

Ion correlations in a micellar solution studied by small-angle neutron and x-ray scattering

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(Received 1 December 1994)

We propose a general and consistent scheme for the analysis of small-angle x-ray and neutron data from quasispherical ionic surfactant micelles in aqueous solution. A two-shell model for the micellar particle structure factor is used, which models the structure in terms of a compact hydrophobic core and a hydrophilic outer shell. The hydrophilic shell contains head groups of the surfactant, water molecules of hydration, and a number of counterions, the number being determined by the counterion condensation mechanism. The partial structure factors for micelle-micelle, micelle-counterion, and counterion-counterion correlations are calculated by a multicomponent mean spherical model (MMSA) of Ronis and Khan. This model can be solved analytically under the conditions of penetrable spheres for point-like counterions. The former condition is essential for treating the highly charged macroion system such as micelles by MMSA. This scheme is applied to a micellar solution composed of an ionic surfactant, cesium dodecyl sulfate. The presence of heavy counterions provides the sensitivity necessary to test the accuracy of the calculated degree of counterion condensation into the outer shell of the micelle.

PACS number(s): 61.20.Gy, 61.10.Lx, 61.12.Ex

I. INTRODUCTION

Aggregation and colligatory properties of ionic micellar solutions, such as aqueous solutions of alkali-metal alkyl sulfates, have been extensively studied by various experimental techniques, including tensiometry, osmometry, and light scattering, both static and dynamic [1–5]. During the last decade, small-angle neutron scattering (SANS) has been proven to be the most powerful technique for determining both the structure of micellar aggregates and the intermicellar correlation derived from electrostatic interactions among micelles and the micelle and its counterions [6–8]. For example, micellar solutions made of alkyl sulfate with various counterions, such as lithium, sodium, and potassium in the presence or absence of mono- or divalent salts, have been extensively studied [9] by SANS. The interpretation of SANS data for a system of nearly spherical micelles is straightforward and has been relatively successful for two reasons. First there is a large contrast between scattering length densities of micelles and solvent when heavy water is used. This means that it is relatively easy to implement the method of contrast variation using different mixtures of heavy water and light water as solvents. It is also possible to selectively deuterate different parts of the alkyl chain of the surfactant while keeping the solvent as heavy water. Second, it turned out that for SANS the counterions play a relatively minor role in the calculation of the scattering intensity, except for maintaining a charge state for the micelles [10]. This latter fact is a consequence of the low contrast of the counterions in aqueous solvent and is a more crucial reason for the ease of the analysis. On the other hand, although the general formula of scattering intensity for the case of small-angle x-ray scattering (SAXS) can be readily written by a simple replacement of the neutron scattering length density distri-

butions by the corresponding electron density distributions, experimental studies of micellar solutions by SAXS are not as abundant as those by SANS in the literature [11]. Aside from a minor experimental complication due to larger absorption by heavy counterions, there is a major theoretical difficulty in data analysis. X-ray scattering intensity distribution from a micellar solution is highly sensitive to the distribution of counterions, as well as to the head groups of surfactant molecules relative to their hydrocarbon tails. The heavier the counterion, the more significant its contribution to different terms of the scattering intensity formula. First, an accurate knowledge of the degree of counterion condensation is needed for calculation of the electron density profile of the hydrophilic layer of the micelle. Second, counterions surrounding the micelles also play a role in the scattering intensity profile in a certain Q range. The scattering contribution from the surrounding counterions comes in through both the micelle-counterion correlation and the counterion-counterion correlation. Calculation of the latter functions is more theoretically challenging than that of the micelle-micelle correlation function from the liquid theory point of view, and, in fact, they are the more interesting quantities to obtain physically. A conventional way of evaluating the micelle-counterion correlation function, or equivalently, its Fourier transform, is by analytical or numerical solutions of the Poisson-Boltzmann equation in a cell model [12,13]. However, with this approach, the counterion-counterion correlation is neglected. Perhaps because of the necessity of this extra complication in data analysis, the use of heavy alkali-metal alkyl-sulfate surfactants has been avoided in previous SAXS studies of ionic micellar systems [11].

In this paper, we give a general formulation of SANS and SAXS intensities for a micellar solution composed of an alkali-metal dodecyl sulfate, which is applicable when

the micelles are quasispherical. The formulation involves calculations of both particle structure factors and interparticle structure factors. The interparticle structure factors are obtained from an analytical solution of a multicomponent mean spherical approximation (MMSA) model with a penetrable macroion sphere. We then use the theory to analyze SANS and SAXS data of a Cs-dodecyl sulfate micellar solution. One of the most important conclusions of this paper is that the degree of the counterion condensation, which is essential for an accurate calculation of the micellar particle structure factor, can be obtained in the process of determining the interparticle structure factor from the SANS data analysis.

II. THEORY FOR THE INTERPARTICLE STRUCTURE FACTORS

In the primitive model (PM), a spherical polyelectrolyte solution is taken as a system composed of charged hard spheres with charge Z_i and diameter σ_i . The solvent is regarded as a continuous dielectric medium with permittivity ϵ . The dominant interactions in the system are the short-range excluded volume and long-range electrostatic interactions. The weaker van der Waals interaction is neglected. Despite its simplicity, the PM has proved to be a reasonable approximation in describing real ionic solutions [14].

The polyelectrolyte solution we consider is composed of macroions with charge Z_M , their counterions with charge Z_c , and salt ions. There are two important parameters in the system: the ratio of the macroion charge to the counterion charge, and the ratio of the macroion size to the counterion size. Usually these two ratios are between 20 and 100 in a typical ionic micellar solution. The large ratios imply significant asymmetry both in spatial dimensions and in magnitude of charges between the macroions and counterions.

Historically, the problem described above was approached by solving coupled integral equations such as the hypernetted chain (HNC) approximation by numerical methods. This involves cumbersome numerical analysis, and the solution is known not to converge for the charge asymmetry ratio above 40 [15]. Furthermore HNC is a thermodynamically inconsistent approximation. In order to achieve the consistency, the procedure of Rogers and Young (RY) has often been used [16]. This latter procedure, however, involves a heavy numerical computation. As a result, it is not suitable for the analysis of experimental small-angle scattering data.

It has been known for some time that an analytical solution for the structure factors can be obtained in certain approximations if one assumes pointlike counterions and salt ions. This is the so called multicomponent mean spherical approximation, which is applicable in principle for any charge asymmetry. The drawback of the MMSA is that it is a linear theory, and the description of charge accumulation near the highly charged surface of macroions is not accurate due to the neglect of nonlinearity. Furthermore, the solution of the MMSA at low macroion densities may exhibit a negative macroion-macroion pair correlation function at contact, which is clearly unphysi-

cal. This difficulty can be overcome by a rescaling of the macroion size together with a condition allowing for nonadditivity of the macroion-counterion diameter. This latter condition allows the counterions to approach the real surfaces of the macroions, even in the cases of rescaling.

The main advantage of the MMSA, however, is its ability to provide an analytical solution for the effective macroion-macroion direct correlation function. Thus it gives an analytical structure factor, which is useful in fitting SANS data of micellar solutions using the effective macroion charge as an empirical parameter. One can therefore extract a realistic macroion-macroion partial structure factor from the experimental SANS data directly. Knowing an accurate macroion-macroion structure factor, one can then use exact relations in the theory to calculate other partial structure factors, such as the macroion-counterion and counterion-counterion structure factors. These partial structure factors, or equivalently the partial pair correlation functions, are essential for evaluating thermodynamic properties such as free energy and osmotic pressure of the solution.

