge) of the micelle \( Z^* \) are the two characteristic parameters to be determined. For evaluation of these two parameters of an ionic micellar solution the newly developed small angle neutron scattering (SANS) technique provides a better alternative than the conventional light scattering in the following two aspects: first SANS spans a wider \( Q \) range (\( Q = (4\pi/\lambda)\sin(\theta/2) \) is the scattering vector) due to shorter wave length (typically a factor of ~ 1000 shorter) and secondly its scattering intensity distribution, \( I(Q) \), when properly analyzed, simultaneously provides the information of both intra and inter particle structure factors from which the aggregation number and the apparent charge can be obtained respectively.

To properly interpret the SANS data of an ionic micellar solution a suitable geometrical model for the micelle and a statistical mechanical theory for calculation of the inter-particle structure factor are necessary. There have been many theories used for characterizing electrolyte solutions such as Debye-Huckel theory, hypernetted chain approximation (HNCA), mean spherical approximation (MSA) and many others [7-12]. Among these theories the HNCA and MSA are particularly interested due to their success in treating simple electrolyte solutions within the primitive model where the solvent effects are taken into account in an approximate way through inclusion of a macroscopic
dielectric constant \( \varepsilon \) [11,12]. For ionic micellar solutions, where the size and charge of micelle and the surrounding ions are highly asymmetric, HNCA has also been claimed to be an accurate theory within the primitive model [13,14,15]. However, HNCA is a nonanalytic theory, and its numerical solution is sufficiently complicated and unstable as to make it unattractive for SANS data analysis. On the other hand, the MSA solution of Ornstein-Zernike (OZ) equation, which is a linearized version of HNCA, is simple enough to yield an analytical solution of \( S_{ij}(Q) \) for an arbitrary mixture of charged particles in a solution using a bare coulomb potential as the asymptotic part of the direct correlation function (this is called a multi-component coulomb fluid or MCCF) [16]. MCCF theory has been verified to be satisfactory in calculating the thermodynamic quantities, such as excess internal energy, Gibb's free energy, and osmotic compressibility, of a simple electrolyte solution and in analyzing SANS data of a highly asymmetric system such as the ionic micellar solutions [17,18]. OZ equation can also be solved analytically with MSA by treating the system as an one component macroion (OCM) system and using DLVO potential as the direct correlation function [19]. OCM was also found to be successful in analyzing SANS data but it yields apparent micellar charge different from that of MCCF [17,18].

In this study, a series of micellar solutions formed by anionic surfactants such as lithium dodecyl sulfate (LDS), sodium dodecyl sulfate (SDS), sodium dodecyl orthoxylene sulfonate (NaC\(_{12}\)OXS), and di-2-ethylhexylsulfosuccinate (AOT), were studied by use of SANS technique.
and analyzed with proper geometric model of micelle along with MCCF theory. HNCA and OCM were also applied to some cases to compare with MCCF theory. A modified OCM theory (MOCM) was adapted to correct the apparent charge of the micelle obtained from OCM analysis because DLVO potential is applicable only in the dilute limit [19]. A rescaling procedure, based on a physical condition proposed by Gillan [20] and the analytical solutions given by Senatore et al [12], was used to remedy the defect of MSA theory due to its neglect of short range interactions among particles. The apparent charges obtained by MCCF and MOCM were interpreted by their corresponding pictures.

In Chapter II the SANS theory and experiment including instruments, settings, sample preparation, data collection and data reduction are presented. In chapter III the geometric model of micelle and its corresponding intra-particle structure factor P(Q) are described. The contrast variation technique is also given in this chapter. Chapter IV devotes to detail discussions of electrolytic theories including (1) brief description of the historical Debye-Huckel theory, (2) construction of OZ equation and HNCA and MSA closures, (3) derivation of the direct correlation function of an effective one-component system to be used in MOCM, and (4) comparision of HNCA, OCM, MCCF, and MOCM theories. In Chapter V and Chapter VI the structures, growths, and interactions of NaC12OXYs and AOT micellar systems are discussed respectively. Chapter VII gives the conclusion of this study. The results of this work that have been published and some detail mathematical formulations are given in appendices.
References:


(7) P. Debye and E. Huckel, Phys. Z, 24, 185 (1923)


(9) L. Blum, Mol Phys., 30, 1529 (1975)


Fig. 1.1 Surfactant aggregates formed in aqueous solutions. A spherical micelle is first formed and transform into the other shapes as surfactant concentration increases. The micelle formed by single chained surfactant molecule tends to transform into prolate spheroid while the micelle formed by doubled chained surfactant molecules like to grow into oblate spheroid.
CHAPTER II

The Small Angle Neutron Scattering Technique

2.1 Neutron Scattering Theory

In this section a brief summary of neutron scattering theory is to be given. Detail description of the theory are available in many literatures [1,2,3].

The incident and scattered neutrons are treated as quantum mechanical waves of wave vector $\mathbf{K} = (2\pi/\lambda)\mathbf{k}$, where $\lambda$ is the wave length and $\mathbf{k}$ is a unit vector specifying the direction of the neutron velocity. The neutron energy $E$ and momentum can then be expressed as

$$E = (\hbar k)^2/2m, \quad (2.1)$$

and $$\mathbf{P} = \hbar \mathbf{k}, \quad (2.2)$$

where $m$ is the rest mass of neutron. In the process of scattering, the neutron-nucleus interaction predominates the scattering properties of the system if neutron-atom magnetic coupling is assumed to be negligible. Furthermore, the first Born approximation can be applied for calculation of the scattering cross section since the neutron-nucleus interaction is short ranged ($\sim 10^{-13}$ cm). With Born appro-
ximation this interaction (~ 36 MeV) is replaced by a pseudo potential \( V(\mathbf{r}) \) of weaker strength but longer range, i.e.,

\[
V(\mathbf{r}) = \left( \frac{2\pi \hbar}{m} \right) \sum_{\ell=1}^{N_2} b_{\ell} \delta(\mathbf{r} - \mathbf{r}_{\ell}),
\]

(2.3)

where \( \mathbf{r}_{\ell} \) is the position vector of the \( \ell \)th nucleus, and \( b_{\ell} \) is the bound scattering length characterizing the low-energy neutron interaction with the \( \ell \) nucleus. The absolute values of \( b_{\ell} \) for all existent nuclei are available [4]. The momentum and energy transfers of the neutron to the nucleus can be then written as

\[
\hbar \mid \mathbf{Q} \mid = \hbar \mid \mathbf{k}_i - \mathbf{k}_f \mid
\]

(2.4)

and

\[
\hbar \omega = E_i - E_f = (\hbar^2/2m)(k_i^2 - k_f^2),
\]

(2.5)

where \( k_i, E_i, k_f, \) and \( E_f \) are respectively the wave vectors and the energies of the incident and the scattered neutrons. It is the intensity distribution of \( \hbar Q \) and \( \hbar \omega \) that one measures in a neutron scattering experiment. More specifically, one measures the double differential scattering cross section \( d^2\sigma/d\Omega d\omega \), defined as the number of neutrons of energy about \( \hbar \omega \) per second per unit incident flux that are scattered into a solid angle \( d\Omega \). Based on the pseudo potential, Eq.(2.3), the neutron scattering theory derives the double differential scattering cross section to be [3]
\[
\frac{d^2 \sigma}{d \Omega d \omega} = \frac{k_f}{k_i} \frac{1}{2\pi} \int dt \exp(-i\omega) \cdot \left\langle \sum_{\ell \ell'} b_{\ell} b_{\ell'}, \exp\left[ iQ \cdot \left( \bar{r}_{\ell}(t) - \bar{r}_{\ell'}(0) \right) \right] \right\rangle,
\]

where the bracket \( \langle \rangle \) denotes the canonical ensemble average of the system at a given temperature and pressure. In fact the quantity inside the \( \langle \rangle \) of Eq.(2.6) should be averaged over all the isotopic and spin states of the scattering media since \( b_{\ell} \) strongly depends on them. Mathematically, one begins by lebelling each nucleus by

\[
\langle \rangle = \sum_{\alpha} \left\langle \sum_{\ell \ell'} b_{\ell}^{\alpha} b_{\ell'}^{\alpha'} \exp\left[ iQ \cdot \left( \bar{r}_{\ell}^{\alpha}(t) - \bar{r}_{\ell'}^{\alpha'}(0) \right) \right] \right\rangle,
\]

where \( \alpha \) denotes the atomic species and \( l_{\alpha} \) a particular nucleus within species \( \alpha \). Separate Eq.(2.7) into \( \alpha = \alpha' \) and \( \alpha \neq \alpha' \) terms we have

\[
\langle \rangle = \left\langle \sum_{\alpha} \sum_{l_{\alpha}} \overline{b_{\ell}^{\alpha}} b_{\ell}^{\alpha} \exp\left[ iQ \cdot \left( \bar{r}_{\ell}^{\alpha}(t) - \bar{r}_{\ell}^{\alpha}(0) \right) \right] \right\rangle + \\
\left\langle \sum_{\alpha \neq \alpha'} \sum_{l_{\alpha} l_{\alpha'}} b_{\ell}^{\alpha} b_{\ell'}^{\alpha} \exp\left[ iQ \cdot \left( \bar{r}_{\ell}^{\alpha}(t) - \bar{r}_{\ell'}^{\alpha'}(0) \right) \right] \right\rangle,
\]

where the bar denotes an average over the isotopic and spin states within species \( \alpha \). The average quantity can be further decomposed into two terms,
\[
\frac{b^\alpha_{\beta} \overline{b}^{\alpha'_{\beta'}}}{b^\alpha_{\beta} \overline{b}^{\alpha'_{\beta'}}} = \left( \frac{(b^\alpha_{\beta})^2}{b^\alpha_{\beta}} - \frac{(b^\alpha_{\beta})^2}{b^\alpha_{\beta}} \right) \delta^\alpha_{\alpha',} \delta^\beta_{\beta',} + \frac{(b^\alpha_{\beta})^2}{b^\alpha_{\beta}}. \tag{2.9}
\]

By combining Eq. (2.6), (2.7), and (2.8) the measured double differential cross section \( \frac{d^2\sigma}{d\Omega d\omega} \) can be separated into two parts, the coherent and the incoherent scatterings,

\[
\frac{d^2\sigma}{d\Omega d\omega} = \left[ \frac{d^2\sigma}{d\Omega d\omega} \right]_{\text{coh}} + \left[ \frac{d^2\sigma}{d\Omega d\omega} \right]_{\text{inc}}, \tag{2.10}
\]

where

\[
\left[ \frac{d^2\sigma}{d\Omega d\omega} \right]_{\text{coh}} = \frac{k_F}{k_i} \frac{1}{2\pi} \int dt \exp(-i\omega t) \left\langle \sum_{\alpha\alpha'} \sum_{\beta\beta'} b^\alpha_{\beta} \overline{b}^{\alpha'_{\beta'}} \right. \]

\[
\exp\left[iQ \left[ \overline{Y}_{\alpha} (t) - \overline{Y}_{\alpha'} (0) \right] \right], \tag{2.11}
\]

\[
\left[ \frac{d^2\sigma}{d\Omega d\omega} \right]_{\text{inc}} = \frac{k_F}{k_i} \frac{1}{2\pi} \int dt \exp(-i\omega t) \left\langle \sum_{\alpha} \sum_{\beta} (b^\alpha_{\beta})^2 \right. \]

\[
\exp\left[iQ \left[ \overline{Y}_{\alpha} (t) - \overline{Y}_{\alpha} (0) \right] \right], \tag{2.12}
\]

and

\[
b^\alpha_{\beta} = \left( \left[ (b^\alpha_{\beta})^2 \right] - \left[ (b^\alpha_{\beta})^2 \right] \right)^{1/2}. \tag{2.13}
\]

In the case of structural study the time dependent part of \( \frac{d^2\sigma}{d\Omega d\omega} \) is removed by integrating over \( \omega \) holding \( Q \) constant. This integration can be achieved by the so called "static approximation", in which the energy
transfer of the incident neutron to the scattering nucleus is assumed to be negligible, i.e.,

\[ |\vec{k}_i| \approx |\vec{k}_f|. \quad (2.14) \]

Thus, the scattering vector \( \vec{Q} \) becomes

\[ |\vec{Q}| = 2k_i \sin(\theta/2) = (4\pi/\lambda) \sin (\theta/2), \quad (2.15) \]

depending only on the scattering angle \( \theta \). With this approximation (the quasi-elastic scattering) the double differential cross sections for incoherent and coherent parts are respectively integrated over \( \omega \) to be

\[ \left[ \frac{d\sigma}{d\Omega} \right]_\text{coh} = \left\langle |\sum_{l}^{N} b_{l}^\alpha \exp (i\vec{Q} \cdot \vec{r}_l) |^2 \right\rangle \quad (2.16) \]

and

\[ \left[ \frac{d\sigma}{d\Omega} \right]_\text{inc} = \sum_{\alpha} N_{\alpha} \left[ b_{\alpha}^\alpha \right]^2, \quad (2.17) \]

where \( b_{l}^\alpha \) is the bound coherent scattering length of the \( l \)th nucleus, \( r_l \) the corresponding position vector, and \( N = \sum N_{\alpha} \) is the total number of nuclei in the scattering media. \( (d\sigma/d\Omega)_\text{coh} \) is a \( Q \)-dependent quantity carrying the informations of particle and inter-particle structures while \( (d\sigma/d\Omega)_\text{inc} \) is a \( Q \)-independent quantity providing a DC level background and often subtracted from the measured total \( (d\sigma/d\Omega) \) spectrum before performing data analysis.
The static approximation applied for integrating the double differential cross section over \( \omega \) has been justified according to the inelastic correction terms of \( \partial \sigma / \partial \Omega \) derived by Placzek [5] and was found to introduce less than 1 \( \% \) error for all the surfactant molecules investigated with \( |\vec{Q}| \) less than 0.3. Thus it is proper to use the static approximation for SANS data reduction and analysis.

In performing SANS experiment for a system such as the micellar solution the useful quantity for analysis is the coherent differential cross section per unit volume of the solution, \( d\Sigma(Q)/d\Omega \), which is

\[
\frac{d\Sigma(Q)}{d\Omega} = n_p \left[ \frac{d\sigma}{d\Omega} \right]_{\text{coh}}, \tag{2.18}
\]

where \( n_p \) is the number of scattering "centers" per unit volume of micellar solution. Eq.(2.18) is true only when all the scattering centers are identical. In the case of micellar solution the scattering center is a cell with one micelle sitting at the center. With this picture and taking \( \hat{R}_i \) to be the position vector of the center of mass of the particle sitting in the \( i \)th cell and \( \hat{x}_{ij} \) the position vector of the \( j \)th nucleus in the \( i \)th cell relative to the center of mass of the \( i \)th particle, we can rewrite \( d\Sigma(Q)/d\Omega \) as
\[
\frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V} \left\langle \left| \sum_{i=1}^{N_p} \exp(iQ \cdot \vec{R}_i) \sum_{\text{cell}_i} b_{ij} \exp(iQ \cdot \vec{x}_{ij}) \right|^2 \right\rangle.
\]

(2.19)

where \(N_p\) is the total number of cells in the scattering volume \(V\). Define the form factor of the \(i\)th cell as

\[
F_i(Q) = \sum_{\text{cell}_i} b_{ij} \exp(iQ \cdot \vec{x}_{ij}),
\]

(2.20)

where \(b_{ij}\) is the scattering length of the \(j\)th nucleus in the \(i\)th cell. Express \(d\Sigma(Q)/d\Omega\) in terms of \(F_i(Q)\) one obtains,

\[
\frac{d\Sigma(Q)}{d\Omega} = \frac{1}{V} \left\langle \left| \sum_{i=1}^{N_p} F_i(Q) \exp(iQ \cdot \vec{R}_i) \right|^2 \right\rangle.
\]

(2.21)

If the solvent is treated as a continuum the form factor of the \(i\)th scattering center (or the particle sitting in the \(i\)th cell) can be written in a Fourier integral form by introducing a scattering length density \(\rho_i\) for \(i\)th particle defined as

\[
\rho_i(\vec{r}) = \left[ \sum_j b_{ij} \delta(|\vec{x}_{ij} - \vec{r}|) \right]/V_i,
\]

(2.22)

and an average scattering length density \(\bar{\rho}_s\) for solvent. \(V_i\) in
Eq. (2.22) is the volume of the $i$th particle. Substitute Eq. (2.22) and $\bar{\rho}_s$ into Eq. (2.20) the integral form of $F_i(Q)$ becomes

$$
F_i(Q) = \int_{\text{particle } i} d^3r \left[ \rho_i(\vec{r}) - \bar{\rho}_s \right] \exp(iQ \cdot \vec{r}) + \int_{\text{cell } i} d^3r \bar{\rho}_s \exp(iQ \cdot \vec{r}). \tag{2.23}
$$

The second integral on the right hand side in Eq. (2.23), to a good approximation, is a delta function at $Q = 0$. Thus, for $Q \neq 0$ only the first survives, i.e.,

$$
F_i(Q) = \int_{\text{particle } i} d^3r \left[ \rho_i(\vec{r}) - \bar{\rho}_s \right] \exp(iQ \cdot \vec{r}), \quad \text{for } Q \neq 0. \tag{2.24}
$$

From Eq. (2.24) it is obvious that the particle form factor depends only on the particle shape once the scattering length density of particle is uniform. Due to this particular feature one can change the contrast (i.e., the difference of the scattering length density of the particle and the solvent) to examine the geometry of the particle. In addition, one can look into a specific portion of a particle if the scattering length density of the particle is not uniform.

To further simplify $d\Sigma(Q)/d\Omega$ for practical uses in analyzing SANS data the colloidal particles in micellar solution are taken to be monodispersed (i.e., all the scattering centers are identical) by which
the form factor in Eq. (2.21) can be factored out of the canonical ensemble average. Thus, the differential cross section becomes, dropping the $i$ subscript in Eq. (2.21),

$$\frac{d\Sigma(Q)}{d\Omega} = n_p \left| F(Q) \right|^2 \frac{1}{N_p} \sum_{l=1}^{N_p} \sum_{l' \neq 1}^{N_p} \exp \left[ i \mathbf{Q} \cdot \left( \mathbf{R}_l - \mathbf{R}_{l'} \right) \right],$$

(2.25)

$$n_p = \frac{N_p}{V}.$$  

(2.26)

Define the intra-particle structure factor $P(Q)$ to be

$$P(Q) \equiv |F(Q)|^2,$$ 

(2.27)

and the inter-particle structure factor $S(Q)$ to be

$$S(Q) \equiv \frac{1}{N_p} \sum_{l=1}^{N_p} \sum_{l' \neq 1}^{N_p} \exp \left[ i \mathbf{Q} \cdot \left( \mathbf{R}_l - \mathbf{R}_{l'} \right) \right],$$ 

(2.28)

the differential cross section can then be written as

$$\frac{d\Sigma(Q)}{d\Omega} = n_p P(Q) S(Q).$$ 

(2.29)

It is easy to see from Eq. (2.27) and (2.28) that $P(Q)$ governs the size and the shape of the scattering particle while $S(Q)$ representing the inter-particle interactions. Thus, the whole SANS analysis devotes to
the calculation of \( P(Q) \) and \( S(Q) \) by giving a proper geometric model for micelle and a suitable statistical mechanical theory for calculation of \( S(Q) \). Detail description of \( P(Q) \) and \( S(Q) \) are to be given in Chapter III and IV respectively. The growth of micelle size, when surfactant concentration increases, is reflected in \( P(Q) \) and can be easily determined through the geometric model of the micelle. On the other hand, \( S(Q) \) gives the structural information, which is mainly governed by inter-particle interactions and micellar concentration, through the pair correlation function \( g(r) \) according to the following relation:

\[
S(Q) = 1 + n_p \int_0^\infty dr \frac{4\pi r^2}{Qr} \left[ g(r) - 1 \right] \frac{\sin(Qr)}{Qr},
\]

(2.30)

where \( g(r) \) has direct physical meaning: the number density distribution of the particles surrounding a central reference particle at distance \( r \).

2.2 SANS Experiment

2.2.1 Instrumentation

A SANS spectrometer, if prudently designed, can approach the sensitivity of the conventional X-ray spectrometers despite the fact that the current available neutron sources have luminosity (number of neutrons per unit area, time, steradian, and wavelength interval) seven to ten orders lower than that of the conventional rotating anode X-ray. This can be achieved by choosing large sample to detector distance (SDD)
and sample collimating slit (~1 cm² versus ~1 mm² in the case of X-ray). The resolution of the total scattering vector \( <\delta Q^2>^{1/2} \) is contributed by four major factors [6],

\[
<\delta Q^2>^{1/2} = \frac{k_1}{\sqrt{12}} \left[ \left( \frac{d_D}{SDD} \right)^2 + \left( \frac{d_E}{SSD} \right)^2 + d_S^2 \right] \left[ \frac{1}{SDD} + \frac{1}{SSD} \right]^2 + \left( \frac{\Delta \lambda}{\lambda} \right)^2 \theta_e^2 \right]^{1/2}
\]

(2.31)

where \( d_E, d_S \), and \( d_D \) are respectively the widths of the entrance slit, sample slit, and detector element. SSD is the source-to-sample distance. In order to obtain high flux the wavelength bandwidth of the monochromator \( \Delta \lambda/\lambda \) has to be optimized. The optimized value of \( \Delta \lambda/\lambda \) requires that SSD = SDD and \( d_E = d_D = 2d_S \). At the optimized condition \( \Delta \lambda/\lambda \) becomes, from Eq.(2.31),

\[
\Delta \lambda/\lambda = \sqrt{3} \ <\delta Q^2>^{1/2}/\lambda
\]

(2.32)

If one requires \( <\delta Q^2>^{1/2}/\lambda \approx 0.05 \), the optimized \( \Delta \lambda/\lambda \) must be close to 0.1 (i.e., 10% spread of wave bandwidth) which is about 150 times the bandwidth used in X-ray experiments. Since \( \Delta \lambda/\lambda \approx 0.1 \) can be achieved in SANS spectrometer one sees that a SANS spectrometer can approach the sensitivity of conventional X-ray spectrometers once all the discussed factors are delicately optimized.

All the experimental measurements of this study were performed at the 60 MW High Flux Beam Reactor (HFBR) located in Brookhaven National
Laboratory (BNL). The BNL HFBR is a D$_2$O moderated reactor using enriched uranium as fuel. The neutrons generated by chain reactions are moderated by D$_2$O to thermal energy at beam port where a 1.9 liter cold source containing liquid hydrogen at 20 °K, 5 atm is used to boost the source neutrons at long wavelength. The neutron beam emerged from this cold source is then guided by a nickel coated neutron guide to pass through a cold beryllium filter and impinges on a multilayer monochromator which selects the wavelength for SANS measurement [7]. The monochromatic beam is then collimated over a length of 2m by a series of apertures (pin holes) of decreasing diameters to further define the neutron beam (e.g., 12mm, 8mm, and 6mm in series) before reaching sample cell. The sample cells used are cylindrical quartz cells with path lengths from 1 to 4 mm depending on the transmissions of the samples. The sample holder/exchanger is a rotating wheel with 8 uniformly distributed sample racks (45° between adjacent racks) on it for mounting samples. The detector used for recording the scattered neutrons is a position sensitive He$^3$ detector with 128x128 pixels covering an area of 50 x 50 cm$^2$. For micellar solutions studied in this work the typical neutron wavelength is ~ 5 A and the sample to detector distance is ~ 140 to 150 cm which results in a Q range of ~ 0.015 to 0.33 A$^{-1}$. The characteristics of BNL neutron spectrometer is given in Table 2.1 and its schematic diagram in Fig. 2.1.

2.2.2 Sample Preparation
The SANS measurements of micellar systems are usually performed for a series of micellar solutions covering as wide the concentration range as possible in order to examine the structure, interactions, and growth as a function of micellar concentration more thoroughly. Thus, a stock solution of the highest concentration (near the maximum solubility) is usually prepared first. The rest of the solutions in the series are then made by dilution of this stock solution so that better relative accuracy can be achieved throughout the whole series of samples. Before SANS measurement is performed sample is injected into the cylindrical quartz cells of path length 1 to 4 mm depending on the surfactant concentration and the transmission of the sample. For low transmission sample (such as the sample with high concentration of hydrogen atoms) 1 mm path length is chosen to avoid multiple scattering which introduces substantial deviation to the absolute intensity measurement. When samples are not in use they are usually kept cool to prevent from deterioration.

The ionic micellar solutions studied in the work include (1) LDS+D₂O, LDS+D₂O+salt, (2) SDS+D₂O, SDS+D₂O+salt, (3) NaC₁₂OXS+D₂O/H₂O mixture, and (4) AOT+D₂O/H₂O mixture. NaC₁₂OXS was measured at various temperatures while all the rests were measured at room temperature.

2.2.3 Data Collection and Reduction

Before measuring micellar samples the SANS spectrometer should be
calibrated according to the standard procedure. In this procedure an 1 mm deionized water (H$_2$O) sample is used for calibration of detector sensitivity because its scattering intensity is largely contributed by isotropic incoherent scattering of H atoms which results in a nearly constant intensity spectrum for all Q. However, this 1 mm H$_2$O sample, due to large incoherent scattering cross section of H atoms, involves too much multiple scattering. According to the recent investigation, in which a series of water samples containing various D$_2$O/H$_2$O mixtures were measured with neutron wave length $\lambda = 5.32$ Å, (four samples [D$_2$O]/[H$_2$O] = 0/100, 5/95, 10/90, and 20/80 were measured) a factor of 0.78 was found between 1 mm H$_2$O and 5/95 samples when compare to the theoretical calculation. This result concludes that all the measurements calibrated according to 1 mm H$_2$O sample have to time a correction factor of 0.78 to obtain the absolute intensity (i.e., d$\Sigma$(Q)/dΩ in unit of cm$^{-1}$) when $\lambda = 5.32$ Å. Besides the sensitivity calibration an empty cell and a cadmium block (for background counting) are also measured for subsequent data normalization.

In order to measure the scattering intensity of the micellar solutions with reasonable statistics, the duration time of data collection are set differently for each individual micellar solution depending on its surfactant concentration and micelle-solvent contrast.

To obtain the absolute intensity spectrum the collected raw data are reduced according to the following formula:
\[
\frac{d\Sigma^i_j}{d\Omega} = \frac{1-T_W}{T_W 4\pi t_W} \frac{I^i_j}{t_s T_s} \frac{I^i_j}{t_W T_W}
\]

(2.33)

where \(\Sigma^i_j\) is the differential cross section per unit volume of the sample solution at pixel \(i,j\); \(t_s\) is the sample cell thickness; \(t_W\) is the path length of the water cell; \(T_W\) is the transmission of water sample; \(I^i_j\) is the scattering intensity of the sample solution at pixel \(i,j\); and \(I^i_j\) is the corresponding scattering intensity of water sample. By this corrected scattering data one obtains the coherent scattering cross section per unit volume of sample solution in unit of \(\text{cm}^{-1}\).
References:


Table 2.1 Parameters of SANS Spectrometer in Brookhaven National Laboratory

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength range</td>
<td>4 - 10 Å</td>
</tr>
<tr>
<td>Wavelength spread (FWHM)</td>
<td>6 - 15 %</td>
</tr>
<tr>
<td>Beam divergence (FWHM, horizontal)</td>
<td>14'</td>
</tr>
<tr>
<td>Flux at Sample (5 Å, 6 mm beam)</td>
<td>$1 - 2 \times 10^6 \text{n/cm}^2 \text{-sec}$</td>
</tr>
<tr>
<td>Detector area</td>
<td>$50 \times 50 \text{ cm}^2$</td>
</tr>
<tr>
<td>Detector Resolution</td>
<td>3 mm</td>
</tr>
<tr>
<td>Sample-detector distance</td>
<td>50 - 200 cm</td>
</tr>
<tr>
<td>Range of scattering angles</td>
<td>$0 - 45^\circ$</td>
</tr>
<tr>
<td>Best spectrometer resolution</td>
<td>1000 Å</td>
</tr>
<tr>
<td>Minimum Q (λ = 5 Å, 2m detector distance)</td>
<td>0.002 Å$^{-1}$</td>
</tr>
</tbody>
</table>
Fig. 2.1 Schematic diagram of SANS spectrometer located in High Flux Beam Reactor, Brookhaven National Laboratory. The specification of this spectrometer are given in Table 2.1
CHAPTER III

INTRA- PARTICLE STRUCTURE FACTOR AND CONTRAST VARIATION

3.1 Intra-particle Structure Factor P(Q)

P(Q), defined through particle form factor (see Eq. (2.24) and (2.27)), strongly depends on particle shape and particle-solvent contrast. For a system containing monodispersed spherical particles the explicit expression of the form factor F(Q) can be derived from Eq. (2.24) to be [1]

\[ F(Q) = v_p (\bar{\rho} - \bar{\rho}_s) \frac{3j_1(QR)}{QR} \]  \hspace{1cm} (3.1)

where \( v_p \) is particle volume, \( \bar{\rho} \) the average scattering length density of the particle; \( R \) is the radius of the particle, and \( j_1 \) is the spherical Bessel function of the first kind. For nearly spherical micellar systems such as the cases studied here, the form factor can be computed, to a reasonable approximation, by using Eq. (3.1) with an effective radius. The intra-particle structure factor P(Q) can then be calculated by taking the orientational average over the entire system which is considered to be isotropic. This approximation, however, is true only when the asymmetric ratio of the particle geometry is less than 2 (e.g., when micelle is prolate the semi-major axis to the semi-minor axis
should be less than 2 for this approximation to be acceptable). The explicit formula for calculating \( F(Q) \) of a nonspherical micelles, such as prolate and oblate micelles, are given in Chapter V (prolate) and Chapter VI (oblate) when NaCl_{12}OXS and AOT micellar systems are discussed. If particles in the system are spherical but polydispersed then the average particle form factor should be calculated by weighting \( F(Q) \) in Eq.(3.1) with particle size distribution function and integrating over all particle sizes. For example, a 3/5/95 AOT/D_{2}O/Decane (3 gm of AOT, 5 cm\(^3\) of water, and 95 cm\(^3\) of decane) microemulsion system has a droplet size distribution describable by Schultz distribution function, thus, the average form factor of the microemulsion droplets is calculated by weighting \( F(Q) \) with Schultz distribution function and integrated over all droplet sizes. The explicit expression of the form factor for this particular distribution has been given [3].

