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Micelles of SDS Surfactants in Concentrated NaCl Solutions

Jin-Hsiang Lo (羅金翔) and Chung-Yuan Mou* (牟中原)
Department of Chemistry, Taiwan University, Taipei, Taiwan 10764, R.O.C.

We investigated the aggregation behavior of rod-like micelles of sodium dodecyl sulfate (SDS) in concentrated NaCl solution by quasi-elastic light scattering (QLS) and viscosity measurement over a range of temperature (25 °C to 50 °C) and NaCl concentration. The reduced viscosity of aqueous SDS in the presence of NaCl has been measured by an Ubbelohde-type capillary viscometer. We show mean hydrodynamic radius of micelles can be determined from viscosity data. We also determined mean hydrodynamic radius using quasi-elastic light scattering. Micellar size decreases with increasing temperature, whereas it increases with increasing ionic strength. The results of viscosity and dynamic light-scattering measurements are interpreted as the extension of length of rod-like micelles. We compare viscosity and light scattering experimental results.

INTRODUCTION

Ionic surfactants in aqueous solution can form various organized structures such as micelles, microemulisions and vesicles. One interesting behavior is the formation of large rod-like micelles in solutions with high ionic strength. The growth in size and shape can be investigated through various properties, including static light scattering,[1] quasi-elastic light scattering (QLS),[2,3] fluorescence,[4] and viscosity studies.[5]

For ionic micelles (cationic and anionic) in aqueous solution, the optimum size is determined by two factors. One is the electrostatic effect of simple salt due to counterion binding on the micellar surface, and the other is due to the hydrophobic interaction of the hydrocarbon chain which is related to the change of hydrogen bonding in water. When one increases the concentration of simple salt added to a micellar solution, the effect is to decrease electrostatic repulsion between ionic head groups; the result is to favor micelle growth in a rod-like shape. A distinct feature of micelles which grow into long rods is thought to be pronounced polydispersity in size distribution. This behavior has been confirmed by light scattering[6] and fluorescence.[4]

The alkylsulfate anionic surfactants have been intensely studied; sodium dodecyl sulfate (SDS) in particular is the material of choice. The pioneer work on this system was done by Mazer et al.;[6] they showed that SDS forms elongated rod-like micelles in 0.6 M NaCl solution. Since then, Benedeck et al.[7,8] and Ikeda et al.[9] have made detailed investigations of the growth of SDS in concentrated NaCl solution, including the thermodynamic parameters of the growth of the micelles. However, there remain questions with regard to the structure of the rod-like micelle; in particular, the flexibility of the rod micelle. A single technique such as QLS is unlikely to provide adquate information. Mishic and Fisch[10] combined QLS and static light scattering to measure the size and shape of grown SDS micelles in concentrated NaCl solution as a function of temperature, amphiphilic concentration, and ionic strength; they interpreted their data in terms of a theory of a flexible (worm-like) rod object.[11] The fit of their data to theories is indirect requiring some manipulations of models that seem to contain too many parameters. We decided to investigate this problem by a different approach by combining the technique of QLS and viscosity measurement. We show that both sets of data can be explained satisfactorily by a model of rigid-rod micelles. There has been no previous study using the technique of QLS in connection with viscosity measurement in the region of high concentration of both surfactants and salts.

EXPERIMENTAL SECTION

Reagents and Solutions

The sodium dodecyl sulfate(SDS) employed in this study was of a highly pure grade (Merck). The water used was doubly distilled and deionized. Purity of reagent-grade sodium chloride is at least 99.5%.

We report here experimental results in which hydrodynamic radius R_h and viscosity of SDS micelles salt solutions measured in 0.5-2g SDS/100 mL aqueous solutions at various temperatures (25-50 °C) in 0.8 and 1 M NaCl solutions. We prepared the solutions by first incubating them in a water bath at 45-50 °C (above the critical micellar temperature, 25-30 °C) to ensure complete dissolution of SDS in NaCl aqueous solutions. Solutions were then kept in an oven at the desired temperature for about 30 min before measurements.