Although the well-known one-component macroion (OCM) theory of Hayter and Penfold [17] and the modification of it, known as the generalized one-component macroion theory [18], have been developed to model the macroion-macroion correlation in solution and used successfully to fit the scattering data, these two theories cannot give partial structure factors or correlation functions between other ionic species in the solution. The MMSA as formulated by Khan and Ronis [19,20] gives not only the effective one-component macroion-macroion correlation function but also the correlation functions between the other species under the condition of penetrable spheres.

A. MMSA theory

The MMSA starts with the system of coupled Ornstein-Zernike (OZ) equations [21],

$$h_{ij}(r) = c_{ij}(r) + \sum_l \rho_l \int d\vec{r}' h_{il}(r') c_{lj}(|r-r'|), \quad (1)$$

and a set of closure relations,

$$g_{ij}(r) = h_{ij}(r) + 1 = 0 \quad \text{for } r < \sigma_{ij}, \quad (2a)$$

$$c_{ij}(r) = -L_B Z_i Z_j / r \quad \text{for } r > \sigma_{ij}, \quad (2b)$$

where σ_{ij} is the diameter for the i, j species and L_B is the Bjerrum length of the solvent, defined as $e^2/\epsilon k_B T$. In the case of additive diameter, $\sigma_{ij} = \sigma_{ij}^A$ with the definition $\sigma_{ij}^A \equiv (\sigma_i + \sigma_j)/2$. In the case of nonadditive diameter, $\sigma_{ij} \neq \sigma_{ij}^A$. The partial structure factor between the i th and the j th species is defined as

$$S_{ij}(Q) = \delta_{ij} + \rho_T (x_i x_j)^{1/2} h_{ij}(Q), \quad (3)$$

where $h_{ij}(Q)$ is the three dimensional Fourier transform of $h_{ij}(r)$, ρ_T the total number density of ions, x_i the fraction of i th species, and δ_{ij} the Kronecker delta.

The rescaled diameter for the one-component theory is determined in the following way. OCM requires that

$g(r)=0$ when $r < \sigma$. But unrescaled MSA theory sometimes results in $g(r) < 0$ until r reaches a value σ_{MM} at which $g(\sigma_{MM})=0$ and beyond which $g(r) > 0$. The effective diameter is therefore σ_{MM} (Gillan's condition). This is often called a rescaled MSA [22].

B. Reduction of a multicomponent system to an effective one-component system

The multicomponent polyelectrolyte system that we consider contains macroions with density ρ_M and charge Z_M ; their original counterions ρ_1, Z_1 ; and added salt ions ρ_i, Z_i ($i=2,3,\dots,1$). By diagonalization of an $l \times l$ matrix $\tilde{c}(Q)$, the multicomponent system can be reduced to a three-component system composed of macroions, counterions, and neutral ions [19]. The densities and charges of the pointlike counterions and neutral particles are given as

$$Z_c = \frac{\sum_{i=1}^l \rho_i Z_i^2}{\rho_1 Z_1}, \quad (4a)$$

$$\rho_c = \frac{\rho_1^2 Z_1^2}{\sum_{i=1}^l \rho_i Z_i^2}, \quad (4b)$$

$$\rho_n = \sum_{i=1}^l \rho_i - \rho_c. \quad (4c)$$

The three-component (M,c,n) system can be further reduced to a two-component (M,c) system under the condition of nonadditivity of diameters. From the OZ equations, one finds that the direct correlation functions are related by

$$\begin{aligned} c_{Mc}^{(2)}(Q) &= c_{Mc}^{(3)}(Q), \\ c_{cc}^{(2)}(Q) &= c_{cc}^{(3)}(Q), \\ c_{MM}^{(2)}(Q) &= c_{MM}^{(3)}(Q) + \rho_n [c_{Mn}^{(3)}(Q)]^2. \end{aligned} \quad (5)$$

The two-component system is finally reduced to an effective one-component system where

$$c_{MM}^{(1)}(Q) = c_{MM}^{(2)}(Q) + \frac{\rho_c [c_{Mc}^{(2)}(Q)]^2}{1 - \rho_c c_{cc}^{(2)}(Q)}. \quad (6)$$

Khan and Ronis showed that the effective one-component system has a Yukawa closure [20]

$$g(r) = 0 \quad \text{for } r < \sigma_{MM}, \quad (7a)$$

$$c_{MM}(r) = \Lambda \frac{e^{-\kappa(r-\sigma_{MM})}}{r} \quad \text{for } r > \sigma_{MM}, \quad (7b)$$

where $\kappa = [4\pi L_B \rho_c Z_c^2]^{1/2}$ is an inverse Debye screening length.

Define $x = r/\sigma_{MM}$, $R_{Mc} = \sigma_{Mc}/\sigma_{MM}$, and $k = \kappa\sigma_{MM}$, the direct correlation function given above can be rewritten as

$$C_{MM}(x) = -\Omega \frac{\exp[-k(x-1)]}{x} \quad \text{for } x > 1, \quad (8)$$

where

$$\Omega = \frac{Z_M^2 e^2}{\epsilon k_B T \sigma_{MM}} \exp(-k) \left[\frac{k}{C\nu + D} \right]^2, \quad (9)$$

$$C = \exp(-k) [\sinh(kR_{Mc}) - kR_{Mc} \cosh(kR_{Mc})], \quad (10)$$

$$D = k \exp(-kR_{Mc})(1 + kR_{Mc}), \quad (11)$$

$$\nu = 24\eta_{MM} \int_1^\infty dx x \exp[-k(x-1)] g_{mm}(x), \quad (12)$$

and η_{MM} is the volume fraction of the one-component system.

The dimensionless potential Ω reduces to the (DLVO) potential under certain conditions. Usually C is negative and its absolute value is much smaller than D . Unless ν is very large, D is dominant over $C\nu$ and the limit of potential

$$\lim_{C\nu \ll D, R_{Mc} \rightarrow \frac{1}{2}} \Omega = \frac{Z_M^2 e^2}{\epsilon k_B T \sigma_{MM}} \left[\frac{1}{1+k/2} \right]^2$$

is exactly the form of the DLVO potential.

