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Interpretation of the intermicellar structure factors in the hypernetted-chain Percus-Yevick approximation

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Intermicellar structure factors extracted from small-angle neutron scattering are analyzed in terms of the primitive model of ionic solutions. A well-defined closure to the Ornstein-Zernike equation is shown to be capable of handling colloidal solutions with high charge and size asymmetry. The micelle-micelle structure factor predicted by a combined hypernetted-chain Percus-Yevick approximation compares favorably with the experimental results for lithium and sodium dodecyl sulfate (LiDS and NaDS) solutions with or without added electrolytes. Compared to the mean spherical approximation the hypernetted-chain Percus-Yevick approximation treats the correlations among ions more accurately and, therefore, the full micellar charge and actual size is used in the analyses even at low volume fraction (concentration) of micelles.

Micelles are aggregates of amphiphilic molecules that are spontaneously formed when the surfactant concentration in aqueous solutions reaches certain threshold value called the critical micellar concentration (CMC).[1] For a typical ionic amphiphilic molecule such as sodium dodecylsulfate (SDS), which has the chemical formula $Na^+OSO_3{}^-\text{-}(CH_2)_{11}CH_3$, the CMC is about 0.008 mol dm^{-3}, or 0.22 wt.%. The formation of micellar aggregates is a cooperative phenomenon driven mainly by a strong hydrophobic interaction between hydrocarbon chains of amphiphilic molecules in water. As a result the minimum micellar aggregate consists of a spherical hydrophobic core with the diameter equal to twice the length of the stretched hydrocarbon tail and a hydrophilic outer layer made up of the ionic head groups of the molecules in contact with water. The micelle carries a net charge Z_M equal to or less than the mean aggregation number (number of monomers in a micelle), $\bar{n}$. The head groups of the ionic micelles are usually fully ionized because of the substantial free-energy decrease due to the solvation of the counterions (Na^+). Thus, each ionic micelle (M) can be pictured as a charged hard sphere of diameter σ_M, including the hydrophobic core and the hydrophilic outer layer, and effective charge Z_M surrounded by a cloud of counterions ($+$). As the monomer ($-$) concentration increases above the CMC, the additional monomers are incorporated into new micelles while the free-monomer concentration remains approximately equal to the CMC.[1]

Various experimental data,[2] including a number of small-angle neutron-scattering (SANS) measurements, in the course of the last few years[3-7] confirm the expectation that the ionic micellar solutions are appreciably nonideal in the whole range of monomer concentrations above the CMC. The SANS intensity distributions, denoted by $I(Q)$, from ionic micellar solutions, show a strong interaction peak which becomes more pronounced as the ionic strength of the solution decreases.[5] The pronounced interaction peak has been interpreted as being due to sharpening of the first diffraction peak of the intermicellar structure factor when the effective Coulomb interaction between micelles becomes long ranged and appreciable compared to k_BT at contact.[3] The SANS intensity distribution for a micellar solution, $I(Q)$, is, to a good approximation, proportional to the product of the intramicellar structure factor, $P(Q)$, and the intermicellar structure factor, $S(Q)$.[8] $P(Q)$ is a monotonically decaying function of Q, the Bragg wave number, and is relatively easy to estimate once the aggregation number $\bar{n}$ of the micelle is specified.[5] The $S(Q)$ factor, on the other hand, an oscillatory function of Q, is sensitively dependent on the form of the intermicellar interaction potential (for example, on the value of Z_M), and in the model calculations also on the statistical-mechanical theory used.

A popular statistical-mechanical model for calculating $S(Q)$ has been the so-called "one-component model" (OCM).[9,10] In analogy to the DLVO theory of colloidal stability,[11] the micellar particles in the OCM are assumed to interact via a screened Coulomb (Yukawa) potential in which the Debye-Hückel screening length is determined by the ionic strength due to the simple ions present. Roughly speaking, this is equivalent to the McMillan-Mayer theory of the solution in which the counterions, coions, and solvent molecules are considered only through their contribution to the micelle-micelle—pair potential. The theory of the Yukawa OCM in the mean spherical approximation (MSA), the YMSA, was first given by Waisman[12] and simplified by Høye and Blum,[13] and by Cummings and Smith.[14] The OCM of ionic micellar solution applied to the calculations of the partial structure factor $S(Q)$ has been repeatedly demonstrated[3–8] to yield excellent agreement with the SANS data, provided the screening parameter κ is appropriately computed and the contact potential V_c is treated as a phenomenological parameter.[16,17] The OCM is, however, not completely satisfactory in two respects: First, in computing the screening parameter one takes into account only the contribution of simple ions in the solution, thus treating the ions and the micelles on an unequal basis, a serious limitation when micellar solutions are concentrated. Second, the effective macroion contact potential in the multicomponent ionic system in which the simple ions are only considered indirectly is, in general, a complicated function of sizes and charges of all the ions and not of the surface charge Z_M and micelle size σ_M alone.[18] Thus, even if one can achieve an excellent fit to the experimental data, the extracted contact potential V_c cannot be easily related to the properties of the macroion itself.