QLS Measurements

Quasi-elastic light scattering measurements were made using Photal LPA-3000/3100 spectrophotometer (Otsuka Electronics). The light source was a 5 mW He-Ne laser with wavelength 632.8 nm; the signal of a photomultiplier with measuring angle 90° was processed in 64 or 128 channels, and a real time digital correlator with time interval method (T.I. method). Samples were filtered through a membrane filter (Millipore) with pore size 0.22 μm to reduce dust interference.

Viscosity Measurements

The reduced viscosities of the solutions were measured by a Cannon-Ubbelohde capillary viscometer (Wescan cat. no. 449005) thermostated at test temperatures ± 0.01 °C. For our system, we chose a small-pore capillary tube for the viscosity measurement such that no non-Newtonian flow behavior could be detected. All glassware was thoroughly cleaned by an acidic cleaning solution. We checked the accuracy of the viscometer by measuring viscosity of pure water and NaCl solutions, which agreed with literature values.

THEORY

The quasi-elastic light scattering technique uses photon correlation to gain information about temporal fluctuations of the liquid solution system. This technique has proved useful in many fields. In this work, the scattered light intensity time-correlation function was analyzed and related to the Brownian diffusion time of the micelle aggregates. For relatively small micelles, the decay of the autocorrelation function is interpreted in terms of the translational diffusion motion of the micelles.[3] The hydrodynamic radius is calculated by means of Stokes-Einstein equation. Experimentally measured photon correlation spectra consist of a sum of exponential decay terms. This property indicates that the micelle size distribution is polydisperse in nature, concurrent with rod-like micelles,[3,12] as we have discussed previously. The reported hydrodynamic radius is an average quantity.[13,14] The method we use is the standard cumulant method,[13,14] although we did make some spot checks using the alternative histogram method.[13,14] For the data reported these two methods give essentially the same average within experimental error.

We give a short review of the theory of QLS. An autocorrelator accepts the digitized scattering light intensity I(t) and computes its normalized time correlation function

$$g^{(2)} = < I(0)\, I(t) > / < I >^2 \tag{1}$$

For photocounts that obey Gaussian statistics, $g^{(2)}(t)$ is related to the first-order electric field correlation $g^{(1)}(t)$ by the Siegert relation.[13]

$$g^{(2)}(t) = 1 + \beta * | g^{(1)}(t) |^2 \tag{2}$$

in which the parameter β, to be determined by fitting, has a value between zero and unity. For relatively small particle undergoing density fluctuations, $g^{(1)}(t)$ is dominated by translational diffusion motion; it is given by

$$g^{(1)}(t) = S(g) * \exp(-q^2 Dt) \tag{3}$$

in which D is the diffusion coefficient, q is the scattering wave vector,

$$| q | = 4\pi n / \lambda * \sin(\theta/2) \tag{4}$$

n is the refractive index, λ wavelength, and θ the scattering angle. S(q) is the static structural factor which is absorbed into β as a fitting parameter. For small, dilute, non-interacting particles, the Stokes-Einstein equation gives the hydrodynamic radius R_h

$$D = k_B T / 6\pi \eta R_h \tag{5}$$

in which k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent. For the rod-like mielle rotational diffusion could make additional contributions to $g^{(1)}(t)$, as investigated by Flamberg and Pecora.[3] According to their results,[3] the rotational contribution should be small for our system because we use greater wave length (smaller q) and shorter rod micelles. Hence we neglect rotational diffusion in the interpretation of our QLS results.

