Electron Paramagnetic Resonance and Small-Angle Neutron Scattering Studies of Mixed Sodium Dodecyl Sulfate and (Tetradecylmalono)bis(N-methylglucamide) Surfactant Micelles

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Small-angle neutron scattering (SANS) and electron paramagnetic resonance (EPR) have been used to characterize mixed micelles comprising the anionic surfactant sodium dodecyl sulfate (SDS) and the sugar-based nonionic surfactant (tetradecylmalono)bis(N-methylglucamide) (C14BNMG). Parallel studies using protonated and deuterated SDS have permitted the calculation of the mole fraction of SDS in the micelle (xSDS). The size of the hydrophobic core of the mixed micelles is essentially invariant with mole fraction xSDS. The volume of the polar shell containing the surfactant headgroups increases with decreasing xSDS. The amount of water present in this shell can be obtained from knowledge of the shell volume and the number and volume of the two types of headgroup occupying the shell. Water comprises about 70% of the polar shell in SDS but is almost completely excluded from the headgroup region of micelles of the nonionic surfactant. EPR has also been used to determine the polarity index, which contains a contribution from the OH groups on the headgroup of the sugar surfactant as well as a contribution from the water. From the rotational correlation time of the spin-probe, a microviscosity has been calculated that increases with decreasing xSDS, perhaps due to steric hindrance of the large glucamide groups or hydrogen bonding between them.

Introduction

Small-angle neutron scattering (SANS) has proved to be a very powerful technique for studying the morphology of the structures formed in aqueous solution by surfactants.1 In principle, analysis of SANS data provides information about the size and shape of the structures, as well as the interaction between them within the context of a particular model. Nevertheless, in practice, sometimes more than one physically reasonable model will fit the scattering data. Thus, it is important to seek other experimental information in order to select the best model. Recently, we have been developing and applying electron paramagnetic resonance (EPR) techniques to study mixed micelles to limit or otherwise “restrain” the SANS analysis. Of particular interest are binary surfactant mixtures of the anionic surfactant sodium dodecyl sulfate (SDS) and a series of nonionic surfactants, (n-alkylalono)bis(N-methylglucamide) (CnBNMG).

Typically, binary surfactant mixtures offer improved performance and cost-effectiveness compared with single-surfactant systems. Many of the benefits arise from nonideal phenomena associated with specific interactions between the two surfactants.2 Several approaches exist to discuss the onset of micellization and composition of the mixed surfactant aggregates formed, the most widely cited being (i) the ideal mixing model of Clint,3 which has been quite successful in describing mixed systems of similar surfactants, (ii) Rubingh’s4 very successful but largely empirical regular solution theory (RST) centered on the parameter β to account for specific interactions between the two surfactants; and (iii) the more comprehensive molecular-thermodynamic models of Blankschtein et al.5 and Bergström et al.6

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Previously, we reported the critical micelle concentrations,7 along with the structural (SANS)9 and dynamic (EPR) characterization8 of binary mixtures of SDS and the nonionic surfactant (dodecylmalono)bis(N-methylglucamide), C12BNMG, which both possess C12 tails. As is found for many mixed anionic–nonionic surfactant solutions, a “synergism” was observed in the CMC behavior—the measured CMC being lower than the prediction from ideal mixing theory. The SDS/C12BNMG pair is a particularly interesting system, as the size and shape of the mixed micelles vary only very slightly with composition. Thus, the mixed micelles are similar in size and shape to the two pure surfactant micelles.8,9,10,12 In essence, replacing an SDS molecule in the micelle by one C12BNMG molecule has little effect on the structure of the micelle, except to displace a volume of solvating water comparable to the difference in the respective headgroup volumes. The dynamics are however quite different across the composition range—the addition of a C12BNMG molecule substantially increases the local viscosity of the headgroup region. As part of the work on these mixed micellar systems,7 we also reported the CMC behavior of asymmetric systems, where the tail length of the nonionic surfactant was decreased or increased by two carbons so that it no longer “matched” that of the SDS. The system containing the longer tail nonionic, (tetradecylmalono)bis(N-methylglucamide) (C14BNMG) showed an interesting switch from antagonistic behavior at low SDS solution mole fractions (fSDS), i.e., the measured CMC being higher than the ideal prediction and, indeed, higher than CMC of C12BNMG to a synergistic behavior at high fSDS. In this paper, we explore this feature in more detail, together with both structural and dynamic behavior.