For a system containing monodispersed cylindrical particles, an analytical expression of the particle form factor can also be derived from Eq.(2.24) [2],

\[
F(Q)_{\text{cyl}} = \left[ \frac{\sin \frac{1}{2} QL_\mu}{\frac{1}{2} QL_\mu} \right] \left[ \frac{2J_1 \left( QR \sqrt{1 - \mu^2} \right)}{QR \sqrt{1 - \mu^2}} \right], \tag{3.2}
\]

\[
\mu = \cos \theta , \tag{3.3}
\]

where \( J_1 \) is the Bessel function of the first kind, \( R \) is the radius of
the cross section of the cylinder and \( L \) is the length of the cylinder. Similarly, \( P(Q) \) of this system is obtained by taking orientational average over the entire system. It is

\[
P(Q)_{\text{cyl}} = \frac{1}{2} \int_{-1}^{1} d\mu \left| F(Q)_{\text{cyl}} \right|^2
\]

However, there is no simple mathematical form for a particle of irregular shape. Thus, the \( d\Sigma(Q)/d\Omega \) of such systems cannot be analyzed using Eq. (2.29) in which the form factor has to be computed. In order to treat such a system the Guinier approximation \[4\] is often applied to determine the radius of gyration of the particle. Guinier approximation has been widely used for evaluating geometric information of noninteracting micellar and microemulsion systems of various particle shapes [5,6]. However, Guinier approximation, besides the fact that it is applicable only at small \( Q \) limit, requires the inter-particle interactions to be negligible at \( Q \to 0 \). It is thus not feasible to use Guinier approximation for analysis of an ionic micellar system whose inter-particle interactions are normally too strong. Therefore, Eq. (2.29) has to be used to analyze SANS data of an ionic micellar solution by computing both \( P(Q) \) and \( S(Q) \) explicitly.

3.2 Contrast Variation Technique

As stated in 2.1, (Eq. (2.24)), the structure of a particular part
of a particle in the solution can be viewed by varying the scattering length density of the solvent so that the only contrast, which neutron can see, is between this particular region of interest and its environment. This so called contrast variation technique has been applied for examination of the molecular structure and the aggregation number of a microemulsion droplet [7] and the surfactant tails distribution within a micellar core [8] assuming inter-particle interaction is negligible at \( Q \to 0 \) (i.e., \( S(Q) \equiv 1 \) at \( Q \to 0 \)). For system with \( S(Q) \equiv 1 \) at \( Q \to 0 \), the \( \frac{d\Sigma(Q)}{d\Omega} \) at \( Q \to 0 \) can be written as

\[
\frac{d\Sigma(Q)}{d\Omega} = n_p P(Q), \text{ for } Q \to 0
\]  

(3.5)

or more explicitly

\[
\frac{d\Sigma(Q)}{d\Omega} = (N_1 - \text{CMC}) \bar{n} \left[ \Sigma b_i - v_M \bar{\rho}_S \right]^2.
\]

\[
\langle |F_N(Q)|^2 \rangle, \quad Q \to 0
\]  

(3.6)

where the first factor denotes the total number of surfactant monomers per unit volume of solution that form micelles, \( \bar{n} \) is the average aggregation number, \( \Sigma b_i \) is the total scattering lengths within a surfactant monomer, \( v_M \) is the dry monomer volume, \( \bar{\rho}_S \) is the average scattering length density of the solvent, and \( F_N(Q) \) is the normalized form factor of the particle having a limiting value of 1 at \( Q = 0 \) when particles are spheres. It is easy to see from Eq.(3.6) that the square root of the scattering cross section is linearly proportional to \( \bar{\rho}_S \) since \( F_N(0) = 1 \) and \( \Sigma b_i \) and \( v_M \) are constant for a given micellar solution. Thus, if one
measures a series of micellar solutions of the same surfactant concentration but using different \( \text{D}_2\text{O}/\text{H}_2\text{O} \) mixtures as solvents, the quantity \( A_0 = \sqrt{d\bar{\Sigma}(0)/d\Omega} \) should fall onto a straight line when plotting versus \( \rho_S \). The \( \rho_S \)-axis interception of this plot gives the contrast matching point \( \bar{\rho}_m \) where \( \sum_{i=1}^{M} \Sigma_{b_i} = V_M \bar{\rho}_m \). From this contrast matching point \( V_M \) can be calculated since \( \Sigma_{b_i} \) is known and \( \bar{\rho}_m \) can be computed according \( \text{D}_2\text{O}/\text{H}_2\text{O} \) ratio at the intercept. In addition, the aggregation number can be obtained from the slope of this straight line using Eq.(3.6).

Although this contrast variation technique is very powerful for determination of molecular parameters of a colloidal particle, it subjects to two major drawbacks: first, it uses only one point of the entire \( d\Sigma(Q)/d\Omega \) spectrum (i.e., \( d\Sigma(0)/d\Omega \)) to construct \( A_0 \) vs \( \rho_S \) plot. This requires very accurate absolute measurement at small \( Q \) which is generally very difficult due to many reasons such as spectrometer calibration procedure, multiple scattering of the calibration sample, time dependent background counting rate, and so on. Secondly, it requires the inter-particle interactions to be negligible at \( Q \to 0 \) which is not feasible in the case of ionic micellar solutions. In order to extend the applicability of this technique so that it can be applied to ionic micellar systems, a so called contrast variation method at finite \( Q \) was proposed in this study. This method relaxes the noninteracting constrain and makes use of the entire \( d\Sigma(Q)/d\Omega \) spectrum. With this method one is able to determine the molecular parameters of an interacting colloidal particle. Detail description of this technique including determination of \( V_M \) and \( \bar{\rho}_m \) is given in Chapter V and VI when it is applied to \( \text{NaC}_{12}\text{OXYS} \) and \( \text{AOT} \) micellar systems.
References:


(2) This relation was recently derived by Prof. S. H. Chen. To author's knowledge, this relation has not been shown in any literature


CHAPTER IV

INTER-PARTICLE STRUCTURE FACTOR S(Q)

4.1 Introduction

As mentioned previously in Chapter II, SANS intensity distribution function consists of two parts, the intra-particle structure factor P(Q) and the inter-particle structure factor S(Q). P(Q), which mainly depends on by particle size and shape, is a decaying function when particles are nearly spherical while S(Q), which is governed by inter-particle interaction, shows an oscillatory behavior. In order to decompose \( d\Sigma(Q)/dQ \) into P(Q) and S(Q) a proper geometric model of the particle for calculation of P(Q) and a suitable statistical mechanical theory for computation of S(Q) are necessary. Calculation of P(Q) has been described in the previous chapter and would be discussed in detail in Chapter V and VI when it is applied to NaC\(_{12}\)OXS and AOT micellar systems. In this chapter a detail description of various statistical mechanical theories that are widely used for calculation of S(Q) is to be presented. For convenience in describing these theories S(Q) and the pair correlation function, g(r), which is related to S(Q) according to Eq.(2.30), will be used interchangeably in the discussion.

In 4.2 the classical Debye-Huckel theory is briefly described. A
summary of DLVO theory is given in 4.3. In 4.4 cluster expansion and
collection of Ornstein-Zernike (OZ) equation, hypernetted chain
approximation (HNCA), and mean spherical approximation (MSA) are given.
Section 4.5 describes the HNCA solutions of OZ equations and the
calculation procedure of S(Q) using HNCA. Section 4.6 devotes to dis-
cussions of one component and multi-component MSA solutions of OZ equa-
tion. In 4.7 rescaling of MSA is presented along with comparison of
HNCA and MSA theories in the calculation of S(Q).

4.2 Debye-Hückel Theory

In an electrolyte solution the relation of the electrostatic poten-
tial \( \Phi_i(r) \) to the charge density \( q_i(r) \) around a given ion \( i \) is
described by Poisson equation,

\[
\nabla^2 \Phi_i(r) = -\left(4\pi/\varepsilon\right)q_i(r),
\]

(4.1)

where \( \varepsilon \) is the dielectric constant of solvent (\( \varepsilon = 78.5 \) for water at 25
\( ^\circ \)C). This equation is exact and involves no approximation. However,
Eq.
(4.1) would not be useful unless \( q_i(r) \) can be expressed in terms of
the electrostatic potential \( \Phi_i(r) \). Since \( q_i(r) \) is a function of the
local number density of the other ions \( j \), it can be expressed in terms
of the local charge density or the pair correlation function as,
\[ q_i(r) = e \sum_j z_j N_j^i(r) \]
\[ = e \sum_j z_j N_j g_{i,j}(r) \]  \hspace{1cm} (4.2)

where \( e \) is the elementary charge, \( N_j^i(r) \) is the number density of \( j \) particle at \( r \) given a reference particle \( i \) at the origin, \( N_j \) is the number density of \( j \) particles in the bulk, and \( g_{i,j}(r) \) is the pair correlation function. To make Eq.(4.1) useful, the so called potential of the average force \( w_{ij}(r) \) is defined according to

\[ g_{i,j}(r) = \exp(-\beta w_{ij}(r)), \]  \hspace{1cm} (4.3)

where \( \beta = 1/k_B T \) is the Boltzmann factor. With this definition \( w_{ij}(r) \) contains all the interactions between particles \( i \) and \( j \). Debye and Hückel approximated \( w_{ij}(r) \) by the electrostatic interaction alone (with all the other interactions ignored), i.e.,

\[ w_{ij}(r) = e z_j \phi_i(r), \]  \hspace{1cm} (4.4)

and arrived the Poisson-Boltzmann (PB) equation,
\[ \nabla^2 \phi_i(r) = - \frac{4\pi}{\varepsilon} e \sum_j z_j n_j \exp[-\beta e z_j \phi_i(r)]. \] (4.5)

Furthermore, they linearized Eq. (4.5) and imposed a charge neutrality condition to yield the Debye-Hückel (DH) equation:

\[ \nabla^2 \phi_i(r) = \kappa^2 \phi_i(r), \] (4.6.a)

where \( \kappa^2 = (4\pi\beta e^2/\varepsilon) \Sigma z_i z_j \) \( \sum z_j \) (4.6.b)

is the Debye-Hückel screening constant. The solution of Eq. (4.6) in the spherical coordinate can be easily found to be

\[ \phi_i = (z_i e/\varepsilon) \exp(-\kappa r)/r. \] (4.7)

The corresponding pair correlation function can then be obtained from Eq. (4.4) by combining with a linearized expansion of Eq. (4.3):

\[ g_{ij}(r) = 1 - (\beta e^2/\varepsilon) z_i z_j \exp(-\kappa r)/r. \] (4.8)

With Eq. (4.8) the partial structure factor \( S_{ij}(Q) \) can be calculated according to Eq. (2.30) and the thermodynamic properties of the system computed from the pair distribution function using standard formula. The explicit expressions of these properties are given as follows:
Excess internal energy:

\[
\Delta E = \frac{2\pi e^2}{\varepsilon} \sum n_i n_j z_i z_j \int_0^\infty dr \frac{r^2 g_{ij}(r)}{r} = -\sum \frac{n_i (Z_i e)^2}{2(\kappa/\varepsilon)} \quad (4.9)
\]

Excess Helmholtz free energy:

\[
\Delta A = k_B T \int_0^{\beta B} \Delta E(\beta') \, d\beta' = -\frac{\kappa^3}{(12\pi\kappa)}, \quad (4.10)
\]

Osmotic coefficient ($\psi$):

\[
\psi - 1 = \beta (\partial \Delta A / \partial V)_T = -\frac{\kappa^3}{(24\pi^2 n_i)} \quad (4.11)
\]

Excess Gibb's free energy:

\[
\Delta G = \Delta A + (\partial \Delta A / \partial V)_T \sum n_i = -\frac{\kappa^3}{(8\pi\kappa)} \quad (4.12)
\]

Activity coefficient ($\gamma_z$):

\[
\ln \gamma_z = \beta \Delta G. \quad (4.13)
\]

The DH theory described above was derived under many assumptions.
which made possible these simple analytical results. A summary of assumptions made in the DH theory of point-like ions is listed below:

1. Approximation of \( w_{ij}(r) \) with electrostatic interaction.
2. All particles in the system are point-like.
3. Linearization of \( \exp[-\beta eZ \phi_j(r_j)] \), which is justified only when \( \phi(r_j) \) is small (i.e., the system is dilute).

Among these assumptions the neglect of excluded volume, which results from assumptions (1) and (2), causes the most severe effect. Lieb and Lebowitz [1] have shown that the internal energy of a point-like electrolyte solution would diverge and cause the system to collapse. To prevent the collapse, Debye and Huckel took into account the size of the central ion and solved DH equation by imposing the continuity of electrostatic field across the boundary of the central ion. The result is

\[
\phi_i(r) = (Z_i e/\varepsilon) \exp[-\kappa(r-\sigma/2)]/[r(1+\kappa\sigma/2)]
\]  

(4.14)

and

\[
g_{ij}(r) = 1 - Z_i Z_j (\beta e^2/\varepsilon) \exp[-\kappa(r-\sigma/2)]/[r(1+\kappa\sigma/2)],
\]  

(4.15)

where \( \sigma \) is the diameter of the central ion. Compare Eq. (4.8) and (4.15).
it is clear that the finite size effect of the central ion would be more and more significant when ionic strength of the system becomes larger. However, this version of DH theory (denoted as MDH), even though taking into account the size effect of the central ion, still neglects the excluded volumes of the ionic atmosphere. The thermodynamic properties calculated by MDH theory are as follows:

\[
\Delta E = - \sum_i \frac{n_i (eZ_i)^2}{\varepsilon} \left[ \frac{\kappa}{2(1+\sigma_k/2)} \right] \tag{4.16}
\]

\[
\Delta A = \Delta E + \frac{\kappa^2}{24\pi \beta} \tag{4.17}
\]

\[
\hat{\phi} - 1 = -\left(\frac{\kappa^2}{2\pi}\right) \sum_1 n_i + \text{(hard core contribution)} \tag{4.18}
\]

\[
\ln\gamma_z = -\beta \sum_i \frac{n_i (eZ_i)^2}{\varepsilon} \left[ \frac{\kappa}{2(1+\sigma_k/2)} \right] \sum_j n_j \tag{4.19}
\]

These two versions of DH theories have been compared to experiments [2,3]. Fig. 4.1 shows the comparison of relative \(\ln(\gamma_z)\) observed experimentally to that calculated by both DH and MDH theories. It is obvious that DH theories of both versions disagree with experimental values when system reaches certain concentration but show fairly good agreement at dilute limit.
4.3 DLVO Potential

The purpose of describing DLVO potential between two spheres is that this potential has been widely used as the pair potential function to solve one component OZ equation using MSA as the closure relation. The detail discussion of why DLVO potential is applied is to be given in 4.6.

The concept used to derive DLVO potential energy between two interacting double layers was proposed by Dube and Levine [4], that is to calculate the free energy change of a system of two identical charged spheres moving from infinitive to a finite distance r keeping the surface potential of the spheres unchanged. The detail derivation can be found in many literatures [5,6]. The result is

$$V_{DLVO}(r) = (\varepsilon \sigma^2 \phi_0 / 4) \exp[-\kappa (r-\sigma)] / r, \ r > \sigma$$  \hspace{1cm} (4.20)

Adapt the surface potential of the central ion in MDH theory one arrives at the so called DLVO potential between two double layers,

$$V_{DLVO}(r) = \frac{e^2 \varepsilon^2}{\varepsilon (1+\kappa \sigma / 2)^2} \frac{e^{-\kappa (r-\sigma)}}{r}, \ r > \sigma$$  \hspace{1cm} (4.21)

This is the potential form often used as the pair potential function in solving one component OZ equation with MSA [7,8,9,10].
4.4 Cluster Expansion

The pair distribution function $g_{ij}(r_{ij})$ from Eq. (4.2) and (4.3) can be expressed in terms of probability function as,

$$g_{ij}(r_{ij}) = p_{ij}(r_i, r_j)/[p_i(r_i) \cdot p_j(r_j)] \tag{4.22}$$

with

$$r_{ij} = |r_i - r_j| \tag{4.23}$$

where $p_{ij}(r_i, r_j)$ denotes the probability of finding ion $i$ at $r_i$ and ion $j$ at $r_j$ simultaneously. For an isotropic system $p_i(r_i) = p_i$ is position independent and $p_{ij}(r_{ij})$ is, in the canonical ensemble,

$$p_{ij}(r, r') = \Sigma_{i,j}^{N} \{ \delta(r - r_i) \delta(r' - r_j) \} \tag{4.24}$$

where $\{ \}$ stands for the average over the configurational canonical partition function:

$$p_{ij}(r, r') = \int ... \int_{r_1}^{r_N} dr_1 dr_2 ... dr_N \Sigma_{i,j}^{N} \delta(r - r_i) \delta(r - r_j) \cdot e^{-\beta U_N(r_1, ..., r_N)} \tag{4.25}$$

with the configurational partition function $Z_N$
\[ Z_N = \int \cdots \int dr_1 \cdots dr_N \exp[-\beta U_N(r_1 \cdots r_N)]. \] (4.26)

The total configurational potential \( U_N(r_1 \cdots r_N) \) is expressed as, in McMillan-Mayer theory [11],

\[ U_N(r_1 \cdots r_N) = \sum_{i>j}^N u_{ij}(|r_i - r_j|) \] (4.27)

where \( u_{ij} \) is pair potential between \( i \) and \( j \). Some properties of \( g_{ij}(r_{ij}) \) are listed as follows:

1. \( g_{ij}(r_{ij}) = g_{ji}(r_{ji}) \) (4.28)
2. \( g_{ij}(r_{ij}) = 0, \quad r_{ij} < \sigma_{ij} (\sigma_{ij} = (\sigma_i + \sigma_j)/2) \) (4.29)
   (i.e., there is no probability of finding \( j \) particle inside particle \( i \)).
3. \( \lim_{r \to \infty} g_{ij}(r_{ij}) = 1 \) (4.30)
4. number density of \( j \) ion in a spherical shell situated between \( r \) and \( r + dr \) from particle \( i \) is
   \[ \frac{dn_i}{dr} = \sum_j 4\pi r^2 p_j g_{ij}(r) \] (4.31)
5. The density-density correlation function
   \( h_{ij}(r_{ij}) \) has a simple relationship with \( g_{ij}(r_{ij}) \),
   \[ h_{ij}(r_{ij}) = g_{ij}(r_{ij}) - 1 \] (4.32)
Substitute \( u_N(\mathbf{r}_1 \cdots \mathbf{r}_N) \) with pair potential function \( u_{ij}(\mathbf{r}_{ij}) \) in Eq. (4.27) into Eq. (4.25) and expand integrand in Eq. (4.22) one obtains

\[
q_{12}(\mathbf{r}_{12}) = \frac{N(N-1)}{Z_1^p_1 Z_2^p_2} \int \prod_{i > j} dr_i \cdots dr_N \left[ f_{ij}(\mathbf{r}_{ij}) + 1 \right] \quad (4.33)
\]

For simplicity \( q_{12}(\mathbf{r}_{12}) \) was used to replace \( g_{ij}(\mathbf{r}_{ij}) \) which makes expression of the integrand more complicate. The function \( f_{ij}(\mathbf{r}_{ij}) \) in Eq. (4.33) is called Mayer's bond function defined as

\[
f_{ij}(\mathbf{r}_{ij}) = \exp[-\beta u_{ij}(\mathbf{r}_{ij})] - 1. \quad (4.34)
\]

Eq. (4.34) can actually be expanded into an infinite series and ordered according to their dependence on number densities of the particles in the system. However, it would be extremely complicate to formulate each term in the series explicitly, especially, the higher order terms. Thus, a diagrammatic representation of these terms is often used [12]. Each graph represents a cluster integral over all possible configurations and a summation over all particles in the system with integrands made up by products of Mayer's bond functions and number densities of the particles. Before representing Eq. (4.33) with diagrams we define the graphic notations as follows: (1) Black circle: field point carrying number densities of the particles. It also denotes summations of all particles with coordinates integrated over the entire space. (2) White circle: root point carrying no integral, summation or number density factor. (3) Bonds: representing the pair function between two species by
connecting them. With these notations and Eq. (4.33) $g_{12}(r_{12})$ can be expanded to be

$$g_{12}(r_{12}) = 1 + \circ \bigcirc + \bigcirc \bigcirc + \bigcirc \bigcirc + \bigcirc \bigcirc + \cdots$$

$$= 1 + h_{12}(r_{12})$$

$$= 1 + f(r_{12}) + \text{(all topological connected diagrams on two white circles without articulation circle which, when removed, would result in breaking of a diagram into two or more diagrams that contain no black circle)}$$

(4.35)

In this $g_{12}$ expansion there is a subset of diagrams that contain no "cutting circle" which, when removed from the diagram, would result in breaking of a diagram into two or more disconnected pieces. This group of diagrams, known to be the direct correlation function $c_{12}(r_{12})$, are

$$c_{12}(r_{12}) = \circ \bigcirc + \bigcirc \bigcirc + \left[ 2 \bigcirc \bigcirc + \bigcirc \bigcirc + \frac{1}{2} \bigg]$$

$$+ \bigcirc \bigcirc + \frac{1}{2} \bigg) + \bigg) + \cdots \right]$$

(4.36)

Compare $h_{12}(r_{12})$ and $c_{12}(r_{12})$ one finds

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\[ h_{12}(r_{12}) = c_{12}(r_{12}) + \int \int n_3 \, n_4 \, c_{13}(r_{13}) \, c_{34}(r_{34}) \, c_{42}(r_{42}) \, d3 + \]

\[ \cdots \]  

\[ (4.37) \]

These convolution type of integrals can be combined to yield

\[ h_{ij}(r_{ij}) = c_{ij}(r_{ij}) + \sum_k n_k \int c_{ik}(r_{ij}) \, d_3 \]

\[ \left( \frac{r_{jk}}{r_{ij}} \right) h_{kj}(r_{kj}) \, d_3 \]  

\[ (4.38) \]

This is the well known Ornstein-Zernike (OZ) integral equation on which modern statistical mechanics is based.

On the other hand, if we represent \( g_{12}(r_{12}) \) by the potential of average force \( w_{12}(r_{12}) \), Eq.(4.3),

\[ g_{12}(r_{12}) = \exp[-\beta w_{12}(r_{12})] \]  

\[ (4.39) \]

\[ -\beta w_{12}(r_{12}) = \ln g_{12}(r_{12}) , \]  

\[ (4.40) \]
and express \(-\beta w_{12}(r_{12})\) with diagrams, we have

\[
-\beta w_{12}(r_{12}) = -\beta u_{12}(r_{12}) + \frac{1}{2} \left( \right) + \left( \right) + \cdots
\]

\[
= -\beta u_{12}(r_{12}) + \text{sum of all diagrams with no bond between two white circles.}
\]

\[
= -\beta u_{12}(r_{12}) + h_{12}(r_{12}) - c_{12}(r_{12}) + d_{12}
\]

where \(d_{12}\) contains all the "bridge diagrams" which can not be represented by convolution of \(c_{12}\) and \(h_{12}\). The hypernetted chain approximation (HNCA) was obtained by neglecting all the bridge diagrams, i.e.,

\[
-\beta w_{12} = \ln g_{12}(r_{12}) \equiv -\beta u_{12}(r_{12}) + h_{12}(r_{12}) - c_{12}(r_{12}).
\]

The general HNCA equation reads

\[
c_{ij}(r_{ij}) = -\beta u_{ij}(r_{ij}) + h_{ij}(r_{ij}) - \ln \left[ h_{ij}(r_{ij}) + 1 \right].
\]

If the short range interaction between particle \(i\) and \(j\) is further neglected (i.e., to approximate \(\ln[h_{ij}(r_{ij})+1] \) with \(h_{ij}(r_{ij})\)) one obtains the mean spherical approximation (MSA),

\[
c_{ij}(r_{ij}) = -\beta u_{ij}(r_{ij}).
\]
From above description it is clear that OZ equation, HNCA, and MSA are consequences of the cluster expansion. Among these results OZ equation is a coupled integral equation with no approximation involved while HNCA and MSA involve different degree of approximations. Since OZ equation is a coupled equation one needs a closure relation to solve it. HNCA and MSA are the two closures frequently used for solving OZ equation. In the following sections we shall discuss how HNCA and MSA are applied to solve OZ equation.

4.5 Hypernetted Chain Approximation

The solution of OZ equation using HNCA closure has been known to be the most accurate theory in modern treatment of a statistical mechanical system. However, HNCA itself is an implicit equation, thus, the solution of OZ equation using HNCA closure can only be obtained through numerical calculation in spite of the pair potential used for \( u_{ij}(r_{ij}) \) in Eq(4.45).

Although several algorithms have been proposed for solving OZ/HNCA equations numerically [13,14,15] the basic concepts are similar. We summarize the step by step procedure in solving OZ/HNCA equations as follows: rewrite the HNCA closure as

\[
c_{ij}(r) = \exp[\gamma_{ij}(r) - \beta u_{ij}(r)] - \gamma_{ij}(r) - 1,
\]

(4.47)
where \( \gamma_{ij}(r) = h_{ij}(r) - c_{ij}(r) \). \hspace{1cm} (4.48)

Define Fourier transform of \( \gamma_{ij}(r) \) by

\[
\tilde{\gamma}_{ij}(Q) = \int_0^\infty \gamma_{ij}(r) \frac{\sin(Qr)4\pi r^2}{Qr} \, dr, \hspace{1cm} (4.49)
\]

one obtains an equation

\[
\tilde{\gamma}_{ij}(Q) = \sum_k n_k \tilde{c}_{ik}(Q) \tilde{h}_{kj}(Q), \hspace{1cm} (4.50)
\]

Upon using the OZ equation

\[
\tilde{h}_{ij}(Q) = \tilde{c}_{ij}(Q) + \sum_k n_k \tilde{c}_{ik}(Q) \tilde{h}_{kj}(Q). \hspace{1cm} (4.51)
\]

Based on Eq.(4.47) to (4.51) the step by step HNCA iteration is performed according the following procedure:

1. give a set of function \( \gamma_{ij}(r) \)
2. compute \( c_{ij}(r) \) using Eq.(4.47)
3. compute \( \tilde{c}_{ij}(Q) \)
4. compute \( \tilde{h}_{ij}(Q) \) from Eq.(4.51)
5. compute \( \tilde{\gamma}_{ij}(Q) \) by use of Eq.(4.50)
6. compute inverse Fourier transform of \( \tilde{\gamma}_{ij}(Q) \)
7. repeat from step 2 until stable solution of \( \gamma_{ij}(r) \) is obtained.
(8) compute $S_{ij}(Q)$ using $g_{ij}(r) = h_{ij}(r) + 1$ and Eq. (2.30).

Although HNCA provides the most accurate result for $S_{ij}(Q)$ and $g_{ij}(r)$ it has two major drawbacks: (1) multi-component HNCA is poorly convergent in the iteration processes, and (2) the range of particle charge and size in which HNCA solution exist is limited. The boundary of this range, which can be defined on the isothermal compressibility - coupling constant plot, is called the spinodal curve. The isothermal compressibility $\kappa_T$ is related to structure factor $S_{ij}(Q)$ by

$$\lim_{Q \to 0} S_{ij}(Q) = \beta \sqrt{\frac{n_i n_j}{n}} \kappa_T$$

(4.52)

Since $\kappa_T$ is a physical quantity it has to be nonnegative. Thus, the $h_{ij}(r)$ and $g_{ij}(r)$ obtained from numerical iteration would not be accepted as HNCA solutions if they correspond to negative isothermal compressibility. The parameter used to determine the spinodal curve is the coupling constant $\Gamma_{ij}$ defined as

$$\Gamma_{ij} = \beta Z_i Z_j e^2 / (a_{ij} \epsilon)$$

(4.53)

where

$$a_{ij} = \left[ \frac{3}{4\pi} \sqrt{n_i n_j} \right]^{-1/2}.$$ 

(4.54)

It is clear to see from Eq. (4.53) that the spinodal curve depends mainly on parameter $Z_i Z_j / a_{ij}$ (or the charge density on the surface of the...
particle). Abernethy et al. have constructed part of the spinodal curve (see Fig. 4.2) [16]. For example, \( \Gamma_{ij} \) for a system of volume fraction 0.2 results in negative \( \kappa_T \) when it is greater than \( \sim 40 \). That is to say that the spinodal point of this system is at \( \Gamma_{ij} \approx 40 \). Similarly, the spinodal point of a system of volume fraction 0.4 is at \( \Gamma_{ij} = 100 \). Unfortunately, most of the ionic micellar solutions investigated in this study have \( \Gamma_{ij} > 200 \) if fully ionization of counterions is assumed which, according the constrain of HNCA described above, are far beyond the region solvable by HNCA. Thus, HNCA is verly limited when applied to strongly interacting micellar solutions. In order to analyze such systems, the simpler but perhaps less accurate MSA closure was used to solve OZ equation. For some particular MSA closures the analytical solutions of OZ equation have been obtained and proved to be satisfactory in calculating thermodynamic properties of simple electrolye solutions and in characterizing the growth of ionic micelles [17-20]. Detail description of various MSA solutions of OZ equation and their mutual relationship are to be discussed in the following sections.