The viscometric technique has been used extensively for polymeric solutions; for micellar solutions the technique is less commonly used because the intrinsic viscosity is not invariant as the micelles grow. The interpretation of viscosity data for concentrated micellar solution is further complicated by the possibility of flexibility[15,16] and entanglement of the rods. In general, we divide the concentration regions into three: dilute, semidilute and concentrated. In the dilute region the viscosity behavior is described by the equation

$$[\eta] = \lim_{c\to 0} \frac{\eta_c/\eta_o - 1}{c} \qquad (6)$$

in which η_o is the viscosity of the solvent, c is concentration of micelles, and $[\eta]$ is the intrinsic viscosity. For a micellar solution, the solvent is taken to be the solution at the critical micellar concentration (cmc). For a system having a large concentration of salt, the cmc value changes little with salt concentration;[17] we take cmc as 8.66×10^{-4}M. Eq. 6 becomes

$$[\eta] = \lim_{c\to 0} \frac{\eta_r - 1}{c} \qquad (7)$$

η_r is the reduced viscosity defined as

$$\eta_r = \frac{\eta_c}{\eta_{cmc}} \qquad (8)$$

$[\eta]$ calculated from Eq. 6 depends on the surfactant concentration ; it reflects the growth of micelles upon increase of micellar concentration. The relation for the concentration dependence of reduced viscosity is given by[15]

$$\eta_r = 1 + [\eta](C - cmc) + 0.75\,(C - cmc)^2\,[\eta]^2 \qquad (9)$$

This equation has been used by Ozeki and Ikeda[15] in their study of the viscosity behavior of aqueous NaCl solution of dodecyldimethylammonium chloride, a rod-like micelle similar to our system. According to the well-known Poiseuille equation, the pressure P is proportional to viscosity and inversely proportional to flow period t. Hence, reduced viscosity is given by the reduced flow period

$$\eta_r \equiv t_c / t_{cmc} \qquad (10)$$

in which t_{cmc} is the flow period for micellar solution at critical micellar concentration, and tc is flow period of sample micellar solution.

For a rod-like micelle, the intrinsic viscosity is related to its axial ratio. If one assumes the micelle to be a rigid rod having length L and a cross-sectional radius R, equivalent to a prolate ellipsoid which has the same volume and major axis L, then the minor axis is 2b = 6R, and the axial ratio is J = L/2b. The intrinsic viscosity of such an ellipsoid is given by,[18]

$$[\eta]/V = J^2/15(\ln 2J - 1.5) + J^2/5(\ln 2J - 0.5) + \frac{14}{15} \qquad (11)$$

Thus, one can calculate the parameter J from measurement of viscosity so to characterize the length of the rod. According to Eq. 11 one assumes the micelle to be rigid.

The next step is to relate the frictional coefficient f (or hydrodynamic radius) to the structural parameter J; e.g. one needs the functional relationship f = f(J). Using

$$k_B T / D = f = 6\pi\eta R_h \qquad (12)$$

one relates J to R_h, once the value J is determined from viscosity measurement. For a rigid rod of length L and cross-sectional radius r, Eq. 12 is generally re-written in the following form

$$kB\,T / D = f = 6\pi\eta\, L\, E(\chi) \qquad (13)$$

with $\chi = \sigma$ or ρ, $\sigma = \ln(L/r)$ and $\rho = L/2r$.

The function $E(\chi)$ has been derived according to various models; they are listed in Table 1, with the calculated hydrodynamic radius labeled R1 to R5. R2 and R3 are from Broersma's early[19] and later[20] relations for long and thin rigid rods; they work well for dilute noninteracting cylinder-like long polymers.[21] R1 represents a model calculation of Flamberg and Pecora[3] that is a slight modification of Broersma's model. The relation of Yamakawa and Fujii[21] (R4) is based on a stiff worm-like model with Oseen-Burgess hydrodynamic interactions between chain elements. Finally, the model in R5, developed by de la Torre et al., represents the rigid particle as assemblies of beads in cylindrical fashion and the beads interact hydrodynamically.[23] R4 agrees with R5 as their treatments are basically the same. It was found previously[23] for a finite cylinder with axial ratio greater than 2 that the results of de la Torre[23] (R5) are in remarkable disagreement with the calculations by Broersma (R2 and R3). Therefore, it is of interest to check these results against our experimental measurements.