C. Analytical solution of the MSA with a Yukawa closure

Waisman [23] showed that a MSA with a Yukawa closure

$$C(x) = -\Omega \frac{\exp[-k(x-1)]}{x} \quad \text{for } x > 1, \quad (13a)$$

$$g(x) = 0 \quad \text{for } x < 1 \quad (13b)$$

has an analytical solution for the direct correlation inside the core of the form

$$\begin{aligned} -C(x) &= a + bx + \frac{1}{2}\eta ax^3 - \nu\Omega \frac{1 - \exp(-kx)}{kx} \\ &\quad - \nu^2\Omega \frac{\cosh(kx) - 1}{2k^2 \exp(k)x} \quad \text{for } x < 1. \end{aligned} \quad (14)$$

By solving a quartic equation and selecting the physical root it is shown that the only unknown parameter in the problem ν is given by [24]

$$\nu = \frac{2k \exp(k) [12\eta(1 + \frac{1}{2}\eta)k + 12\eta(1 + 2\eta)]}{12\eta(1 + \frac{1}{2}\eta)k + 12\eta(1 + 2\eta) + [(1 - \eta)^2 k^3 + 6\eta(1 - \eta)k^2 + 18\eta^2 k - 12\eta(1 + 2\eta)] \exp(k)}. \quad (15)$$

So $S_{MM}(Q)$ can be calculated from the above direct correlation functions using our revised version of the Hayter-Penfold FORTRAN package. This solution of ν from Eq. (15) is, in principle, a good approximation in the high

temperature limit. By the high temperature limit we mean that the dimensionless contact potential Ω is very small. Using this approximate solution we can calculate the pair correlation function $g(r)$ by Fourier transform-

ing the structure factor. We then check the accuracy of the ν value thus calculated by using the definition given in Eq. (12) in terms of the $g(r)$. For our present case, we obtain an agreement to within 10%. This is not surprising, since the MSA itself requires the potential to be small. However, for a dilute and highly charged system, Ω is large and the MSA turns out to be a poor approximation. It gives a very high peak in the structure factor $S(Q)$ and an unreasonable $g(r)$ inside the core. Fortunately, this problem can be solved by the rescaling procedure in conjunction with the nonadditivity condition. This latter procedure allows the macroion-macroion diameter to be enlarged while keeping the macroion-counterion diameter unchanged. The dimensionless contact potential obtained after the rescaling is usually smaller than 0.1, and the high temperature approximation is valid. The structure factor $S(Q)$ thus calculated can be used to fit SANS data easily. Furthermore, other partial structure factors can be evaluated analytically in terms of the $S(Q)$ within this MMSA model, as shown in the following sections.

D. Determination of other correlation functions

Knowing $S_{MM}(Q)$, all other correlation functions can be evaluated in Q space through the following relations. Define $h_{ij}^s = \sqrt{\rho_i \rho_j} h_{ij}$ and $c_{ij}^s = \sqrt{\rho_i \rho_j} c_{ij}$; OZ equations for the three-component system (macroions, counterions, and neutral particles) are

$$\Gamma_M = \frac{kL_B Z_M Z_c [2\gamma \exp(kR_{Mc}) \cosh(kR_{Mc}) - 1]}{2\gamma \exp(kR_{Mc}) [\sinh(kR_{Mc}) - kR_{Mc} \cosh(kR_{Mc})] + 1 + kR_{Mc}}, \quad (19b)$$

$$\gamma = \nu \exp(-k)/k. \quad (19c)$$

So once $S(Q)$ is known from analysis of SANS data, all the other partial structure factors and the corresponding partial correlation functions can be calculated. Since the counterions and salt ions are taken as pointlike particles, the macroion-counterion radius is the radius of the micelle. Although the macroion-macroion diameter is extended by the rescaling, the nonadditivity condition allows $R_{Mc} < \frac{1}{2}$. As a result, the counterions can still come close to the actual micellar surface.

III. SCATTERING INTENSITY DISTRIBUTION FROM AN IONIC MICELLAR SOLUTION

A. Scattering intensity of micellar-counterion system

In this section, we shall derive an intensity formula for the simpler case of a micelle-counterion system. The

$$\begin{aligned} \frac{d\sigma_{\text{coh}}}{d\Omega} &= \frac{1}{V} \left\langle \left| \sum_{l=1}^{N_1} b_1 e^{i\vec{Q}\cdot\vec{r}_l} + \sum_{l=N_1+1}^N b_l e^{i\vec{Q}\cdot\vec{r}_l} \right|^2 \right\rangle \\ &= \frac{1}{V} \left\langle \left| \sum_{l=1}^{N_1} b_1 e^{i\vec{Q}\cdot\vec{r}_l} \right|^2 + \left| \sum_{l=N_1+1}^N b_l e^{i\vec{Q}\cdot\vec{r}_l} \right|^2 + 2 \operatorname{Re} \left[\left| \sum_{l=1}^{N_1} b_1 e^{i\vec{Q}\cdot\vec{r}_l} \right| \left| \sum_{l=N_1+1}^N b_l e^{i\vec{Q}\cdot\vec{r}_l} \right| \right] \right\rangle \end{aligned} \quad (21)$$

species 1 species 2 species 1 and 2

$$\begin{aligned} h_{MM}^s &= c_{MM}^s + c_{MM}^s h_{MM}^s + c_{Mc}^s h_{Mc}^s + c_{Mn}^s h_{Mn}^s, \\ h_{cc}^s &= c_{cc}^s + c_{cc}^s h_{cc}^s + c_{Mc}^s h_{Mc}^s, \\ h_{nn}^s &= c_{Mn}^s h_{Mn}^s, \\ h_{Mc}^s &= c_{Mc}^s + c_{Mc}^s h_{MM}^s + c_{cc}^s h_{Mc}^s, \\ h_{nc}^s &= c_{Mc}^s h_{Mc}^s, \\ h_{Mn}^s &= c_{Mn}^s + c_{Mc}^s h_{nc}^s. \end{aligned} \quad (16)$$

The partial structure factors are evaluated as [25] [note that $S(Q) = S_{MM}(Q)$],

$$S_{Mn}(Q) = c_{Mn}^s(Q) S(Q), \quad (17a)$$

$$S_{nn}(Q) = 1 + [c_{Mn}^s(Q)]^2 S(Q), \quad (17b)$$

$$S_{Mc}(Q) = \frac{Q^2}{k^2 + Q^2} c_{Mc}^s(Q) S(Q), \quad (17c)$$

$$S_{cn}(Q) = \frac{Q^2}{Q^2 + k^2} c_{Mc}^s(Q) c_{Mn}^s(Q) S(Q), \quad (17d)$$

$$S_{cc}(Q) = \frac{Q^2}{k^2 + Q^2} + \left[\frac{Q^2}{k^2 + Q^2} \right]^2 [c_{Mc}^s(Q)]^2 S(Q), \quad (17e)$$

$$c_{Mc}^s(Q) = 4\pi \sqrt{\rho_M \rho_c} [\Gamma_M R_{Mc}^3 j(QR_{Mc}) - L_B Z_M Z_c \cos(QR_{Mc}) / Q^2], \quad (18a)$$

$$c_{Mn}^s(Q) = 4\pi \sqrt{\rho_M \rho_n} \Gamma_n R_{Mc}^3 j(QR_{Mc}), \quad (18b)$$

where

$$\Gamma_n = -1 / (1 - \eta_{Mn}) \quad \text{with} \quad \eta_{Mn} = 4\pi \rho_M R_{Mc}^3 / 3 \quad (19a)$$

and

added salt, if any, is only taken into account as a background effect of contributing to the ionic strength of the solution.

Suppose there are two species in a system of volume V . The numbers of the two species are N_1 and N_2 , respectively. The total particle number is $N = N_1 + N_2$. The coherent scattering cross section per unit solid angle per unit volume is defined as

$$\frac{d\sigma_{\text{coh}}}{d\Omega} = \frac{1}{V} \left\langle \left| \sum_{l=1}^N b_l e^{i\vec{Q}\cdot\vec{r}_l} \right|^2 \right\rangle. \quad (20)$$

Expand according to the two species,

In the second line of Eq. (21), the first term in large angular brackets is for species 1 only and the second term is for species 2 only, while the last term is for both species 1 and 2.