Recently, Senatore and Blum[19] and Naegele *et al.*[20] have proposed to calculate the partial structure factors of the ionic micellar solution by treating it as a multicomponent ionic fluid in the spirit of the primitive model of ionic solutions.[21] In this approach the macroions and the simple ions are represented as charged hard spheres embedded in a dielectric continuum (water). The charge of each ion is at its center and the dielectric constant of the spheres is taken to be equal to that of the solvent. The primitive model has been shown to give a good account of structural and thermodynamic properties of low-valent electrolytes.[22] Probably the most satisfactory way of calculating the structure of such models is the hypernetted-chain approximation (HNCA), but the simpler, analytically solvable mean spherical approximation (MSA) has often been shown to yield useful results.[24,25] The MSA applied to ionic systems has the following properties:

(a) In the high-charges, high-density limit, it becomes identical to the HNCA (Ref. 26).

(b) The long-range ($r \rightarrow \infty$) part of the direct correlation functions is asymptotically correct.[23,27]

However, when the charges are not too high and the concentration is low, as in the micellar systems of present interest, the MSA pair-correlation functions become increasingly inaccurate at small interionic separations. For the case of ionic colloids, a simple way of correcting this difficiency is to redefine the polyion diameter and charge.[28] This amounts to including some of the counterions next to the macroion into a redefined colloidal particle. The chemical binding effects—if they exist—can also be accounted for in this way. Sheu *et al.* have shown that SANS spectra of salt-free micellar solutions and solutions containing various amounts of 1-1 electrolytes can be satisfactorily analyzed using the primitive-model MSA supplemented by the above rescaling procedure.[28,29] This type of rescaled MSA (RMSA) analysis has the advantage that the screening of the intermicellar Coulombic interactions is treated self-consistently by introducing the generalized screening parameter,[30] and the charges and the sizes of all ionic species are explicitly taken into account. The analyses of the SANS data by the OCM and by the RMSA have been shown to give the same aggregation number of the micelle, but different effective surface charges.[28,29] Denoting the OCM surface charge by Z^* and the RMSA charge by Z_0, one had, in general, $Z^* > Z_0$. Furthermore, Z_0 was found to agree well with the so-called "dressed charge"[16,29] of the micelle which is about 15—25% of the aggregation number $\bar{n}$. Thus, one can interpret Z_0 as a dressed charge of the bare micelle of charge n carrying a cloud of counterions physisorbed on its surface.

Apart from the point that a proper interpretation of Z_0 is required, it is pertinent to stress the fact that the aggregation number $\bar{n}$ and the structure factor $S(Q)$ extracted from SANS data are well defined and reliable. In the field of ionic solutions there are few reliable ion-ion partial structure factors obtained from either neutron- or x-ray-diffraction experiments.[31,32] It is thus gratifying to find that SANS technique has now been developed to a point that the partial structure factor of macroions can be reliably measured, at least for solutions with relatively low ionic strengths, as in micellar solutions.

In some sense micellar solutions pose a challenge to ionic solution theory because they are generally characterized by highly asymmetric charge and size distributions. Applications of the HNCA, usually considered to be the most accurate integral-equation approximation method, have been reported,[33–39] but there is some evidence that its inherent limitations may become quite serious in highly asymmetric polyelectrolyte solutions;[38–41] in any case the convergence of standard iteration schemes can not always be attained in these systems.[38–41] It is also known[42] that the HNCA is less satisfactory for treatment of highly charged, flat interfaces where it yields thermodynamically unstable charge distributions with an excessive accumulation of the counterions near the large charged particle.