4.6 Mean Spherical Approximation (MSA)

As described in the previous section, MSA is a linearized version of HNCA by neglecting the logarithmic term which governs the short range interactions between particles. With this approximation the MSA closure contains no \( h_{ij}(r_{ij}) \),

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\[ c_{ij}(r) = -\beta u_{ij}(r). \] (4.55)

Thus, the only effort in solving OZ equation with MSA is to give \( u_{ij}(r) \) a proper form. Two most common forms of \( u_{ij}(r) \) are: Coulomb potential form, commonly used in solving multi-component OZ equations (abbreviated as MCCF),

\[ c_{ij}(r) = \frac{-\beta z_i z_j e^2}{\varepsilon} \quad \text{(MCCF)} \] (4.56)

and Yukawa potential form (screened Coulomb potential) which is widely applied while solving one component OZ equation (abbreviated as OCM),

\[ c_{ij}(r) = A \left( e^{-\kappa r}/r \right) \quad \text{(OCM)} \] (4.57)

where \( \kappa \) is Debye-Hückel screening constant and \( A \) is the prefactor and is normally a function of charge and size of the particle. The respective analytical solutions of OZ equation using these two closures have been obtained [21,22] and the structure factors so calculated has been applied to SANS data analysis of ionic micellar solutions and shown to be satisfactory [20,21,22]. However, when DLVO potential is used as direct correlation function in OCM picture, the micellar charge, \( Z_{OCM} \), extracted through SANS data fitting is different from that obtained from MCCF, \( Z_{MCCF} \). To clarify this point and obtain the real charge using these theories, we first give a brief discussion on the analytical solution of OZ equation using MCCF and OCM closures. We then prove that if one represents the MCCF with an effective one component macroion (MOCM)
system, in which the other components are assumed to be point-like, the
effective direct correlation function \( c_{\text{eff}}(r) \) has a Yukawa form with a
prefactor \( A' \) (see Eq. (4.57)) different from that of the DLVO potential (see Eq. (4.21)) but leads to it at the dilute limit. This con-
sequence explains why MCCF and OCM give identical \( S(Q) \) when they are
used for SANS data analysis but give different charges. Thus, if one
uses MOCM instead of OCM to analyze SANS data of an ionic micellar solu-
tion both charge and \( S(Q) \) extracted should be comparable to that of MCCF
if the counterion sizes are negligible compare to micelles.

4.6.1 Multi-component Coulomb Fluid (MCCF)

In MCCF the so called primitive model is adapted where the solvent
(in this case water) is regarded as a continuum with a dielectric con-
stant \( \epsilon \). The counterions, coions, (if any), and the micelles are
treated as charged hard spheres of finite sizes and the direct correla-
tions among them are of bare potential forms,

\[
c_{ij}(r) = -\beta \frac{Z_i Z_j e^2}{\epsilon}, \quad r > \sigma_{ij} \quad [\equiv \frac{\sigma_i + \sigma_j}{2}] \quad (4.58)
\]

where \( \sigma_i \) and \( \sigma_j \) are diameters of particle \( i \) and \( j \) respectively. For
hard sphere, the density distribution of particle \( j \) inside particle \( i \) is
simply zero, i.e.,

\[
h_{ij}(r) = -1 \text{ for } r < \sigma_{ij}. \quad (4.59)
\]
With boundary condition Eq. (4.59) and the closure Eq. (4.58) the multicomponent OZ equations can be solved analytically using Baxter's method [24]. The result is

$$S_{ij}(Q) = \delta_{ij} 2\pi \sqrt{N_i N_j} \left[ G_{ij}(-iQ) - G_{ij}(iQ) \right]/iQ \quad (4.60)$$

where

$$G_{ij}(s) = \int_0^\infty dr g_{ij}(r)e^{-sr} \quad (4.61)$$

is a complicated function of the physical parameters $Z_i$ and $\sigma_i$. The explicit expressions of $G_{ij}(iQ)$ is given in reference [21]. In this derivation an important quantity $2\Gamma$, known to be the generalized screening parameter, is obtained by solving the following implicit equation,

$$(2\Gamma)^2 = \frac{4\pi \beta \varepsilon^2}{\varepsilon} \sum_{i=0}^{M} N_i \left[ \frac{Z_i - (\Pi/2\Lambda)\sigma_i^2 P_n}{1 + \Gamma \sigma_i} \right]^2 \quad (4.62)$$

where $M$ is number of particle kinds, $\Delta$ and $P_n$ are function of $\Gamma$ and the physical parameters, $Z_i$, and $\sigma_i$. Their explicit expressions are available in ref. [21]. $\Gamma$ takes into account the size effects of the particle in the system on screening power. It leads to $\kappa$ if all sizes, except micelle, are assumed to be point-like and the summation index $i$ in Eq. (4.62) is taken from 1 to $M$ instead of from 0 to $M$ (This is to assume that micelles have no contribution to screen constant).
Since $S_{ij}(Q)$ so calculated involves basic parameters $\sigma_i$ and $Z_i$, one can extract these parameters when using MOCF theory for SANS data analysis. Some theoretical and experimentally extracted $S_{ij}(Q)$ are given in Fig. 4.3, 4.4, 4.5, 5.7, 5.8, and 6.6.

4.6.2 One Component Macroion Theory (OCM)

Instead of using bare coulomb potential for $c_{ij}(r)$ OCM uses DLVO potential, Eq.(4.21), for $c(r)$ and the boundary condition $h(r) = -1$ for $r < \sigma_0$ to solve one-component OZ equation. The structure so obtained is [7],

$$S_{00}(Q) = 1 + 2\pi N_0 [\tilde{G}_{00}(-iQ) - \tilde{G}_{00}(iQ)]/iQ \quad (4.63)$$

where $\tilde{G}_{00}(s)$ has the same definition as Eq.(4.61) with both $i$ and $j$ equal to 0. The explicit form of $\tilde{G}_{00}(s)$, in terms of $Z_0$ and volume fraction of the micelle $\eta = (\pi/6)N_0\sigma_0^3$, is also given in ref. [21]. In the process of solving OZ equation using OCM one has to solve a quadratic equation (Eq. II.15 of ref. [21]) to get an intermediate parameter $\gamma_0$ which is directly related to $\tilde{G}_{00}$. $\gamma_0$ is one of the roots of the quadratic equation that has minimum absolute value [20].

The structure factor so calculated $S_{00}(Q)$ has been applied to analyze SANS data of ionic micellar solutions by several colloidal
workers [8,9,10] and shown to be successful. However, the charges of the micelles extracted are not sufficiently accurate due to approximation introduced by DLVO potential. The charge obtained by OCM can be corrected by replacing DLVO with the effective correlation function $c^{\text{eff}}(r)$ in solving OZ equation. Derivation of $c^{\text{eff}}(r)$ and $S_{00}(Q)$ thus calculated (i.e., MOCM) is to be described in next section.

4.6.3 Modified One-Component Macroion Theory (MOCM)

It has been shown that the accuracy of $S_{00}(Q)$ and the associated micellar parameters, such as charge and size, depend heavily on the forms chosen for direct correlation function while solving OZ equation with MSA in primitive model [21,22]. Since two potential forms commonly used for $c(r)$, MOCF and OCM, discussed in the previous subsections show different micellar charges it is necessary to investigate these two charges by examining their direct correlation function. Here we derive the effective one-component direct correlation function of MOCF and compare it to DLVO which is used in OCM theory.

To derive $c^{\text{eff}}(r)$ we start by modeling the micelle of number density $n_0$ and charge $Z_0 e$ and the ions in the solution (number density $n_i$, charge $Z_i e$, i=1,2,⋯) as a highly asymmetric electrolyte obeying the charge neutrality condition

$$n_0 Z_0 + \sum n_i Z_i = 0.$$  \hfill (4.64)
In this model the interactions between charged species are taken to be

\[ u_{ij}(r) = \infty \quad r < \sigma_{ij} \]
\[ = Z_i Z_j e^2 / \varepsilon r \quad r > \sigma_{ij} \] (4.65, 4.66)

The structure of such an asymmetric electrolyte solution can be described by the pair correlation function \( g_{ij}(r) \) (and thus \( S_{ij}(Q) \)) and the total correlation function \( h_{ij}(r) \). The total correlation functions relate to direct correlation function according to OZ equations

\[ \tilde{h}_{ij}(Q) = \tilde{c}_{ij}(Q) + \sum_{l=0}^{M-1} n_l \tilde{c}_{il}(Q) \tilde{h}_{lj}(Q), \quad i, j, l = 0, 1, \ldots \] (4.67)

where \( M \) is total number of species in the system and

\[ \tilde{h}_{ij}(Q) = \int d^3 r \exp(-iQ \cdot r) h_{ij}(r) \] (4.68)

For micellar-micellar correlation, particularly, one has

\[ \tilde{h}_{00} = \tilde{c}_{00} + n_0 \tilde{c}_{00} \tilde{h}_{00} + n_1 \tilde{c}_{01} \tilde{h}_{01} + \cdots . \] (4.69)

Express \( \tilde{h}_{01} (i \neq 0) \) by \( \tilde{c}_{ij} \) (\( i,j=0,1,2,\ldots \)) one arrives the following equation for \( \tilde{h}_{00} \),
\[
\tilde{h}_{oo} = \tilde{c}_{oo} + \tilde{c}_o^T \left[ \bar{I} - \tilde{c}_o^* \right]^{-1} \tilde{c}_o + \\
n_0 \left[ \tilde{c}_{oo} + \tilde{c}_o^T \left[ \bar{I} - \tilde{c}_o^* \right]^{-1} \tilde{c}_o \right] \tilde{h}_{oo}
\] (4.70)

where the column matrix \( \tilde{c}_o \) has elements

\[
(\tilde{c}_o)_i = \sqrt{n_i} \tilde{c}_{oi}(Q) \quad i = 1, 2, \cdots ,
\] (4.71)

\[
(\tilde{c}^*)_{ij} = \sqrt{n_in_j} \tilde{c}_{ij}(Q) \quad i = 1, 2, \cdots ,
\] (4.72)

and \( \bar{I} \) is \( M \times M \) unit matrix. By defining the effective direct correlation function between micelles to be

\[
\tilde{c}^{\text{eff}}(Q) = \tilde{c}_{oo}(Q) + \tilde{c}_o^T \left[ \bar{I} - \tilde{c}_o^* \right]^{-1} \tilde{c}_o ,
\] (4.73)

one obtains the effective one component OZ equation for micelles,

\[
\tilde{h}_{oo}(Q) = \tilde{c}^{\text{eff}}(Q) + n_0 \tilde{c}^{\text{eff}}(Q) \tilde{h}_{oo}(Q) .
\] (4.74)

In spatial space it reads
\[ h_{00}(r) = c_{\text{eff}}(r) + n_0 \int_{\text{all space}} c_{\text{eff}}(r) h_{00}(|r - r'|) \, d^3r'. \quad (4.75) \]

Assume all the ions, except micelle, are point-like we write

\[ c_{ij}(r) = -\beta \frac{Z_i Z_j e^2}{\varepsilon r} + c_{ij}^S \quad i,j=0,1, \ldots, r > 0 \quad (4.76) \]

where \( c_{ij}^S \) represents the deviation of \( c_{ij}(r) \) from coulombic form which is satisfactory asymptotically. Since all the ions, except micelle, are point-like, it is easy to see that

\[ c_{00}^S(r) = 0, \quad \text{for } r > \sigma_0, \]
\[ c_{0i}^S(r) = 0, \quad \text{for } i=1,2, \ldots \text{ and } r > \sigma_0 / 2, \]
\[ c_{ij}^S(r) = 0, \quad \text{for } i,j=1,2, \ldots \text{ and } r > 0. \quad (4.77) \]

Taking Fourier transform of \( c_{ij}(r) \) in Eq. (4.76) and substitute into Eq. (4.73) one obtains [27,28],

\[ \tilde{c}_{\text{eff}}(Q) = \tilde{c}_{00}^S(Q) + \sum_{i=1}^{M-1} \tilde{c}_{0i}^S \quad - \frac{(\tau_0 + \sum_{i=1}^{M-1} \tau_i \tilde{c}_{0i}^S)^2}{Q^2 + \kappa^2} \quad (4.78) \]

where \( \tau_i = (4\pi B n_i)^{1/2} Z_i \quad i=0,1,2,3 \ldots \quad (4.79) \)
\[ I_B = \beta e^2 / \epsilon. \]  \hspace{1cm} (4.80)

The next step is to perform the inverse Fourier transform of \( \tilde{c}^{\text{eff}}(Q) \) to give \( c^{\text{eff}}(r) \) for \( r > \sigma_0 \) which is regarded as the effective pair potential defined to be, in MSA closure,

\[ \beta u^{\text{eff}}(r) = - c^{\text{eff}}(r). \]  \hspace{1cm} (4.81)

The inverse Fourier transform of the first term in the right-hand side of Eq. (4.78) gives no contribution for \( r > \sigma_0 \) (see Eq. (4.77)) and so does the second term which can be seen from convolution theorem and Eq. (4.77). Thus, the only effort needed is to perform the inverse Fourier transform of the last term in r.h.s of Eq. (4.78). To perform the inverse Fourier transform \( c_{0i}^s \) has to be known. The analytical form of \( c_{0i}(r) \) for \( r < \sigma_0 / 2 \) has been given by Hiroike \[29],

\[ c_{0i}(r) = - \frac{1}{1-\eta} - \frac{2Z_0^2 \lambda B^2 \zeta}{\sigma_0} \quad r < \sigma_0 / 2, \]  \hspace{1cm} (4.82)

where \( \eta \) is the micellar volume fraction and

\[ \zeta = (\Gamma \sigma_0 + \xi) / (1 + \Gamma \sigma_0 + \xi), \]  \hspace{1cm} (4.83)

\[ 4\Gamma^2 = \kappa^2 \tau_0^2 / (1 + \Gamma \sigma_0 + \xi)^2, \]  \hspace{1cm} (4.84)

\[ \xi = 3\eta / (1 - \eta). \]  \hspace{1cm} (4.85)
Substitute Eq.(4.82) into Eq.(4.76) and take the Fourier transform of $c_0^S(R)$ one obtains

$$
\tilde{c}_0^S(Q) = C_i \frac{\sin(QR)}{Q^3} + D_i \left( \frac{R}{Q^2} \right) \cos(QR), \quad (4.86)
$$

where

$$
C_i = - \left[ \frac{4\pi}{1 - n} + \frac{4\pi Z_o Z_1 L_B \xi}{R} \right], \quad (4.87)
$$

$$
D_i = C_i + \frac{(4\pi Z_o Z_1 L_B)}{R}, \quad (4.88)
$$

and $R = \sigma_0/2$ is the radius of the micelle. We then take the inverse Fourier transform of the last term in r.h.s. of Eq.(4.78), employing theorem of residues, to get the effective direct correlation function $c^{\text{eff}}(r)$ as

$$
c^{\text{eff}}(r) = -Z_0^2 L_B \kappa^2 \left( e^{-\kappa \rho}/\rho \right) \text{ for } r > \sigma_0, \quad (4.89)
$$

where

$$
X = \cosh(\kappa R) + U \left[ \kappa R \cosh(\kappa R) - \sinh(\kappa R) \right], \quad (4.90)
$$

and

$$
U = \xi/(\kappa R)^3 - \zeta/(\kappa R). \quad (4.91)
$$

It is clear from Eq.(4.89) that the effective one component direct correlation function has a Yukawa form but with a prefactor different from that of DLVO potential. However, at dilute limit, i.e., $n_0 \to 0$,
the prefactor of Eq. (4.89) reduces to that of DLVO pair potential (see Eq. (4.21)), i.e.,

\[
\lim_{n_0 \to 0} \left( -Z_0^2 \frac{I_B \chi^2}{n_0} \right) = \frac{-\beta \exp(\kappa \sigma) Z_0^2 \varepsilon^2}{\varepsilon \left[ 1 + \kappa \sigma / 2 \right]^2}.
\]

(4.92)

From the fact that the effective one component direct correlation function \( c^{\text{eff}}(r) \) has also a Yukawa form but with different prefactor from that of DLVO potential one can easily explain why both OCM and MCCF give satisfactory \( S_{00}(Q) \) but different charges of micelles.

Using this effective direct correlation function one can solve one component OZ equation to calculate \( S_{00}(Q) \) for SANS data analysis. The micellar charge thus extracted from SANS data should be nearly identical to that obtained from MCCF once the sizes of the ions in the solution are negligible compare to micelle. Fig. 4.3 shows MOCM correction to OCM charges for SDS micellar solutions. Note, \( \alpha_{\text{MOCM}} \) (fractional charge of the micelle) is in general small than that of OCM (i.e., \( \alpha_{\text{OCM}} \)). The MCCF charges for SDS (see appendix D) are also smaller than \( \alpha_{\text{OCM}} \) indicating the significance of MOCM correction. However, \( \alpha_{\text{MCCF}} \) is not the same as \( \alpha_{\text{MOCM}} \) because the size effects of counterions were neglected in MOCM picture.

In spite of the fact that MSA shows reasonable applicability in analyzing SANS data, there is a natural drawback of MSA due to neglect of the short range correlation which is taken into account in HNCA. This defect of MSA is reflected by having negative \( g_{00}(r) \) at \( r = \sigma_0 \) in
solving OZ equation. This unphysical result of MSA occurs when volume fraction $\eta < 0.2$. In order to recover this defect many rescaling mechanisms have been proposed based on Gillan’s condition [24,28] which artificially increases the micellar size until $g_{o0}(\sigma_o') = 0$. The new boundary of the micelle $\sigma_o'$ represents the MSA interaction boundary. All the proposed rescaling mechanisms give satisfactory $S_{o0}(Q)$ but renormalize the charge of the micelle to a lower value depending on the rescaling mechanism. Detail description of this aspect is given in the following section.

4.7 Rescaling of MSA And Its Comparison With HNCA

It is well known that ionic surfactants form micellar aggregates in aqueous solutions spontaneously when concentration of the surfactant monomers exceeds a threshold value called critical micellar concentration. The formation of micellar aggregates in aqueous solution is a cooperative process driven by strong hydrophobic interactions between the tails of the surfactants in the aqueous environment. The energetically favorable self association is however counterbalanced by a decreasing entropy of dispersion upon micellization. Thus near CMC micelles are formed with a well defined minimum size consistent with the geometrical packing constrain of the tail groups of the surfactant molecules. For example, a surfactant such as SDS has hydrocarbon tail of length $l = 16.7$ Å and a steric volume of $V_T = 350 \text{ Å}^3$ which results in formation of a minimum compact spherical micelle of aggregation of 53
Similarly, NaC_{12}OXYS has corresponding parameters $l = 13.75$ Å and $V_T = 370$ Å$^3$ resulting in a minimum aggregation number of 30. For surfactant concentration not too far above the CMC (without electrolyte added) the micellar aggregates grow slowly in size while their shape changes from spherical to spheroidal. Take the case of NaC_{12}OXYS at concentration of 4gm/dL and temperature of 53.6 °C, the measured mean aggregation number is 49.8 indicating micelles of spheroidal shape with an axial ratio 1.69 or an equivalent sphere of diameter 48.3 Å. The SANS experiment shows that the micellar system at this condition is nearly monodisperse so it can be considered as a two-component macroion-counterion system. In this case the micelles are charged macroions with surface charges equal to or less than the mean aggregation number $\bar{n}$ in equilibrium with the counterion (Na$^+$) cloud surrounding them. The situation is similar to an electrolyte solution except that in the micellar solutions the charge and size between micelle and counterion are highly asymmetric.

For the theoretical treatment of this type of systems the similarities with simple electrolyte solutions prompt the application of the primitive model for ionic solutions [2]. According to this simple model, the charge aggregates and the small ions are treated as uniformly charged spheres immersed in a solvent of a dielectric continuum with dielectric constant $\varepsilon$. The solvent averaged pair potentials are then assumed to be given as
\[ u_{ij}(r) = \frac{Z_i Z_j e^2}{\varepsilon r} \quad \text{for } r > \sigma_{ij} \quad (4.93) \]

where \( r \) is the distance between the particles \( i \) and \( j \) of valences \( Z_i \) and \( Z_j \), and diameters \( \sigma_i \) and \( \sigma_j \), and \( e \) is the elementary charge. The most successful statistical mechanical treatments of this model have so far been based on the application of the OZ equation for the total correlation functions \( h_{ij}(r) \) between ion pair \( i \) and \( j \):

\[ h_{ij}(r) = c_{ij}(r) + \sum_k n_k \int c_{ik}(r) h_{kj}(|r-r'|) \, d^3r' \quad (4.94) \]

coupled with the approximate closure relations for the direct correlation function \( c_{ij}(r) \) [32]. In the case of MSA one takes the closure relations as:

\[ c_{ij}(r) = -\beta u_{ij}(r) \quad \text{for } r > \sigma_{ij} \quad (4.95) \]

\[ h_{ij}(r) = -1 \quad \text{for } r < \sigma_{ij} \quad (4.96) \]

In the case of HNCA:

\[ c_{ij}(r) = -\beta u_{ij}(r) + h_{ij}(r) - \ln[h_{ij}(r)+1] \quad (4.97) \]

By comparison with computer simulations of the primitive model electrolyte solutions, HNCA has been confirmed to be an accurate theory.
for the structural and thermodynamic properties of 1-1 and 1-2 electrolyte solutions [33,34]. Recently, the application of HNCA has been extended to the study of highly asymmetric charge systems such as the ionic colloidal solutions [35-41] but its accuracy is not yet verified for these extremely conditions. One of the problems of HNCA in dealing with highly charged systems at low concentration is that the conventional numerical iteration often fails to converge [16,40]. This is due to the fact that there is a broad range of states within which nonphysical compressibility values would be obtained from results of the HNCA calculation (Eq.(25) to Eq.(29) of reference 16). The boundary of the instability (spinodal curve) can be defined in terms of two variables, namely, the volume fraction $\eta$ of the solution and the reduced temperature $T_R$ as

$$T_R = k_B T / u_{01}(\sigma_{01})$$

(4.98)

where 0 denotes the macroion and 1 the counterion. $u_{01}(\sigma_{01})$ is a measure of the maximum strength of macroion-counterion interaction. Unfortunately, typical micellar solutions of macroion charge above 50 and volume fractions less than 0.05 would correspond to states beyond the spinodal curve [16] in the $T_R - \eta$ plane for a meaningful HNCA solution to be found. For these reasons and for the fact that HNCA is a non-analytic theory, the simpler but perhaps less accurate MSA approach becomes relevant. One major advantage of MSA is that its solution to a multi-component coulomb fluid has been obtained analytically [21,24]. Thus no numerical instability would be encountered. However, MSA tends
to produce a nonphysical negative pair correlation function between macroions near the contact when the volume fraction is low and charge is high. In order to overcome this defect we previously proposed a rescaled MSA (RMSA) [24] for calculations of inter-micellar structure factors when the solutions are dilute and micellar charges are high, thus extending the applicability of the MSA to a broader range covering all the experimental conditions. In this RMSA, the effective macroion diameter $\sigma'_0 > \sigma_0$ is introduced according to a condition $\gamma_{00}(\sigma'_0) = 0$ for cases where $\gamma_{00}(\sigma_0)$ is negative. With this impenetrable model [24] the macroion-counterion contact distance would be increased. One thus assumes that the ions within the expanded volume belong to part of the rescaled colloidal particle of diameter $\sigma'_0$ with a consequence that charge $|Z'_0| < |Z_0|$. It is obvious that, at given $Z'_0$, the detailed counterion distribution $\gamma_{01}(r_{01})$ within $r_{01} < \sigma'_0/2$ has no effect on the MSA solution of the convolution integrals in Eq. (4.94) as long as $\gamma_{00}(r)$ is spherosymmetrical and the only long range contribution to $c_{01}(r_{01})$ is the direct coulomb interaction.

The results of SANS experiment can be analyzed in terms of different approximate theories of electrolyte solutions including MSA, RMSA, and HNCA. In all these theories, the micellar charge $Z_0$ is treated as an adjustable parameter. A central quantity in these analyses is the mean aggregation number of the micelles, $\bar{n}$. From several previous SANS studies of ionic micellar solutions [8,9,10] it is amply clear that the position of the prominent interaction peak observed in all the SANS experiments at low ionic strengths is uniquely related to $\bar{n}$. Assuming the
micellar system to be reasonably monodispersed, one can generally write
the differential cross section per unit volume as
\[ \frac{d\Sigma(Q)}{d\Omega} = I(Q) = n_p P(Q) S(Q) \]  
(4.99)

The first factor \( n_p \) is the number of micelles per unit volume which can
be determined from the concentration of the surfactant molecules once \( \bar{n} \)
is specified. The particle structure factor \( P(Q) \) for a compact micellar
aggregate can also be shown to depend on \( \bar{n} \) and the hydration number \( N_H \)
of the head group which is usually a constant for a given surfactant
molecule (for example, for NaC\(_{12}\)OXY at 53.6 °C, \( N_H \approx 20 \)). Thus, the
extraction of the intermicellar structure factor \( S(Q) \) (which is an
abbreviation of \( S_{oo}(Q) \)) from measured \( I(Q) \) depends essentially on being
able to specify \( \bar{n} \) correctly. A conventional method of simultaneously
deducing \( \bar{n} \) and \( S(Q) \) from the experimental data is to use the one-com-
ponent (OCM) model for calculation of \( S(Q) \) [7]. In this model one needs
two input parameters, the effective surface charge \( Z_{OCM} \) and the effec-
tive hard sphere diameter \( \sigma_0 \). The latter quantity is uniquely related
to \( \bar{n} \) and the hydration number. The whole spectrum \( I(Q) \) is then least
square fitted to Eq.(4.99) using these two adjustable parameters. This
fitting is unique because \( \bar{n} \) largely determines the position of the
interaction peak and \( Z_{OCM} \) controls the height and the width of the peak.
In the previous communication [24] we showed that \( S(Q) \) can also be
calculated from a two-component MSA (i.e., two-component MOCF) or RMSA
of the primitive model. This latter model can achieve an equally good
fit to SANS data with essentially the same \( \bar{n} \) but a different charge \( Z_{MSA} \).
(or $Z_{\text{RMSA}}$). $Z_{\text{MSA}}$ is usually smaller than $Z_{\text{OCM}}$. We found that $Z_{\text{MSA}}$ is close to the value of the so-called dressed charge of the micelle [42] and the resulting $S(Q)$ extracted from the experiment is nearly identical to the OCM model.

Recently, we showed that an HNCA related closure called HNCA/Percus Yevick approximation [42] is also capable of yielding the same $S(Q)$ with the fully ionized macroion charges in the case of low concentrations. The micelle-micelle structure factor $S(Q)$ so calculated also shows fair agreement with that extracted from the SANS data using RMSA. We observed that this agreement can be made better if the charge of the micelle is properly reduced. Thus it is of interest to test the MSA and RMSA against HNCA which is generally considered to be a more reliable integral equation theory for electrolyte solutions.

To test the MSA we selected a concentrated system for which the micellar volume fraction is high ($\eta = 0.3$) and compared all three partial structure factors $S_{ij}(Q)$ calculated by MSA and HNCA. Next, to test the RMSA we selected less concentrated systems where volume fractions of micelles are respectively 0.05, 0.1 and 0.2. We limit the comparison between the RMSA and HNCA only to the micelle-micelle partial structure factor $S_{00}(Q)$ which we denoted previously $S(Q)$ for simplicity. Finally, the HNCA is directly applied to the analysis of SANS data from NaC_{12}OXYS at 4gm/dL.

The detailed descriptions of the methods and of the numerical
techniques used in the model calculation have been given in the previous communications [25,40]. In all HNCA calculations, 2048 uniformly spaced sampling points with the step size $\Delta = 0.025$ nm were used. This is enough to satisfy relatively well the Stillinger-Lovett moment conditions. The zeroth moment is typically of the order $10^{-3}$ and the second moment of the order of 0.1. The model parameters are collected in Table 4.1. For an easier comparison with former works, the reduced temperatures $T_r$'s are also given for all of the systems studied. The height of the first peak in the micelle-micelle partial structure factor, defined according to the equation

$$S_{ij}(Q) = \delta_{ij} + \sqrt{n_i n_j} \tilde{h}_{ij}(Q),$$

(4.100)

is also included. In Eq. (4.100) $\delta_{ij}$ is the Kronecker delta function, $n_i$ the number density of species $i$ and $\tilde{h}_{ij}(Q)$ the Fourier transform of $h_{ij}(r)$.

We first consider a system of relatively high micellar volume fraction $\eta=0.3$. For this case MSA can be solved without rescaling and thus, all three partial structure factors, $S_{00}(Q)$, $S_{01}(Q)$, and $S_{11}(Q)$ calculated by MSA should be reliable. In Fig. 4.4 we compare the results of HNCA for the system 1 of Table 4.1 with the corresponding MSA results of system 2 with $|Z_{\text{MSA}}(2)| < |Z_{\text{HNCA}}(1)|$. As seen from Fig. 4.4, very good agreement between the results of the two theories is achieved for all three partial structure factors. In order to get the good agreement, the effective charge of the micelle is reduced from -20 to -17 in MSA calculation. This charge renormalization arises from an
inherent weakness of MSA which under estimates the accumulation of the counterions near the micellar surface. Apart from the problem of a proper interpretation of the effective micellar charge, it appears that MSA can be quite useful in studies of all three partial structure factors in system for which the rescaling is not needed. The same conclusion has been reported previously [44].

