Enthalpy and Entropy of Scission in Wormlike Micelles
Hanqiu Jiang,† Karsten Vogtt,‡ Jacqueline B. Thomas,‡ Gregory Beaucage,*‡ and Andrew Mulderig†

†Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0012, United States
‡P&G Analytical Sciences, 8700 Mason-Montgomery Road, Mason, Ohio 45040, United States

Supporting Information

ABSTRACT: The free scission energy is the thermodynamic parameter that governs the contour length of wormlike micelles (WLMs). It is the contour length and the propensity to coil and entangle that determine the viscoelastic properties of this commercially important substance class. The free scission energy $\Delta E_{sc}$ and the associated change in enthalpy $\Delta H_{sc}$ and entropy $\Delta S_{sc}$ on scission have been determined for a mixed anionic/zwitterion surfactant system (sodium laureth sulfate and cocamidopropyl betaine) at various salt concentrations (3–5 wt % NaCl). Both enthalpy $\Delta H_{sc}$ and entropy $\Delta S_{sc}$ changes decrease linearly with increasing NaCl concentration. At NaCl concentrations above 4 wt %, $\Delta S_{sc}$ even adopts negative values. The term $\Delta S_{sc}$ decreases more rapidly than $\Delta H_{sc}$ around room temperature and causes the observed elongation of WLMs upon addition of NaCl. It is suggested that $\Delta S_{sc}$ is initially positive due to fewer bound counterions per surfactant molecule at end caps compared to the intact, cylindrical parts before scission, leading to a net release of ions upon scission. Negative values of $\Delta S_{sc}$ are attributed to hydrophobic hydration occurring at the end caps at high salt concentrations. $^{23}$Na NMR measurements indicate the presence of immobilized ions, supporting a previously proposed ion-cloud model based on neutron scattering results.

INTRODUCTION
Surfactant molecules with hydrophilic head-groups and hydrophobic tails may self-assemble into aggregates, known as micelles, in aqueous solution.† Micelles do not have a fixed structure, they constantly form and disrupt structure in a dynamic equilibrium.‡,§ The equilibrium is controlled by a balance between the repulsive interactions of head-groups and the attraction of hydrophobic tails.¶ These properties are related to the chemical nature of surfactant molecules and are often altered through the addition of salt or other additives.¶ Inorganic salt is a particularly important additive used industrially to screen the electrostatic repulsions between surfactant head-groups and enhance the formation of elongated micelles.¶

In the past decades, the impact of inorganic salts on micellar formation has been extensively studied and reported.¶,§† Several techniques, such as rheology and scattering, were employed in these studies. It is well known that the addition of halide salts may induce a depression of the critical micellar concentration and the transition of micelle geometry from spheres to rods of increasing length to flexible wormlike structures. These changes may be induced by the reduction of electrostatic repulsion as well as hydration between head-groups upon addition of counterions.

The growth of WLMs relies on an increase in the end cap energy relative to the energy of a similar cylindrical section of WLM. This difference is proportional to the WLM scission energy $E_{sc}$. The scission energy was defined in the mean-field theory of Cates and Candau by the following relationship:¶

$$N = \phi^{1/2} \exp \left( \frac{E_{sc}}{2k_B T} \right)$$

(1)

where $N$ is the average number of surfactant molecules in a WLM, $\phi$ is the surfactant’s volume fraction, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature in K. The equation is valid for neutral systems and has been successfully employed for those that are highly electrostatically screened.¶ However, there are few reported values in the literature for $E_{sc}$ employed to determine the scission energy indirectly using a relation between the activation energy of breakage and the terminal relaxation time. Values between 50 and 120 kJ/mol are found for $E_{sc}$ depending on the amphiphile type and solvent condition. However, Couillet et al. point out that high values of $E_{sc}$ lead to unrealistically large values for the contour length.¶ They suggest that $E_{sc}$ is more accurately a free energy consisting of an enthalpic and an entropic part, and that the Arrhenius plots employed in the rheology-based method miss the entropic contribution. In a recent work, we scrutinized relation 1 and the possibility for an entropic contribution to

Received: August 28, 2018
Revised: October 28, 2018
Published: October 23, 2018
$E_{sc}$ was found that the introduction of a term $T\Delta S_{sc}$ indeed yields more realistic and consistent contour lengths. The Gibbs free energy of scission can be formulated as

$$
\Delta F_{sc} = 2RT \ln \left( \frac{\pi R_1^2 z^2 \rho_{WLM} N_a \times 10^{-24}}{m_{surf} \phi_{1/2}} \right) = \Delta H_{sc} - T \Delta S_{sc}
$$