**Experimental Section**

**Materials.** Sodium dodecyl sulfate (Aldrich) was recrystallized from ethanol until no dip in the surface tension–concentration plot could be detected around the CMC. The perdeuterated SDS (Aldrich) was not recrystallized prior to use. The nonionic surfactant (Kodak European Research, U.S. patent 5,298,191) is depicted in Chart 1. It was purified extensively with reverse-phase HPLC prior to use. All other reagents were of analytical grade and used as received. The solvent used was D2O and H2O in the SANS and EPR measurements, respectively.

**Small-Angle Neutron Scattering.** The SANS measurements were performed on the fixed geometry, time-of-flight QM diffractometer (ISIS Spallation Neutron Source, Oxfordshire, U.K.) over a Q-range of approximately 0.008 to 0.22 Å−1. Samples were contained in thermostated 2 mm path length, UV-spectrophotometer grade, quartz cuvettes (Helma). All measurements were carried out at 45 °C. Experimental measuring times were between 40 and 80 min.

All scattering data were normalized for the sample transmission and incident wavelength distribution, corrected for instrumental and sample backgrounds using an empty quartz cell, and for the linearity and efficiency of the detector response. The data were put onto an absolute scale using a well-characterized partially deuterated polyethylene-blend standard sample.

**Chart 1. Nonionic Surfactant (Tetradecylmalono)bis(N-methylglucamide), C12BNMG**

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SANS Data Fitting and Analysis. The intensity of scattered radiation, I(Q), as a function of the wave vector, Q, is given by

\[ I(Q) = V_m^2 n_m (\rho_m - \rho_p) P(Q) S(Q) + B_{inc} \]  

where P(Q) describes the morphology of the scattering species, S(Q) describes the partial spatial arrangement of the micelles in solution, n_m is the number of micelles/unit volume, V_m is the volume of the micelle, and B_{inc} is the incoherent, background scattering. \( \rho \) is the neutron scattering length density of the micelle (subscript m) and the solvent (subscript s). The first three factors in eq 1 (viz, \( V_m^2 n_m (\rho_m - \rho_p) \)) are combined into a single parameter to “scale” the model intensity to the absolute value. With postfitting, the scalar may be recalculated using the parameters describing the micelle morphology/composition and the molar concentration of micelles to validate the fit. The calculated and observed values should lie within ~10%.

The model of the micelle adopted here is that of a charged particle with an elliptical core–shell morphology. For the SDS/C12BNMG case, a rather crude version9 of this model was used. The elliptical core was assumed to be dodecane and its minor radius constrained to be 16.7 Å (the all-trans length of a dodecyl tail). The shell thickness and difference between the core and shell scattering length densities were the principal fitting parameters, but these are not independent. Nonetheless, an approximately linear dependence of the shell thickness on micelle composition x_{SDS} was observed. As x_{SDS} → 1, the scattering length density of the shell (\( \rho_{shell} \)) tends to that of water, and the contrast (\( \rho_{shell} - \rho_p \)) decreases. Thus, the distinction between the shell and the continuous phase becomes poorly defined and the accuracy in determining the shell thickness drops significantly.

For the data presented here, a more refined version of the model has been employed. On the basis of the number of dodecyl and tetradecyl alkyl chains in the micelle, composition weighted-average values of the volume of the alkyl tail, volume of the polar head, and, thus, the scattering length densities of the different regions of the micelle can be calculated. However, attempts to fit the data using these averages were not successful. The fits are more consistent and the values of the parameters deduced more physically realistic when we assume that two of the CH2 groups in the tetradecyl tail do not reside in the core region but in the shell. Thus, the core effectively comprises dodecyl tails and has a corresponding scattering length density.

The average volume of the headgroup and average scattering length density of the dry headgroup region were input as constants. The values of the constants were calculated from the composition of the micelle and the values for the respective dry headgroup volumes. For the nonionic surfactant, the two -CH2 -linked N-methyl glucamides have a volume of 527 Å³, and incorporating 51 Å³ for the 2 CH2 groups yields the total headgroup volume of...
...608 Å$^3$ and the scattering length density of the headgroup fragments of the nonionic surfactant was taken to be $\rho_{\text{nonionic}} = 1.2 \times 10^{-6}$ Å$^{-2}$.