Experimentally interesting situations, however, often involve the systems with the surfactant concentration too low and the interactions among micelles too strong for the ordinary MSA to be applicable. The RMSA described in full detail in ref.[24,25] is therefore of great practical importance. In Fig. 4.5 we compare the HNCA intermicellar structure factors of system 3, 5, and 7 with those of system 3, 4, 6, and 8 obtained from RMSA. From Fig. 4.4 we see that RMSA can reproduce the HNCA micelle-micelle structure factor $S_{00}(Q)$, as successfully as does MSA when the rescaling is not necessary. Note, however, the renormalized charge required for the calculated RMSA structure factor to fit that of the HNCA is rather low. This is consistent with the rescaling concept of ref.[24]. In this article the renormalized charge of the micelle is interpreted as the sum of the charges of the micelle itself and that of all the counterions located within the rescaled cosphere of radius $r = \sigma_0'/2$. In a recent paper [28] an attempt was made to evaluate the reliability of RMSA presuming erroneously that no counterion was allowed to penetrate the surface of the rescaled micelle. Consequently, if no renormalization of the micellar charge was made there would be no surprise that the "RMSA*" curve shown in Fig. 1 of ref. [28] falls out
of the prediction of the alternative RMSA proposed in ref. [28]. In that RMSA the numerical solution of the RMSA was given for the system in which the counterions are allowed to penetrate the res. 1ed macroion surface so that the macroion-counterion distance is kept uncharged in the process of rescaling. This is an interesting alternative to the RMSA of ref. [24], since it may be used for the studies of the counterion-micelle and for the counterion-counterion correlations. On the other hand, it is clear that these two versions of the RMSA do not differ significantly as far as the inter-micellar structure factor is concerned. One, however, has to bear in mind that the renormalized charges in the two cases must necessarily be different.

Finally, we turn to the performance of HNCA in analyzing the experimental intermicellar structure factors extracted from SANS data using RMSA. In Fig. 4.6 we give the HNCA partial structure factor $S_{00}(Q)$ of system 11 in Table 4.1 together with the RMSA curve which has previously been fitted to the SANS results for a 4 gm/dL solution of NaC\textsubscript{12}OXXS in D\textsubscript{2}O at 53.6 °C [3]. The effective micellar charges that fit the experimental data are $Z_{\text{HNCA}} = -18$ and $Z_{\text{RMSA}} = -10.0$. Both charges are well below the mean aggregation number $\bar{n} = 49.8$ at the given conditions. The difference between these two effective charges is consistent with the rescaling concept outlined above. To illustrated the effect of the micellar charge, we give in the inset of Fig. 4.6 three curves of $S_{00}(Q)$ computed by HNCA for system 9, 11, and 14 of Table 4.1. The micellar charges are respectively -10.0, -18, and -32. $Z_{\text{HNCA}} = -32$ is the highest charge for which we were still able to solve the HNCA equa-
tions at this low concentration. The only visible effect of the charge in this case is found to be on the height of the peak values of $S_{00}(Q)$. The peak values that correspond to these micellar charges are also given in Table 4.1. It is obvious that the peak value varies rapidly with the charge at low charge. With increased charge this dependence slows down. This is probably due to condensation of counterions in the thin double layer around the micelle. A related saturation effect has been observed in the simulation studies of the osmotic properties of planar, cylindrical and spherical colloids at about the same macroion surface charge density as here [45,46,47].

On the whole, it appears that the MSA and RMSA are in a very good agreement with the HNCA when used for the calculation of intermicellar structure factor, although the macroion charge has to be treated as an adjustable parameter. It is hard to trace the sources of the difference between the mean aggregation number of the micelles and its effective charge in the case of HNCA. It might be due to the existence of short range van der Waals attractive forces that we neglect in this treatment. It might also be due to the fact that HNCA does not treat the counterion-macroion correlation near the contact completely accurately in the case of high asymmetry of charges. Even with more realistic physical models, such as inclusion of the van der Waals attraction between macroions, the micelle-counterion systems may not be treated successfully by the conventional HNCA approach because the molecular nature of the solvent is neglected in the primitive model. It seems possible that the micellar growth in the solution is controlled by the same thermodynamic
relations as that described in ref. [16] for determination of the spinodal curve. The micelles, under certain conditions, will reach the sizes and the charges that bring the systems close to or beyond the two phase coexistence boundary (spinnadol cure on $T_r - \eta$ plane), the range where HNCA is poorly convergent or not solvable. With RMSA one is able to compute the correct $S(Q)$ over a range broader than HNCA by handling an artificial system of higher volume fraction and weaker electrostatic interactions. Thus, the MSA together with the concept of both ref. [24] and [28] would be useful and powerful in analyzing SANS data and in characterizing micellar solutions.
References:


(14) K. Ng, J. Chem. Phys. 61, 2680 (1974)


Table 4.1 The model parameters of the selected systems studied. The concentrations are given in mole per cm$^3$, the ionic diameter in nm. The temperature is kept 313 °K for system 1 - 8 and 326.6 °K for system 9 - 14.

<table>
<thead>
<tr>
<th>system</th>
<th>$-z_0$</th>
<th>$T_r$</th>
<th>$\eta$</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$\sigma_0$</th>
<th>$\sigma_1$</th>
<th>$\sigma_2$</th>
<th>method</th>
<th>$S_{00}(Q_{\max})$</th>
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<tr>
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<td>0.19</td>
<td>0.3</td>
<td>7.60</td>
<td>152</td>
<td>---</td>
<td>5.0</td>
<td>0.5</td>
<td>0</td>
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<td>---</td>
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<tr>
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<td>17</td>
<td>0.22</td>
<td>0.3</td>
<td>7.61</td>
<td>129</td>
<td>---</td>
<td>5.0</td>
<td>0.5</td>
<td>0</td>
<td>MSA</td>
<td>---</td>
</tr>
<tr>
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<td>30</td>
<td>0.13</td>
<td>0.05</td>
<td>1.294</td>
<td>39</td>
<td>---</td>
<td>5.0</td>
<td>0.5</td>
<td>0</td>
<td>HNCA, RMSA</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
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<td>0.05</td>
<td>1.294</td>
<td>17</td>
<td>---</td>
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<td>0.5</td>
<td>0</td>
<td>RMSA</td>
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</tr>
<tr>
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<td>0.1</td>
<td>2.54</td>
<td>101</td>
<td>---</td>
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<tr>
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<td>5.1</td>
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<td>---</td>
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<td>0</td>
<td>HNCA</td>
<td>---</td>
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<td>0.2</td>
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<td>0.07</td>
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<td>40.2  2.5</td>
<td>4.8</td>
<td>0.4</td>
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<td>50.3  2.5</td>
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<td>0.4</td>
<td>1.0</td>
<td>HNCA</td>
<td>1.330</td>
<td></td>
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$C_0$, $C_1$, and $C_2$ are concentrations of macro ion, counter ion, and co ion, respectively.
Fig. 4.1 Comparison of DH and MDH calculations of activity coefficients \( \gamma_2 \) (in relative unit) to experimental data. It is clear that both DH and MDH theories agree with experimental data only at the dilute limit. These curves are taken from reference 3 of chapter 4.
Fig. 4.2 Isothermal compressibility $\kappa_T$ as a function of the coupling constant $\Gamma_{ij}$. The HNCA solutions are acceptable only when their corresponding $\kappa_T$ is nonnegative. From the curve it is easy to see that for a system of 0.2 micellar volume fraction the maximum coupling constant for HNCA solution to be meaningful is about 40. For most of the ionic micellar systems investigated here the coupling constant, if fully ionization of the counterions is assumed, are much greater than 40 when micellar volume fraction is 0.2. This constrain limits the applicability of HNCA.
Fig. 4.3 OCM and MOCM fitting to SDS micellar solutions at $T = 40^\circ C$. The fractional charge of the micelles extracted by MOCM is consistently smaller than those obtained from OCM suggesting that using DLVO potential would over estimate the micellar charges. The MCCF charges of these two cases are very different from those of MOCM due to following reasons: (1) MCCF takes into account of the size effects and (2) the rescaling concept of MCCF is different from that of MOCM (see section 4.6) significantly.
Fig. 4.4 The partial structure factors for system 1 (square) and system 2 (solid lines) calculated by HNC and MSA respectively. All three partial structure factors obtained from these two methods are nearly identical providing the MSA charge is properly reduced.
Fig. 4.5 the comparison of intermicellar partial structure factors calculated by HNCA for systems 3, 5, and 7 (square) with those obtained from RMSA for systems 4, 6, and 8 (solid lines). The agreement is excellent while the charges of the macroions are substantially reduced in RMSA calculations.
Fig. 4.6 The $S_{00}(Q)$ obtained by fitting HNCA to SANS data with $Z_{\text{HNC}} = 18$ (O) for system 11 with the corresponding RMSA curve calculated by setting $Z_0 = -10$. This gives the best fit to the SANS data (solid line).
5.1 Introduction

NaC\textsubscript{12}OXS is an ionic surfactant with a double alkyl chains of carbon number m+n+3=12 attach to a sulfonated aromatic head group. The chemical structure of this molecule and various distances within the molecule are depicted in Fig. 5.1. A high purity form of this compound has been synthesized and characterized by Valint [1]. The CMC in pure D\textsubscript{2}O is about 0.53 mM at room temperature and about 2.5 mM at T = 40 - 50 °C. The maximum solubility in pure D\textsubscript{2}O at T = 50 °C is 133 mM and at this highest concentration the solution is optically transparent with low viscosity. An earlier SANS measurement (by J. S. Huang) indicated that the scattering intensity distribution is dominated by a strong interaction peak signifying the importance of the double layer interaction between micelles at all concentrations above 6.6 mM. We are interested in the structure of a normal micelle formed from a double chain surfactant mainly as a follow-up study to the earlier studies of micellar aggregates formed from single chain ionic surfactants such as LDS and SDS [2,3]. We have recently studied the structure of diC\textsubscript{6} lecithin (zwitterionic surfactant) micelle in aqueous solution [4]. It was shown that this double chain zwitterionic surfactant forms spheroidal micelles near CMC.
In section 5.2, we briefly describe the experimental procedures, including the sample preparation and SANS measurements. We then present in section 5.3 the basic structural model of the micelle and go into a detailed description of a contrast variation method using faintie Q data by which we determine the model parameters. This is followed with discussions of the results in section 5.4, emphasizing the interpretation of the aggregation number and the effective charge of the micelle extracted from the experiment. Section 5.5 summarizes our findings about the structure and the correlation between micelles.

5.2 Experiment

Sample.

The average carbon numbers of the two hydrophobic tails of the surfactant, NaC_{12}OXS, are 1.5 and 7.5 respectively (see Fig. 5.1). The surfactant is characterized by a high performance liquid chromatographic method based on a reverse phase paired-ion chromatography. The solvent used for preparation of samples was gold label D_{2}O supplied by Aldrich Chemical Co. with purity better than 99.8 atom % of deuterium. For preparations of micellar solutions at different concentrations, a 5 % (by weight) solution was prepared at room temperature initially, the lower concentration solutions were then made by dilution of this stock solution for experimental consistency.
SANS Measurements.

The experiments were conducted at the High Flux Beam Reactor at Brookhaven National Laboratory using low angle spectrometer [5]. The neutron wavelength was \( \lambda = 5.45 \) Å and the sample-to-detector distance was 176 cm. A position sensitive detector with 128 x 128 pixels subtending an area of 50 cm x 50 cm was used to record the scattered neutrons. The range of the magnitude of scattering vector, \( Q = (4\pi/\lambda) \sin(\theta/2) \), where \( \theta \) is the scattering angle, covered in the experiment was from 0.02 to 0.22 (Å\(^{-1}\)).

The detector sensitivity was calibrated, pixel by pixel, using an isotropic scatterer. In this experiment we used a 1-mm water sample. A separate measurement of the detector background and the empty cell scattering were made for the subsequent data correction.

The collected raw data were corrected by first subtracting out the contributions from the background and the quartz cell. The corrected data is then divided by the water data to correct for the detector sensitivity. Normalization of the data to an absolute intensity scale was made by using the transmission of 1 mm water sample. This normalized two-dimensional data is then circularly integrated along the iso-Q contour to yield the differential cross section per unit volume of sample as a function of \( Q \). This way of data reduction and normalization has already been discussed in our previous publication [6]. The diffe-
rential cross section, $d\Sigma(Q)/d\Omega$, contains a component due to incoherent scattering of hydrogen atoms. We computed this contribution $d\Sigma_{inc}(Q)/d\Omega$ using the known number density of hydrogen atoms in the solution and an incoherent scattering cross section of hydrogen which was taken to be 80 barns. This incoherent contribution was subtracted out from the scattering cross section $d\Sigma_s(Q)/d\Omega$ to obtain a coherent scattering cross section $d\Sigma(Q)/d\Omega = I(Q)$ which was then used in the subsequent analysis.

5.3 Method of Data Analysis

Since the SANS intensity distribution from the NaC\textsubscript{12}OXS micellar solution shows a strong interaction peak in the range of concentration studied, the conventional technique of external contrast variation based on the extrapolated $Q=0$ intensity $I(0)$ [2], is not applicable. We decided therefore to assume an explicit structural model from the outset and work out its full consequences including the monomer packing in the micellar core and the intermicellar interactions. In fact an advantage of SANS method is that the scattering cross section can in principle be computed in detail without ambiguity once the structure and the interaction of the system are specified. Thus the structural determination of a system reduces to a quantitative numerical testing of the models. In our attempt to arrive at the structure of the micellar aggregate we have tested a number of such models and arrived at the following specific model which was found to be quantitatively satisfactory.
A. Structural Model.

Figure 5.2 depicts the basic model of the micelle. The micelle consists of a hydrophobic core of scattering length density \( \rho_1 \), a hydrophilic head group region of thickness \( \delta \) and scattering length density \( \rho_2 \). The hydrocarbon tail length of NaC\(_{12}\)OXS surfactant molecule is estimated to be 13.75 Å by summing up the bond-to-bond distances [7], \( b = 13.75 \) Å, according to its chemical structure shown in Fig. 5.1. The basic structural parameters in this model, which is independent of the surfactant concentration, are the volume of a surfactant tail in the hydrophobic core \( V_T \) and the polar head volume \( V_H \). The purpose of the contrast variation measurement is to determine these two basic parameters.

B. Contrast Variation at Finite \( Q \).

Adapting the basic model of the micelle shown in Fig. 5.2 the SANS cross section for a system of monodispersed nonspherical micelles can be written in the following suggestive form [8]:

\[
\frac{d\Sigma(Q)}{d\Omega} = (N_1 - \text{CMC}) \bar{n} \left[ \sum_{i} b_i - \frac{V}{1 - \rho_S} \right]^2 < |F(Q,\mu)|^2 \frac{s(Q)}{s(Q_{\text{c}})}. \tag{5.1}
\]

The first factor \( (N_1 - \text{CMC}) \) is the number density of the monomers which form micelles, the second factor \( \bar{n} \) is the average aggregation number of a micelle. The third factor is the "contrast", i.e., the difference of the scattering length of a dry monomer from that of the solvent of equivalent volume. The fourth factor is a normalized particle structure
factor $P(Q) = \langle |F(Q,\mu)|^2\rangle$ and finally the fifth factor is the orientationally averaged inter-particle structure factor $\overline{S(Q)}$. More explicitly, $\overline{S(Q)}$ is defined as

$$\overline{S(Q)} = 1 + \frac{\langle |F(Q,\mu)|^2 \rangle}{\langle |F(Q,\mu)|^2 \rangle} [S(Q) - 1]$$  \hspace{1cm} (5.2)$$

where $S(Q)$ is the inter-micellar center-center structure factor to be calculated by a liquid theory. The angular dependent particle form factor $F(Q,\mu)$ depends on the magnitude of the scattering vector $\hat{Q}$ and on the orientation of the ellipsoidal particle (major and minor axes $a$ and $b$ respectively) through a direction cosine $\mu = \hat{Q} \cdot \hat{a}$. It can be written as

$$F(Q,\mu) = f \frac{3j_1(U_1)}{U_1} + (1-f) \frac{3j_1(U_2)}{U_2}$$  \hspace{1cm} (5.3)$$

where $j_1$ is the spherical Bessel function of the first kind and

$$U_1 = Q \int \mu^2 \frac{a^2}{\mu^2 + (1 - \mu^2) b^2}$$  \hspace{1cm} (5.4)$$

$$U_2 = Q \int \mu^2 (a + \delta)^2 + (1 - \mu^2)(b + \delta)^2$$  \hspace{1cm} (5.5)$$

and $f = V_T (\rho_1 - \rho_2)/(|\Sigma b_1| - V_M \rho_S)$.

(5.6)$$

The quantity $\Sigma b_1 = 3.34 \times 10^{-4} A$ is the sum of the scattering length of
all the atoms in a monomer, and $\rho_s$ is the scattering length density of the solvent.

$$\rho_s = \beta \rho_{D_2O} + (1 - \beta) \rho_{H_2O}$$  (5.7)

where $\beta$ is the volume fraction of $D_2O$ in the solvent. The scattering length density of the hydrophilic layer $\rho_2$ is composed of contributions from three groups of molecules in that layer. They are the water molecules associated with the head group $\rho_{1}^{H}$, the hydrophilic part of the monomer excluding sodium $\rho_{2}^{H}$, and the sodium ions bound to the head groups $\rho_{3}^{H}$. Therefore, the scattering length density $\rho_2$ can be written as:

$$\rho_2 = \rho_{1}^{H} + \rho_{2}^{H} + \rho_{3}^{H}$$  (5.8)

where

$$\rho_{1}^{H} = N_H [\beta \Sigma b_{D_2O} + (1 - \beta) \Sigma b_{H_2O}] \bar{n} / V_{sh}$$  (5.9)

$$\rho_{2}^{H} = \bar{n} \Sigma b_{HD} / V_{sh}$$  (5.10)
\[ \rho_3 = \frac{n}{\bar{n}} (1 - \alpha) b_{Na}. \] (5.11)

\[ \Sigma b_{D_2O} = 1.9153 \times 10^{-4} \text{ A} \text{ and } \Sigma b_{H_2O} = -0.1677 \times 10^{-4} \text{ A} \text{ are the total scattering lengths of } D_2O \text{ and } H_2O \text{ molecules respectively. } N_H \text{ is the average number of water molecules associated with a head group. } \Sigma b_{HD} \text{ is the sum of scattering lengths of the head groups. This sum could contain part of the contribution from the oxylene ring. } b_{Na} = 0.363 \times 10^{-4} \text{ A} \text{ is the scattering length of Na, and } \alpha (= Z_0/\bar{\mu}) \text{ is the normalized fractional charge of a micelle. The volumes of the hydrophilic layer } V_{sh} \text{ and the hydrophobic core } V_C \text{ can be computed according to the following equations:}

\[ V_{sh} = \frac{(4\pi/3)[(a+\delta)(b+\delta)^2 - ab^2]}{(5.12)} \]

\[ V_C = \frac{(4\pi/3)ab^2}{\pi V_T}, \] (5.13)

and \[ V_H = V_M - V_T = (\pi/6)\delta^3. \] (5.14)

The number of solvent molecules associated with a monomer head group, \( N_H \), can also be calculated from the equation:

\[ N_H = \left[ \frac{V_{sh}}{\bar{n}} - (V_M - V_T)(1 - \alpha) + (V_M - V_T - V_{Na}) \alpha \right] / V_S \] (5.15)

where \( V_{Na} = 9 \text{ A}^3 \) is volume of \( Na^+ \) and \( V_S = 30.27 \text{ A}^3 \) is volume of the solvent (water) molecule.
Let us summarize the procedure for calculating $dI(Q)/d\Omega$ at each $Q$ as follows: To compute this quantity we need 8 parameters: the major and minor axis, $a$ and $b$, the thickness of the hydrophilic shell $\delta$, $V_M$, $V_T$, $N_H$, and $\alpha$. The minor axis $b$ is known from the molecular geometry of the tail and $a$, $\delta$, and $N_H$ are derived parameters. Starting from the basic molecular parameters $V_M$ and $V_T$ (and hence $V_H$ and $\delta$ from Eq.(5.14)) and two micellar parameters $\Pi$ and $\alpha$ we can compute the semi-major axis $a$ and shell thickness $\delta$ using Eq.(5.13) and (5.14) from which the volume of the hydrophilic layer $V_{sh}$ can be computed by use of Eq.(5.12) and (5.15). Therefore, if we pick a convenient concentration at which to determine the two molecular parameters $V_M$ and $V_T$ (and the two micellar parameters $\Pi$, $\alpha$ at that concentration) we can make a model fit to the SANS data at any other concentrations to determine the two micellar parameters $\Pi$ and $\alpha$ from which micellar growth and inter-micellar interactions are specified.

The method of contrast variation at finite $Q$ we propose here for the determination of the two molecular parameters, $V_M$ and $V_T$ is based on Eq.(5.1). From Eq.(5.1) we can define a $Q$-dependent quantity $A(Q)$ which can be derived from the differential cross section by
\[ A(Q) \equiv \left[ \frac{d\Sigma(Q)}{d\Omega} / P(Q) / S(Q) \right]^{1/2} \]

\[ = \sqrt{(N_1 - \chi M) \bar{M}} \left| \Sigma_{b_1} - V_M \rho_S \right|. \]

We observe from Eq. (5.17) and (5.18) that \( A(Q) \), when averaged over all \( Q \), i.e., \( <A(Q)> \) should be a linear function of \( \rho_S \). Thus, if we choose a convenient monomer concentration to fix the prefactor in Eq. (5.18) and measure a series of micellar solutions of various \([D_2O]/[H_2O]\) mixtures as solvents, the quantity \( <A(Q)> \), when plotted against \( \rho_S \), should be linear if the model of the micelle is consistent with the data. The slope and the zero intercept of this line will then give \( \bar{M} \) and \( V_M \). In computing \( A(Q) \) at each \( Q \) one needs to compute \( P(Q) \) and \( S(Q) \) which requires specification of the four basic parameters of the model: \( V_M, V_T, \bar{M}, \) and \( \alpha \). To calculate \( P(Q) \) we use the structural model of NaC\(_{12}\)OXYS micelle described previously. For \( S(Q) \) we use the primitive model of two-component coulomb fluid (MOCF) described in 4.6. The contrast variation measurements were done at five \( \rho_S \) values, the first four data were used to fix the four parameters and the fifth one was to test the consistency of the model. Another consistency check can also be made by comparing the two parameters: \( \bar{M} \) and \( V_M \) obtained from the linear regression analysis of \( <A(Q)> \) vs \( \rho_S \) plot and the corresponding parameters extracted from individual \( d\Sigma(Q)/d\Omega \) curve fitting.

C. Inter-particle Structure Factor \( S(Q) \)
To calculate $S(Q)$ we use the MCCF theory described in 4.6 assuming two components in the micellar solution, namely, the micelle and the counterion. Since all the concentrations investigated here correspond to micellar volume fractions far below 0.2, above which rescaling is not needed, the inpenetrable model of rescaling procedure described in Chapter IV was used to recover the unphysical $g_{00}(r)$ at micelle-micelle contact. The renormalized micellar charges due to rescaling are interpreted as the surface charge of the micelle on the interaction boundary (i.e., on the surface of the rescaled micelle of radius $\sigma_0'/2$ where $\sigma_0'$ is the rescaled diameter of the micelle). This surface charge is essentially the charge sensed by the other micelle through coulomb interaction. In fact there is a counterion cloud arround the micellar surface thus it is plausible to include some counterions near the micellar surface as part of the micelle. As for defining the interaction boundary in the case where rescaling is needed it is truly model dependent. For example, the penetrable model described in 4.6, in which the distance between counterion and micelle is kept constant in the process of rescaling, always gives higher micellar charge than inpenetrable model used here because the interaction boundary of these two models are quite different [3,10]. When system is rescaled using inpenetrable model the physical picture is similar to that of the "dressed micelle" model proposed by Evan et al (called EMN theory hereafter) [11]. In that model the counterions arround the micelle are assumed to be physisorbed by the micelle and can not be resolved from micelle. Thus, the renormalized micellar charge obtained from MCCF together with inpenetrable rescaling model can be compared to that calculated from EMN theory using
the $\sigma_0'$ as micellar diameter and $2\Gamma$ as screening constant.

5.4 Results and Discussion

Fig. 5.3 shown the $d\Sigma(Q)/d\Omega$ vs. $Q$ plots of the contrast variation series. Various 2 gm/dL NaC$_{12}$OXYS micellar solutions using different [D$_2$O]/[H$_2$O] mixtures as solvents at $T = 53.6 \, ^{0}\text{C}$ were chosen for this purpose. The fitting parameter were $V_M$, $V_T$, $\bar{M}$, and $\alpha$ as described previously. The fitting procedure was: first, assign a set of values for these four parameters; secondly, calculated the derived parameters $a$, $\delta$, and $N_H$; and then $d\Sigma(Q)/d\Omega$ according to Eq.(5.1); and finally, check the chi-square by comparing the calculated $d\Sigma(Q)/d\Omega(Q)$ to that obtained from SANS measurement. As one can see from Fig. 5.3 the agreement is excellent and the parameters $\bar{M}$, $\alpha$, $V_M$, and $V_T$ extracted are listed in Table 5.1. We then reconfirm values of $\bar{M}$ and $V_M$ from a linear regression analysis of $<\Lambda(Q)>$ vs $\rho_S$ plot. The analysis is shown in Fig. 5.4. The contrast matching point was found to be at [D$_2$O]/[H$_2$O] = 16/84 and $\bar{M}$ and $V_M$ were found to be 41 and 610 $\text{Å}^3$ from the slope and the contrast matching point. We thus selected a set of values $V_T = 370 \, \text{Å}^3$ and $V_M = 610 \, \text{Å}^3$ for the subsequent analysis of micellar solutions at different concentrations. In lower part of Fig. 5.3 we display the data of 2 gm/dL NaC$_{12}$OXYS micellar solution at 100 % H$_2$O solvent and the predicted $d\Sigma(Q)/d\Omega$ using the four parameters extracted from the upper graph. The agreement is satisfactory.
Fig. 5.5 shows $d\Sigma(Q)/d\Omega$ and the corresponding model fitting of a series of NaC$_{12}$OXS micellar solutions with concentration ranging from 0.25 gm/dL to 5 gm/dL at $T = 53.6$ °C. The fitting were made by setting $V_M = 610$ Å$^3$ and $V_T = 370$ Å$^3$ and using $\bar{N}$ and $\alpha$ as fitting parameters. Fig. 5.6 shows the analogous model fitting of the other series of solutions at $T = 40$ °C. The extracted aggregation number $\bar{N}$, the fractional charges $\alpha$, and the associated informations are shown in Table 5.2.

In Fig. 5.7 and 5.8 we show the inter-micellar structure factors extracted from experimental data by MOCF, for the case of 2 gm/dL and 4 gm/dL micellar solutions at $T = 40$ °C. Also displayed are their fitted $S(Q)$ based on OCM theory [12,13]. These fittings were achieved by adjusting the effective micellar charges (and hence the Debye screening constant $\kappa$) holding micellar size unchanged. It is easy to see that the agreement is reasonable and that the effective charges from MOCF are consistently lower. The small deviation of $S(Q)$ between these two approaches is mainly due to the fact that MOCF takes into account the size effects of both micelles and the counterions while OCM treating the counterions as point-like ion.

In Table 5.2 we listed the extracted parameters at different concentrations and two temperatures. Also the fractional charge calculated by EMN theory are listed [11]. In this theory we calculate a Gibb's free energy due to formation of a double layer around a single micelle situated in the micellar solution with all the rest of monomers dissociated in solution to keep the charge neutrality. The Gibb's free energy
is then differentiated with respect to $\kappa$ to obtain the "surface excess" of the counterions physisorbed onto the micelle surface. The formula for calculating $\alpha_{\text{EMN}}$ is given at Eq. (9) of Appendix A. $\alpha_{\text{MCCF}}$ is indeed close to $\alpha_{\text{EMN}}$ as can be seen from Table 5.2.

In Fig. 5.9 we plot the aggregation number $\bar{N}$ at two temperatures as function of $(X - X_{\text{CMC}})^{1/2}$ where $X$ and $X_{\text{CMC}}$ are respectively the mole fractions of the monomer and that of the CMC. According to a ladder model of micellar growth, this plot should be a straight line with a slope relating to the difference of two free energy parameters entering the theory [14]. We note that at $X_{\text{CMC}}$ the minimum aggregation number $\bar{N}_0 = 30$ at $T = 53.6$ °C. The plot is a straight line at low concentrations but seems to deviate from the linearity at the higher concentrations. This may be due to the fact that at this concentration the isotropic micellar phase is very close to the mesomorphic phase of the surfactant-water mixture where the ordered structure consisting of large aggregation begins to form.

5.5 Summary

The anionic surfactant sodium dodecyl orthoxylene sulfonate forms isotropic micellar phase in water up to 5 gm/dL monomer concentration in the vicinity of the room temperature. We have studied, in the isotropic phase, the micellar structure, the inter-aggregate interaction and the growth of the aggregates as functions of concentration and temperature.
The minimum micelle formed near CMC is shown to have a compact spherical packing of 30 monomers. The hydrophobic core is dry and has a radius equal to the fully stretched chain length of $b = 13.75$ Å. The hydrophilic head layer has a thickness $\delta = 7.81$ Å and there are on an average 20 water molecules associated with each polar head group.