Define the structure factor $S_{ij}(Q)$ between the i th and j th particles as the following:

$$S_{11}(Q) = \frac{1}{N_1} \left\langle \sum_{i,l'=1}^{N_1} e^{i\vec{Q}\cdot(\vec{R}_i - \vec{R}_{l'})} \right\rangle, \quad (22a)$$

$$S_{22}(Q) = \frac{1}{N_2} \left\langle \sum_{i,l'=1}^{N_2} e^{i\vec{Q}\cdot(\vec{R}_i - \vec{R}_{l'})} \right\rangle, \quad (22b)$$

$$S_{12}(Q) = \frac{1}{\sqrt{N_1 N_2}} \left\langle \sum_{i=1}^{N_1} \sum_{l'=1}^{N_2} e^{i\vec{Q}\cdot(\vec{R}_i - \vec{R}_{l'})} \right\rangle. \quad (22c)$$

So the total cross section is given by the following equation:

$$\begin{aligned} \frac{d\sigma_{\text{coh}}}{d\Omega} = & \frac{N_1}{V} |F_1(Q)|^2 S_{11}(Q) + \frac{N_2}{V} |F_2(Q)|^2 S_{22}(Q) \\ & + \frac{\sqrt{N_1 N_2}}{V} 2 \operatorname{Re}[F_1(Q)F_2(Q)] S_{12}(Q), \end{aligned} \quad (23)$$

where the $|F(Q)|^2$ is the particle form factor and will be discussed in detail in the next section.

Now consider the situation of an anionic surfactant micelle, which is composed of an aggregation of \bar{N} monomers. Suppose the total surfactant concentration is C , excluding the remaining monomer, with a critical micellization concentration (cmc). The first species in this system is the micelle, and the second one is the counterion whose charge state is $+1$. Suppose the micelle has an effective charge of $-Z$. The concentration of micelles in the solution is thus given by $N_1 = C/\bar{N}$ and the concentration of the counterions is $N_2 = N_1 Z$. The complete scattering cross section for this two-component system is

$$\begin{aligned} \frac{d\sigma_{\text{coh}}}{d\Omega} = & \frac{C}{N} \{ |F_1(Q)|^2 S_{11}(Q) + Z |F_2(Q)|^2 S_{22}(Q) \\ & + 2\sqrt{Z} \operatorname{Re}[F_1(Q)F_2(Q)] S_{12}(Q) \}. \end{aligned} \quad (24)$$

$$I(Q) = \frac{d\sigma_{\text{coh}}}{d\Omega} = \frac{C}{N} \left\{ \bar{N}^2 \left[\sum_{\text{monomer}} b_i - V_m \rho_s \right]^2 \bar{P}(Q) S_{\text{MM}}(Q) \right.$$

$$\left. + 2\bar{N}\sqrt{Z} \left[\sum_{\text{monomer}} b_i - V_m \rho_s \right] \left[\sum_{\text{counterion}} b_i - V_c \rho_s \right] \bar{f}(Q) S_{\text{Mc}}(Q) + Z \left[\sum_{\text{counterion}} b_i - V_c \rho_s \right]^2 S_{\text{cc}}(Q) \right\}. \quad (26)$$

The orientational averaged normalized form factors are

$$\bar{f}(Q) = \int_0^1 d\mu \left[\xi \frac{3j_1(U_1)}{U_1} + (1-\xi) \frac{3j_1(U_2)}{U_2} \right] \quad (27a)$$

and

Note that the size of the counterion is much smaller than that of the micelle. In the range of the scattering vector Q available for small-angle neutron and x-ray scatterings, it is reasonable to assume that the counterion is a point charge with a particle form factor independent of Q .

B. The intensity formula and the particle form factors

The general form of the particle form factor is given by the following equation:

$$F(Q) = \left[\sum b_i - V_p \rho_s \right] \bar{f}(Q), \quad (25a)$$

$$|F(Q)|^2 = \left[\sum b_i - V_p \rho_s \right]^2 \bar{P}(Q), \quad (25b)$$

where V_p is the volume of the particle, i.e., the volume of excluded solvent, $\sum b_i$ the total scattering length of the particle, and ρ_s the scattering length density of the solvent. $\bar{f}(Q)$ and $\bar{P}(Q)$ are the normalized particle form factors.

The assumption of a point counterion simplifies the counterion normalized form factor as unity. However, to evaluate the form factor of the micelle, a structural model has to be developed. A micelle is an aggregation of \bar{N} monomers with a certain fraction of counterions surrounding it. Here a two-shell model is adopted, being well justified by theories and previous neutron scattering experiments. In the two-shell model, the micelle has a hydrophobic core composed of the hydrocarbon tails, a hydrophilic outer layer composed of the head groups, some fraction of counterions, and hydrated solvent molecules. The shape of the micelle is pseudospherical or ellipsoidal. The short axis of the inner ellipsoid b is equal to the extended dodecyl chain length, and the long axis a is determined by the conservation relationship of the total core volume. The outer layer has a thickness of t .

Based on the two-shell model, the total scattering intensity can be written as

$$\bar{P}(Q) = \int_0^1 d\mu \left[\xi \frac{3j_1(U_1)}{U_1} + (1-\xi) \frac{3j_1(U_2)}{U_2} \right]^2, \quad (27b)$$

where

$$U_1 = Q[\mu^2 a^2 + (1-\mu^2)b^2]^{1/2}, \quad (28a)$$

$$U_2 = Q[\mu^2(a+t)^2 + (1-\mu^2)(b+t)^2]^{1/2}, \quad (28b)$$

and the dimensionless partition number ζ is proportional to the difference of the scattering length densities of the core and the layer,

$$\zeta = \frac{V_i(\rho_{\text{core}} - \rho_{\text{layer}})}{(\sum b_i - V_m \rho_s)}, \quad (29)$$

where V_i is the volume of the dodecyl chain.

The MMSA theory is used to evaluate the structure factors $S_{ij}(Q)$. An effective charge is essential to determine the Debye screening length, the electrostatic potential in the one-component MSA theory, and the density of the free counterions. The nonadditivity conditions are satisfied in the following way. Suppose the physical diameter of the micelle is σ , so the radii of the micelle, namely, σ_{Mc} , is half of σ . The nonadditive micelle-micelle diameter σ_{MM} required by the MMSA theory is a product of σ and a rescaling factor (no less than 1), which is usually adopted in rescaled MSA. The micelle-counterion diameter is characterized as σ_{Mc}/σ_{MM} , which is smaller than $\frac{1}{2}$.