RESULTS AND DISCUSSION

We have made viscosity measurement over a range of temperature 25 °C to 50 °C and NaCl concentration at 0.8M

Table 1. Equations for Diffusion Function of Cyclinders

R1 : $E(\rho) = 2\ln\rho - 1.46 - 7.4(1/\ln 2\rho - 0.34)^2 - 4.2(1/\ln 2\rho - 0.39)^2$
R2 : $E(\sigma) = 2\sigma - 0.19 - 8.24/\sigma + 12/\sigma^2$
R3 : $E(\sigma) = 2\sigma - 0.614 - 21.6/\sigma^2 + 55/\sigma^3 - 31/\sigma^4$
R4 : $E(\rho) = 2[\ln\rho + 0.3863 + 0.5/\rho - 0.0625(1/\rho)^2 + 0.00195(1/\rho)^4]$
R5 : $E(\rho) = 2\ln\rho + 2\,(0.312 + 0.565/\rho + 0.1/\rho^2)$

and 1.0M. A typical result is plotted in Fig. 1 for the case of 0.8M salt concentration. When the concentration of SDS increases the reduced viscosity also increases. The reduced viscosity is then treated by using Eq. 9 to obtain intrinsic viscosity which is listed in Tables 2 and 3. According to Fig. 1 when temperature increases the reduced viscosity decreases; this condition reflects the decreasing size of micelles. The cases of 0.8M and 1.0M salt concentration show similar viscosity behavior.

Gamboa and Sepulveda[24] previously measured viscosities of some ionic micellar solutions in the presence of added salts. They interpreted their results in terms of a transition from spheres to rods, and estimated the length of the rod micelle from the intrinsic viscosity. Because the equation they used includes only the first term of the right-hand-side of our Eq. 11, it is inaccurate. We used Eq. 11 to calculate the length parameter J for all cases and list the results in Tables 2 and 3. We further took the partial molar volume of SDS to be 246.4 mL/mol[25] and cross-sectional diameter to be 50 Å.[26] The cylinder lengths are calculated and listed in the same tables.

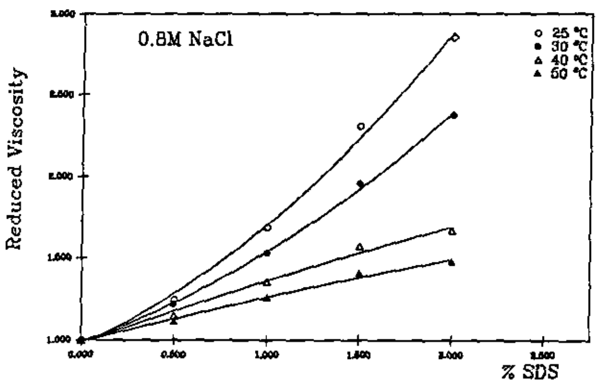

Fig. 1. Reduced viscosity of rod-like SDS micellar solution in 0.8M NaCl solution at various SDS contentrations and temperatures.

The equations listed in Table 1 have been used to calculate the effective hydrodynamic radii presented in Tables 2 and 3. The results are also plotted in Figs. 2 and 3. In the same tables, R6 and R7 are the results of QLS measurements; R6 represents the hydrodynamic radii measured by Mishic and Fisch,[10] and R7 data are the results of this work. They are in essential agreement. Mishic and Fisch[10] indicated that their treatment based on flexible rods is not distinguishable from one based on rigid rods. Our rigid-rod model is then more economic in the sense that we use fewer parameters in fitting.