Since the double layer repulsion between micelles is always appreciable in this ionic micellar system we proposed a method of contrast variation at finite $Q$. This technique has been used before for the determination of micellar structure by Triolo et al [15] but we believe our implementation of it and the interpretation of the results are considerably different. The main purpose of the contrast variation measurement is to determine two molecular parameters which are assumed to be invariant to the solution condition. The parameters are the effective tail volume $V_T$ in the hydrophobic core and the effective hydrophilic head group volume $V_H = V_M - V_T$. We obtained $V_T = 370$ Å$^3$ which is nearly identical to the tail volume of the dodecyl chain in LDS and SDS micelles we studied before [2,3,6]. The $V_H = 240$ Å$^3$ is also a very reasonable value considering the geometry of the molecule (see Fig. 5.1).

The inter-micellar structure factor can be calculated using a primitive model of a two-component fluid in the mean spherical approximation (MCCF). This two component model is a slightly improved version of the traditionally used OCM model [12,13] because it takes into account the finite size effects of the particles in the solution on screening power.
We interpret the effective surface charge extracted to be the dressed micellar charge which can be calculated by solving a Poisson-Boltzmann theory [11]. The growth of micelles at low and moderate concentrations follows the ladder model but deviates from it near the boundary of the mesomorphic phase.
References:

(1) P. Valint, Exxon Research & Engineering Co., Annandale, NJ 08801


(9) G. Senatore and Blum, J. Phys. Chem., 89, 2676 (1985)


Table 5.1 Extracted basic parameters of NaC\textsubscript{12}OXYS contrast variation series of micellar solutions

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>[NaC\textsubscript{12}OXYS]</th>
<th>[D\textsubscript{2}O]/[H\textsubscript{2}O]</th>
<th>$\bar{n}$</th>
<th>$V_T$(A$^3$)</th>
<th>$V_M$(A$^3$)</th>
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<tr>
<td>100/0</td>
<td></td>
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<td>2 gm/dL</td>
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<td>375</td>
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<td>41.8</td>
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<td>40/60</td>
<td></td>
<td></td>
<td>41.7</td>
<td>370</td>
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Table 5.2 Parameters extracted from SANS data of NaC\textsubscript{12}OXYs micellar solutions

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<th>T(°C)</th>
<th><a href="%25">NaC\textsubscript{12}OXYs</a></th>
<th>$\bar{n}$</th>
<th>$\sigma_M$(A)</th>
<th>a(A)</th>
<th>a/b</th>
<th>$2\Gamma_{\sigma M}$(A)</th>
<th>$\alpha_{MCCF}$</th>
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Fig. 5.1 The structure of sodium dodecyl orthoxylene sulfonate. The average carbon numbers of the two hydrophobic tails are 7.5 and 1.5 respectively and the average stretched chain length is 13.75 Å (see ref. 7 of Chapter V).
Fig. 5.2 Schematic structure of NaC_{12}OXYS micelle. The minor radius $b$ of the ellipsoidal micelle is assumed to be the fully stretched length, 13.75 Å and the hydrophobic core to be compact.
Fig. 5.3 The differential cross section per unit volume of micellar solution, $dI(Q)/d\Omega$, as a function of the scattering vector $Q$ for 2% NaC$_{12}$OXYS micellar solutions in solvents of various D$_2$O/H$_2$O ratios at $T = 53.6$ °C. All the fittings are excellent the extracted parameters, $\Phi$, $\alpha$, $V_M$, and $V_T$ are nearly identical (see Table 6.1).
Fig. 5.4 $\langle A(Q) \rangle$ as a function of D$_2$O fraction in solvent. The result shows a linear behavior and the contrast matching point, where $\langle A(Q) \rangle = 0$, was found to be at [D$_2$O]/[H$_2$O] = 16/84. The corresponding molecular parameters thus found are $V_M = 610 \text{ A}^3$ and $V_T = 370 \text{ A}^3$. 

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Fig. 5.5 $d\Omega(Q)/d\Omega$ vs Q plot with concentration ranging from 0.25 gm/dL to 5 gm/dL at $T = 53.6^\circ C$. The extracted values of the parameters are shown in Table in 5.1.
Fig. 5.6 The same plot as Fig. 5 with concentration 0.25 gm/dL to 4 gm/dL at T = 40 °C.
Fig. 5.7 Inter-micellar structure factor $S(Q)$ extracted from experiment by MOCF (□) for the case of 2 gm/dL NaC$_{12}$OXS micellar solution at $T = 40^\circ$C. The solid line is the OCM fitting of the same system. $Z_{OCM}$ is much higher than that of MOCF.
Fig. 5.8 Same plot as fig. 7 for the case of 4 gm.dL.
Fig. 5.9 The average aggregation number $\bar{n}$ as a function of $(X - X_{\text{CMC}})^{1/2}$. $X$ and $X_{\text{CMC}}$ are the mole fractions of surfactant monomer and that of CMC respectively. The extrapolated minimum $\bar{n}$ is about 30.
CHAPTER VI

THE STRUCTURE AND GROWTH OF DI-2-ETHYLHEXYL SULFOSUCCINATE
MICELLES IN AQUEOUS SOLUTIONS

6.1 Introduction

AOT is a double chain anionic surfactant of molecular weight 444.5 gm/mole having a small ionic head group and relatively short (about C_6) but bulky hydrocarbon tails of fully stretched length 12.57 Å^3. This length can be calculated by summing up all the bond-to-bond distances within the molecule (see Fig. 6.1) [1]. Due to this hydrophilic/phydrophobic imbalance, AOT is poorly soluble in water but readily soluble in oil. At room temperature the maximum solubility of AOT in H_2O is about 1.35 % by weight [2] and is about 1.1 % in D_2O. Above this concentration but less than 29 % it is known to form a mesomorphic phase consisting of parallel rod-like aggregates of AOT molecules in hexagonal array with the length of the rod about 24 Å. In between 29 and 82 % of AOT in H_2O, a lamellar phase is formed with Bragg spacing increasing from about 28 Å to 112 Å, depending on the water content. The amphiphilic layer thickness is however kept between 19 to 21 Å without significant change as the water content varies [3].

We have investigated other micellar systems formed from other anionic surfactants such as LDS, SDS. Both of these two surfactants
have only one hydrophobic tail. It was found that the micelles vary in shape from spherical to prolate spheroidal as the surfactant concentration increases [4,5,6]. In addition, we have recently studied an ionic micellar system formed by an anionic surfactant NaC_{12}OKYS which has a long and a short tail with a length ratio of ~ 5.0 (see Fig. 5.1) [7]. The micelles formed by this surfactant are prolate spheroids but with axial ratios less than that of both LDS and SDS micelles when the micellar volumes are about the same. It is thus interesting to know if a micelle formed by a double-chain surfactant with comparable tail lengths will grow from spherical to an oblate spheroidal when concentration increases.

We determined the AOT micellar structure by measuring the SANS intensity distribution of the micellar solutions at various concentrations and analyzed them with different geometric packing models. Based on the least square fitting to these models we arrived at the conclusion that the AOT micelle grows from a spherical minimum micelle at CMC to an oblated spheroidal micelle as the surfactant concentration increases.

In section 6.2 we briefly describe the experimental procedure including the sample preparation and SANS experiements. In section 6.3 we present the structural model of an AOT micelle, the method of contrast variation at finite Q, and the method for calculation of the inter-micellar structure factor. In section 6.4 we discuss the results obtained from the SANS data analysis emphasizing the AOT micellar structure and its growth as a function of concentration. We summarize our
findings briefly in Section 6.5.

6.2 Experiment

Sample.

Surfactant AOT used for SANS experiment in this work is obtained from Fluka Chemical Co., and was further purified by J. Sung to attain a purity of better than 99.8% [8]. The solvents were a gold label D₂O with 99.8 atom % of deuterium and a deionied H₂O. The samples used for the contrast variation measurements were 0.8% AOT micellar solutions prepared respectively in mixed solvents of [D₂O]/[H₂O] = 100/0, 85/15, 70/30, and 55/45. For the concentration series we first made a stock solution of 1.0% concentration and then prepared the lower concentration solutions by dilution of this stock solution for experimental consistency.

SANS Experiment.

SANS experiments were conducted at the High Flux Beam Reactor of Brookhaven National Laboratory using a low angle biological spectrometer [9,10]. The neutron wave length was λ = 5.45 Å with a spread Δλ/λ = 10 %.

The sample-to-detector distance was 111.8 cm. A position sensitive detector with 128 x 128 pixels subtending an area of 50 cm x 50 cm was used to record the scattered neutrons. With this setting the magnitude
of the scattering vector $\hat{Q}$ ranges from 0.016 to 0.33 Å$^{-1}$. The time
durations of the measurements in this study range from 1.0 hour to
several hours depending on AOT concentration and particle-solvent
contrasts. The calibration of detector sensitivity, the empty cell and
background corrections and the data normalization procedure have been
described in Chapter III, Chapter V and literature [11].

6.3 Data Analysis.

For every AOT micellar system investigated, a strong interaction
peak was clearly presented in the SANS intensity distribution. Due to
the strong interaction among micelles the conventional contrast
variation technique, which has been widely used for the case of reversed
micelle and microemulsion system, is no longer applicable. In order to
make the contrast variation technique applicable to such a strongly
interacting system, we proposed a contrast variation method at finite $Q$.
The detail description has been given in Chapter V and reference 7.

A. The Structural Model of AOT Micelle.

In Fig. 6.2 we depict a structural model of AOT micelle in D$_2$O. It
consists of two regions: a compact hydrophobic core with a semi-minor
axis a and a semi-major axis b equal to the fully stretched tail length
12.57 Å (Fig. 6.1), and an outer layer of thickness $\delta_0$ containing the
polar head groups and the associated solvent molecules. We have tested
both prolate and oblate spheroid models for AOT micelles and found that
the oblate spheroid model gives consistently better fits to the SANS
data than the prolate spheroid model. Based on this structural model,
in which $\delta_0$ is defined by the boundary of water penetration (and thus
hydrophilic portion of the AOT molecule), two model parameters, the dry
AOT molecular volume $V_M$ and the dry polar head volume $V_H$, can be
determined by the contrast variation method at finite $Q$ to be described
below.

B. Contrast Variation at Finite $Q$

For a monodispersed non-spherical micellar system, the differential
cross section per unit volume, neglecting the contribution from
surfactant monomers, measured by SANS can be written as [11]

$$\frac{d\Sigma(Q)}{d\Omega} = (N_1 - CMC) \bar{n} \sum_{i}^{M} \left( \sum_{b_i} - \alpha b_{Na} \right) - \left( V_M - \alpha V_{Na} \right) \bar{\rho}_S \right)^2 \cdot$$

$$< | F(Q,\mu) | ^2 > \overline{S(Q)} \quad (6.1)$$

The first factor $(N_1 - CMC)$ is the number density of AOT monomers that
form micelles, the second factor $\bar{n}$ is the mean aggregation number of
the micelle describing the average number of surfactant molecules that
form a micelle. The third factor consists of three terms: $\sum_{i}^{M} \sum_{b_i}$ is the
total neutron scattering lengths of the AOT molecule including that of
the counterion $b_{Na}$, $\alpha$ is the fraction of counterion dissociation of a
micelle, $V_{Na}$ is the volume of the counterion and $\bar{\rho}_S$ is the average
scattering length density of the solvents. The fourth factor is the normalized intra-particle structure factor \( P(Q) = \langle |F(Q,\mu)|^2 \rangle \) and finally the fifth factor \( \overline{S(Q)} \) is the orientationally averaged inter-particle structure factor defined as

\[
\overline{S(Q)} = 1 + \frac{\langle |F(Q,\mu)|^2 \rangle}{\langle |F(Q,\mu)|^2 \rangle} [S(Q) - 1]
\]  

(6.2)

where \( S(Q) \) is the center-center structure factor between micelles. It can be calculated by solving a two-component Ornstein-Zernike equation [12] in the mean spherical approxiamtion (MSA) with a coulomb closure. The particle form factor \( F(Q,\mu) \), which is determined by the particle shape, depends on the momentum transfer \( \hat{Q} \) and the orientation of the symmetric axis (in this case the semi-major axis \( b \)) of the particle. For an oblate spheroid \( F(Q,\mu) \) can be written as \( \mu = \hat{Q} \cdot \hat{b} \) :

\[
F(Q,\mu) = f \left[ 3j_1(U_1)/U_1 \right] + (1-f)\left[ 3j_1(U_2)/U_2 \right],
\]

(6.3)

with \( U_1 = Q \left[ \mu^2 b^2 + (1 - \mu^2) a^2 \right] \),

(6.4)

\[
U_2 = Q \left[ \mu^2 (b + \delta_0)^2 + (1 - \mu^2) (a + \delta_0)^2 \right],
\]

(6.5)

and \( f = V_T \left( \bar{\rho}_1 - \bar{\rho}_2 \right) \left[ (2b_1 - \alpha b_{Na}) - (V_M - \alpha V_{Na}) \bar{\rho}_s \right] \),

(6.6)

where \( j_1 \) is spherical Bessel function of the first kind, \( V_T = V_M - V_H \) is the dry AOT tail volume, and \( \bar{\rho}_1 \) and \( \bar{\rho}_2 \) are the scattering length densities of the hydrocarbon core and the outer layer respectively. For
AOT micelle, $M = 3.804 \times 10^{-4}$ A, $b_{Na} = 0.363 \times 10^{-4}$ A, and $v_{Na} = 9$ Å$^3$. The scattering length density of a $[D_2O]/[H_2O]$ mixed solvent can be expressed in terms of $\beta = [D_2O]/[H_2O]$ as

$$\bar{\rho}_s = \beta \bar{\rho}_D + (1-\beta) \bar{\rho}_H,$$  \hspace{1cm} (6.7)

where $\bar{\rho}_D$ and $\bar{\rho}_H$ denote respectively the scattering length density of $D_2O$ and $H_2O$. Since the outer layer of the AOT micelle contains the polar head groups, the counterions, and the associated solvent molecules, the scattering length density of this layer $\bar{\rho}_2$ should be formulated according to its composition as

$$\bar{\rho}_2 = \rho_1^H + \rho_2^H + \rho_3^H$$  \hspace{1cm} (6.8)

where $\rho_1^H$, $\rho_2^H$, and $\rho_3^H$ are the scattering length densities of the hydrophilic layer contributed by the solvent molecules, the polar heads, and the counterions respectively. They can be calculated according to the following equations:

$$\rho_1^H = \bar{\rho}_s \times \frac{v_s N_H \pi}{v_{sh}}$$  \hspace{1cm} (6.9)

$$\rho_2^H = \frac{\pi \sum b_1}{v_{sh}},$$  \hspace{1cm} (6.10)

and $\rho_3^H = \pi (1 - \alpha) \frac{b_{Na}}{v_{sh}}$  \hspace{1cm} (6.11)

where $v_s = 30$ Å$^3$ is the volume of a water molecule, $N_H$ is the averaged
hydration number per AOT polar head, $V_{sh}$ is the volume of the outer layer and $\Sigma b_i$ is the total scattering length of the AOT polar head excluding the counterion. Since the hydrophobic core is compact and the thickness of the outer layer is $\delta_0$, we can calculate the hydrophobic core volume $V_c$, the outer layer volume $V_{sh}$, and the averaged hydration number $N_H$ according to the following equations:

$$V_{sh} = (4\pi/3) [(a + \delta_0)^2 (b + \delta_0) - a^2 b], \quad (6.12)$$

$$V_c = (4\pi/3) a^2 b = \Pi V_T, \quad (6.13)$$

$$N_H = \left[ (V_{sh} / \Pi - V_H - (1 - \alpha) V_{Na}) / V_S \right], \quad (6.14)$$

$$V_T = V_M - V_H', \quad (6.15)$$

and $$\delta_0 = [6(V_H - V_{Na})/\Pi]^{1/3}. \quad (6.16)$$

Based on the structural model proposed above the procedure for calculation of $d\Sigma(Q)/d\Omega$ is summarized as follows: there are 8 parameters that characterize the micellar structure as well as inter-particle structure factor, namely, $a$, $b$, $\delta_0$, $V_M$, $V_T$, $N_H$, $\Pi$, and $\alpha$. Among them $b$ is assumed to be 12.57 Å and $a$, $N_H$, $\delta_0$ can be calculated according to Eq. (6.13), (6.14), and (6.16). Thus, the four basic parameters to be determined by SANS experiments are $\Pi$, $\alpha$, $V_M$, and $V_H$ where $\Pi$ and $\alpha$ are concentration dependent micellar parameters while $V_M$ and $V_T$ are the molecular parameters of a monomer and are expected to be weakly
dependent on the monomer concentration. We thus picked a convenient concentration (0.8 % of AOT in this case) at which to perform SANS measurements for a series of micellar solutions in different [D$_2$O]/[H$_2$O] mixtures and fit the intensity distributions according to the proposed structural model to determine $V_\Pi$ and $V_M$. We then use the extracted $V_M$ and $V_H$ values for the subsequent analyses of the micellar solutions at other concentrations using $\bar{\eta}$ and $\alpha$ as the fitting parameters.

The contrast variation method at finite $Q$ used here for determination of $V_M$ and $V_H$ is based on the form of Eq. (6.1). We define a $Q$-dependent quantity $A(Q)$ as

$$A(Q) = \left[\frac{d\Sigma(Q)}{dQ} / P(Q) / S(Q)\right]^{1/2}.$$  \hspace{1cm} (6.17)

From Eq. (6.17) we see that $A(Q)$, when averaged over all $Q$, represents the square root of the first three prefactors of the scattering cross section formulated in Eq. (6.1) and is independent of $Q$. Thus $\langle A(Q) \rangle$ can be calculated from SANS data at all $Q$ together with the model calculations of $P(Q)$ and $S(Q)$. Since $\langle A(Q) \rangle$ is linearly proportional to $\bar{\rho}_S$ ($\bar{\eta}$ should be the same for all the contrast variation series of AOT micellar solutions) the contrast matching point, where the scattering intensity vanishes, can be determined by extrapolating $\langle A(Q) \rangle$ vs $\bar{\rho}_S$ curve to zero. From the scattering length density at the matching point $\bar{\rho}_m$ the dry volume of the AOT molecule $V_M$ can be obtained. We then used the $V_M$ and the slope of the contrast variation curve (Fig. 6.4) to compute the mean aggregation number $\bar{\eta}$ of AOT micelles at 0.8 % surfactant
concentration. The mean aggregation number so obtained was then tested against that extracted directly from fitting SANS data to further verify the structural model preassumed. The other alternative of determining $V_M$ (and thus $N$) is to assign an amplitude factor $Amp$ and express the scattering intensity as

$$\frac{d\Sigma(Q)}{d\Omega} = Amp < |F(Q,\mu)|^2 > S(Q)$$

(6.18)

and use $Amp$ as an adjustable parameter in fitting SANS data. The square root of the extracted $Amp$ value should be consistent with $<A(Q)>$. This provides another alternative to verify the proposed AOT structural model.

C. Inter-particle Structure Factor $S(Q)$

The inter-micellar structure factor $S(Q)$, dependent on the micellar excluded volume effect and the inter-micellar double layer interaction, was calculated by solving the two-component Ornstein-Zernike equation using the mean spherical approximation (MSA). The basic parameters for $S(Q)$ calculation are sizes and charges of the particles in the solution. The detail description of computing $S(Q)$ has already been given in many articles [6,7,13,14]. In the case of AOT micellar solutions the volume fractions are much less than 0.2 below which the rescaling procedure proposed previously [6] has to be applied in computing $S(Q)$. The micellar charge extracted from SANS data by fitting $S(Q)$ calculated this
way is renormalized in the course of rescaling. This renormalized charge is interpreted as the effective surface charge of the micelle where the effective surface of the micelle was taken to be the rescaled micellar surface.

6.4 Results and Discussion

Fig. 6.3 shows the experimental (square) and the fitted (solid) curves of the scattering intensity versus Q plots for the case of 0.8 % AOT concentration in mixed solvents. The agreement is excellent for the whole series of solutions. The fitting parameters used are $\bar{\Pi}$, $\alpha$, $V_M$, and $V_H$. The extracted parameter values are tabulated in Table 6.1. Fig. 4 shows the $<A(Q)>$ versus $p_S$ plot (or called the contrast variation plot). The contrast matching point was found to be at $[\text{D}_2\text{O}]/[\text{H}_2\text{O}] = 17/83$ by extrapolating $<A(Q)>$ to zero on $p_S$ axis. The Amp values, which were used to verify the contrast matching point obtained from Fig. 4, are also tabulated in Table 6.1. From Amp values we also found the same contrast matching point which confirms the validity of the model we proposed for AOT micelle. The dry volume of AOT monomer was determined to be 611 A$^3$ which agrees with the value obtained from a contrast variation measurement of AOT reverse micelle in decane [15]. By fixing the $V_M$ and $V_H$ (65 A$^3$) so determined we then fit the SANS data of a series of solutions of concentrations ranging from 0.2 to 1.0 % using only two adjustable parameters, $\bar{\Pi}$ and $\alpha$. The results are shown in Fig. 6.5. The extracted parameter values are also tabulated in Table 6.1.
Fig. 6.6 shows the inter-micellar structure factors extracted from the concentration series. The absolute $S(Q)$ value of the 0.6 % solution shown in the graph is shifted up by 1.0 and that 0.3 % by 2.0 and so on. It is clear from Fig. 6.6 that the micellar system becomes more and more ordered as concentration increases. In Fig. 6.7 we show the mean aggregation number as function of the square root of the mole fraction of monomers that form micelles ($X_{\text{CMC}} = X_1$ is the mole fraction of the free monomer). This plot is suggested by a thermodynamic model of micellar formation and growth called ladder model [16]. All the data points seem to fall onto a straight line. We therefore linearly extrapolated the data points to obtain the minimum aggregation number $N_0 = 15 \pm 1$ at CMC which is generally very difficult to measure due to low scattering intensity. The minimum aggregation number so obtained is reasonable from a simple geometric consideration. The volume of the spherical dry hydrophobic core is $4\pi b^3/3 = 8379 \ \text{Å}^3$. Using the dry monomer tail volume $V_T = 611 - 65 \ \text{Å}^3 = 546 \ \text{Å}^3$ found from the contrast variation measurement one gets the aggregation number $N_0 = 8379/546 = 15.3$.

6.5 Summary and Conclusion

The anionic surfactant AOT forms normal micelle in D$_2$O up to 1.1 gm/dL concentration at room temperature. By using SANS technique we have determined the micellar structure and its growth in dilute region. The minimum micelle formed near CMC was found to have a compact
spherical packing containing 15 AOT monomers with a radius \( b = 12.57 \) \( \text{Å} \) which is equal to the fully stretched hydrocarbon tail length. The thickness of the hydrophilic layer is about 5 \( \text{Å} \) (Fig. 6.2) and there are about 22 water molecules associated with each head group. Due to the strong interactions among micelles we used the contrast variation method at finite \( Q \) to determine two molecular parameters that characterize the monomer in a micelle. These two values were found to agree with an independent measurement in the case of reverse micelle \([15]\). The AOT micelle grow moderately from spherical to oblate spheroidal confirming our expectation that a surfactant having two alkyl chains of comparable tail lengths tends to grow from spherical to oblate spheroidal in shape when concentration increases. Finally, the micellar growth was found to depend on the monomer concentration similar to a relation suggested by the ladder model \([16]\).
References:


(3) K. frontell, J. Coll. and Int. Sci., 43, 156 (1973)


(8) J. Sung, Exxon Research and Engineering Co., Ammendale, NJ 08801


(10) B. P. Schoenborn, V. Ramakrishnan and D. Schneider, Physica, 137B, 214 (1986)


(12) L. S. Ornstein and F. Zernike, Prsc. Acad. Sci. (Amsterdam) 17, 793 (1914)


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Table 6.1 The parameters extracted from SANS data fitting of AOT micellar solutions.
Fig. 6.1 Molecular structure of an AOT monomer. The tail length is about 12.57 Å calculated by summing up all the bond-to-bond distances within the tail. The hydrophilic head diameter was found to be about 5 Å.
Fig. 6.2 AOT micellar structure model. The micelle consists of a compact core of semi-major axis $b$, which is taken to be the fully stretched length of the tail, semi-minor axis $a$ to be determined by the model, and a hydrophilic head layer. The contrast between solvent and the hydrophilic layer is small due to water penetration. The dry volumes of the head and the whole surfactant monomer are 65 and 611 Å$^3$ respectively.
Fig. 6.3 SANS intensity distributions of 0.8 % AOT in various [D₂O]/[H₂O] mixed solvents. The calculated values (solid) agree with measured values (Q) very well. The parameter values extracted are nearly identical confirming the applicability of the contrast variation method using finite Q data (see Table 6.1).
Fig. 6.4 $\langle A(Q) \rangle$ plot as a function of $D_2O/H_2O$ ratio in the solvent. By linear extrapolation the contrast matching point was found to be at $[D_2O]/[H_2O] = 17/83$. The $\pi$ can be calculated according to Eq. (6.1) and $\bar{\rho}_s$ at the contrast matching point.
Fig. 6.5 SANS intensity distributions of micellar solutions with various AOT concentrations in D$_2$O. The parameter values extracted are shown in Table 6.1.
Fig. 6.6 $S(Q)$ plots of AOT/D$_2$O micellar system. The system becomes more and more ordered as AOT concentration increases. The scales for $S(Q)$ at 0.6%, 0.8% and 1% are shifted up by 1, 2, and 3 respectively.
Fig. 6.7 AOT micellar growth as a function of surfactant concentration (in unit of molar fraction). All the data seem to fall onto a straight line consistent with the thermodynamic model suggested by Missel et al (see ref. 16 of Chapter VI).
CHAPTER VII

CONCLUSION AND FUTURE RESEARCH

In this study small angle neutron scattering technique was demonstrated to be a powerful technique in characterizing ionic micellar systems. Through SANS measurements and model analyses of the intensity distributions various anionic surfactants were found to form minimum spherical micelles at CMC with sizes equal to compact packing of the hydrophobic tails of the surfactants. As surfactant concentration increases the micelle grows gradually transforming from spherical to prolate/oblate spheroidal depending on the surfactant molecules. An interesting trend was found, namely the micelles formed by single tail surfactant tend to grow from spherical to prolate spheroidal while the micelle formed by double chain surfactant seems to go to from spherical to oblate spheroidal in shape. The hydrophobic core of micelles were found to be free of water molecules. The penetration of water was found to be limited to the hydrophilic layer. The molecular parameters such as dry volume of the surfactant monomer and its tail were successfully determined by a contrast variation method at finite scattering vector \( \Omega \) proposed in this study. This method extends the applicability of the conventional contrast variation technique so that it is applicable to treat the micellar/microemulsion systems with strong inter-particle interactions.
The apparent charges of micelles, for all the cases studied here, are much less than the fully ionized micellar charges. This is independent of the different electrolytic theories used for calculation of the inter-particle structure factor from which the apparent is extracted. This result suggests that there exist counterion condensation phenomena near the micellar surface.

Since the statistical mechanical theories developed at this stage are not sufficiently to treat the charge condensation phenomena quantitatively, more theoretical efforts should be directed toward this point in the future. Examination of the counterion distribution near the micellar surface may ultimately provide an understanding of the phase transition/separation of ionic micellar systems.
Experimental Test of a Theory of Dressed Micelles: The Case of the Monovalent Counterion

Yong-Sheng Chao, Eric Y. Shen, and Sow-Hsin Chen

Nuclear Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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Small-angle neutron scattering (SANS) has been used to determine the aggregation number, the size, and the interparticle structure factor of ionic micellar solutions consisting of the ionic detergent lithium dodecyl sulfate (LDS) and heavy water. The experiments cover a range of concentrations, [LDS] = 0.008–1.107 M, and salt [LiCl] = 0.0–1.0 M. The structure factors for all cases can be well fitted by assuming the intermicellar potential to be the screened Coulomb form with an effective charge \( z^* \). We have tested the values of \( z^* \) thus obtained against a recent theory of the "dressed micelles" by Evans, Mitchell, and Ninham. Our results agree reasonably well with the theory for micellar solutions of moderate detergent concentrations and moderate amount of salt. Experimental results, however, disagree with the theory in the cases of low salt and high detergent concentrations. We also extracted the effective interfacial tension \( \gamma \) from these comparisons. \( \gamma \) varies from 15.0 to 10.7 dyn/cm for low and high salt cases.

I. Introduction

A series of SANS experiments carried out over the past several years revealed that in ionic micellar solutions the intermicellar interaction plays a dominant role in determining the thermodynamic and equilibrium structural properties of the solutions at moderate and high detergent concentrations. At low salt the interaction is significant even at the critical micellar concentration (cmc), which is usually at the mM level. The reason is that the intermicellar interactions are long-ranged when the ionic strength of the solution is low. According to the DLVO theory of colloidal interactions, the double-layer repulsion between two charged particles has a screened Coulomb form when the ionic strength of the solution is low. However, the experimental interparticle structure factor, \( S(Q) \), can be well fitted by using the standard liquid theory, assuming the screened Coulomb form of the potential up to the ionic strength as high as 1.0 M. An effective surface charge \( z^* \) of the micelle can be extracted from the comparison of the theory and experiment. It has been convincingly demonstrated from the experiments that \( z^* \) is generally much less than \( z \), which means the cmc should be numerically equal to the aggregation number \( \theta \). Thus, there are two well-established experimental facts to be reconciled by the theory: the double-layer repulsion between two charged micelles can be well represented by the screened Coulomb form; but the charge which enters into this effective potential is a renormalized charge \( z^* < z \). This latter fact has been addressed theoretically in two recent papers by Alexander et al. on the polyion system and by Evans et al. on the ionic micelle system.