The scattering intensity formula of the micellar system is generally applicable to both neutron scattering and x-ray scattering. However, the relative weights of the three terms given in Eq. (26) are quite different in the two cases. In neutron scattering, when the solvent is purely deuterated water, the scattering intensity is dominated by the scattering of micelle due to the simple estimation of $(\sum_{\text{counterion}} b_i - V_c \rho_s)/(\sum_{\text{monomer}} b_i - V_m \rho_s) \cong V_c/V_m < 0.05$. This contrast explains why the previous analysis of the SANS data of micellar solutions is successful by evaluation of micelle-micelle interaction alone. However, it may not be true in the case of x-ray scattering of the same system, because scattering from counterions may not be negligible in some Q range. The heavier the counterion is, the more it scatters. With a selection of the counterion, the term $(\sum_{\text{counterion}} b_i - V_c \rho_s)$ can be quantitatively comparable with the term $(\sum_{\text{monomer}} b_i - V_m \rho_s)$. Furthermore, since the electron density profile is rather different from the neutron scattering length density profile, the parameters used to calculate the form factors are highly sensitive to the ionization factor α . Both $(\sum_{\text{monomer}} b_i - V_m \rho_s)$ and ζ are strongly dependent on α . The former determines the absolute intensity scale, and the latter controls the shape of the scattering pattern at large Q ,

$$\sum_{\text{monomer}} b_i = b_{\text{tail}} + b_{\text{head}} + (1 - \alpha)b_{\text{ion}} \quad (30a)$$

and

$$V_m = V_{\text{tail}} + V_{\text{head}} + (1 - \alpha)V_c. \quad (30b)$$

As can be seen from the above discussion, an absolute intensity analysis of both SAXS and SANS data will place significantly strict constraints on the fitting parameters.

IV. SANS AND SAXS EXPERIMENTS

The micellar solution is composed of cesium dodecyl sulfate $[C_{12}SO_4(CH_2)_{11}CH_3]$ in D_2O . Cesium (Cs^+) is chosen as the counterion because its atomic number is

large ($Z = 55$). The surfactant with a purity of 99% was synthesized in our own laboratory. D_2O (99.98%) pure was purchased from Cambridge Isotope Laboratory. A 3% solution was used for both neutron and x-ray scattering measurements taken at 40°C. SANS experiments were performed at the biology low angle diffractometer in the high flux beam reactor of Brookhaven National Laboratory. The average wavelength used was $\lambda = 5 \text{ \AA}$ with $\Delta\lambda/\lambda = 9\%$. The sample-to-detector distance was 1.3 m. The measurement covered a Q range from 0.01 to 0.34 \AA^{-1} , where $Q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the wave-vector transfer in the scattering, and θ is the scattering angle. The sample was contained in a flat quartz cell with a path length of 1 mm. A SAXS measurement was made at the 20-m SAXS instrument in the Solid State Division of Oak Ridge National Laboratory. The rotating anode x-ray source used a copper target with a characteristic wavelength of 1.54 \AA . The source-to-sample distance and sample-to-detector distance were 3.126 and 1.70 m, respectively, covering a Q range from 0.01 to 0.35 \AA^{-1} . The sample was contained in a copper holder with two Kapton windows having a thickness of 50 μm . The path length of the sample was 0.66 mm with a transmission of 23.5%. To account for the scattering contribution from micellar solution, the SAXS of a solution with a concentration at cmc was also measured and subtracted from the 3% data. In addition, SAXS measurements of a micellar solution having a similar surfactant with a lighter counterion, namely, sodium dodecyl sulfate (SDS), were also made for comparison.

V. DATA ANALYSIS AND DISCUSSION

The total scattering intensity is the sum of the coherent scattering, as described by Eq. (26), and a constant incoherent background. More specifically, the isotropic incoherent scattering in SANS comes mainly from the incoherent cross sections of hydrogen and deuterium atoms in the sample. The incoherent scattering for SAXS, on the other hand, comes from the Compton scattering of x rays by all the electrons in the sample. Coherent scattering lengths of the relevant molecules for neutrons and x rays are listed in Table I. Material constants for the surfactant are listed in Table II.

A FORTRAN code based on a gradient searching nonlinear least squares fitting method [26] was written and used to fit both SANS and SAXS intensities in absolute scales. The procedure starts by fitting SANS data to extract the first trial set of the three independent parameters, namely, the effective charge Z^* , the mean aggregation number \bar{N} , and the thickness of hydrophilic layer t .

TABLE I. Geometrical and thermal constants of Cs dodecyl sulfate molecules.

Carbon tail volume	360 \AA^3
Counterion volume	25 \AA^3
Head group volume	75 \AA^3
Short axis length	16.7 \AA
Cmc at 40°C	6.9 mM
D_2O molecule volume	30.27 \AA^3

TABLE II. Scattering lengths of the surfactant and solvent molecules for neutrons and x rays. The unit of neutron scattering lengths is in 10^{-4} Å. The unit of x-ray scattering lengths is in r_0 , the classical radius of electron, $r_0 = 2.818 \times 10^{-13}$ cm.

b	X-ray (units of r_0)	Neutron (10^{-4} Å)
Hydrocarbon tail $C_{12}H_{25}$	97	-1.3740
Head group SO_4^-	49	2.6065
Counterion Cs^+	54	0.542
Solvent D_2O	10	1.9153

All the other parameters, such as the volume fraction, the fractional ionization factor, the hydration number per head group, the axial ratio of the inner shell ellipsoid, and the average diameter of the micelle, as well as the scattering length densities of the hydrophobic core and the hydrophilic layer, are deduced under the constraints of the internal relationships among the material parameters and the three independent fitting parameters. Since SANS intensity is directly proportional to \bar{N} and \bar{N} is also related to the volume of the micelle, this parameter is particularly well determined by SANS data fitting, while the other two parameters are only approximately known. This set of parameters is then fed into SAXS data fitting procedure using Eq. (26) and further refined. SAXS intensity at large Q is determined mostly by the particle structure factor $P(Q)$ of the micelle. The dominant contribution to $P(Q)$ comes from the number of counterions in the hydrophilic layer. Thus SAXS data give a severe constraint on the value of Z^* . The parameter t , which turns out to be 5.65 Å, is important in giving the right amount of hydration and volume of the micelle, and is determined jointly by SANS and SAXS data. This procedure is repeated a couple of times to obtain the final set of fitting parameters, which is given in Table III. The fitted intensities and the experimental data of SANS and SAXS in absolute scales are shown in Figs. 1 and 2, respectively. χ^2 of the SANS data fitting is about 3, and the fit is essentially perfect in the entire Q range. SAXS intensity distribution is reproduced quite well for Q larger than 0.05 Å⁻¹, but there is a visible discrepancy in the lower Q region. The relative intensities of the three terms described in Eq. (26) for the SAXS intensity profile is given in Fig. 3.

It should be emphasized that the three parameters used

TABLE III. Key parameters extracted from fitting SANS and SAXS data. The aggregation number, the hydrophilic layer thickness, and the fractional ionization factor are fitted parameters. The other parameters are deduced from the internal relationships of the materials constants.