Modeling of the structure of the headgroup region of the anionic surfactant is complicated by the potential for the sodium counterions to dissociate to some degree; i.e., the degree of dissociation of sodium counterions ($\alpha_{Na^+}$) may vary. If all the sodium ions are bound ($\alpha_{Na^+} = 0$), this results in a volume of the headgroup of 74.2 Å$^3$ and, hence, $\rho_{\text{NaSulfate}} = 3.1 \times 10^{-4}$ Å$^{-2}$. If the sodium ions are completely dissociated ($\alpha_{Na^+} = 1$), the volume decreases to 60.6 Å$^3$ and $\rho_{\text{NaSulfate}} = 3.8 \times 10^{-4}$ Å$^{-2}$. Recent work on the closely related system SDS/C$_{12}$BNMG has shown that $\alpha_{Na^+}$ increases from $\alpha_{Na^+} = 0.27$ at $x_{SDS} = 1$ to $\alpha_{Na^+} = 0.70$ at $x_{SDS} = 0.3$; i.e., the fraction of counterions bound to the micelles is strongly dependent on the micelle composition. It is not known how the degree of sodium ion dissociation depends on micelle composition for the SDS/C$_{12}$BNMG combination of surfactants. One could assume that it would not be too different to the SDS/C$_{12}$BNMG case. However, it is the average headgroup scattering length density and volume that are required and these are volume-weighted averages of the two surfactant headgroups present in the polar shell. Due to the much greater volume of the sugar headgroup, adopting an incorrect value for $\alpha_{Na^+}$ will only have a significant effect on the overall headgroup region scattering length density for SDS-rich cases. Under those conditions, $\alpha_{Na^+}$ must tend toward 0.27. Thus any discrepancy introduced by assuming $\alpha_{Na^+} = 0.27$ is greatly reduced. Therefore, we took a constant value of $\alpha_{Na^+} = 0.27$, corresponding to the situation for simple SDS micelles. Thus, the fitting parameters describing the form factor calculation are the charge and the hard-sphere radius.

The structure factor $S(Q)$ was calculated using the Hayter and Penfold model for spheres of a given micellar charge and ionic strength, incorporating refinements for low volume fractions and a penetrating ionic background. This $S(Q)$ also allows the determination of the Debye radius and the inverse Debye length. The hard-sphere radius was allowed to vary, but the volume fraction was constrained. This method of calculating the structure factor, which assumes spherical particles, remains valid for a small degrees of micelle ellipticity, as is the case here. The ionic strength is governed by the concentrations of the unimeric SDS and the free sodium counterions of the sodium surfactant in the micelle. The last contribution may be calculated knowing the degree of dissociation of the sodium counterions, $\alpha_{Na^+}$, which we have assumed to have a constant value of 0.27. Thus, the only fitting parameters in the structure-factor calculation are the charge and the hard-sphere radius.

**Electron Paramagnetic Resonance.** Experimental details for the EPR measurements are identical to those described previously (10) and therefore, only essential details are repeated here. Stock solutions of SDS were stored in D$_2$O, and the measured intensity $I(Q)$ depends on the micellar composition via the square of the scattering length density difference $(\rho_{\text{m}} - \rho_{\text{p}})^2$. $\rho_{\text{m}}$ depends in turn on the deuterium content of the micelle. This assumes there is no isotope effect on the micelle size and shape. The micellar composition may be conveniently extracted from the EPR spectrum by fitting expressions that relate to local minima in the least-squares fits.


$(16)$ Bales, B. L.; Stenland, C. J.; Phys. Chem. 1993, 97, 3418.

from SANS measurements without any data fitting merely from the ratio of the scattering intensities $R(Q)$ obtained with h- and d-SDS at the same composition via

$$V_{\text{SDS}} = \frac{(\sqrt{R(Q)} - 1)(\rho_{\text{C_{14}BNMG}} - \rho_{\text{D_{2}O}})}{(\rho_{\text{h-SDS}} - \rho_{\text{C_{14}BNMG}}) - \sqrt{R(Q)}(\rho_{\text{d-SDS}} - \rho_{\text{C_{14}BNMG}})} \quad (7)$$

where

$$R(Q) = \frac{I(Q) h-SDS, C_{14}BNMG - B_{\text{inc}} h-SDS, C_{14}BNMG}{I(Q) d-SDS, C_{14}BNMG - B_{\text{inc}} d-SDS, C_{14}BNMG}$$