(2)

where $R$ is the gas constant, $N_a$ is the Avogadro constant, $T$ is the temperature in Kelvin, and $\Delta H_{sc}$ and $\Delta S_{sc}$ are the enthalpy and the entropy of the scission, respectively. The parameters $m_{surf}$, $\rho_{surf}$, and $\phi_r$ are the mass of a single surfactant molecule in g/mol, the mass density of the micelles in g/cm$^3$, and the volume fraction of the WLMs, respectively. The WLMs are envisioned as a chain of cylindrical subunits with a length $L_1$ and a radius $R_1$ in this approach, summing up to a total number of subunits $z$. These structural parameters are determined by small-angle neutron scattering (SANS) using a hybrid scattering function, where the index “1” refers to the structure of the subunits, whereas the index “2” indicates parameters belonging to the global, overall chain structure. These structural parameters are determined by small-angle neutron scattering (SANS) using a hybrid scattering function, where the index “1” refers to the structure of the subunits, whereas the index “2” indicates parameters belonging to the global, overall chain structure. This would shift the reaction process from a mechanism yielding two end caps, Figure 1, to one yielding...
stripping model is qualitative and based on two values of \( \Delta H_{sc} \) at different salt concentrations (3 and 6 wt % NaCl). To put this hypothesis on a more solid foundation, one needs to show that \( \Delta H_{sc} \) decreases proportionally to the branch content, \( n_{br}/z \), where \( n_{br} \) is the number of branches per chain and \( z \) is the average number of subunits in a chain.

A surprising result is the occurrence of a negative entropy of scission, \( \Delta S_{sc} \), at high salt concentrations.\(^{3,3} \) Given that WLMs in solution exhibit densities similar to the surfactants in solid state (\( \sim 1.1 \text{ g/m}^3 \)), one can, in first approximation, neglect the entropy change upon scission of the WLM’s hydrophobic core and attribute \( \Delta S_{sc} \) solely to the changes in the organization of the associated (counter) ions. Indications for the presence of an ion cloud surrounding the WLMs have been demonstrated\(^{32,33} \) for the present mixed surfactant system. The number of ions associated with the WLMs scales linearly with the bulk concentration of salt. This finding will be further verified in this work by \( ^{23} \text{Na} \) nuclear magnetic resonance (NMR) measurements. It is known that end caps have a lower capacity of binding counterions due to their lower surface charge density.\(^{33} \) The free energy required for the creation of the ion cloud would need to uptake heat from the environment to leave the ion cloud and become mobile bulk ions. Alternatively, one may formulate that the release of partially immobilized, i.e., “cold” ions into the bulk effectively decreases the ion’s temperature. This heat transfer \( \Delta Q/T \) from the environment in the direction of the WLM system at constant temperature and pressure would account for a positive entropy change from the perspective of the WLM dispersion. A positive entropy change on scission has previously been related to counterions.\(^{35,36} \)

The positive entropy change on scission can be explained using an ion-cloud model;\(^{33} \) however, the occurrence of a negative scission entropy at high salt concentrations requires further explanation. Given the differences in \( \Delta H_{sc} \) and \( \Delta S_{sc} \) at high and low salt concentrations and just considering scission via breakage or branch stripping, there are two manifest sources for a negative \( \Delta S_{sc} \). First, depending on the ion-binding properties of branch points, the onset of branching may give rise to an uptake of ions upon branch stripping. If the ion-binding capacity of a given branch point is lower than that of the resulting cylindrical segment plus end cap (see Figure 2), then branch stripping would lead to the binding of ions and accordingly to a negative contribution to \( \Delta S_{sc} \).