Aggregation number \bar{N}	100
Effective charge Z^*	25
Hydrophilic layer thickness t (Å)	5.65
Ionization factor α	24.8%
Value fraction η	3.07%
Average diameter (Å)	52.6
Hydration per head group	9.8

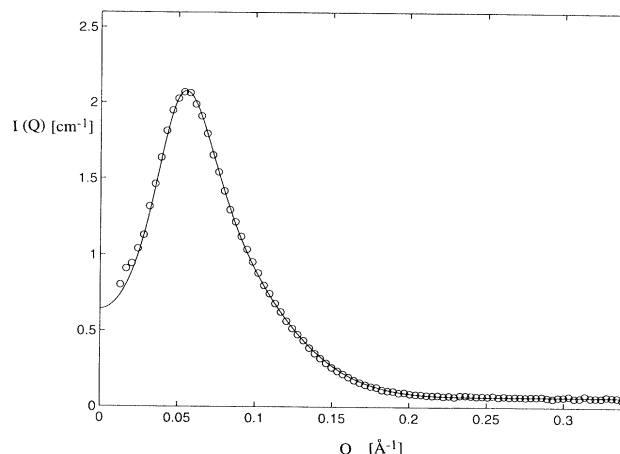


FIG. 1. SANS intensity distribution of 3% CsDs in D_2O at 40°C. The open circles are the experimental data. The solid line is the fitted curve. The fit takes into account the scattering contribution from micelles. The intermicellar structure factor is calculated using the MMSA theory, and the particle structure factor is calculated based on a two-shell model.

to fit SANS and SAXS data are kept the same. The effective charge obtained by fitting SANS data, in the first place, is essentially used to evaluate the particle structure factor $P(Q)$ for the SAXS intensity. We use the term charge condensation to describe the incorporation of counterions into the hydrophilic layer of the micelle. Thus the effective charge of the micelle Z^* is the difference between the mean aggregation number \bar{N} and the condensed charges. The fractional ionization α ,

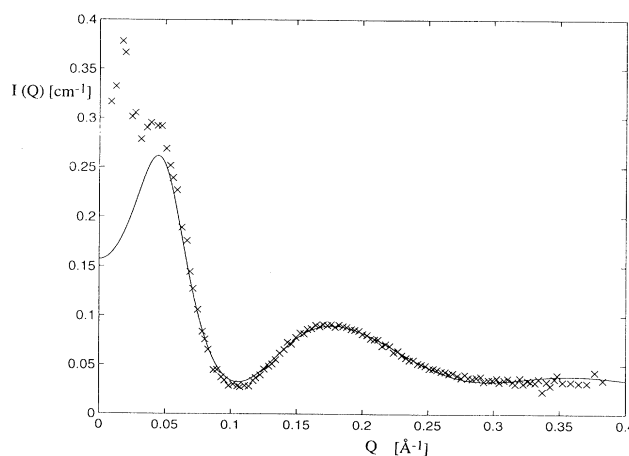


FIG. 2. SAXS intensity profile of 3% CsDs in D_2O at 40°C. The crosses are the experimental data. The solid line is the theoretical calculation based on Eq. (26). The micelle-micelle structure factor is first obtained from SANS analysis, and the micelle-counterion and counterion-counterion structure factor are evaluated from Eq. (17). The counterions are taken as point-like particles. The micellar particle structure factor is calculated by a replacement of neutron scattering length densities for the case of the neutron with electron densities for the case of x ray.

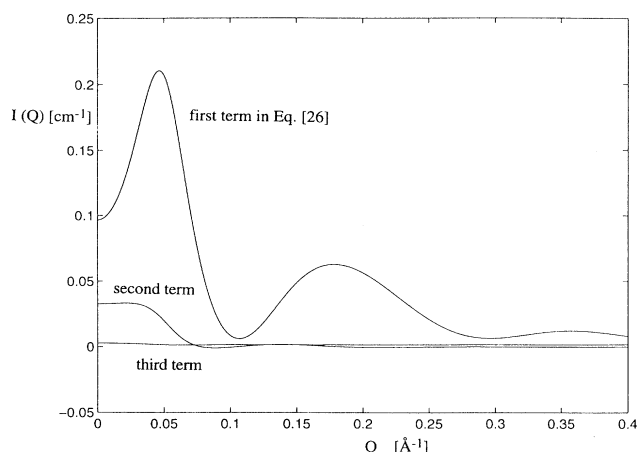


FIG. 3. Relative weights of the three terms, namely, the micelle-micelle term, the micelle-counterion term, and the counterion-counterion term, as described in Eq. (26) of the calculated SAXS profile. The summation of the three components is the theoretical calculation of SAXS intensity. The scattering profile at large Q is dominated by the micelle-micelle term.

which is the ratio of Z^* to \bar{N} , turns out to be 24.8% which is higher than that obtained by the OCM analysis of SANS data alone [27]. The effective charge of the macroion obtained by different theories could vary widely. It can also depend sensitively on the type of counterion in the case of the micelle aggregate. For example, in HNC or RY theory the full charge (equivalent to the aggregation number) is often used to calculate the $S_{MM}(Q)$ numerically [13,16,19]. Our result in this paper shows that this is in principle incorrect because 75% of the counterion has to reside in the hydrophilic shell to account for the x-ray intensity distribution in the high Q region. In this paper, we essentially use SAXS intensity at the large Q region to determine the effective charge. This way it is more likely to obtain the real number of counterions inside the micelle because of the sensitivity of the particle structure factor to the presence of heavy counterions in the hydrophilic layer. The partition number ζ of the two shells defined in Eq. (29) and used in Eq. (27) is 0.8 for neutron scattering, but -2 for x ray scattering. Thus the particle structure factors for the micelle in SANS and SAXS cases are quite different. The normalized particle structure factors for neutron and x-ray scatterings are illustrated in Fig. 4. The electron densities for the hydrophobic core, the hydrophilic layer, and the solvent are 0.269, 0.460, and 0.327 $e/\text{\AA}^3$ respectively, according to the best fit parameters.

The partial structure factors $S_{MM}(Q)$, $S_{Mc}(Q)$, and $S_{cc}(Q)$ are shown in Fig. 5. The micelle-micelle structure factor is well determined by fitting SANS data, and the other two structure factors can be calculated from the MMSA theory. The partial structure factors $S_{Mc}(Q)$ and $S_{cc}(Q)$ are evaluated accurately from Eq. (17c) and Eq. (17e), respectively. The Fourier transform of the three structure factors can be easily made to give the corresponding pair correlation functions. The pair correlation functions $g_{MM}(r)$ and $g_{Mc}(r)$ are given in Figs. 6 and 7,

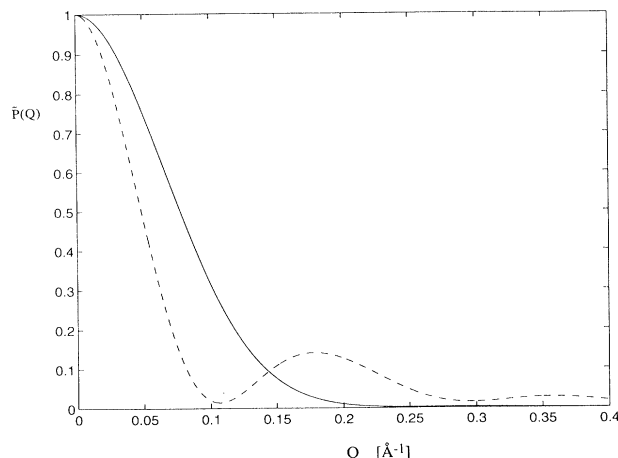


FIG. 4. Normalized particle structure factors of the micelle for the cases of neutrons and x rays. The solid line is the form factor, evaluated based on the neutron scattering length density profile of the micelle. The dashed line is the form factor based on the electron density profile of the micelle. The shape of the normalized particle structure factor is mainly determined by the dimensionless partition factor in Eq. (29). This number is 0.8 for the case of neutrons, but -2 for the case of x rays.

respectively. Figure 6 shows that $g_{MM}(r)$ is essentially zero until 75 \AA , while the actual micellar diameter is 52.6 \AA according to Table III. It is clear that the former is the rescaled diameter. $g_{Mc}(r)$ in Fig. 7 is essentially the counterion distribution around the micellar surface. It shows that most of the excess counterions accumulate within 25 \AA of the surface. This function can also be calculated by solving the Poisson-Boltzmann equation in the cell model numerically [13].