The mean value of the ratio ($R(Q)$) for $Q$ values up to $Q = 0.1 \text{ Å}^{-1}$ is used in this calculation of $x_{\text{SDS}}$. The results of the analysis are shown in Figure 1a, where the micelle composition $x_{\text{SDS}}$ is plotted in terms of the solution mole fraction $R_{\text{SDS}}$ at a total surfactant concentration of 25 mM. Shown in Figure 1b is the CMC as a function of the solution mole fraction $R_{\text{SDS}}$. The two curves describe similar behavior. At low $R_{\text{SDS}}$, $\text{CMC}_{\text{mixture}} > \text{CMC}_{\text{ideal mixing}}$ but $x_{\text{SDS}} < R_{\text{SDS}}$, i.e., the behavior is antagonistic. In contrast, at high $R_{\text{SDS}}$, the more common synergistic behavior is observed as $\text{CMC}_{\text{mixture}} < \text{CMC}_{\text{ideal mixing}}$ and $x_{\text{SDS}} < R_{\text{SDS}}$.

The scattering profiles of the two simple surfactants are shown in Figure 2. The parameters defining the fits are given in Table 1. For the SDS case, the core radius ($R_{\text{core}}$) is found to be equivalent to the all-trans length of the dodecyl tail (16.7 Å) with a shell thickness ($\delta_{\text{shell}}$) of 3.6 Å, comparable to other SANS studies. 14 In the fitting of the profile, the charge on the micelle corresponds to a 22% dissociation of Na\(^+\) counterions, in good agreement with other studies and with our assumption of $\alpha_{\text{Na}} = 27\%$. The fit to the profile of the C14BNMG is equally good. In this case, the shell is much thicker at 7.2 Å, consistent with the greater volume of the headgroup unit (527 Å\(^3\) plus 81 Å\(^3\) for the two CH\(_2\) groups). It is also entirely consistent with the equivalent result for the dodecyl homologue C12BNMG (headgroup volume 527 Å\(^3\)), where the shell thickness was 6 Å. 8,9 Most importantly, the quality of these fits provides tacit confirmation that the calculated values are physically reasonable. Also shown in Figure 2 are the structure factors pertaining to those fits. The nonionic surfactant (solid line) essentially shows a monotonic decay in $S(Q)$ as $Q$ tends to zero, representing a soft, virtually uncharged repulsive interaction. As found with the SDS/C12BNMG case, the hard sphere $S(Q)$ alone could not describe the low $Q$ scattering. The SDS structure factor (broken line) shows the expected damped oscillatory form associated with electrostatically interacting systems.

Equally good fits are observed for the various mixed systems with deuterated/protonated SDS combinations.
and, hence, aggregation number are essentially invariant with composition that is important when discussing the different estimates of mean size each technique may make. However, assuming either \( x_{SDS} = 0.27 \) or taking a separate experiment, no further interpretation should be made. However, assuming either \( x_{SDS} = 0.27 \) or taking the SDS/C12BNMG value of \( x_{Na^+} \) at the corresponding composition does not invalidate the main conclusion expressed here that \( x_{Na^+} \) increases as \( x_{SDS} \) decreases.

Examples are given in Figure 3a for \( x_{SDS} = 0.5 \) and Figure 3b for \( x_{SDS} = 0.1 \). As shown in Table 1, for all of the different anionic–nonionic mixed compositions, the same model of the micelle fits data sets obtained with both h/d contrasts, once the difference in the core scattering length density has been accounted for. This inherently confirms that only a single micelle type exists in these solutions rather than two micelle types each rich in one of the two components.