In principle, a rigorous approach to calculating the equilibrium micellar-micellar correlation function would have to take into account the existence of the counterions and co-ions in the solvent which in this case can be taken as a continuous dielectric medium with a dielectric constant \( \varepsilon \). One would then solve the three-component Ornstein-Zernike equations with a suitable closure relation for the direct correlation functions. Such an approach has been taken by Medina-Noyola and McQuarrie. In order to have a tractable theory one usually makes a mean spherical approximation (MSA) whereby the direct correlation functions are equated to negative of the bare Coulomb interactions divided by \( k_BT \). Medina-Noyola and McQuarrie showed that in the limit where the diameters of the counterions and co-ions are negligible compared to the charged colloidal particles and also in the limit of infinite dilution of the colloidal particle, the effective colloidal interaction is the screened Coulomb form of the DLVO potential. More recently, Senatore and Blum estimated that this approximation is good provided the ratio of the sizes of the counterions and co-ions to the micelles is less than 0.1. This condition is usually met in ionic micellar systems so far studied.

In these theories, which model after the primitive model of ionic solutions, it is not clear what is the value of the surface charge of the micelle one supposes to use in writing down its bare Coulomb interactions with ions. It is clear from the experiments that the surface charge of the micelle would have to be less than its fully ionized value in order to compare favorably with these theories. It has been known from thermodynamic theory of micelle formation that the concept of the counterion binding and the associated fractional surface charge is the with experimental cmc. It is, however, doubtful that the thermodynamic theory formulated in terms of solution of the Poisson–Boltzmann equation can even be applied to concentrated micellar solutions. It is clear from the physical ground that the degree of the dissociation of the counterions from the micelle is determined from the competition between the solvation energy of counterions, which favors the ionization, and micellar-micellar repulsive interaction, which favors the recombination. Thus, at cmc the thermodynamic theory is reasonable because the intermicellar repulsions are weak, but at large detergent concentration where the micellar-micellar interactions become dominant one expects to see the phenomenon of the charge reduction (renormalization) of the micelle. In this latter regime, the liquid theory approach is clearly needed.

In this paper, we present the experimentally measured values of these renormalized surface charge, \( z^* \), for ionic detergent solutions which span detergent concentrations from the cmc to 35 g/dL, and salt concentrations from 0.0 to 1.0 M. We compare our results with the theory by Evans, Mitchell, and Ninham. We are able to identify in the process the range of validity of the theory based on the solution of the Poisson–Boltzmann equation.
Theory of Dressed Micelles

of an isolated micelle. It is remarkable that using only two input parameters from the experiment, namely, the ionic strength of the solutions and the aggregation number of the micelle, one is able to compute the effective surface charge parameter, \( \alpha = x^* / \bar{a} \) which agrees with the simple expression over a wide range of salt concentrations up to moderate micellar concentrations of the solutions.

II. Theory

The analytic expressions for calculation of the effective charge and surface tension of a dressed micelle given by Evans et al. were derived from solution of the nonlinear Poisson–Boltzman equation.\(^{10}\) For a spherical micelle of radius \( R \) (radius of the hydrophobic core plus the head group size) and aggregation number \( \bar{a} \) in a 1–1 electrolyte solution, the P–B equation is

\[
\nabla^2 \psi = \frac{d^2 \psi}{dr^2} + \frac{\psi}{r} + 8 \pi n a e \frac{\psi}{k_B T} \sinh \left( \frac{\epsilon \psi}{k_B T} \right)
\]

(1)

with boundary conditions

\[
\psi(r) = 0 \quad \text{as} \quad r \to \infty
\]

\[
\frac{d \psi}{dr} = \frac{4 \pi n a e}{\epsilon} \quad \text{at} \quad r = R
\]

(2)

where \( n_a \) is the bulk electrolyte concentration, \( \epsilon \) the dielectric constant of the solvent, \( \psi(r) \) the electrostatic potential at \( r \), and \( e \) the surface charge density of the micelle. Introducing two dimensionless variables \( x \) and \( y \)

\[
y = \frac{\epsilon \psi}{k_B T}, \quad x \equiv xe \]

where the Debye screening length \( \lambda \) is given by

\[
\lambda = \left( \frac{8 \pi n a e^2}{k_B T} \right)^{1/2}
\]

(3)

Eq 1 and 2 become

\[
\frac{d^2 y}{dx^2} + \frac{2}{x} \frac{dy}{dx} = \sinh y
\]

(3)

\[
\frac{dy}{dx} \bigg|_{r=R} = -\frac{4 \pi n a e}{\epsilon k_B T} = -\frac{s}{\lambda}
\]

(4)

where \( \alpha \bar{a} \) is the area per head group in the micelle with aggregation number \( \bar{a} \), and the surface charge density \( e = e / \alpha \bar{a} \). Writing the dimensionless surface potential \( y_0 = \psi(R) \), the approximate solution of (3) and (4) gives first order in \( (xR)^{-1} \) (an accuracy of about 3% for \( xR = 0.5 \)).\(^{10}\)

\[
\cosh \frac{y_0}{2} = \left[ \left( 1 + \frac{2}{xR} \right)^{1/2} + \frac{xR}{2} \right]^{1/2} - \frac{2}{xR}
\]

(5)

Given \( y_0 \) one can then calculate the electrostatic part of the surface Gibbs free energy per monomer in the micelle by\(^{9,10}\)

\[
g_{\text{el}} = \alpha \bar{a} \int_0^x \psi_0 \, dx = \frac{k_B T}{\lambda} \int_0^x n_a \, dy
\]

(6)

An explicit evaluation of \( g_{\text{el}} \) can be made by using eq 5 in eq 6 to obtain\(^{9}\)

\[
g_{\text{el}} = 2k_B T \left[ \ln \left( \frac{x}{2} + \left[ 1 + \left( \frac{x}{2} \right)^2 \right]^{1/2} \right) - \frac{1}{1 + \left( \frac{x}{2} \right)^2} \right]^{1/2} - \frac{4}{xR} \ln \left( \frac{x}{2} + \left[ 1 + \left( \frac{x}{2} \right)^2 \right]^{1/2} \right)
\]

(7)

It is possible to improve the accuracy of eq 5 to the next order in \( (xR)^{-1} \). This was done in a paper by Ohshima, Healy, and White.\(^{14}\) They have written the relation between the scaled surface charge density \( s \) and the scaled surface potential \( y_0 \), to an accuracy of \( (xR)^{-2} \), as

\[
s = 2 \sinh \left( \frac{y_0}{2} \right) \times
\]

\[
\left[ 1 + \frac{1}{\sqrt{\cosh^2 \left( \frac{y_0}{4} \right)} + \frac{1}{(xR)^2}} \right]^{-1/2} \frac{8 \ln \left[ \sinh \left( \frac{y_0}{4} \right) \right]}{\sinh \left( \frac{y_0}{2} \right)}
\]

(5')

To calculate \( g_{\text{el}} \) we can do a partial integration of eq 6 to get

\[
g_{\text{el}}(s) = k_B T \left[ y_0 - \frac{1}{2} \int_0^s s' \, dy' \right]
\]

(6')

In this way \( g_{\text{el}} \) can be computed numerically. However, we find this improvement gives values of \( g_{\text{el}}(s) \) which are nearly the same as \( g_{\text{el}}^{(1)} \), as can be seen from comparison in Table III.\(^{10}\)

To calculate the fractional effective surface charge \( \alpha \), the adsorption excess of counterions on the micellar surface was considered. A thermodynamic argument gave\(^{10}\)

\[
\frac{d}{dx} \left( \frac{g_{\text{el}}}{n_a} \right) = -\frac{\Gamma k_B T \, d\alpha}{n_a} = -2 \Gamma k_B T \frac{\alpha}{\epsilon} \frac{dx}{x}
\]

(8)

where \( \Gamma \) is the adsorption excess of counterions on a given micelle (i.e., the number of ions adsorbed onto the surface of the aggregation number \( \bar{a} \)). Whence

\[\alpha = \frac{\bar{a}}{a} = 1 + \frac{\Gamma}{\bar{a}} = 1 + \frac{\epsilon}{2} \frac{d}{dx} (g_{\text{el}} / k_B T)
\]

(9)

Using eq 4 for \( s \) and eq 7 for \( g_{\text{el}}^{(1)} \), we get, after differentiation

\[\alpha^{(1)} = \frac{1 - \frac{x}{\bar{a}}}{1 + \left( 1 + \left( \frac{x}{2} \right)^2 \right)^{1/2}} \left[ 1 + \frac{1}{(xR)^2} \right]^{-1/2} \left[ 1 + \frac{1}{\sqrt{\cosh^2 \left( \frac{y_0}{4} \right)} + \frac{1}{(xR)^2}} \right]^{1/2}
\]

(10)

We can also use \( g_{\text{el}}^{(1)} \) from eq (6') and differentiate numerically to get \( \alpha^{(1)} \). The comparison of \( \alpha^{(1)} \) and \( \alpha^{(1)} \) is given in Table III. The effective interfacial tension can also be calculated from the relation:

\[\gamma = \frac{d\alpha}{dx} = \frac{k_B T}{\sqrt{\bar{a}}} \left( \frac{y_0 - \frac{g_{\text{el}}}{k_B T}}{\bar{a}} \right)
\]

(11)

Equations 9 and 10 in conjunction with \( g_{\text{el}}^{(1)} \) are to be used for the subsequent calculations of \( \alpha^{(1)} \) and \( \alpha^{(1)} \). \( \alpha^{(1)} \) is obtained by using \( g_{\text{el}}^{(1)} \) in eq 10 and is also given in Table III. The input parameters to the theory are \( \bar{a} \) and \( \lambda \).

The fractional effective surface charge of a dressed micelle, \( \alpha \), can also be extracted independently from SANS experiments by a self-consistent fitting of the scattering cross section per unit volume \( I(Q) \) with two parameters, namely, the aggregation number \( \bar{a} \) and the effective surface charge of the micelle \( \lambda \).

The SANS data are processed to obtain the differential cross section per unit volume \( d^2 I / dQ \), which we also call the scattered intensity function \( I(Q) \). The intensity function has the form

\[I(Q) = n_a F^2(Q) - F(Q) I^2(Q) + F(Q) I(Q)^2
\]

(11)

where \( n_a = \epsilon n_a / 10^4 \) is the number of micelles per unit volume, \( N_a \) being Avogadro's number, \( \epsilon \) the molar concentration of LDS monomers in the micellar state, \( S(Q) \) the interparticle structure

Figure 1. Schematic picture of the model of LDS micelles we used to analyze SANS data. \( P(Q) \) factor depends largely on the hydrophobic core while \( S(Q) \) factor depends on the total volume of the micelle including an outer layer of the head group region having a thickness of 5.56 Å. In D_{2}O solvent the scattering length density profile of the micelle is depicted in the lower half of the figure.

factor, and \( F(Q) \) the single particle form factor of the micelle. In eq 11 the form factor is averaged over both the polydispersity and the random orientations. If the monodispersed micelles are assumed, then

\[
F^2(Q) = F(Q)^2 = P(Q)
\]

and eq 11 becomes

\[
I(Q) = n_{p} P(Q) S(Q)
\]

In order to fit \( I(Q) \) self-consistently by \( \eta \) and \( z^* \), the three factors \( n_{p} F(Q), \) and \( S(Q) \) should only depend on \( \eta \) and \( z^* \). It is clear that \( n_{p} \), for a given system, depends only on \( \eta \) only.

By the definition

\[
F(Q) = \int_{0}^{\infty} \exp(i\vec{q}\cdot\vec{r})[\rho_{s}(r) - \rho_{m}(r)] \, dr
\]

where \( \rho_{s}(r) \) and \( \rho_{m}(r) \) are the scattering length densities of the micellar core and the solvent, respectively. \( F(Q) \) for a randomly oriented prolate ellipsoid can be calculated as

\[
P(Q) = [k_{c} - \rho_{m}] V_{c} \int_{0}^{\infty} \left[ \frac{\sin QR_{s} - QR_{s}\cos QR_{s}}{(QR_{s})^{3}} \right] \, dQ
\]

where \( R_{s} = [a_{2}^{2} + b^{2}(1 - \mu^{2})^{1/2}] \) is the radius of an equivalent spherical micelle, \( \mu \) is the cosine of the angle between the direction of the semimajor axis of the ellipsoid \( a \) and the scattering vector \( \vec{q} \), \( V_{c} = \pi a_{2} b \), \( a_{2} = \frac{4\pi a_{2} b}{3} \), and \( a_{2} = 360 \) Å is the volume of the tail. Taking \( b \) to be 16.7 Å, the fully stretched length of the tail, \( a_{2} \), can then be calculated by the relation \( a_{2} = 4\pi R^{3}/V \). Thus the calculation of \( F(Q) \) depends only on \( \eta \).

The calculation of \( S(Q) \) assumes the micelle to be a rigid charge sphere of diameter \( d \), interacting through a dimensionless screened-Coulomb potential

\[
\beta U(x) = G \exp(-kx)/x \quad x \geq 1
\]

\[
\beta U(x) = x \quad x < 1
\]

where \( k = \alpha d \) is the dimensionless Debye screening constant, \( x = r/d, \beta = 1/k_{B}T, \) and \( G \exp(-k) \) is the contact potential denoted as \( \text{GEK} \)

\[
\text{GEK} = (\beta x^{2}e^{2}/d)(1 + k/2)^{2}
\]

The results obtained for ref 10 a set of data on LDS micellar solutions previously published by Bendedouch et al., the result is given in Table I.

<table>
<thead>
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<th>( \text{LDS} )</th>
<th>( \text{LiCl} )</th>
<th>( \alpha_{\text{app}} )</th>
<th>( \alpha_{\text{calc}} )</th>
<th>( \gamma ), dyn/cm</th>
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<td>0.34</td>
<td>0.37</td>
<td>11.6</td>
<td>310</td>
</tr>
</tbody>
</table>

\( \alpha = z^*/\eta, \gamma = \text{effective surface tension of micellar/water interface.} \)

To calculate \( S(Q) \) by this model, one needs three input parameters: \( k, \eta, \) and the volume fraction \( \eta = \frac{n_{p}}{a_{2}d^{2}}/6 \). First we calculate the effective radius of the hydrocarbon core \( R \) by

\[
R^{3} = ab^{3} = (3/4\pi)\eta a_{2}
\]

Then \( d \) can be obtained by (see Figure 1)

\[
d = 2(R + 5.56 \text{ Å})
\]

From the definitions of \( k \) and \( \eta \), it is clear that both \( k \) and \( \eta \) are functions of \( \eta \) only. Thus, \( S(Q) \) is essentially a function of \( \eta \) and \( z^* \) only. It was noted in ref 3 that the parameter \( \eta \) essentially determines position and \( z^* \) the width and height of the interaction peak (see Figure 2).

The fitting procedure is self-consistent in the sense that the size parameter \( R \) (or \( \eta \)) which determines the \( P(Q) \) also influences the interaction strength through the parameter \( \eta \) which determines the factor \( S(Q) \). The value of \( \alpha = z^*/\eta \) is thus influenced by both the particle size and the strength of coupling.

III. Discussion of the Results

We apply the theory of ref 10 to a set of data on LDS micellar solutions previously published by Bendedouch et al; the result is given in Table I.
### Table II: Analysis of SANS Data of the New Series

<table>
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<th>[LDS]</th>
<th>[LiCl]</th>
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*See section II for definitions of symbols.

### Table III: Comparison of Different Approximate Formulas for $\gamma$, $\gamma^{(1)}$, $\gamma^{(2)}$, and $\alpha$

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*$\gamma_{e}^{(EM)}$ is from (A.11), $\gamma_{e}^{(EM)}$ from (A.15), and $\alpha_{e}^{(EM)}$ from (A.14) of ref 10.

Figure 3. Extracted $S(Q)$ for the case shown in Figure 2. Solutions with higher LDS concentrations show sharper first diffraction peak due to the increase in the local ordering. It also indicates that 0.02 M of LiCl is not sufficient to screen the electrostatic repulsion between micelles completely even at low LDS concentration.

Figure 5. Extracted $S(Q)$ for the two cases shown in Figure 4. Note that an increase in salt concentration hardly affects the resultant $S(Q)$ function. The aggregation number however increases substantially.

Figure 6. Scattering intensities for 0.07344 M LDS with 0.1 M (−), and 0.2 M (O) LiCl. The $\alpha$ values obtained by the model analysis and experiment show excellent agreement in these two cases.

In addition to these data we undertook a new series of experiments on a similar system but at lower salt and detergent concentrations. The experimental procedure and data analysis are similar to that given in ref 3, and also described in section II. Figure 2 gives the SANS intensity $I(Q)$ as a function of $Q$ at a series of detergent concentrations ranging from 2.5 to 20 g/dL at a constant salt concentration 0.02 M. The analyses results are given by solid lines. The extracted $S(Q)$ are given in Figure 3. It is seen that the agreement between the theory and the experiment is excellent. Figure 4 gives two cases corresponding to the detergent concentration of g/dL at two higher salt concentrations.

0.1 and 0.2 M. Figure 5 again shows the extracted $S(Q)$ for the two cases. Figure 6 gives two results for even higher salt concentrations 0.5 and 1.0 M. Again the agreement of the model analysis and experiment are seen to be good. But it is found that the fitting procedure at high salts is insensitive to variation in $\alpha$. Figure 7 shows the analyses using considerably higher values of $\alpha$ but with the aggregation number kept the same as in Figure 6. The results of the model analyses and their comparison with the dressed micellar theory are summarized in Table II.

Looking carefully through Table I and II, one notices the following trend: the effective interfacial tension $\gamma$ varies slowly over a wide range of detergent concentrations and salts, the values lie between 11.2 and 15.3 dyn/cm. The parameter $\alpha$ shows...
although we already remarked that at high salts the $\alpha$ is poorly
determined from experiment. (3) At moderate salt concentrations
(0.1 < [LiCl] < 0.5) agreements between theory and experiments
are quite reasonable.

Figure 8 summarizes the results of theory of dressed micelles
for $\alpha$. The parameter $\alpha$ is essentially a function of the aggregation
number of the micelle and the ionic strength of the solution. These
functional relationships are given by solid lines. The experimental
values determined from SANS data for moderate salt concen-
trations are also placed in the graph. Roughly speaking, the central
c part of the graph is the region where one finds agreement between
the theory and the experiment.

IV. Conclusion

We have demonstrated in a previous publication[4] that the two
parameters $n$ and $\alpha$ are uniquely determined from analyses of
SANS data. In view of the excellent agreement between the analyses
and the experimental data we believe the values of $n$ and $\alpha$
as obtained are reliable. Thus the comparison of $\alpha_{\text{calc}}$ with that
given by the dressed micelle theory would genuinely test the
validity of the theory.

The disagreement as we pointed out in section III at low ionic
strength is partially due to the fact that the parameter $\alpha R$ is small
(less than unity). For this condition it is known that the accuracy
of solution of the Poisson–Boltzmann equation is poor. Another
source of error is in the fundamental formula, eq 8. It seems to
us that this thermodynamic relation is valid only when $n_0$
is dominated by the counterion concentration. The disagreement
at high ionic strength is again understandable. In this regime the
Debye length $\kappa^{-1}$ is comparable to the distance between head
groups in the micelle and the continuum approximation made in
Poisson–Boltzmann equation is again in question. The dressed
micelle theory in principle ought to fail at high detergent concen-
trations because in this theory intermicellar interaction is not
considered. This deficiency of the theory can in principle be
remedied by formulating the theory in terms of a proper three-
component primitive electrolyte model. Nevertheless, the concept
of a dressed micelle is a useful one and to a limited extent our
experiments have substantiated its region of validity.

Acknowledgment. Acknowledgment is made to the donors of
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Chemical Society, and to the National Science Foundation.

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APPENDIX B

Intermicellar Interactions in Lithium Dodecyl Sulfate Solutions. Effects of Divalent Counterions

Yong-Sheng Chao, Eric Y. Shao, and Sew-Hain Chen

Nuclear Engineering Department, 24-209 Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139 (Received: March 20, 1985; In Final Form: May 16, 1985)

Small angle neutron scattering (SANS) has been used to study the growth and interactions ofionic micelles formed from lithium dodecyl sulfate (LDS) in D₂O. In particular, effective interactions between the micellar aggregates have been studied as functions of the surfactant concentrations and the added salts MgCl₂ and CaCl₂. At low salt concentration [salt] = 0.02 M, the double layer repulsion dominates the intermicellar interaction and we observe an increase in the effective micellar charge but a decrease in the micellar aggregation number as the LDS concentration increases from 1 to 20 g/dl. At high salt concentrations [MgCl₂] = 0.3 M, the effective intermicellar interaction becomes attractive and the aggregation number increases with the LDS concentration. The extracted fractional surface charge of the micelles at low salt is compared with the recent theory of "dressed micelles" and a moderate agreement is found.

I. Introduction

In a series of SANS experiments on lithium dodecyl sulfate (LDS) solutions, we have measured the small angle neutron scattering intensity distribution (spectra) due to the presence of micelles and their mutual interactions. For solutions without added electrolyte, the SANS spectra show a pronounced interaction peak due to electrical double layer interaction between micelles which is so characteristic of an ionic micellar system with high surface charge density. We have studied the effects of added 1-1 electrolyte (LiCl) on the strength of the double layer interaction. In particular, we have addressed the question of how to interpret an effective surface charge of the micelle which can be determined experimentally.

For the model LDS ionic micellar system, we have shown that the micellar growth as a function of the LDS concentration and added electrolyte is one-dimensional and thus the shape (ellipsoidal) and size are determined by specifying the parameter A (aggregation number). This simplifying feature, plus a previous experiment which fixes the average scattering length density of hydrophilic micellar core, allows us to calculate the particle form factor part of the scattering cross section uniquely, once A is specified. The interparticle structure factor part of the cross section can be computed by the standard liquid theory dealing with interacting spherical particles.

The interaction in this case is the double layer repulsion between micelles, which is of the Yukawa form well-known from the classical DLVO theory. In this theory the only input parameter is the effective charge z⁺, or equivalently, the fractional surface charge, f = z⁺/A. Thus, from a quantitative analysis of the SANS spectrum, one extracts two unique parameters, and f, the former gives the growth and the latter the degree of ionization of the micelle.

In a recent paper, we interpreted the parameter f so extracted according to the theory of dressed micelles formulated by Evans, Mitchell, and Ninham (henceforth referred to as EMN). This theory was formulated only for a 1-1 electrolyte solution and comparison of the theory and experiment shows reasonable agreement.

We report in this paper an investigation of the LDS micelle growth and the degree of ionization as functions of LDS concentration and added 2-1 electrolytes, MgCl₂ and CaCl₂. The case of divalent counterions such as Mg²⁺ and Ca²⁺ is interesting because there is evidence that the traditional Poisson-Boltzmann equation approach to the double layer interaction, which forms the basis of the DLVO theory, seems to be invalid. We have extended the dressed micelle theory of EMN to the case of mixed 1-1 and 2-1 electrolytes, taking the result from Ohshima, Healy, and White. We discussed comparison of this theory and the experimental results on f in this paper.

Besides the fractional surface charge, the main interests of this paper are the observation that the aggregation number of the

(8) Evans, D. F.; Mitchell, D. J.; Ninham, B. W. J. Phys. Chem. 1983, 88, 6344 (this paper is referred to as EMN).
micelle decreases as a function of the LDS concentration at low salt when the double layer repulsion is dominant; but the aggregation number increases rapidly as a function of LDS concentration at high salt when the intermicellar interaction switches to an attractive one.

II. Experiment and Data Analysis

Samples. LDS was supplied by Sigma Chemical Co. with a specified purity of 99%. Gold label D₂O was obtained from Aldrich Chemical Co. with 99.8 atom % of deuterium. CaCl₂ and MgCl₂ were Mallinskrodt analytical reagents.

In the preparation of solutions, the samples with highest concentration were made first, and the others were obtained by dilution to give better relative accuracy in the concentrations for a series of measurements. The sample was contained in a cylindrical quartz cell having a path length ranging from 1 to 4 mm. The transmission was kept in the range of 70%-85%.

Data Collection Reduction. The experiments were conducted at the High Flux Beam Reactor at Brookhaven National Laboratory using the H-9 low angle biology spectrometer. The neutron wavelength was λ = 4.75 Å and the sample-to-detector distance was 85.8 cm. The position sensitive detector with 100 × 100 pixels recorded scattered neutrons at scattering angle θ having Bragg wavenumber Q = 4π sin(θ/2)/λ in the range of 0.022-0.245 Å⁻¹. Background scattering and the contributions from the solvent and the quartz window were subtracted pixel by pixel by using a standard subroutine in the laboratory. The attenuation of the neutron beam in the sample was corrected by dividing the scattered intensity by the transmission. A 1-mm H₂O sample was used to standardize the measured intensity into an absolute scattering intensity. The absolute cross section per unit volume of the sample is calculated according to

\[
d\Sigma_i^i = \frac{1 - T_w}{T_w + r_i T_w} \frac{I_i^i}{I_w T_w}\frac{I_w}{I_w T_w}
\]

where \(\Sigma_i^i\) is the absolute cross section per unit volume of the sample at the pixel \(i, j\), \(T_w\) is sample thickness, \(r_w\) is water thickness, \(I_w\) is transmission of the sample solution (with empty cell part removed), \(T_w\) is transmission of water, \(I_i^i\) is scattered intensity of the sample solution at the pixel \(i, j\), and \(I_w^i\) is scattered intensity of water at the pixel \(i, j\).

Data Analysis. The model for the LDS micelle was the same as described in CSC.° The differential cross section per unit volume as a function of Q for a collection of monodisperse micelles with core radius R can be written as

\[
I(Q) = n_i P(Q) S(Q) T(Q)
\]

where \(n_i\) is the number density of micelles. The particle form factor, \(P(Q)\), for a randomly oriented prolate ellipsoid can be calculated according to

\[
P(Q) = (\rho_c - \rho_o)^2 V_e^2 \int_0^1 \left[ \frac{3 \sin u - u \cos u}{u^2} \right] \, du
\]

where \(u = Q(a/2 + b(1 - \mu^2))^{1/2}\), \(R = (a b^2) \mu \) is radius of the equivalent spherical core, and \(u = \cosine of the angle between the direction of the semimajor axis of the ellipsoid and the scattering vector \(Q\). \(\rho_c\) and \(\rho_o\) are the scattering length densities of the micellar core and the solvent, respectively. \(V_e = 4 \pi R^3 / 3 = n_R \lambda^3\), where \(n_R\) is the aggregation number and \(\lambda = 350 \lambda^3\) is the volume of the tail. The structure factor \(S(Q)\) was calculated by solving the Ornstein-Zernike equation in the mean spherical approximation (MSA) using Hayer and Penfold's algorithm. The micellar-micellar interaction potential is to be that of the screened Coulomb form with a contact potential given by

\[
Gek = \frac{\beta 2^2 \mu^2}{2 \omega a(1 + k/2)^2}
\]

where \(\beta = 1/\kappa T\), \(\mu^2\) is the effective charge of the micelle, \(2 \omega a = \kappa a^2\) is the dimensionless Debye screening constant. We choose the radius of the micelle \(R\) according to

\[
a = R + 5.56 \AA
\]

which was determined in a previous experiment.¹ The Debye screening constant \(\kappa\) is calculated from the equation

\[
\kappa = \left( \frac{8 \pi e^2 N_A a}{10^3 k_B T} \right)^{1/2}
\]

where

\[
I = cmc + [salt] + (f/2)[\text{LDS} - cmc]
\]

is the ionic strength of the micellar solution, cmc is the critical micelle concentration, and \(N_A\) is the Avogadro number. This is a consistent definition of \(\kappa\) when the micelle is regarded as partially ionized.¹²

It was found in a preliminary analysis that the micellar-micellar interaction potential becomes attractive when the divalent salt concentration is higher than 0.1 M. Thus, we analyzed the case of low and high salt concentrations separately by using different sets of input parameters. For the case [salt] = 0.1 M, where the potential is repulsive, the core radius \(R\) and the effective charge \(z^e\) of the micelle were used as inputs in the data fitting as described in CSC. For the case [salt] = 0.5 M, where the interaction is attractive, the core radius \(R\) and the contact potential \(Gek\) (negative) were used as the input parameters. In this case, \(Gek\) is the parameter characterizing the van der Waals attraction between micelles.

III. The Double Layer Free Energy according to the Poisson–Boltzmann Equation

In order to calculate the fractional surface charge, \(f\), and the effective interfacial tension, \(\gamma\), of the micelle, we first compute the double layer contribution to the Gibbs's free energy per monomer forming the micelle according to

\[
\frac{\delta a}{k_B T} = \frac{1}{s} \int_0^{\gamma_0} I y_0 \, dy_0 = \frac{1}{s} \int_0^{\gamma_0} s \, dy_0
\]

where \(\gamma_0(s) = e \phi(s)/k_B T\) is the dimensionless surface potential and \(s = 4 \pi e^2 / e k_B T n_m\) is the dimensionless surface charge density.

In order to perform the integration on the right-hand side of eq \(8\), we need a functional relationship between the surface potential and the surface charge density. For the case of the mixture of 1-1 and 2-1 electrolytes, an approximation relationship (to first order in \(\kappa a^2\)¹¹ has been given by Ohshima et al.¹¹ The formula reads

\[
s = pt + 2 \kappa a^2 \left\{ (3 - p) t - \left( \frac{3}{\eta} \right)^{1/2} \frac{1 - \eta}{2} \ln \left( \frac{1 + \eta/3(t - \eta/3)}{(1 - \eta/3)(t + \eta/3)} \right) \right\}
\]

where \(p = 1 - e^{-\gamma R}, [1 - \eta/3]^{1/2}, \eta = n_2 \eta = n_1 + n_2, n_1 = 1-1 electrolyte concentration (=LDS concentration), and n_2 = 2-1 electrolyte concentration.