A way of mitigating this problem by using a new closure approximation, termed the hypernetted-chain Percus-Yevick (HNC-PY) approximation, has been proposed recently by Bratko, Friedman, and Zhong.[39] In the HNC-PY approximation the Ornstein-Zernike (OZ) integral equation

$$h_{ij}(r_{ij})=c_{ij}(r_{ij})+\sum_k n_k \int c_{ik}(r_{ik})h_{jk}(r_{jk})d^3r_k \qquad (1)$$

is supplemented by the HNCA closure for the macroion-macroion correlations

$$c_{MM}(r_{MM})=-\beta u_{MM}(r_{MM})+h_{MM}(r_{MM}) -\ln[1+h_{MM}(r_{MM})]\ , \qquad (2)$$

and for the remaining correlations, by the Percus-Yevick closure,

$$c_{ij}(r_{ij})=(1-e^{\beta \bar{u}_{ij}})[1+h_{ij}(r_{ij})],\quad \beta=1/k_BT\ . \qquad (3)$$

In the above equations, $c_{ij}(r_{ij})$ and $h_{ij}(r_{ij})$ are the direct and total correlation functions for the pair of components

i and j,[23] n_i is the number density of the component i, and $\bar{u}_{ij}(r_{ij})$ is the solvent averaged pair potential of components i and j. Within the primitive model of ionic solutions,

$$\bar{u}_{ij}(r_{ij}) = \begin{cases} \dfrac{Z_i Z_j e^2}{4\pi\epsilon r_{ij}} \text{ for } r \geq \sigma_{ij} & (4) \\ \infty \text{ for } r_{ij} < \sigma_{ij} \,, & (5) \end{cases}$$

where

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \,. \tag{6}$$

$Z_i e$ is the charge of the species i, and ϵ is the dielectric constant of the pure solvent. It is found[39] that the HNC-PY integral equation can be solved in a wider charge-concentration range than the HNCA alone.

Furthermore,[39] the macroion-macroion distributions of the HNC-PY approach compare favorably with the available HNCA and Monte Carlo results despite the PY approximation employed in treating the ion-polyion correlations. The HNC-PY correlation functions g_{M+} are close to those of the HNCA at distances large enough so that g_{MM} is nonzero. This, in turn, means that the charge of individual micelles together with the surrounding cloud of the counterions as seen from the other aggregates does not depend essentially on the choice between the two closure approximations.

In the present communication we apply the HNC-PY approximation to calculate the intermicellar structure factor $S(Q)$,

$$S(Q) = 1 + n_M \tilde{h}_{MM}(Q) \,, \tag{7}$$

for comparison with data obtained recently[16,28] from the SANS measurements in solutions of sodium and lithium dodecylsulfate at different concentrations and with or without added simple electrolyte. For this purpose we solve the HNC-PY approximation for a number of model systems corresponding to the real systems studied experimentally (Table I). We use the primitive model of ionic solutions with the model parameters taken from earlier works[16,28,39] and assume that the charge of the micelle, Z_M, is equal to the aggregation number $\bar{n}$. The micelle, counterion, and coion diameters, σ_M, σ_+, and σ_-, the concentration of the amphiphile, c_a, the concentration of the free of nonmicellized amphiphile, c_a^f, and that of the simple salt (LiCl) added, c_s, are given in Table I. The reduced temperatures $T_r = k_B T / u_{M+}(\sigma_{M+})$, a measure of the polyion-counterion interaction, are also included for a comparison with the former work.[39] The values of the ionic diameters are rounded in order to facilitate the discretization required for the numerical solution of the OZ equation. In system 1–4 in the table the value $\sigma_- = 0.6$ nm is the rounded value of the Stokes hydrodynamic radius of free surfactant determined from the measured coefficient of self-diffusion of dodecylsulfate ion.[43] For simplicity, the estimate $\sigma_- = 0.4$ nm, corresponding roughly to the Cl^- ion,[44] is ascribed to all coions in the presence of 0.02 mol dm^{-3} LiCl, where Cl^- represented the dominant coion species. The integral equations were solved according to the Rossky-Dale algorithm[45] using the fast-Fourier-transform routine. The number of sampling points obtained in the discretization was 1024 or 2048 and the spacing between the points was between 0.02 and 0.05 nm, depending on the concentration. The convergence, often attained with the use of the mixing parameter,[46] was generally slow and required from 5×10^2 to 1.5×10^3 iterations at the highest aggregate charges of $Z \sim 10^2$.