The shell thickness (\( \delta_{shell} \)) decreases monotonically with increasing \( x_{SDS} \), Figure 4a, while the core radius (\( R_{core} \)) and, hence, aggregation number are essentially invariant with \( x_{SDS} \) (Table 1). The dependencies of core radius and shell thickness on micelle composition are very similar to those observed in the SDS/C12BNMG case. However, a discrepancy in aggregation number arises: our work using time-resolved fluorescence quenching TRFQ yields \( N_{agg} \approx 45 \) for simple SDS micelles,\(^8\) while SANS gives \( N_{agg} \approx 70 \). This is commonly found when comparing different experimental approaches\(^{18}\) and may arise through the different estimates of mean size each technique is sensitive to. TRFQ gives the number concentration of micelles, while SANS measures a volume-squared weighted size (eq 1). Hence, for systems with any polydispersity, the aggregation number from TRFQ will be lower than that calculated from the mean size measured by SANS. However, it is the trend in aggregation number with composition that is important when discussing variations in micelle properties. These trends are well-reproduced in SDS micelles\(^{18}\) irrespective of the technique used.

In the calculation of the ionic strength, we have assumed that 27% of the sodium ions are dissociated from the micelle surface. From the charge on the micelle extracted from the fit (Table 1), a derived value of \( x_{Na^+} \) can be calculated [(charge per micelle)/(\( N_{agg}x_{SDS} \))]. For \( x_{SDS} < 0.5 \), the assumption of \( x_{Na^+} = 0.27 \) is rather crude. The discrepancy between the assumed and recalculated values of \( x_{Na^+} \) is significant. From the calculated charge on the micelle, we can see that the degree of sodium counterion binding/SDS molecule in the micelle is not constant over the whole mole fraction range and increases at low \( x_{SDS} \), Figure 4b. A similar observation has been made by electrochemical magnetic resonance EMR\(^{11}\) for the SDS/C12BNMG system, and those results are also shown in Figure 4b. If the degree of dissociation is greater than 0.27 (i.e. \( x_{Na^+} \) underestimated), the real ionic strength and, hence, screening length will be greater. This in turn dampens the electrostatic interaction between the micelles, leading to a low estimate for the charge on micelle. For example, refitting the \( x_{SDS} = 0.2 \) data set using an estimate for \( x_{Na^+} \) derived from the SDS/C12BNMG system, \( x_{Na^+} = 0.6 \), leads to a charge on the micelle of 13e rather than the tabulated value of 11e. On the basis of this value for the charge, \( x_{Na^+} = 0.7 \), in better agreement with the initial estimate of \( x_{Na^+} = 0.6 \). Unless \( x_{Na^+} \) is known from a separate experiment, no further interpretation should be made. However, assuming either \( x_{Na^+} = 0.27 \) or taking the SDS/C12BNMG value of \( x_{Na^+} \) at the corresponding composition does not invalidate the main conclusion expressed here that \( x_{Na^+} \) increases as \( x_{SDS} \) decreases.

Clearly, the sodium ion and sulfate headgroup prefer to be fully dissociated and hydrated but such an arrangement would lead to a significant unfavorable electrostatic interaction between adjacent headgroups over the micelle surface. This repulsion is screened by that fraction of sodium ions bound to the micelle surface. However, as the headgroups become more separated with decreasing SDS mole fraction, the fraction of sodium ions required to screen the electrostatic repulsion decreases. Alternatively, since the concentration of \( Na^+ \) in the sample is less, the activity of \( Na^+ \) associated with the micelle is reduced to be in equilibrium with the activity in the aqueous phase. Either way, \( x_{Na^+} \) increases with decreasing \( x_{SDS} \). However, for the lowest micelle mole fraction studied in the SDS/C12BNMG case (\( x_{SDS} = 0.13 \)), \( x_{Na^+} \) appears to show a sudden drop in value. This could be due to dehydration of the headgroup region with the consequence that there is insufficient water to solvate the sulfate ions. In contrast, no equivalent decrease in \( x_{Na^+} \) was found for the SDS/C14BNMG at a similarly low value of \( x_{SDS} \). Whether or not the latter system might show a decrease at an even lower \( x_{SDS} \) is an interesting question, so clearly further measurements are required in the low mole fraction region. Perhaps, it should also be remembered that the above conclusions are drawn from two very different measurement techniques, so further work should be done to compare the techniques. Given that other measurements show the behavior of SDS/C12BNMG and SDS/C14BNMG systems to be similar, it is encouraging to see that the two techniques give similar data and trends for the two systems in Figure 4b.