According to Figs. 2 and 3, the hydrodynamic radii measured by means of QLS agree well with the results of Torre et al. and Yamakawa et al. whereas the results based on Broersma's relation overestimate R_h by about 10%. In

Table 2. QLS and Viscosity Datas of SDS Solutions in 1M NaCl

Temperature: 30°C SDS conc.(M)[%]	η_r	[η]	J	L	R1	R2	R3	R4	R5	R6	R7
(8.66E-04)	1.00	-	-	-	-	-	-	-	-	-	-
(1.73E-02)[0.5]	1.26	13.4	24.9	1243	192	197	189	166	167	-	167
(3.47E-02)[1.0]	2.41	23.9	35.1	1757	243	250	240	215	218	217	225
(5.20E-02)[1.5]	3.79	26.9	37.8	1888	256	262	253	227	230	-	230
(6.94E-02)[2.0]	4.65	23.9	35.2	1761	244	250	241	216	218	223	228
Temperature: 40°C SDS conc.(M)[%]	η_r	[η]	J	L	R1	R2	R3	R4	R5	R6	R7
(8.66E-04)	1.00	-	-	-	-	-	-	-	-	-	-
(1.73E-02)[0.5]	1.20	10.6	21.5	1075	174	180	172	149	150	-	-
(3.47E-02)[1.0]	1.52	11.8	23.0	1151	182	188	180	157	158	148	117
(5.20E-02)[1.5]	2.25	15.4	27.2	1358	204	209	201	177	179	-	133
(6.94E-02)[2.0]	2.97	15.8	27.5	1375	205	211	203	179	181	148	142
Temperature: 50°C SDS conc.(M)[%]	η_r	[η]	J	L	R1	R2	R3	R4	R5	R6	R7
(8.66E-04)	1.00	-	-	-	-	-	-	-	-	-	-
(1.73E-02)[0.5]	1.14	7.60	17.5	874	153	157	150	128	129	-	-
(3.47E-02)[1.0]	1.27	6.83	16.3	816	146	151	144	122	123	110	-
(5.20E-02)[1.5]	1.63	9.17	19.7	984	165	170	162	139	141	-	-
(6.94E-02)[2.0]	1.98	9.60	20.2	1012	168	173	165	142	144	123	97

Notes: (1) R1 to R7 are hydrodynamic radii / Å as explained in text.
(2) [η] : units are 1/M.

Table 3. QLS and Viscosity Datas of SDS Solutions in 0.8M NaCl

Temperature: 25°C SDS conc. (M) [%]	ηr	[η]	J	L	R1	R2	R3	R4	R5	R6	R7
(8.66E-04)	1.00	-	-	-	-	-	-	-	-	-	-
(1.73E-02)[0.5]	1.24	12.7	24.0	1202	188	193	185	162	163	-	-
(3.47E-02)[1.0]	1.68	13.6	25.1	1253	193	198	190	167	168	142	140
(5.20E-02)[1.5]	2.30	15.8	27.5	1375	205	211	203	179	181	-	156
(6.94E-02)[2.0]	2.85	15.2	26.9	1343	202	208	199	176	177	165	168
Temperature: 30°C SDS conc. (M) [%]	ηr	[η]	J	L	R1	R2	R3	R4	R5	R6	R7
(8.66E-04)	1.00	-	-	-	-	-	-	-	-	-	-
(1.73E-02)[0.5]	1.21	11.3	22.4	1123	179	185	177	154	155	-	-
(3.47E-02)[1.0]	1.53	10.9	21.9	1096	177	182	174	151	153	117	-
(5.20E-02)[1.5]	1.96	12.6	23.9	1196	187	192	184	161	163	-	111
(6.94E-02)[2.0]	2.37	12.3	23.6	1180	185	191	183	159	161	135	118
Temperature: 40°C SDS conc. (M) [%]	ηr	[η]	J	L	R1	R2	R3	R4	R5	R6	R7
(8.66E-04)	1.00	-	-	-	-	-	-	-	-	-	-
(1.73E-02)[0.5]	1.14	8.03	18.1	905	156	161	154	131	133	-	-
(3.47E-02)[1.0]	1.35	7.75	17.7	885	154	159	151	129	130	85	-
(5.20E-02)[1.5]	1.57	8.37	18.6	929	159	164	156	134	135	-	-
(6.94E-02)[2.0]	1.67	7.12	16.8	838	149	153	146	124	125	85	-
Temperature: 50°C	-	-	-	-	-	-	-	-	-	-	-
SDS conc. (M) [%]	ηr	[η]	J	L	R1	R2	R3	R4	R5	R6	R7
(8.66E-04)	1.00	-	-	-	-	-	-	-	-	-	-
(1.73E-02)[0.5]	1.11	6.69	16.1	805	145	150	143	121	122	-	-
(3.47E-02)[1.0]	1.26	5.84	14.7	737	138	142	135	113	114	-	-
(5.20E-02)[1.5]	1.40	6.31	15.5	775	142	146	139	117	118	-	-
(6.94E-02)[2.0]	1.47	5.40	14.0	700	133	138	131	109	110	-	-