Finally a comparison of SAXS spectra of sodium dode-

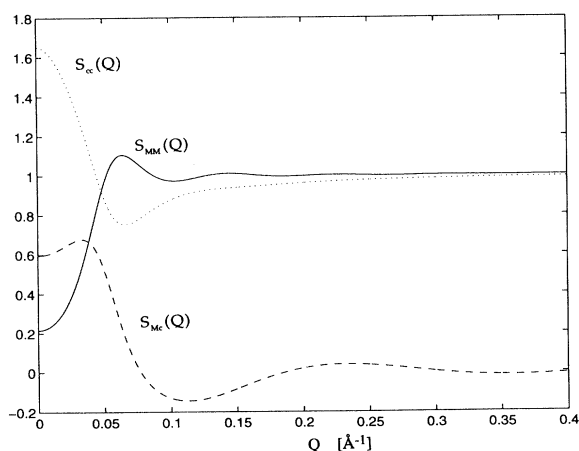


FIG. 5. Partial structure factors of the micellar system. The solid line is the micelle-micelle structure factor $S_{MM}(Q)$, the dashed line is the micelle-counterion structure factor $S_{Mc}(Q)$, and the dotted line is the counterion-counterion structure factor $S_{cc}(Q)$. The micelle-micelle structure factor is obtained by fitting SANS data, whereas the other two structure factors are obtained by using the MMSA theory.

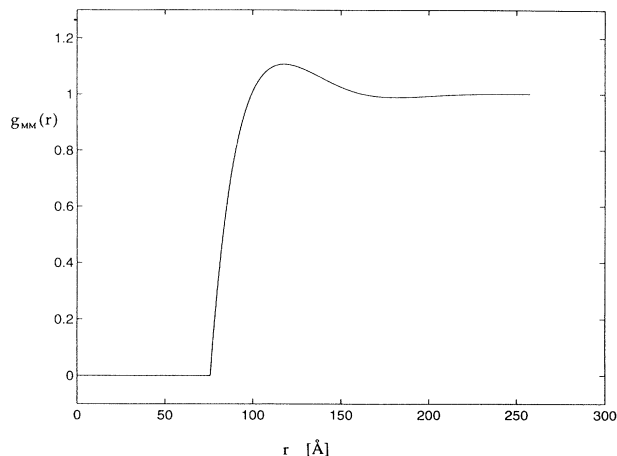


FIG. 6. Micelle-micelle correlation function $g_{MM}(r)$, obtained by taking the Fourier transform of its corresponding structure factor $S_{MM}(Q)$. The nearest intermicellar distance is given by the product of the average diameter of the micelle and a rescaling factor.

cyl sulfate and cesium dodecyl sulfate is shown in Fig. 8. The only difference between the two surfactants is the type of counterions they have. Their SANS spectra look very similar, meaning that the aggregation numbers or the sizes are similar. The lighter sodium ions scatter fewer x rays, so the intensity is mainly coming from the first term in Eq. (26). SAXS profiles for the systems with the same counterions but at different concentrations usually have the same shape at large Q , where the particle structure factor dominates. However, SAXS profiles for the systems with different counterions have shifted peaks relative to each other, meaning that the electron density profiles in and around the micelles are quite different. Since the hydrocarbon core is the same for both cases, the difference comes essentially from the counterion distribution around the surface and the counterion conden-

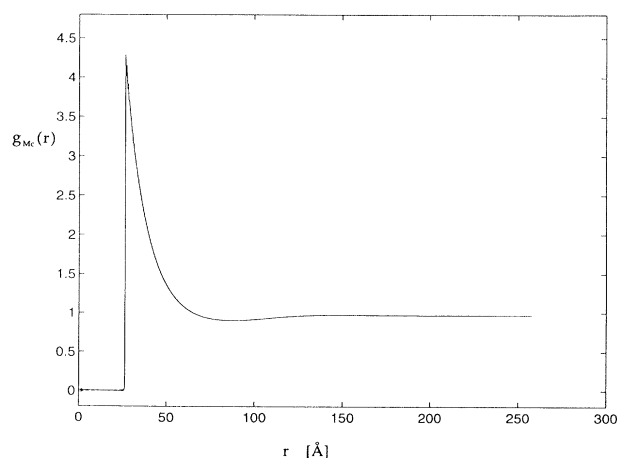


FIG. 7. Micelle-counterion correlation function $g_{Mc}(r)$, obtained by taking the Fourier transform of its corresponding structure factor $S_{Mc}(Q)$. The correlation function describes the counterion distribution around the micelle.

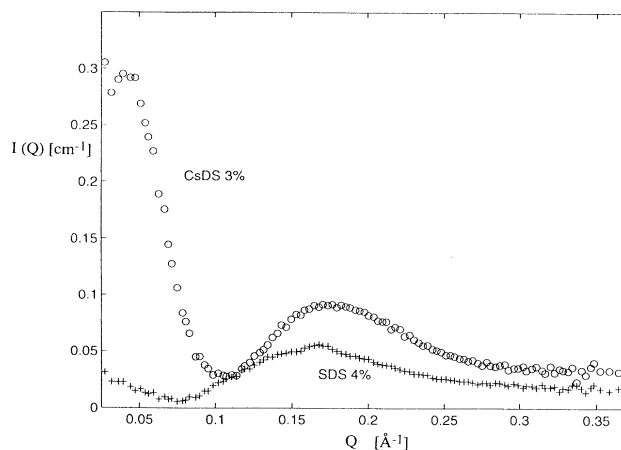


FIG. 8. SAXS intensity distributions of sodium dodecyl sulfate (SDS) and cesium dodecyl sulfate (CsDs). The only difference between the two surfactants is the type of counterions. A 3 wt % CsDs and a 4 wt % SDS have similar molar concentrations. The similarity of their SANS distributions indicates similar aggregational behavior of the two surfactants. However, their SAXS distributions show an obvious shift of peak position. This is due to the different electron density profiles of the hydrophilic outer layers of the micelles.

sation inside the hydrophilic outer layer of the micelles. We do not analyze the SAXS distribution of the SDS case because a similar case has been fully treated by Zemb and Charpin, and Itri and Amaral [11]. It is to be noted that in the two above references the counterion condensation was not calculated theoretically. They simply used the electron density of the hydrophilic layer as a fitting parameter.