The fractional surface charge \(f\) is given by

\[
f = 1 + \frac{\kappa d g_{m} / k_B T}{2} dx
\]

where \(\kappa\) is the Debye screening constant defined as

\[
\kappa = \left( \frac{8 \pi e^2 (n_1 + n_2)}{e k_B T} \right)^{1/2}
\]

Finally, the effective surface tension \(\gamma\) can be computed from

\[
\gamma = \left( \frac{\partial g_{m}}{\partial n_m} \right)
\]
IV. Discussion of the Results

The LDS concentrations used in the experiment vary from 1 up to 20 g/dL. The concentrations of MgCl₂ vary from 0.02 (low salt) to 0.1 (moderate salt) and further to 0.5 (high salt) in order to see the reversal of the interactions from repulsive to attractive. In the case of calcium salt, experiments were done only for the low salt case because a further increase in the salt concentration soon results in precipitation of the detergent. Figure 1A shows the results of the low salt series for MgCl₂. The ordinate \( I(Q) \) denotes the differential scattering cross section per unit volume given in eq 2. The coordinate \( Q \) is the wave vector transfer defined as \( Q = 4\pi \sin \theta/2)/\lambda \) where \( \theta \) is the scattering angle and \( \lambda = 4.75 \text{ Å} \). The points denoted by different symbols are experimental results, and the solid lines are the fitted curves according to the procedure described in section II. The fit is done by specifying two input parameters \( c_i \) (or equivalently \( R_i \) and \( g^2 \)) and going through a nonlinear least-squares fitting routine. The fit is uniformly good with \( \chi^2 \) of about 3. It is also a unique fit because the position of the interaction peak largely determines \( R \) and the height and width of the peak depend on \( g^2 \). The fit depends sensitively on \( c_i \) and we can determine \( R \) to an accuracy of ±1 unit. The accuracy of \( g^2 \) is better at low salt because at moderate and high salts the double layer interaction is so attenuated that the effect on the intensity spectra is weak.

Figure 1b shows the extracted intermicellar structure factors as a function of LDS concentration (in M) at a constant salt concentration [MgCl₂] = 0.02 M. One can say that there are the experimentally determined structure factor in the following sense: as we stated above, the fitting procedure is sensitively dependent on \( c_i \) because the interaction peak is formed as a result of the combined effects of the decaying \( P(Q,R) \) function (which is sensitively dependent on \( \theta \)) and the first differential peak of \( S(Q) \), the position of which depends on \( \theta \) and hence on \( R_i \). Thus the position of this peak determines uniquely the value of \( c_i \). Since \( P(Q,R) \) is a unique function of \( c_i \), \( S(Q) \) so extracted from \( I(Q) \) is a correct experimental structure factor which is rather insensitive to the model used to compute it. For example, even if the one-component macromolecule (OCM) description § of the intermicellar structure is not completely accurate, the experimentally extracted \( S(Q) \) could still be accurate, provided one regards the \( g^2 \) so determined to be a model-dependent parameter. Conversely, if one is able to show that the \( g^2 \) obtained from the model fitting is reasonable by an independent argument (such as by the EMN theory), then one would have experimentally demonstrated that the OCM model is valid and the assumed DLVO micellar interaction is a good one.

Figure 2a,b gives the analogous pair of functions \( I(Q) \) and \( S(Q) \) for LDS of various concentrations at 0.02 M CaCl₂. The striking feature of Figure 1b and Figure 2b is that the structure factor \( S(Q) \) in low salts depends strongly on the micellar concentration. The solution is highly nonideal even at 1% (0.037 M) detergent concentration. Table I summarizes the results of the model fitting in the columns \( \theta \) and \( f_{\text{emp}} = (2g^2)/\theta^2 \). The first interesting point to note is that \( \theta \) decreases as the concentration of LDS increases. The reference point is that the minimum micelle in this case corresponds to \( \theta = 53 \) and was determined in ref 1. The second interesting point to note is that the \( g^2 \) in the case of solutions with 0.02M MgCl₂ increases from about 9 to 27 as LDS increases from 1 to 10 g/dL, while in the case of 0.02 M CaCl₂ solutions it increases from 16 to 25 when LDS concentration varies from 2.5 to 20 g/dL. Thus one can say that Ca²⁺ ions are slightly more effective than Mg²⁺ ions in reducing the surface charge of the micelle at the corresponding detergent concentrations.

To see the specific effect of the divalent counterions on the surface charge and on the growth of the micelle more clearly, we compare in Table II the relative effect of a monovalent counterion Li⁺ and a divalent counterion Ca²⁺. The salt concentrations in both cases are 0.02 M which is relatively small compared to the detergent molar concentration. It is seen from the table that at low detergent concentration where the effects of the added counterions are expected to play an important role one sees clearly the enhanced ability of Ca²⁺ over that of Li⁺ in increasing \( \theta \) and decreasing \( g^2 \). However, as the LDS concentration increases much beyond the salt concentration the effects of the added salts become

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\( f \) | expnl | calcld |
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<td>0.387</td>
<td></td>
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</table>

Figure 2. (a) I(Ω) vs. Q for a series of micellar solutions in D2O with 0.02 M of CaCl2 added. Data plotted are for [LDS] = 0.0918 (O), 0.184 (F), 0.367 (X), and 0.734 (M). The extracted S(Ω) vs. Q for the corresponding cases in a. We call this series a low salt series in the text and the fitted parameters η and f_0 were given in Table 1.

Table II: Comparison of Aggregation Number and Effective Surface Charge of Micelles in Low Salt Series at that of 1-1 Electrolyte LiCl

<table>
<thead>
<tr>
<th>[LDS]</th>
<th>[LiCl]</th>
<th>[CaCl2]</th>
<th>η</th>
<th>z^*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0918</td>
<td>0.02</td>
<td>59</td>
<td>20.58</td>
<td></td>
</tr>
<tr>
<td>0.184</td>
<td>0.02</td>
<td>63</td>
<td>23.63</td>
<td></td>
</tr>
<tr>
<td>0.367</td>
<td>0.02</td>
<td>72</td>
<td>25.13</td>
<td></td>
</tr>
<tr>
<td>0.734</td>
<td>0.02</td>
<td>76</td>
<td>26.14</td>
<td></td>
</tr>
<tr>
<td>0.0918</td>
<td>0.02</td>
<td>98</td>
<td>15.78</td>
<td></td>
</tr>
<tr>
<td>0.184</td>
<td>0.02</td>
<td>88</td>
<td>18.92</td>
<td></td>
</tr>
<tr>
<td>0.367</td>
<td>0.02</td>
<td>78</td>
<td>23.87</td>
<td></td>
</tr>
<tr>
<td>0.734</td>
<td>0.02</td>
<td>77</td>
<td>24.64</td>
<td></td>
</tr>
</tbody>
</table>

less effective as compared to the ionized Li^+ counterions from the monomer forming the micelles. We see then the two cases approach nearly the same limiting values, η = 77 and z^* = 25.

In Table I we also list the calculated fractional surface charge f_0 and the interfacial surface tension energy γBoh/k_BT from the EMN theory. We see that there is a moderate agreement between f_0 and f_0. It is expected that the Poisson–Boltzmann equation for the case of 1-1 electrolyte is not as accurate as for the 1-1 electrolyte, so this level of agreement between the theory and experiment is more than one can hope for.

Figure 3 shows the result of four LDS concentrations ranging from 0.5 to 10 g/dL all at salt concentration [MgCl2] = 0.1 M. The solid lines represent the fitted curves according to the OCM theory. Again the degree of the fit is good and the parameters extracted are listed in Table III. It is seen that at this moderate salt concentration the aggregation number stays nearly constant at around 91–95. The double layer interaction is so much attenuated especially at low LDS concentration, again showing the stronger screening power of Mg^2+ as compared to Li^+.

When we increase the salt concentration further to [MgCl2] = 0.5 M, the situation changes dramatically. The data are shown in Figure 4 for LDS concentrations ranging from 1 to 10 g/dL. It is clear from the figure that the intermicellar interactions has to be an attractive one to explain the sharp rising of I(Ω) at small Q^2. We used a model micellar interaction potential consisting of a hard core plus an attractive Yukawa tail. The range of the attractive tail is chosen to be such that η = 10. The contact potential GeV is negative and has a magnitude of several k_BT, depending on the detergent concentration. The results are listed in Table III. It is worth noting that the aggregation number in this case increases rapidly with the concentration of LDS. It has been demonstrated before that for added salt with a monovalent counterion Li^+ the effective intermicellar interaction switches to attractive only for [LiCl] greater than 1.5 M.

V. Conclusion

We have shown that the one-component macromolecule model of the interacting micelles remains a reasonable one for LDS micelles...
Application of a rescaled mean spherical approximation to strongly interacting ionic micellar solutions

Eric Y. Sheu, Chuan-Fu Wu, and Sow-Hsin Chen

Nuclear Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Lesser Blum

Physics Department, University of Puerto Rico, Rio Piedras, Puerto Rico 00931
(Received 19 July 1985)

We analyze a set of small-angle neutron scattering (SANS) data of micellar solutions using a rescaled mean spherical approximation (MSA). The rescaling is shown to overcome the inaccuracy of MSA for the cases of dilute and strongly coupled solutions. The theory is in excellent agreement with SANS data for dilute as well as concentrated solutions. The counter-ion size effect is explicitly taken into account and the extracted renormalized micellar charges are reasonable but smaller, compared to that from the rescaled one-component macro-ion approximation.

Micelles are spherical or nearly spherical aggregates of soap molecules in water that are spontaneously formed when the concentration of soap molecules is increased above a certain threshold value called the critical micellar concentration (CMC). A soap molecule such as lithium dodecyl sulfate is made up of a charged head group (\(-\text{OSO}_3^-\mathrm{Li}^+\)), which is hydrophilic, and a hydrocarbon tail [\(\text{CH}_2(\text{CH}_3)_11\text{H}\)] which is hydrophobic. As a result, the structure of a micellar aggregate consists of a hydrophobic core of close-packed hydrocarbon tails, and a head-group outer layer emerging into water which is charged because some fraction of the "counter-ions" \(\mathrm{Li}^+\) has dissociated into water. Typically, near the CMC (8 mM) the micellar aggregate has a minimum size with a diameter of about 44 Å and an aggregation number of about 54.\(^1\) The degree of ionization \(\alpha\), which is the ratio of the renormalized charge \(Z^*\) to the aggregation number \(\bar{n}\), is estimated to be between 0.20 and 0.25 (Ref. 2) near the CMC. A proper liquid theory which takes into account interactions among the charged micelles, between the micelles and the counterions, and the counter-ions themselves is needed to calculate the renormalized charge \(Z^*\). The effects of the solvent are taken into account in an approximate way through inclusion of a macroscopic dielectric constant \(\varepsilon\). This so-called primitive model\(^1\) has been shown to have some range of validity in the case of simple electrolyte solutions. In the case of micellar solutions the situation is slightly different because both the charge and size of micelles are much larger than the other ions in the solution. Applications of the primitive model to this kind of highly asymmetric electrolyte solutions have been made by Elkoubi, Turq, and Hansen\(^4\) and Patey\(^5\) using hypernetted chain approximation (HNC), and the results seem to be satisfactory. However, HNC is a non-analytic theory, and its numerical solution is sufficiently complicated as to make it unattractive for analyses of experimental data. On the other hand, the mean spherical approximation (MSA), which is a linearized version of the HNC, is simple enough to yield an explicitly analytical solution for an arbitrary mixture of ions in a solution.\(^6\) The solution of the MSA has been tested against experimental data on osmotic coefficients of 1-1 electrolyte solutions\(^7\) and also to some extent against the equivalent solution of the HNCA in the case of NaCl solutions,\(^4\) and the accuracy of it was demonstrated to be satisfactory. In this paper we shall apply a multicomponent MSA to micellar solutions with only the counter-ions present (i.e., no added salt). We analyze small-angle neutron scattering (SANS)-data from micellar solutions containing detergent lithium dodecyl sulfate (LDS) and sodium dodecyl sulfate (SDS), both taken at the same concentrations so that one can see the effects of the size of the counter-ions on the aggregation number \(\bar{n}\) and on the renormalized surface charge \(Z^*\). We shall show that a simple model of micellar structure\(^7\) plus the MSA for calculation of the intermicellar structure factor allow us to fit the data nicely and thus uniquely extract parameters \(\bar{n}\) and \(\alpha\) from each SANS intensity spectrum. An alternative analysis using the one-component macro-ion (OCM) approximation\(^1, 9\) gives the same aggregation number \(\bar{n}\) but higher values of \(\alpha\). We then argue that \(\alpha\)'s extracted by using the MSA are more realistic than that from the CCM by comparing the results to the prediction of a theory of dressed micelles by Evans, Mitchell, and Ninham.\(^2\) In two recent publications, Senatore and Blum\(^10\) and Nägele, Klein, and Medina-Noyola\(^11\) discussed possible applications of the MSA to micellar solutions. They pointed out that as far as the intermicellar structure factor is concerned the MSA gives comparable results at the first diffraction peak as the HNCA for dense solutions. The first diffraction peak is the most important region for analysis of SANS data. However, since they did not implement the rescaling procedure, the structure factors calculated for solutions with micellar volume fractions less than 0.2 become inaccurate. Therefore, they did not attempt to analyze SANS data by the MSA.

We model the micellar solution as consisting of a system of charged hard spheres immersed in a dielectric medium (water) of a dielectric constant \(\varepsilon\). The size, charge, and number density of the micelles are denoted by \(\sigma_\text{m}\), \(Z_\text{m}\), and \(n_\text{m}\) respectively, and the corresponding quantities for ions by \(\sigma_i\), \(Z_i\), and \(n_i\), with \(i = 1\) (counter-ions) and 2 (co-ions), etc. The pair correlation functions \(g_{ii}(r)\) are found by solving the coupled Ornstein-Zernike (OZ) equations:

\[
\lambda g_{ii}(r) = C_{ii}(r) + \sum_j \gamma_j \int d^3r_j h_{ij}(|r - r_j|) C_{ij}(r_j)
\]

where

\[
h_{ii}(r) = C_{ii}(r) + \sum_j \gamma_j \int d^3r_j h_{ij}(|r - r_j|) C_{ij}(r_j)
\]
using the closure

\[ \eta_{\text{eff}}(r) = -1, \quad r < \sigma_{\text{eff}} . \]

\[ C_{\text{eff}}(r) = -\beta Z_\text{eff} Z_\text{ref} / r, \quad r \geq \sigma_{\text{eff}} . \]

Here \( \eta_{\text{eff}}(r) = g_{\text{eff}}(r) - 1 \) are the total correlation functions, \( C_{\text{eff}}(r) \) the direct correlation functions, \( \beta = 1/k_B T \), and \( \sigma_{\text{eff}} = (\sigma_a + \sigma_b)/2 \). The condition Eq. (2) is an exact statement for a hard-core system, but the condition Eq. (3) is only asymptotically true at larger \( r \). Thus the MSA becomes increasingly more accurate as the volume fractions of the hard spheres increases. A closed-form solution for \( g_{\text{eff}}(r) \) or equivalently \( C_{\text{eff}}(r) \) can be obtained by Baxter’s method.12 For our purpose, it is most direct to write down the partial structure factor \( S_{\text{eff}}(Q) \), which is

\[ S_{\text{eff}}(Q) = \delta_{\text{eff}} + 2\pi (n_a n_b)^{1/3} [G_{\text{eff}}(-iQ) - G_{\text{eff}}(iQ)] / iQ , \]

where \( G_{\text{eff}}(iQ) \) is a complex function defined in terms of a Laplace transform of \( \eta_{\text{eff}}(r) \), i.e.,

\[ G_{\text{eff}}(s) = \int_0^{\infty} e^{-s} \eta_{\text{eff}}(r) dr . \]

An explicit expression for \( G_{\text{eff}}(s) \) has been given by Blum4 and Senatore and Blum10 in terms of the physical parameters of the system and a generalized screening parameter \( \Gamma assignment \). In the limit \( \sigma_a = 0 \) and \( n_a = 0 \), \( \Gamma_c \) reduces to the well-known Debye screening parameter conventionally defined as

\[ \chi^2 = 4 n_B \beta e^2 / e \sum n_i Z^2 . \]

In general, \( \Gamma_c \) is less than \( \chi \) for dilute and moderately dense solutions. This is because the finite-size ions have reduced screening power. In the calculation of \( \Gamma_c \) the contribution of micelles is taken into account consistently, while in the conventional Debye-Hückel theory13 it is left out as in Eq. (6).

Although Eq. (4) is an elegant solution for the partial structure factors of a multicomponent Coulomb fluid, it is known that for low ionic concentrations and for strong Coulomb couplings the MSA solution gives negative \( g_{\text{eff}}(r) \) in the neighborhood of the minimum-approach distance. This phenomenon will in turn give rise to an inaccurate partial structure factor \( S_\text{MSA}(Q) \) for typical micellar solutions with micellar volume fraction \( \phi \) less than about 0.2. This is a serious defect of MSA since the interesting range of micellar solutions almost always includes \( \phi \approx 0.2 \).

In order to overcome this defect, we suggest the following approximate modification to the solution of the MSA when \( g_0(\sigma_0) \) becomes negative. In this case, we seek for \( \sigma_0' > \sigma_0 \), which will satisfy Gillan’s condition,14 \( g_0(\sigma_0') = 0 \). We can do this integrated by first choosing, for example, \( \sigma_0' = \sigma_0 + 5 \) Å, recalculate \( \Gamma_c \), including modification of the volume fraction to a new value \( \phi' = (\pi/6) n_0 \sigma_0^2 \), and use them to calculate a new \( S_\text{MSA}(Q; \Gamma_c') \). We then Fourier transform \( S_\text{MSA}(Q; \Gamma_c') \) at one point \( r = \sigma_0' \) to check whether \( g_0(\sigma_0') \) is positive or negative. If it is positive, we halve the increment and repeat the calculation. If it is negative, we double the increment and again repeat the calculation. This procedure usually leads to a rapid convergence of \( \sigma_0 \) to the right rescaled value satisfying the Gillan condition. \( S_\text{MSA}(Q; \Gamma_c') \) thus obtained is then the correct intermicellar structure factor to be used for the neutron cross-section calculation.

The physical basis for the rescaling procedure can be seen from the following argument.16 If we define an average intermicellar spacing by \( \alpha = (3/4\pi n_0)^{1/3} \), then we can introduce a Coulombic coupling constant \( \gamma \) by

\[ \gamma = 2\beta v_0 (r = 2a) = \frac{\beta Z_\text{eff} e^2}{\epsilon_0} . \]

\( \gamma \) is the ratio of the intermicellar Coulomb interaction energy to the thermal energy at the average intermicellar distance. When \( \gamma < 1 \), we have a weak-coupling case, and the actual contact distance \( \sigma_0 \) is the relevant quantity for the calculation of \( S_\text{MSA}(Q; \Gamma_c) \). But when \( \gamma > 1 \), one has a strong-coupling case, and the relevant distance is \( \alpha \) instead. This is because in this case the micelles would seldom approach close enough to each other to sense the contact distance \( \sigma_0 \), and we are allowed to choose a \( \sigma_0' \) such that \( \sigma_0 < \sigma_0' < 2a \). Increasing \( \sigma_0 \) to \( \sigma_0' \) would bring in more of the short-range correlation missing in MSA ansatz Eq. (3) into the problem. At the same time one has \( \phi' > \phi \), an increased volume fraction which makes the MSA more accurate.

In ionic micellar solutions, values of \( \gamma \) are usually about 10, and one is always dealing with the strong-coupling case. Thus, as soon as \( \phi \) falls below 0.2, the MSA becomes inaccurate, and the rescaling is necessary. The rescaling procedure we propose above will improve accuracy of \( S_\text{MSA}(Q) \) but probably not \( S_\text{MSA}(Q) \), since now the ions cannot approach the micelles closer than the distance \( \sigma_0'(1 + \phi) \). This is not important in analyses of SANS data since neutron structure factor involves only \( S_\text{MSA}(Q) \).

Previously, we have analyzed similar SANS data using a one-component macro-ion theory.1,9 In this theory one regards the counter-ions as point charges distributed around the micelles, which can be eliminated from the problem by introducing a Debye screening parameter \( \sigma \) [Eq. (6)]. As a result, the intermicellar effective interaction is renormalized into a Yukawa form:

\[ v_\gamma(r) = \frac{(Z\sigma)^2 e^{\sigma_0 - \sigma_0'/2}}{\epsilon_0 [1 + \kappa \sigma_0' \beta^{-1} Z^2]} ; \quad r > \sigma_0 . \]

This particular form of the macro-ion interaction is called the Derjaguin-Landau-Verwey-Overbeek double-layer potential in the colloid literature.13 That the effective macro-ion pair potential is of the Yukawa form can be justified from a more accurate liquid theory, but the coefficient in front of it turns out to be a complicated function of the physical parameters of the system.17 Thus \( \sigma' \), which appears in Eq. (8), does not have a well-defined meaning of an effective charge, as opposed to the renormalized charge \( Z_\text{eff} \) in the MSA, which has a well-defined meaning of the effective micellar charge which enters the pair interaction. In the OCM theory18 one takes \(-\beta v_\gamma(r)\) as the direct correlation function outside the core in solving the one-component OZ equation for the macro-ions. OCM analyses of SANS data1,9 turned out to result in uniformly excellent agreement with experiment. However, in this case, one needs to understand the meaning of the extracted parameter \( Z' \). We have discussed this question very recently19 and showed that \( Z' \) so obtained in general agrees with what one expects from a theory of dressed micelles,2 except for the case when there are only counter-ions and micelles present.
in the solution. In the latter case $Z^*$ obtained from OCM analyses seem to give too high a value by about a factor of 2. In using OCM in conjunction with $\nu_f(\tau)$, one also needs to rescale the MSA solution when the volume fraction of micelles is below about 0.2. Hansen and Hayter\textsuperscript{20} implemented a rescaling procedure for the case of the one-component Yukawa fluid and showed that near the first diffraction peak of $S(Q)$ the rescaled MSA yielded a comparable accuracy to that from the one-component HNCA.

SANS measurements were done at the Biology Small Angle Spectrometer at the high-flux reactor of Brookhaven National Laboratory. Incident neutrons had wavelengths $\lambda = 4.83$ Å, with the sample situated at a distance 1.43 m from the two-dimensional detector. This geometry allowed a coverage of a $Q$ range, $0.022 \leq Q \leq 0.303$ Å$^{-1}$, where the Bragg wave number in the scattering, $Q = 4\pi \sin(\theta/2)/\lambda$, is a function of the scattering angle $\theta$. We shall denote by $I(Q)$ the differential cross section per unit volume of the sample, which was obtained from processing the experimental data.\textsuperscript{1} It can be shown\textsuperscript{15} that under fairly general conditions,

$$I(Q) = N_p P(Q) S'(Q)$$

where $N_p$ is the number of micelles per unit volume, $P(Q)$ is the particle-structure factor, and $S'(Q)$ is the orientationally averaged interparticle structure factor:

$$S'(Q) = 1 + \frac{1}{(F(Q))^2} \left[ -[S(Q) - 1] \right].$$

$F(Q)$ in the equation is the form factor of the micelle, and the bracket denotes the orientation-averaged when the shape of the micelle deviates from sphericity.

Figure 1 shows $I(Q)$ vs $Q$ plots for LDS solutions at concentrations 2.5, 5.0, 10, and 20 g/dL. Points are experimental intensities in an absolute scale of cm$^{-1}$, and solid lines are the MSA fits to the data. Figure 2 gives the similar results for SDS solutions. The only difference in the physical parameters of LDS and SDS solutions is in the counter-ion size. The hydrated lithium ion has a diameter of $\sigma_{Li} = 3.90$ Å, and the hydrated sodium ion has a diameter of $\sigma_{Na} = 2.60$ Å. These values are taken from Triolo, Grigera, and Blum\textsuperscript{1} obtained by the best fit to thermodynamics data of 1-M electrolyte solutions. One sees that the agreement between the MSA and the experiment is uniformly good. We also analyze the same data using the OCM theory in a way described in Ref. 1. The quality of fit to the data is about the same as using the MSA, but values of the fitted parameters are different. We summarize the results in Table I. It can be seen that the aggregation number $\tilde{n}$ from

<table>
<thead>
<tr>
<th>Table I. Parameters for LDS and SDS solutions.</th>
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<tbody>
<tr>
<td>Conc. (mol/L)</td>
</tr>
<tr>
<td>LDS</td>
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<td></td>
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<tr>
<td></td>
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<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td>SDS</td>
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</tbody>
</table>
the two schemes of fit are consistent to within 5%. This is because \( \bar{n} \) is largely determined by the position of peak in \( I(Q) \), as remarked previously.\(^1\) However, values of \( \alpha \), which is the fractional surface charge of the micelle, are different by a factor of 2. \( \alpha_{\text{OCM}} \) is always larger than \( \alpha_{\text{MSA}} \). It can be shown\(^2\) from a theory of dressed micelles (EMN) that, in the case of LDS, \( \alpha = 0.2 \) and should be fairly insensitive to the salt added. It has been shown that the theory of EMN should be fairly good for dilute solutions with added salt.\(^3\) This means that for micellar solutions without added salt, such as the case we considered here, the reasonable values of \( \alpha \) should be also about 0.2. Table I lists values of \( \alpha_{\text{EMN}} \) calculated in a way described in Ref. 19, and they show good agreement with \( \alpha_{\text{MSA}} \).

Figure 3 compares two \( S_0(Q) \) extracted from SANS data of a 10-g/dL LDS solution by using MSA (solid line) and OCM (dashed line), respectively. One sees that they are nearly identical. Similar results are also obtained from solutions of other concentrations. This proves the point that the MSA treatment of a multicomponent Coulomb fluid is nearly equivalent to the OCM treatment of an equivalent one-component Yukawa fluid, as far as \( S_0(Q) \) is concerned. However, in MSA, the screening constant \( Z_0 \) used in the calculation is more consistent, and the \( Z_0 \) extracted from the fit has a simpler physical meaning.

In conclusion, we have demonstrated that in conjunction with a simple rescaling procedure, the rescaled MSA treatment of a multicomponent Coulomb fluid can be used to analyze SANS data from strongly interacting micellar solutions with very good results. In particular, one can easily incorporate into the theory the size and charge effects of counter-ions and co-ions in the solution. The charge \( Z_0 \) extracted from SANS data can be identified as the renormalized surface charge\(^4\) of micelles, which agrees with an independent estimate\(^5\) made for ionic micellar solutions near CMC. Nevertheless, the ultimate justification for the accuracy of rescaled MSA requires further theoretical work.

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Effects of Ion Sizes on the Aggregation and Surface Charge of Ionic Micelles in 1:1 Electrolyte Solutions

Eric Y. Shen, Chuan-Fu Wu, and Sow-Haii Chen*

Nuclear Engineering Department, 24-209, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (Received: November 19, 1985; In Final Form: January 8, 1986)

A rescaled mean spherical approximation (RMSA) has been developed to model the interparticle structure of strongly interacting micellar solutions by treating them as multicomponent Coulomb fluids. In this model the counterion and co-ion sizes can be explicitly taken into account in determining the intermicellar structure factor. A series of small angle neutron scattering (SANS) data of lithium and sodium dodecyl sulfate micellar solutions containing various kinds of 1:1 electrolytes have been analyzed by the model in conjunction with a two-shell model for the micellar structure factor. The theory is capable of generating excellent fits to the SANS intensity distributions. Two parameters, the average aggregation number \( N \) and the fractional surface charge \( \alpha \) of the micelle, have been systematically extracted from the experimental data. It is shown that both \( N \) and \( \alpha \) are strong functions of the counterion size but are only weakly dependent on the co-ions sizes.

I. Introduction

It has been well established from a number of SANS experiments\(^1\)-\(^5\) in the course of the past several years that ionic micellar solutions are appreciably nonideal in the whole range of concentrations above the critical micellar concentration. It is a common characteristic of SANS intensity distributions (spectra) from ionic micellar solutions that they exhibit a strong interaction peak which is more pronounced as the ionic strength of solutions decreases.\(^6\) The pronounced interaction peak has been interpreted as due to the sharpening of the intermicellar structure factor when the effective Coulomb interactions between micelles become long-ranged and appreciable as compared to \( k_B T \). The SANS spectrum, for a micellar solution, is to a good approximation, the product of the particle structure factor and the interparticle structure factor.\(^7\) The particle structure factor, \( P(Q) \), is a monotonically decaying function of \( Q \), the Bragg wavenumber of the scattering, and is relatively simple to evaluate once the aggregation number of the micelle is specified.\(^8\) The intermicellar structure factor, \( S(Q) \), on the other hand, is an oscillatory function of \( Q \) and is sensitively dependent on the form of the intermicellar interaction and on the statistical mechanical theory used to calculate the structure factor.