The polarity index \( H(25^\circ C) \), linearly related to the hyperfine coupling constant, is shown in Figure 5a as a
The polarity index increases with the mole fraction of SDS above $x_{SDS} \sim 0.2$ for both cases as more water is pulled into the headgroup region due to the much smaller sulfate headgroup. Over the region of composition $0.3 < x_{SDS} < 0.8$, the two sets of data are reasonably parallel with the SDS/C_{12}BNMG micelles with composition $x_{SDS} = 0.1$ for h-SDS (○) and d-SDS (■) in D_{2}O. The solid lines correspond to fits to the constrained model as described in the text.

The polarity index is dependent on the water present in the headgroup region and the $\text{OH}$ groups on the sugar. From the SANS analysis, $\phi_{\text{water}}$ is obtained as a fit parameter. It may also be calculated from eq 8,

$$\phi_{\text{water}} = \left[ V_{\text{shell}} - N_{\text{agg}}(x_{SDS}V_{\text{SDSheadgroup}} + (1 - x_{SDS})V_{\text{sugarheadgroup}})\right]/V_{\text{shell}}$$

where $V_{\text{shell}}$ is the volume of the shell and $N_{\text{agg}}x_{SDS}V_{\text{SDSheadgroup}} + (1 - x_{SDS})V_{\text{sugarheadgroup}}$ corresponds to the volume occupied by the headgroups.

Figure 3. (a) Intensity of scattered radiation as a function of wave vector, $Q$, for mixed sodium dodecyl sulfate (SDS)/(tetradecylmalono)bis(N-methylglucamide) (C_{14}BNMG) micelles with composition $x_{SDS} = 0.5$ for h-SDS (○) and d-SDS (■) in D_{2}O. The solid lines correspond to fits to the constrained model as described in the text. (b) Intensity of scattered radiation as a function of wave vector, $Q$, for mixed sodium dodecyl sulfate (SDS)/(tetradecylmalono)bis(N-methylglucamide) (C_{12}BNMG) micelles with composition $x_{SDS} = 0.1$ for h-SDS (○) and d-SDS (■) in D_{2}O. The solid lines correspond to fits to the constrained model as described in the text.

Figure 4. (a) SANS-derived shell thickness for (○) h-SDS/C_{14}BNMG and (■) h-SDS/C_{12}BNMG binary mixtures as a function of micellar composition $x_{SDS}$ of 25 mM mixed micelles comprising sodium dodecyl sulfate, SDS, and (tetradecylmalono)bis(N-methylglucamide), C_{12}BNMG. (b) Degree of sodium ion dissociation $\alpha_{Na^{+}}$, as a function of SDS micelle mole fraction $x_{SDS}$ for SDS in 50 mM mixed micelles of SDS/(tetradecylmalono)bis(N-methylglucamide), C_{12}BNMG (SANS results; h-SDS, ○; d-SDS, ■), and SDS/(dodecylmalono)bis(N-methylglucamide), C_{12}BNMG (electrophoretic NMR results from ref 11, □).
This formulation is similar to that defining $H(25\,^{\circ}\text{C})$, from which the number of –OH groups, $N_{\text{OH}}$, on the nonionic surfactant contribution to $H(25\,^{\circ}\text{C})$ may be estimated:

$$H(25\,^{\circ}\text{C}) = \{V_{\text{shell}} - N_{\text{agg}}(x_{\text{SDS}}V_{\text{SDSheadgroup}} + (1 - x_{\text{SDS}})V_{\text{sugarheadgroups}} + (1 - x_{\text{SDS}})V_{\text{H}_{2}\text{O}}N_{\text{OH}})\} / V_{\text{shell}}$$  (9)

Here each –OH group has the same effective volume as a single water molecule, $V_{\text{H}_{2}\text{O}} = 30\,\text{Å}^3$. Remember, $N_{\text{OH}}$ must lie between 0 and 10.

Figure 5. (a) EPR-derived polarity $A^*$ and linearly-related polarity index $H(25\,^{\circ}\text{C})$ of mixed micelles comprising sodium dodecyl sulfate, SDS, and (tetradecylmalono)bis(N-methylglucamide), C$_{14}$BNMG (●), and sodium dodecyl sulfate, SDS, and (dodecylmalono)bis(N-methylglucamide), C$_{12}$BNMG (○), as a function of micelle composition $x_{\text{SDS}}$. (b) EPR-derived polarity index $H(25\,^{\circ}\text{C})$ (○) and SANS-derived shell water volume fraction $\phi_{\text{water}}$ (●) of mixed micelles comprising sodium dodecyl sulfate, SDS, and (tetradecylmalono)bis(N-methylglucamide), C$_{14}$BNMG, as a function of micelle composition $x_{\text{SDS}}$.