*The notes are the same as the table 2.

the study of rodlike micelles or polymers, one seaks to determin the cross-sectional radius r and the length L of the cylinder, provided that the length parameter J can be determined by another technique. Tirado and Torre[27] claimed that the use of Broersma's relation caused to be a strongly underestimated. In the J range of our interest, the difference could reach 30%. We constrained constant the cylinder radius when calculating R_h. Thus, Broersma's

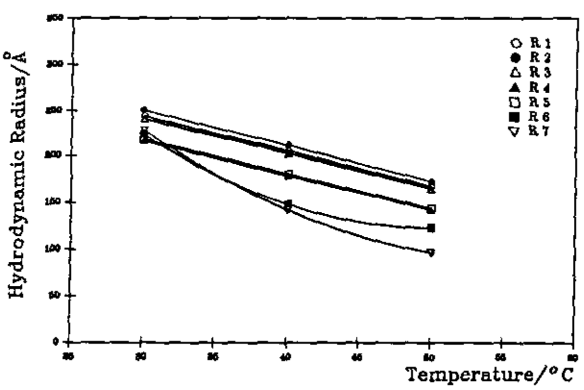

Fig. 2. Hydrodynamic radius calculated by various methods. The contentration of the solution is 2% SDS and 1M NaCl.

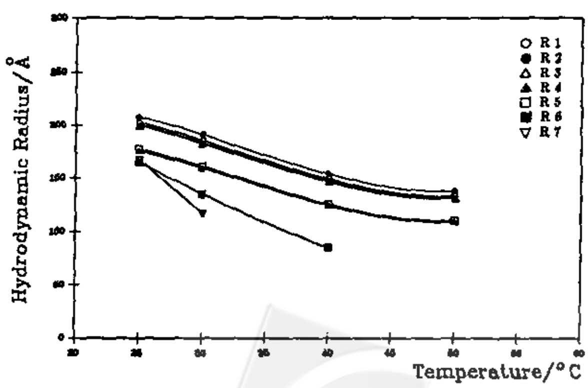

Fig. 3. Hydrodynamic radius calculated by various methods. The concentration of the solution is 2% SDS and 0.8M NaCl.

relation would lead to an overestimation of Rh by about 10%, as we observed in comparing R1 and R7. We therefor conclude that the frictional relationships derived by Yamakawa and de la Torre and coworkers are in good agreement with our experiments. We consider that Broersma's calculation is correct in only the limit of infinite J but its estimation of the end effect is not very good when the rod is finite in length.

In conclusion, we have examined the size and shape of the rod-like micelle system of SDS in concentrated NaCl solution with two techniques, quasi-light scattering and viscosity measurements. We have shown that one can obtain the cross-sectional radius r and length L of the cylinder, while the length parameter J can be determined by viscosity technique. This method will be useful for other rod-like suspensions of biopolymers for example. We have shown further that from the viscosity data the SDS micelles can be treated as essentially rigid rods. Previously, Nagarajan[16] analyzed viscosity data of dodecylammonium chloride in concentrated salt solution and also concluded that they can be interpreted better by assuming a rigid-rod model than by flexible rods. In selecting methods for treating frictional coefficients, we find that the method of de la Torre and Yamakawa agrees well with experiments.

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Key Words

Micelle; Light scattering; Viscosity.

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