In the past, a popular statistical mechanical model for calculating \( S(Q) \) has been the so-called "one-component macroion model" (OCM).\(^9\) OCM is modeled after the DLVO theory of colloidal stability which introduces an effective colloidal macroion double layer interaction in the form of a Yukawa potential with a Debye screening parameter, \( \kappa \), and a contact potential \( V_c \) which is a function of the surface charge \( Z^* \) and macroion size \( \sigma_{OCM} \). In this approach the effects of counterions and co-ions are treated approximately through their contribution to the ionic strength of the solution which in turn determines the screening parameter \( \kappa \). From the statistical mechanical liquid theory point of view, this approximation amounts to ignoring the sizes of counterions and co-ions (i.e., point charges) and to the use of the mean spherical approximation for calculation of the structure factor \( S(Q) \).\(^10\)

The OCM model of micellar solutions has been repeatedly demonstrated\(^11\)-\(^13\) to yield excellent fits to the SANS data when \( \kappa \) is appropriately computed and the contact potential \( V_c \) is treated as a phenomenological parameter.\(^11\)-\(^13\) This approach is, however, not completely satisfactory in two respects: First, in computing the screening constant \( \kappa \), one takes into account only the contribution from the small ions in the solution. Thus one treats the ions and the micelles on an unequal basis. This asymmetry in the theory would no doubt be a serious limitation when micellar solutions are concentrated. Secondly, the OCM model is a contracted theory in which small ions are eliminated from the solution which originally consists of a multicomponent ionic mixture. Thus the contact potential of the effective macroion interaction is, in general, a complicated function of all of the ion sizes and is not a function of the surface charge \( Z^* \) and the size \( \sigma_{OCM} \) of the macroion alone.\(^14\) Because of the latter problem, even if one can achieve an excellent fit to the experimental data, the extracted contact potential \( V_c \) cannot be easily related to properties of the macroion itself.

In two recent papers, Sanatone and Blum\(^15\) and Nägele et al.\(^16\) pointed out the possibility of calculating the structure factor \( S(Q) \) of ionic micellar solutions by treating them as multicomponent Coulomb fluids in analogy to the "primitive model" used in the electrolyte solution theory.\(^17\) In this approach, one treats both the macroions and small ions in a consistent way, taking into account both their charges and sizes, and postulating their mutual interactions as bare Coulomb interactions in a dielectric medium of water. It has been shown in the context of 1:1 and 2:1 electrolytes that the primitive model gives quite satisfactory accounts of thermodynamic and structure properties of the dilute as well as concentrated solutions.\(^18\),\(^19\) A proper liquid theory to use is the so-called hypernetted chain approximation (HNC)\(^20\) but it has also been demonstrated that in many cases the simpler so-called mean spherical approximation (MSA) would yield similar results.\(^21\) The advantage of using the MSA in multicomponent

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Coulomb fluids is that the structure and thermodynamic properties can be obtained entirely analytically. A disadvantage of the MSA is that, due to the nature of its approximation, it gives rise to unphysical pair correlation functions at short distances when the volume fraction of the macromer becomes low. Thus the MSA in its original form is unsatisfactory for analyses of the structure of ionic micellar solutions because the low concentration range of micellar solutions is often quite important.

In a recent brief communication, we have pointed out that this unphysical feature of the MSA at low concentrations can be eliminated by a rescaling procedure. We have demonstrated that, by implementing the rescaling procedure, SANS data for micellar solutions without added salt can be satisfactorily analyzed by the MSA. In the present paper we shall further extend the analyses to SANS data for micellar solutions with various added 1:1 electrolytes. Our purpose is, first, to explain the model for computing the particle structure factor \( P(Q) \) and the interparticle structure factor \( S(Q) \) in full detail. Second, to investigate the size effects of counterions and co-ions on the micellar aggregation number \( n \) and the effective fractional surface charge parameter \( a \). We also performed a parallel analysis of the data using the OCM model. We show that although the aggregation number \( n \) extracted by MSA and OCM are similar, the fractional surface charge parameters \( a \) are different. We then compare the values of \( a \) extracted from experimental data with a recent theory of dressed micelles proposed by Evans, Mitchell, and Ninham (EMN). The comparison shows that while the \( a_{\text{MSA}} \) 's extracted from the MSA fits agree reasonably with the theory of EMN, \( a_{\text{OCM}} \) 's from the OCM fits differ appreciably from it. We then argue that \( a_{\text{MSA}} \) is a more reasonable quantity to take for the effective micellar surface charge.

II. SANS Experiment

Sample and Cell. Both lithium and sodium dodecyl sulfates (LDS and SDS) were supplied by Sigma Chemical Co. with specified purity better than 99\% and were used without further purification. The uniformities of their carbon chain lengths were checked by the manufacturer by gas and thin-layer chromatography. Gold label D_{2}O with >99.8 at \% deuterium was used as the solvent of the micellar solutions. The other chemicals used in this experiment, such as various kinds of salts, were of reagent grade.

The micellar solutions were prepared by dissolving known amounts of surfactant in D_{2}O solvent. In order to obtain better relative accuracy in concentrations for a series of measurements, the most concentrated sample was prepared first and the rest of the series was made by dilution. Following the dilution, salts were

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**Table 1: Effective Ion Sizes Taken from Ref 33**

<table>
<thead>
<tr>
<th>Cation</th>
<th>( r_{+} ) Å</th>
<th>Anion</th>
<th>( r_{-} ) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^{+})</td>
<td>3.90</td>
<td>F(^{-})</td>
<td>2.72</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>2.58</td>
<td>Cl(^{-})</td>
<td>3.60</td>
</tr>
<tr>
<td>K(^{+})</td>
<td>1.82</td>
<td>Br(^{-})</td>
<td>3.90</td>
</tr>
<tr>
<td>Cs(^{+})</td>
<td>1.15</td>
<td>F(^{-})</td>
<td>4.32</td>
</tr>
</tbody>
</table>

---

 added to the micellar solutions to complete the sample preparation. Since the dry volumes of the surfactants and the additives are known, their molar concentrations can be accurately calculated for the later data analyses. The prepared sample was injected into a cylindrical quartz cell for scattering measurement and was kept frozen when not in use to avoid deterioration.

Data Collection and Reduction. The SANS experiments were conducted on the low angle biology spectrometer located in the high flux beam reactor at Brookhaven National Laboratory. The thermal neutron beam emerging from an in-pile liquid hydrogen source passes through a cold Be filter and impinges on a multilayer monochromator which selects a wavelength $\lambda = 4.83$ Å with a spread $\Delta \lambda / \lambda = 5\%$. The monochromatic beam is then collimated over a length of 2 m by a series of apertures (pin holes) of decreasing diameter $(12.8, 6 \text{ mm})$. A position-sensitive detector with $128 \times 128$ pixels covering an area of $64 \times 64$ cm$^2$ was used to record the scattered neutrons. The sample-to-detector distance was chosen to be 138.8 cm which, together with the detector dimension, spans a $Q$ range of 0.0147 to 0.350 Å$^{-1}$. Samples were contained in flat cylindrical quartz cells with a window thickness of 1 mm and path lengths ranging from 1 to 4 mm.

Raw scattering data were collected from 20 min to 1.5 h, depending on the micellar concentration, and were first manipulated in the standard fashion$^{27}$ to subtract the background and the contributions from the incoherent scattering of the solvent and from the quartz cell. The attenuation of the neutron beam in the sample was corrected by separate transmission measurements for each sample. The treated data were further reduced by correcting for detector sensitivity. The detector sensitivity was calibrated by using a 1-mm H$_2$O sample. The absolute scattering intensity (differential cross section per unit volume of sample) is calculated according to

$$\frac{d\Sigma_{ij}}{dQ} = \frac{1 - T_e}{T_e} \frac{I_{ij}/I_iT_i}{I_{ij}/I_iT_i}$$

where $\Sigma_{ij}$ is the differential cross section per unit volume of the sample at the pixel $i,j$; $I_i$ is the sample thickness; $T_e$ the water thickness; $T_i$ is the transmission of the sample solution (with empty cell contribution subtracted); $T_e$ is the transmission of water; $I_{ij}$ is the scattered intensity of the sample solution at pixel $i,j$; and $I_{ij}$ is the scattered intensity of water at pixel $i,j$.

III. Model for the Particle Structure Factor

According to our previous investigation,$^{26}$ a lithium dodecyl sulfate (LDS) micelle in water for surfactant concentrations from one up to 1.107 M can be represented by an ellipsoid with a two-layer structure as depicted in Figure 1. The inner hydrophobic region is a compact core consisting largely of the hydrocarbon tails of LDS monomers. The semimajor axis, $b = 16.7$ Å, is the fully stretched length of the dodecyl chain and the semimajor axis $a$ is linearly related to the aggregation number $n$ according to

$$\frac{n \rho}{2} = \frac{4\pi}{3} a b^2$$

where $\rho = 364 \pm 22$ Å$^3$ is the steric volume of the C$_{12}$ chain. The scattering length density $\rho_i$ of this region is equal to $-0.38 \times 10^{-4}$ Å$^{-3}$ which is the value for a typical liquid hydrocarbon. The outer
hydrophilic region consists of the polar head groups and the water molecules of hydration. At present the structure of this outer region is not known in sufficient detail and we simply assume it to be a layer with thickness δ and scattering length density p₂. The value of p₂ is positive and is only about 10% different from the solvent (D₂O) value p₁ = 6.34 × 10⁻⁶ Å⁻².

This structural model does not take into account the thermal motions of monomers in and out of the micelle. This fluctuation would give rise to a finite thickness of the hydrophobic–hydrophilic interface which would then constitute a third region. However, all our experiments so far indicate that inclusion of the third layer is not necessary to fit the data, and in any event the two additional parameters introduced by this more complicated model would be certain to result in a nonunique fit.

In the above-mentioned two-region or two-shell model, the form factor $F(Q)$ of the micelle is calculated according to the scattering length density profile depicted in the lower part of Figure 1. For an ellipsoid with the major axis inclined at an angle β to the direction of the scattering vector $Q$, the form factor is given by

$$F(Q,a) = 4π \rho \frac{a^2 b^2 (p_1 - p_2)}{3} \frac{3/2}{u_1} + 4π \frac{a}{3} (a + b)(p_2 - p_1) \frac{3/2}{u_2}$$

where

$$u_1 = Q[(a^2 + b^2)(1 - \mu^2)]^{1/2}$$

$$u_2 = Q[(a + b)^2 + (b + b^2)(1 - \mu^2)]^{1/2}$$

$$\mu = \cos β$$

The thickness of the outer region δ can be calculated by using $a$ and $b$ from eq 2 according to the formula

$$\frac{4π}{3} (a + δ)(b + δ)^2 = h(p_m + p_r (1 - a) + p_w N_w)$$

where $p_m$ is the volume of a monomer excluding the counterion, $p_r$ is the hydrated volume of the counterion, $p_w$ is the volume of the water molecule, and $N_w$ is the average number of water molecules hydrating a polar head. The values of $p_m$, $p_r$, and $p_w$ are known to be 400, 31.04, and 30.0 Å³, respectively, and that of $N_w$ is assumed to be 10 in the cases of LDS and SDS micelles.

The aggregation number $h$ and the fractional surface charge $a$ are the two parameters used for SANS data fitting. Thus, for a set of $h$ and $a$ values the scattering length density of the outer shell $p_2$ is calculated according to

$$p_2 = \frac{h[b(\text{OSO}_7^-) + (1 - a) p_r + N_w p_{\text{D}_2\text{O}}]}{V_{\text{outer shell}}}$$

where $b(M)$ denotes the scattering length of species M, and the particle structure factor $P(Q)$ can be calculated according to

$$P(Q) = \langle |F(Q)|^2 \rangle = \int_0^1 dT |F(Q,\alpha)|^2$$

For a nearly monodispersed system of ellipsoidal micelles, one can, to a good approximation, decompose the differential cross section per unit volume (eq 1) into the product of three factors:

$$\frac{d\Sigma}{d\Omega}(Q) = I(Q) = N_p P(Q) S(Q)$$

where $N_p$ is the number of micelles per unit volume, and $P(Q)$ is the particle structure factor defined in eq 6. $S(Q)$ is the orientationally averaged structure factor related to the particle

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center–center structure factor \( S(Q) \) by the formula\(^4\)

\[
S(Q) = 1 + \frac{(F(Q))}{(\langle F(Q) \rangle)^2} (S(Q) - 1) \tag{8}
\]

\((F(Q)))\) is the angular average of the form factor given in eq 3, i.e.

\[
(F(Q))) = \frac{1}{\ne} \int_0^\ne d\mu F(Q,\mu) \tag{9}
\]

**IV. Model for Interparticle Structure Factor**

In this section we shall describe the model used to calculate the center–center structure factor \( S(Q) \) for micelles which has been defined in eq 8. In order to calculate \( S(Q) \) of a system of particles in thermal equilibrium at temperature \( T \), one requires a model for the micellar solution and a statistical mechanical theory for the equilibrium structure of the solution.

For the sake of simplicity and for lack of a better model we shall adopt the so-called “primitive model” of the solution.\(^1\) In this model one regards the solvent (water) as a continuous medium with a dielectric constant \( s \) (about 79 at room temperature). The micelles and the counterions and co-ions are assumed to be describable as charged hard spheres. The equilibrium pair correlation functions \( g_0(r) \) or the total correlation functions \( h_0(r) = g_0(r) - 1 \) can be obtained by solving the multicomponent Ornstein–Zernike (OZ) equation:²

\[
h_0(r) = C_0(r) + \sum_{\ne} \frac{Z^2}{\ne} \int d\mu \mu(r,\mu) C_0(r) \tag{10}
\]

supplemented with a set of closure relations. For a hard sphere system one has exact relationships

\[
h_0(r) = \frac{1}{r} \quad r < \sigma_0
\]

where \( \sigma_0 = (\sigma_i + \sigma_j)/2 \) and \( \sigma_i \) and \( \sigma_j \) are the hard core diameters of the particle species \( i \) and \( j \). We shall define the indices in such a way that \( i = 0, 1, 2, 3, \ldots \) denote respectively the micelle, the dissociated counterion, the added counterion, and the co-ion, etc. We take the diameter of the micelle \( \sigma_0 \) to be the equivalent-sphere diameter defined as \( \sigma_0^1 = \sqrt{\pi(a + \delta)(b + \delta)} \) (see eq 4). This approximation should be good when the axial ratio \( a/b \) is less than 2.

For a charged system it has been known\(^18,19\) that a set of accurate closures are the HNCA closures\(^17\) which relate the direct correlation functions \( C_i(r) \) back to the total correlation functions, namely

\[
C_i(r) = h_0(r) - \ln [1 + h_0(r)] - \frac{Z_i^2 \sum_i \rho_i^2}{r \kappa_0 T} \tag{12}
\]

HNCA is, however, a nonanalytic and its numerical solution procedure is sufficiently complicated as to make it unattractive for analyses of experimental data. Furthermore, for a highly asymmetric electrolyte solution such as a micellar solution, where \( z_i/z_j (i \neq 0) \) can be 20 or more, the numerical procedure for solving HNCA is known to be poorly convergent.

If one were to neglect the short-range interparticle correlations near the contact, then one may put \( h_0(r) \ll 1 \) eq 12 and obtain an approximate set of closure relations

\[
C_i(r) = -\frac{Z_i^2 \sum_i \rho_i^2}{r \kappa_0 T} \tag{13}
\]
Figure 7. Same as Figure 5 but for 0.5 M of added salts. Compared to Figure 5 one can see an increased screening effects as reflected on the left wings of the peaks. However, only slight differences between these peaks are observed for different sizes of co-ions.

which is called the mean spherical approximation (MSA). It is to be noted here that in this article the abbreviation MSA always means solution of a multi component OZ equation (eq 10) with closure relations eq 11 and eq 13.

Blum\textsuperscript{22} showed in 1975 that the structure and thermodynamics of multicomponent Coulomb fluids (MCCF) could be solved analytically in MSA by Baxter's method.\textsuperscript{30} The solution was obtained in terms of physical parameters of the system such as the number density $\rho$, the size $\sigma$, and the charge $Z_i$ and a generalized screening parameter $2\Gamma$ given by solution of an implicit equation:

\begin{equation}
(2\Gamma)^2 = \frac{4\pi\varepsilon^2}{\kappa_B T} \sum_{i} \left( Z_i - \frac{\pi}{2\Delta} \frac{\sigma_i^3 \rho_i}{1 + \Gamma \sigma_i} \right)^2
\end{equation}

where

\begin{equation}
\Delta = 1 - \frac{\pi}{6} \sum_{i} \rho_i \sigma_i^3
\end{equation}

\begin{equation}
P_s = \sum_{i} \frac{\rho_i Z_i}{1 + \sigma_i} \left( 1 + \frac{\pi}{2\Delta} \sum_{i} \frac{\rho_i \sigma_i^3}{1 + \Gamma \sigma_i} \right)
\end{equation}

It is important to note from eq 14 that the well-known Debye-
Hückel limit\textsuperscript{17} is obtained by putting $\phi_0 \to 0$ and $\sigma_i \to 0$ for $i \neq 0$. In this limit

$$\frac{2\Gamma^2}{\varepsilon} = \frac{N_e^2}{k_BT} \sum \psi_i Z_i^2 = \varepsilon$$

(17)

For the purpose of SANS data analyses we need only $S(Q) = S_{OCS}(Q)$. According to Szentore and Blum\textsuperscript{15} one can write

$$S_{OCS}(Q) = 1 + 2\psi_0 \tilde{G}_{OCS}(iQ)$$

(18)

where $\tilde{G}_{OCS}(iQ)$ is the Laplace transform of the pair correlation function $g_{OCS}(r)$, namely

$$\tilde{G}_{OCS}(iQ) = \int_0^\infty dr \, \tilde{r} g_{OCS}(r) \exp(-iQr)$$

(19)

$G_{OCS}(Q)$ is a complicated function of all the physical parameters and $2\Gamma$ and an explicit expression of it was given by Szentore and Blum.\textsuperscript{15}

Because the right-hand side of the OZ equation (eq 10) is dominated by $C_1(r)$ for low volume fraction of ionic species and because the $C_1(r)$ given in eq 13 neglects the short-range correlations between particles the MSA solution for $g_{OCS}(r)$ tends to become unphysical when the volume fraction of micelles $\phi_0 = (\psi_0/6)\rho_0^2$ becomes low. The unphysical solution manifests itself by giving rise to a pair correlation function, at contact $g_{OCS}(0) < 0$, which is not allowed in a hard-core system. This occurs usually for $\phi_0 < 0.2$ and is a serious defect of MSA since the interesting range of micellar solution almost always includes $\phi_0 < 0.2$.

In order to overcome this defect recently suggested the following approximate modification to MSA when $g_{OCS}(0)$ becomes negative. In this case we seek for a rescaled value $\sigma'_0 > \sigma_0$ which satisfies a condition

$$g_{OCS}(\sigma'_0) = 0$$

(20)

This is called Gillan’s condition in the context of the one-component plasma problem.\textsuperscript{31} Thus, in order to implement the rescaling, initially a value $\sigma'_0 = \sigma_0 + \Delta \sigma_0$ is chosen. Recompute $\Gamma'$ according to eq 14, including modification of the volume fraction to a new value $\psi'_0 = \psi_0 + \Delta \psi_0/6$ and use them to calculate a new $S_{OCS}(\Gamma')$. Then evaluate the Fourier transform of $S_{OCS}(\Gamma')$ at $r = \sigma'_0$ to check whether $g_{OCS}(\sigma'_0)$ is positive or negative. If it is positive then reduce $\Delta \sigma_0$ to half and go through the cycle. If it is negative then double $\Delta \sigma_0$ and go through the cycle. This process usually converges rapidly leading to $\sigma'_0$ satisfying eq 20. $S_{OCS}(\Gamma')$ thus obtained is the correct intermicellar structure factor to be used for the neutron cross-section calculation.

The physical basis for rescaling can be seen as follows: if the unphysical behavior of $g_{OCS}$ inside the micellar core is the result of neglecting the short-range correlations in the closure relation (eq 13), it can be remedied approximately by increasing the effective size of the micelle. This rescaling does not alter the long-range part of the micellar interaction because the form of the Coulomb potential depends only on the center–center distance and does not depend on where the charges reside around the micelle. We have implemented the calculation of $S_{OCS}(Q)$ for $i/j = 0$ to 3 in a Fortran package which can be run on a PDP-11 series computer with memory size no less than 256 kbytes.\textsuperscript{31}

Previously we have analyzed similar SANS data using the one-component macroion (OCM) theory\textsuperscript{3,4,12,13}. In this theory one regards the counterions as point charges distributed around the micelles, which can be eliminated from the problem by introducing a Debye screening constant $\varepsilon$ (eq 17). As a result, the intermicellar effective interaction is renormalized into a Yukawa form:

$$V(r) = \frac{(Z\varepsilon)^2}{\varepsilon^2} \exp\left(-\frac{r}{\varepsilon}\right)$$

(21)

This particular form of the macroion interaction is called the DLVO double layer potential in the colloid literature.\textsuperscript{8} That the effective macroion pair potential is of the Yukawa form can be justified from a more accurate liquid theory but the coefficient in front of it is in general a complicated function of the physical parameters of the system.\textsuperscript{14} Thus $Z\varepsilon$, which appears in eq 21, does not have a well-defined meaning of any specific of the micelle unless the DLVO form given in eq 21 is a good approximation in a particular situation. We shall denote the structure factor calculated using an one-component MSA closure having an effective potential given in eq 21 $S_{OCS}(\varepsilon)$.

An independent and approximate way of estimating the effective surface charge of the micelle has been given recently by Evans, Mitchell, and Ninham.\textsuperscript{24} In this theory of “dressed” micelles one computes the double layer free energy of a single micelle situated in the solution, $\delta_{rad} = \delta_a$ is a function of two physical parameters $\varepsilon R$ and $\sigma_a$ where $R$ is the radius of the dressed micelle and $\sigma_a$ is the effective surface area per monomer. Then the fractional dressed surface charge is given by\textsuperscript{12}

$$\alpha_{EMN} = \frac{Z\varepsilon}{\varepsilon_{rad}} = 1 + \frac{\varepsilon}{2\sigma_a} \frac{\varepsilon_{rad}}{k_BT}$$

(22)

where $\delta_a$ is the dressed micellar charge. In practice one can calculate $\delta_a$ from $\varepsilon$. Thus $\alpha_{EMN}$ can be calculated after a SANS data analysis which gives $\varepsilon$.

V. Discussion of the Results

The procedure for calculating a SANS spectrum \( I(Q) \) is as follows: the three basic input parameters are \( N, \sigma, \) and \( N_H \). As we mentioned before it was found that a choice of \( N_H = 10 \) is sufficient to fit all the data we present in this paper. Starting from \( N \) and \( \sigma = |Z_d|/\rho \) we first calculate the number of micelles per unit volume \( N \), from the known monomer concentration of the solution, the cmc and \( \eta \). The volume of the micellar cores is then calculated from eq 2 and \( \alpha \) determined. Values of \( \beta \) and \( \delta \), the scattering length density and the thickness of the outer shell, are then calculated from eq 4 and 5. From these parameters the optical structure factor \( P(Q) \) can be completely determined from eq 3 and 6. To obtain \( S_{Q\omega}(Q) \) we need to know the physical parameters \( \rho_2, \alpha_2, \) and \( Z_2 \). To obtain \( S_{Q\omega}(Q) \) we need to know the physical parameters \( \rho_2, \alpha_2, \) and \( Z_2 \). To obtain \( S_{Q\omega}(Q) \) we need to know the physical parameters \( \rho_2, \alpha_2, \) and \( Z_2 \). To obtain \( S_{Q\omega}(Q) \) we need to know the physical parameters \( \rho_2, \alpha_2, \) and \( Z_2 \). To obtain \( S_{Q\omega}(Q) \) we need to know the physical parameters \( \rho_2, \alpha_2, \) and \( Z_2 \).

These values are taken directly from the work of Triolo et al., where they obtained these values by fitting MSA to osmotic coefficient data of many 1:1 electrolyte solutions. All charges \( Z_2 \), except \( |Z_d| \), are known numbers. Using these physical parameters we can calculate \( S(Q) \) from MSA as described in section IV. Finally, we calculated \( S(Q) \) according to eq. 9 and 10 and substitute it into eq 7 to obtain \( I(Q) \).

Previously, we used a one-shell model for calculation of \( P(Q) \). This is an approximation in which we put \( \rho_2 = \rho \) and \( \alpha_2 = \alpha \), which is the full size of the micelle by taking \( \delta = 5.56 \AA \) and calculating \( \alpha_2 \) to \( |Z_d| = 2(\alpha + \delta) \). Figure 2 we compare results of one-shell and two-shell models for the case [SDS] = 0.117 M and [LiCl] = 0.1 M. For this case the one-shell model results in the fitted parameters \( \eta = 77, \alpha = 230, \) and \( \beta = 4.3 \times 10^{-5} \AA^{-2} \) while those of the two-shell model are \( \eta = 74, \alpha = 234, \) and \( \beta = 5.34 \times 10^{-5} \AA^{-2} \). We see that the \( S(Q) \) so extracted by the two models are parally identical. The only difference in these two models is the values obtained for \( \eta \), which is different by \( \sim 4\% \). We feel that the two-shell model described in section III is more appropriate and thus shall use it in all subsequent analyses.

It is of interest to first compare the results of analyses using MSA and OCM. For [SDS] = 0.117 M and [NaCl] = 0.1 M the analyses give \( \eta = 82 \pm 1 \) in both cases but \( \sigma_{\text{MSA}} = 0.203 \) and \( \sigma_{\text{OCM}} = 0.405 \). The extracted \( S(Q) \) are shown in Figure 3. It is seen that they are identical for all practical purposes. This feature is rather universal for all data analyzed and we are led to the conclusion that MSA and OCM can both be used to extract a reliable structure factor \( S(Q) \).

We have analyzed five sets of data using the two-shell model

Figure 9. The counterion size (\( \sigma_c \)) dependence of the aggregation number, \( N \), and the fractional surface charge, \( \alpha \), of the micelle. Both \( N \) and \( \alpha \) show strong dependences on \( \sigma_c \), and saturate as \( \sigma_c \) becomes greater than 4.0 \( \AA \).

Figure 10. (a, top) The fractional surface charge of micelle for solutions with [LDS] = 0.31 M and [NaCl] = 0.1 M plotted as a function of the co-ion size \( \sigma_c \), for both cases decreases gradually as \( \sigma_c \) increases. (b, bottom) The co-ion size (\( \sigma_c \)) dependence of the aggregation numbers for solutions with [LDS] = 0.31 M, [salt] = 0.1 M (C); [LDS] = 0.62 M, [salt] = 0.1 M (A); [LDS] = 0.31 M, [salt] = 0.3 M (B); and [LDS] = 0.62 M, [salt] = 0.5 M (E). It is obvious that \( \eta \) is insensitive to the co-ion size.

for \( P(Q) \) in conjunction with MSA for \( S(Q) \). These results are presented in Figures 4-8. The parameters extracted from the analyses are summarized in Table II. In the first series we used [SDS] = 0.117 M and successively added 0.1 M [MCl] where M stands for Li, Na, K, and Cs.

Recalling that the micelle is negatively charged the purpose of this series of experiments is to study the effect of the size of the cations on \( \eta \) and \( \alpha \). The results of the fits are displayed in Figure 9 which shows clearly an excellent agreement between theory and experiment. The general trends are as follows: as the size of the hydrated cations increases the aggregation number decreases and the fractional charge decreases. In series 1 through 5 we studied LDS micellar solutions with different amounts of added lithium halides. Figure 5 gives the result for the series with [LDS] = 0.31 M and [salt] = 0.1 M; Figure 6 gives the result for series of [LDS] = 0.62 M and [salt] = 0.1 M; Figure 7 gives the result for the series of [LDS] = 0.31 M and [salt] = 0.1 M; and Figure 8 gives the result for the series of [LDS] = 0.62 M and [salt] = 0.5 M. The general trends are that the aggregation number of the micelle is nearly independent of the hydrated cation size, but the fractional charged decreases slowly with increasing anion size. The results of \( \alpha \) and \( \eta \) versus \( \sigma_c \) are summarized in Figure 10, a and b.

We have analyzed the same sets of data using OCM and have also calculated the "dressed" micellar charge according to EMN theory. All these results are also summarized in Table II. It is worth noting that \( \sigma_{\text{MSA}} \) is always close to \( \sigma_{\text{OCM}} \) but different from \( \sigma_{\text{OCM}} \). It is, therefore, tempting to interpret \( \sigma_{\text{OCM}} \) as the "dressed" fractional micellar charge calculated in the EMN theory.

VI. Conclusions

We have demonstrated that the rescaled mean spherical approximation (RMSA) is a useful theory for analysis of the
structure of ionic micellar solutions by treating them as multi-component Coulomb fluids. From this analysis, three physical parameters of the micelle, namely, the average micellar aggregation number $n$, the fractional dressed charge $\alpha$, and the effective hydration number $N_h$ of the head group, can be extracted. This can be done in the micellar phase for any concentration of the ionic surfactant and for any amount of added 1:1 electrolytes up to 0.5 M. Two quantities extracted from the experiment are of immediate interest: micellar growth as functions of the concentration of the surfactant and added salts; and the center–center structure factor $\phi(Q)$ for each case. Furthermore, the $\phi(Q)$'s are accurately obtained from SANS data for a wide range of $Q$. This structural information can be used to test a more accurate microscopic theory of intermicellar structure in the future. We emphasize that the $\phi(Q)$'s we presented in this paper are very weakly dependent on the MSA that we used to extract them. This is because $n$ is largely dependent only on the position of the interaction peak in a SANS spectrum. The MSA approach we use in this paper has an advantage over the OCM approach used in the past because the counterion and co-ion sizes can be explicitly taken into account in the data analysis. The variation of the fractional dressed micellar charge $\alpha_{\text{MSA}}$ as a function of cation and anion sizes is interesting and is intuitively reasonable. The microscopic meaning of the micellar charge $Z_0$ is, at present, not completely clear and may depend on the nature of the approximation inherent in MSA. It is, however, plausible that $Z_0$ is indeed the dressed micellar charge which has been defined and calculated approximately in EMN theory.

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