Assuming that tumbling corresponds to the slowest motion of the micelle, $\tau_{\text{micelle}}$ may be calculated from eq 11 using the SANS data for $R_{\text{micelle}}$:

$$\tau_{\text{micelle}} = \frac{4\pi\eta_{\text{water}}R_{\text{micelle}}^3}{3kT}$$  (11)

Here $\eta_{\text{water}}$ is the bulk viscosity of water.

On the other hand, $\tau_{\text{relative}}$ is determined by the local dynamics and structure of the micelle:

$$\tau_{\text{relative}} = \frac{4\pi\eta_{\text{local}}R_{\text{probe}}^3}{3kT}$$  (12)

Here $\eta_{\text{local}}$ corresponds to a local or “microviscosity” and $R_{\text{probe}}$ is a parameter that describes the effective hydro-
dynamic radius of the spin-probe. For 16-DSE, a value for $R_{\text{probe}}$ of 3.75 Å has been found over a wide range of viscosities by varying water/methanol solvent composition and/or temperature. This is obviously not the actual size of the probe molecule but the effective size based on the microdynamics, a point that is discussed extensively, and validated, in ref 8.

The measured rotational correlation time ($\tau_{\text{measured}}$) and the microviscosity ($\eta_{\text{local}}$) of the spin-probe are shown in Figure 6 for both the SDS/C_{12}BNMG and SDS/C_{14}BNMG binary mixtures. With decreasing SDS mole fraction, the values of these parameters increase for both surfactant combinations. The increase in microviscosity is probably due to steric hindrance arising from the bulky sugar headgroups, which may experience significant inter-glucamide hydrogen bonding. Since these micelles do not change size or shapes significantly with $x_{\text{SDS}}$ and the overall tumbling of the micelle contributes little to the measured rotational correlation times, the transformations described by eqs 11 and 12 have little effect on the shapes of the curves obtained. The microviscosity of the shell of simple C_{14}BNMG micelles is greater than that of C_{12}BNMG, which is rather surprising as both headgroup regions are similar in structure and contain very little water. The larger C_{12}BNMG micelle has a greater headgroup volume, but its aggregation number is somewhat higher. The first few molecules of nonionic surfactant to enter the SDS micelle have a far more pronounced effect on the microviscosity for the SDS/C_{12}BNMG case than for the SDS/C_{14}BNMG case, the latter showing a constant microviscosity down to $x_{\text{SDS}} = 0.8$. This is also reflected by the greater number of OH groups contributing to $H(25 \degree C)$ for the C_{14} nonionic surfactant at $x_{\text{SDS}} > 0.8$.

Over the composition range $0.3 < x_{\text{SDS}} < 0.8$, the microviscosity of SDS/C_{14}BNMG micelles is less than that of SDS/C_{12}BNMG, consistent with the higher fraction of water in the headgroup region. However, the SDS/C_{14}-BNMG microviscosity is also more sensitive to $x_{\text{SDS}}$, presumably because the C_{14}BNMG micelles have a higher microviscosity than C_{12}BNMG micelles.

**Conclusions**

SANS and EPR have been used to study the structure of mixed anionic/nonionic surfactant micelles of SDS/C_{14}-BNMG. An elliptical core–shell morphology was found to describe the SANS data. The shell thickness decreases monotonically with mole fraction of SDS in the micelle ($x_{\text{SDS}}$), but the core radius was invariant with $x_{\text{SDS}}$ at 16.7 Å. Accordingly, the aggregation number of the mixed micelles does not vary with composition. At low $x_{\text{SDS}}$, the sugar headgroups occupy the majority of the headgroup region and the microviscosity of this region is rather high. At high $x_{\text{SDS}}$, the smaller sulfate headgroup results in a thinner headgroup region but one with a significantly greater volume fraction of water. Accordingly, the microviscosity is much lower at high $x_{\text{SDS}}$. 

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