Moreover, the increase in salt concentration may stabilize and increase the density of the WLM’s cylindrical part more than at its end caps. If the addition of salt energetically favors the presence of surfactants in the densely packed cylindrical WLM segment, then the average number of surfactant molecules in the end caps decreases. This in turn would lead to an increased exposure of the hydrophobic hydrocarbon chains to water at the end caps. At room temperature, hydration of hydrophobic groups leads to a decrease in entropy,\(^{37-39} \) possibly due to the organization of water around hydrophobic groups. Moreover, both increase in hydrophobic hydration as well as the transfer of less surfactant molecules from the cylindrical environment into a hemispherical environment in the end cap at high salt concentrations would be expected to decrease \( \Delta H_{sc} \). Although entropically unfavorable, the hydration of hydrophobic residues is usually enthalpically favorable around room temperature.\(^{37,40} \)

The change in \( \Delta S_{sc} \) for the NaCl concentration series can be explored to decide which of these two explanations, branch stripping or hydrophobic hydration, is more plausible. In ref 13 just two values at a higher (6.13%) and a lower (3.01%) NaCl concentration at 0.25% SLE1S are available for \( \Delta S_{sc} = \pm 2 \text{ J/(mol K)} \) for high salt, \( 100 \pm 20 \text{ J/(mol K) for low salt} \) and \( \Delta H_{sc} = \mp 49.6 \pm 0.5 \text{ kJ/mol for high salt, 87 \pm 5 kJ/mol for low salt} \). This does not allow for the verification of an association of the change \( \Delta S_{sc} \) with the onset/progress of branching. As outlined below, the utilization of SANS allows the assessment of the branch density, \( n_{br}/z \), of WLMs. The determination of \( n_{br}/z \) and \( \Delta S_{sc} \) for a NaCl concentration series can help to determine which of the two explanations given above, branch stripping or hydrophobic hydration, is in agreement with the observations.

Employing eq 2, \( \Delta F_{sc} \), \( \Delta H_{sc} \), and \( \Delta S_{sc} \) can be determined from the structural properties of the WLMs, namely, their contour length \( L_z \) and radius \( R_L \). In this process, the WLMs are modeled as chains with cylindrical segments, where the index 1 refers to the cylindrical subunits and the index 2 refers to the global, convoluted, and branched structure. Small-angle neutron scattering can be utilized to determine the structure. On the basis of a hybrid unified Guinier/power-law approach, the scattered intensity of WLMs can be separated according to their structural hierarchy.\(^{31,42,46} \)

\[
I(q) = I_1(q) + I_2(q)
\]

where \( I(q) \) is the overall scattering intensity and \( I_1(q) \) is the scattering intensity contributed by the cylindrical subunits the overall scattering intensity

\[
I(q) = \int_0^{\infty} N(R_s)G_1P_{cyl}(q, R_s, L_1) dR_s
\]

where \( P_{cyl}(q) \) is the form factor for a cylinder.

A distribution function \( N(R_s) \) accounts for polydispersity of the cross-sectional radius of the cylindrical subunits, \( R_s, L_1 \) is the length of the cylindrical subunits. The value \( G_1 = I_1(0) \) is given by \( N/V(\Delta \rho)^2 V_{cyl1} \), where \( N/V \) is the number density of cylindrical subunits, \( V_{cyl1} = (\pi R_s^2 L_1) \) is the volume of the cylinders and \( \Delta \rho \) is the difference between the scattering length density \( \rho_{cyl1} \) of the cylindrical subunits and the solvent \( \rho_s \). \( I_1(q) \) is the scattering intensity of the higher structural level with interconnected subunits that is formulated as follows

\[
I_1(q) = G_2 e^{-(q^2 R_s^2)/3} + B_2 e^{-(q^2 R_z^2)/3}G_1^2 q^2 \text{erf} \left( \frac{q R_z}{2} \right)
\]

where \( q = \frac{q}{\text{erf}(x)} \) and \( \text{erf}(x) \) is the error function.

The scattering function is fully described by Vogtt et al.\(^{26} \) Of special importance is the weight average number of subunits \( z \) that can be calculated from the scattered intensity at zero angle \( G_1 \) for the structural levels \( i = 1, 2 \).

\[
z = \frac{G_2}{G_1} + 1
\]

Using \( z \), the parameter \( n_{br} \) can be calculated as follows.\(^{43} \)

\[
n_{br} = \frac{z^2}{d_{cyl}} - 1
\]

where \( d_{cyl} \) is the fractal dimension of the WLM. The parameter \( c \) is the connectivity dimension \( c = d_{cyl}/d_{min2} \), where \( d_{min2} \) is the minimum dimension of the fractal-like object. For linear
WLMs, assuming a self-avoiding walk of the cylindrical subunits, $d_{min,2} = 5/3$. The connectivity dimension $c = 1$ for unbranched WLMs and $c > 1$ for branched systems given that the formation of other structures than cylinders can be ruled out. For $d_{c2} = 1.67$, $c = 1$ and the chains are unbranched or linear. For $d_{c2} > 1.67$, the chains are branched.