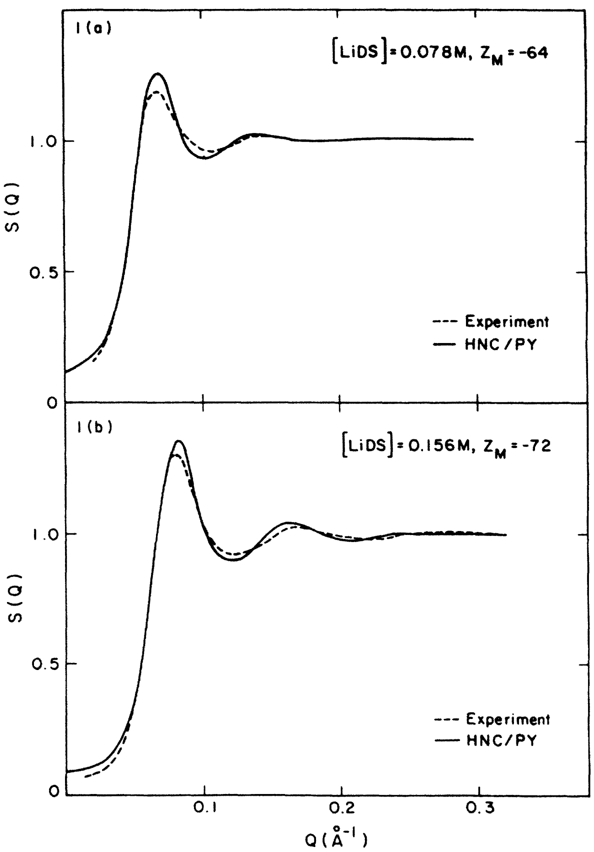

FIG. 1. Intermicellar partial structure factor $S(Q)$ of LiDS solutions, system (a) 1 and (b) 2 of Table I.

In Figs. 1–3 the partial structure factors $S(Q)$ from the theory are compared with those determined previously[16,28] from SANS measurements. Considering that the model parameters are taken from thermodynamic data without further adjustment, the agreement between the theory and the experiment is satisfactory. However, there are systematic small deviations between the theory and experiments visible near the first diffraction peak. It is not likely that different methods (MSA or OCM) used in experimental extraction of the structure factor can produce this amount of difference. Therefore, we must conclude that the discrepancies are genuine and are due to imperfections of the theory. It is important to note that no rescaling of the size or of the charge of the aggregates has been made here. The previous success of the rescaled MSA and of the OCM theories, both treating the micelles together with the closest counterions as new, less charged colloidal particles, seem to indicate an incomplete ionization of the micelles.

TABLE I. The model parameters corresponding to lithium and sodium dodecylsulfate solutions. The ionic diameters are given in nm and the concentrations in mol dm^{-3}. The free-surfactant concentration c_a^f is taken to be 0.008 mol dm^{-3} in all cases. c_s denotes the concentration of LiCl added.

System	$-Z_M$	T_r	Counterion	c_a	c_s	σ_M	σ_+	σ_-
1	64	0.050	Li$^+$	0.078		4.2	0.4	0.6
2	72	0.047	Li$^+$	0.156		4.4	0.4	0.6
3	87	0.039	Na$^+$	0.065		4.5	0.3	0.6
4	98	0.036	Na$^+$	0.130		4.7	0.3	0.6
5	59	0.046	Li$^+$	0.0918	0.02	3.5	0.4	0.4
6	63	0.043	Li$^+$	0.1836	0.02	3.5	0.4	0.4

On the other hand, the relatively high diffusion coefficients of the counterions in aqueous solutions of sodium and lithium dodecylsulfate[43,47] can be interpreted satisfactorily by assuming a complete dissociation.[48–50] The results of the present work show that the SANS results can also be analyzed using the full aggregate charge when a suitably powerful approximation method is applied. Thus, the rescaling concept can be viewed as an analogue of Manning's condensation hypothesis for linear polyelectrolytes[52] In these theories the apparent association is introduced to account for very strong Coulombic interactions which are otherwise mishandled by less powerful approximation methods. It is gratifying to observe the substantial agreement between the results of the rescaled MSA with those obtained by the more refined HNC-PY approach when the same model parameters fitting the SANS data in the RMSA are used. However, considering the convenience of having an analytical solution in the RMSA as compared to the nontrivial numerical procedure[45] involved in solving the HNCA or the HNC-PY approximation, further application of the rescaled MSA in the analyses of the intermicellar correlations is expected.