VI. CONCLUSION

We present in this paper a theoretical framework for a consistent analysis of a set of SANS and SAXS intensities of an ionic micellar solution, including counterions. The analysis deals with both intensities on an absolute scale. As an example, a pair of SANS and SAXS intensities of a 3% cesium dodecyl sulfate in D_2O at $40^\circ C$ has been measured and analyzed with the same set of parameters. There are three essential parameters for the system: the effective charge, the thickness of the hydrophilic layer, and the mean aggregation number of the quasispherical micelle. The separate contributions of micelle-micelle, micelle-counterion, and counterion-counterion correlations are calculated from a MMSA theory. The determination of the set of three parameters is not unique based on SANS data alone, but it can be determined with a much narrower margin by a further constraint of SAXS data. SANS data are analyzed first to extract an accurate micelle-micelle structure factor, using the effective charge as a fitting parameter. The micelle-counterion and counterion-counterion structure factors can then be obtained from general relations within the MMSA model, once the micelle-micelle structure factor is known. The final set of the three structural parameters of the micelle is obtained from a joint refinement of SANS and SAXS

intensities. Thus the combined analysis of SANS and SAXS data from the same sample allows us to derive both the micelle-counterion and counterion-counterion structure factors, which are essential ingredients in a satisfactory ionic solution theory for thermodynamic properties of the solutions. The micelle-micelle pair correlation function and the counterion distribution in the vicinity of the micellar surface can then be evaluated by taking Fourier transforms of the corresponding structure factors. The particle structure factors for neutrons and for x rays are modeled consistently in a two-shell model. We determine the degree of counterion condensation in the process of extracting the micelle-micelle structure factor from experimental data and use it to calculate the particle structure factor. The general intensity formulas fit both SANS and SAXS data well at most of the Q range. However, there is a discrepancy between the theory and measured data for a very small Q region in the SAXS intensity. This discrepancy may be due to an inaccurate counterion-counterion structure factor calculated from the MMSA model and its weighting factor in the intensity formula. Application of MMSA to analyses of more

extensive experimental data is needed for further assessment of the behavior of counterion-counterion structure factor in the small Q region. If in fact the counterion-counterion structure factor is the source of discrepancy between the theory and SAXS intensity, then a careful SAXS study of ionic micellar solutions with heavy counterions is a potential tool for further elucidation of the poorly understood counterion-counterion correlation problem.

ACKNOWLEDGMENTS

The research of Y. C. Liu and S. H. Chen was supported by U.S. DOE Grant No. DEFG02-90-ER454529. Y.C.L is grateful for partial financial support from the Texaco Research Center, Beacon, New York. The authors would like to thank the Biology Department of Brookhaven National Laboratory for SANS spectrometer time. We are indebted to Dr. D. Schneider for technical assistance. Similar acknowledgment goes to the Solid State Division of Oak Ridge National Laboratory for SAXS beam time and Dr. J. S. Lin for technical assistance in using the 20 m SAXS instrument.

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- [1] H. F. Huisman, Proc. K. Ned. Wet., Acad. Ser. B **67**, 367 (1964).
- [2] N. A. Maser, G. B. Benedek, and M. C. Carey, J. Phys. Chem. **80**, 1076 (1976); C. Y. Yong *et al.*, *ibid.* **82**, 1375 (1978); P. J. Missel *et al.*, *ibid.* **84**, 1044 (1980); P. J. Missel *et al.*, *ibid.* **87**, 1264 (1983).
- [3] C. Tanford, *Hydrophobic Effects* (Wiley-Interscience, New York, 1973).
- [4] J. N. Israelachvili, D. J. Mitchell, and B. W. Ninham, J. Chem. Soc. Faraday Trans. 2 **72**, 1525 (1976).
- [5] B. Lindman and H. Wennerström, Phys. Rep. **52**, 1 (1979).
- [6] J. B. Hayter and J. Penfold, J. Chem. Soc. Faraday Trans. 1 **77**, 1851 (1981); J. B. Hayter and T. Zemb, Chem. Phys. Lett. **93**, 91 (1982); J. B. Hayter and J. Penfold, Colloid Polymer Sci. **261**, 1022 (1983).
- [7] D. Bendedouch, S. H. Chen, and W. C. Koehler, J. Phys. Chem. **87**, 153 (1983); D. Bendedouch, S. H. Chen, and W. C. Koehler, *ibid.* **87**, 2621 (1983); S. H. Chen, Ann. Rev. Phys. Chem., **37**, 351 (1986); Physica **137B**, 183 (1986).
- [8] E. Y. Sheu and S. H. Chen, J. Phys. Chem. **92**, 4466 (1988); B. Cabane, R. Duplessix, and T. Zemb, J. Phys. (Paris) **46**, 2161 (1985).
- [9] Y. S. Chao, E. Y. Sheu, and S. H. Chen, J. Phys. Chem. **89**, 4862 (1985); **89**, 4395 (1985); E. Y. Sheu, C. F. Wu, and S. H. Chen, *ibid.* **90**, 4179 (1986).
- [10] J. B. Hayter, in *Physics of Amphiphiles*, edited by V. Degiorgio and M. Corti (North-Holland, Amsterdam, 1985), p. 59.
- [11] T. Zemb and P. Charpin, J. Phys. (Paris) **46**, 249 (1985); R. Itri and L. Amaral, Phys. Rev. E **47**, 2551 (1993).
- [12] S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, and P. Pincus, J. Chem. Phys. **80**, 5776 (1984).
- [13] D. Bratko, D. Wang, and S. H. Chen, Chem. Phys. Lett. **163**, 239 (1990).
- [14] G. Stell, *Modern Theoretical Chemistry Vol 5, Part A: Statistical Mechanics*, edited by B. J. Berne (Plenum, New York, 1970), p. 47.
- [15] L. Belloni, J. Chem. Phys. **99**, 43 (1985).
- [16] F. J. Rogers and D. A. Young, Phys. Rev. A **30**, 999 (1984); R. Klein, in *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution*, Vol. 369 of *NATO Advanced Studies Institute Series C: XXX* edited by S. H. Chen, J. S. Huang, and P. Tartaglia (Kluwer Academic, Dordrecht, 1992).
- [17] J. B. Hayter and J. Penfold, Mol. Phys. **42**, 109 (1981).
- [18] E. Y. Sheu, Ph.d. thesis, MIT, 1987; S. H. Chen, E. Y. Sheu, J. Kalus, and H. Hoffmann, J. Appl. Cryst. **21**, 751 (1988); in *Micellar Solutions and Microemulsions—Structure, Dynamics and Statistical Thermodynamics* (Springer-Verlag, New York, 1990), Chap 1.
- [19] S. Khan, T. L. Morton, and D. Ronis, Phys. Rev. A **35**, 4295 (1987).
- [20] S. Khan and D. Ronis, Mol. Phys. **60**, 637 (1987).
- [21] L. Blum, Mol. Phys. **30**, 1529 (1975); G. Senatore and L. Blum, J. Phys. Chem. **89**, 2676 (1985).
- [22] M. Gillan, J. Phys. C **7**, L1 (1974); J. P. Hansen and J. B. Hayter, Mol. Phys. **46**, 651 (1982).
- [23] E. Waisman, Mol. Phys. **25**, 45 (1973).
- [24] J. S. Hoye and G. Stell, Mol. Phys. **32**, 195 (1976); J. S. Hoye and L. Blum, J. Stat. Phys. **16**, 399 (1977).
- [25] See also G. Senatore, in *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution* (Ref. [16]), p. 175.
- [26] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969, p. 237).
- [27] Y. C. Liu, P. Baglioni, J. Teixeira, and S. H. Chen, J. Phys. Chem. **98**, 10208 (1994).