It remains to examine to what extent any of the above approximation methods is suitable for studies of thermodynamic or transport phenomena in ionic colloids where the knowledge of accurate ion-ion and ion-polyion correlations may also be important. Recent results of the complete HNCA theory seem promising for both the treatments of the equilibrium[38,39] and dynamic[39] phenomena under the conditions in which solutions to the HNCA can still be obtained. Compared to the HNCA, the HNC-PY has been shown[39] to extend the range of the model parameters for which the OZ equation can be solved to those characteristic of the most typical ionic micellar solutions. Its applicability for studies of various thermodynamic properties and ion diffusion in these systems will be discussed in a forthcoming communication.

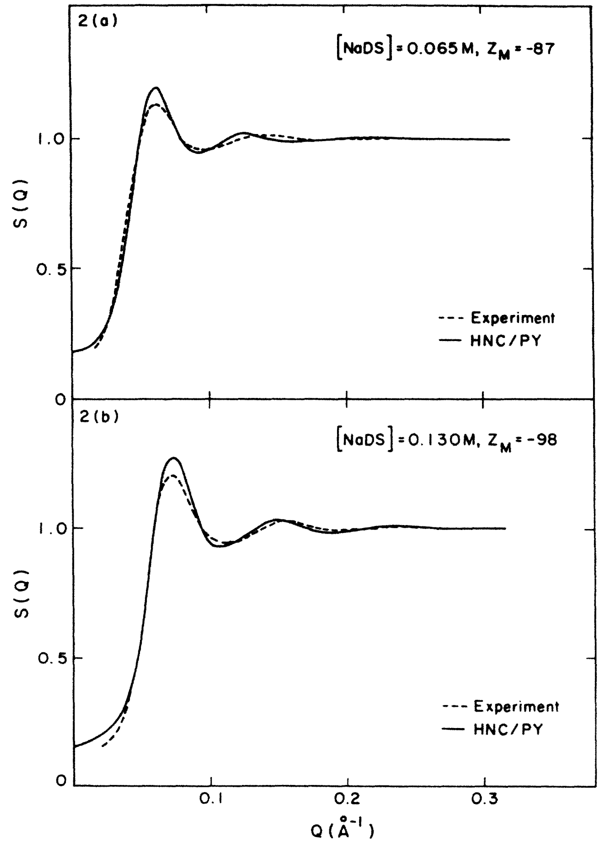

FIG. 2. Intermicellar partial structure factor $S(Q)$ of NaDS solutions, systems (a) 3 and (b) 4 of Table I.

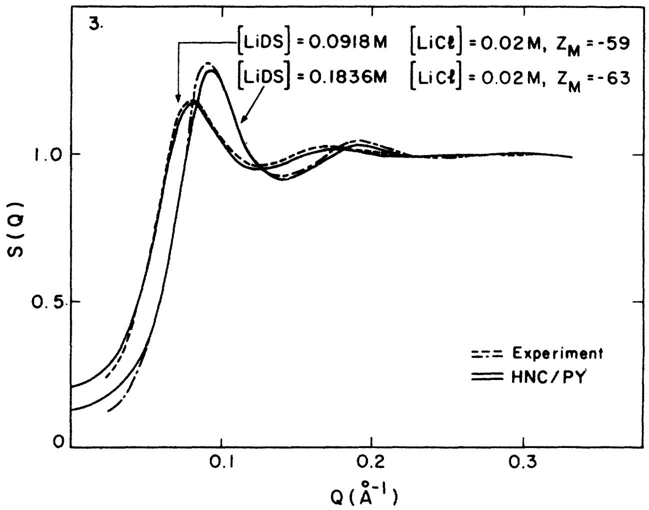

FIG. 3. Intermicellar partial structure factor $S(Q)$ of LiDS solutions, systems (a) 5 and (b) 6 of Table I.

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