With these parameters, the change in the scission entropy $\frac{d\Delta S_{sc}}{d\phi_{NaCl}}$ as well as the change in the scission enthalpy $\frac{d\Delta H_{sc}}{d\phi_{NaCl}}$ with the salt mass fraction can be compared with the development of branching. Then, the applicability of the possible explanations for the observed $\Delta S_{sc}$ and $\Delta H_{sc}$ can be evaluated.

**MATERIALS AND METHODS**

Surfactant mixtures were made from a mix of a common anionic surfactant, sodium laureth-1 sulfate (SLE1S, commercially available as STEOLCS-170) at 0.179 wt % (5.70 mM), and a zwitterionic surfactant, cocamidopropyl betaine (CAPB, commercially available as Amphotol HCA-HP) at 0.021 wt % (0.648 mM), with a molar ratio of 9:1 in deuterated water, as shown in Figure 3. (Both surfactants are available from Stepan Chemical, Northfield, Ill.) This binary surfactant mixture was chosen because it has been seen to produce stable WLM structures and serves as a model for more complicated commercial surfactant mixtures. A series of salt concentrations, NaCl at 3.01, 3.56, 4.01, and 5.00 wt % (0.57, 0.67, 0.75, and 0.94 M), were investigated at three temperatures, 15, 25, and 35 °C. The salt and surfactant concentration ranges were selected to ensure the presence of WLMs in dilute condition as shown in the pseudo-phase diagram given in Figure 4. At salt concentration around 6%, the surfactant system becomes hazy and shows the tendency to phase separate. Data points in Figure 4 are evaluated based on the SANS results from the measured samples. The corresponding scattering profiles have been plotted selectively in Figure S4 of the Supporting Information.

SANS data were measured on the GP-SANS instrument at Oak Ridge National Laboratory, Oak Ridge, TN. Data were reduced by procedures provided by the beam line. Data sets after reduction and background correction were fitted as described in ref 26. Previous SANS data of a concentration series33 have shown that samples at a weight fraction of 0.2% are sufficiently dilute to avoid any overlap between WLMs.

NMR measurements were performed to verify the premise of the ion-cloud model33 that ions are immobilized near the micelles in numbers far greater than a monolayer, and that this ion cloud does not display saturation. NMR samples were prepared by placing Na+ surfactant solutions in 5 mm NMR tubes. An external reference standard of Na-Dy(PPP)$_2$ ([Na$^+$] = 0.40 M) in a coaxial 2 mm NMR tube was then inserted for each experiment. A $\Pi/2$ pulse length of 16 $\mu$s was measured and used for all $^{23}$Na NMR experiments. The experiments were performed at 25 °C and recorded at 105.84 MHz on a Bruker Avance III 400 MHz (9.4 T) spectrometer equipped with a 5 mm broadband probe. The same NMR parameters and data analysis were adopted for single-quantum (SQ) and double-quantum filtered (DQF) experiments as reported in previous studies.44 For each sample, SQ and DQF experiments were recorded with an identical number of scans (64), repetition times, and receiver gains. The SQ and DQF spectra were processed and analyzed using MestReNova software (Mestrelab Research, S.L., Santiago de Compostela, Spain).

**RESULTS AND DISCUSSION**

Figure 5 is a log–log plot of scattered intensity versus scattering vector for samples with increasing NaCl concen-

Figure 4. Pseudo-phase diagram of the studied mixed surfactant system at 25 °C. Gray dotted lines are drawn just for the guidance of eyes. Points highlighted with red dotted lines correspond to the samples in this study.

Figure 5. Log–log plot of scattered intensity versus scattering vector for samples with 0.2% MS at 25 °C with varying NaCl concentrations.
from a concentration series. The large-scale structural features ($L_2$ and $z$) for the samples at higher salt concentration have relatively large error bars, as given in Table S1 in the Supporting Information, because the changes occur at the lower $q$-limit of the SANS instrument. The micellar contour length ($L_2$), as well as number of cylindrical subunits ($z$), was found to increase with salt concentration, whereas opposite trend was observed with increasing temperature. The length of cylindrical subunits, $L_2$, is around 600 ± 100 Å. Variations in $L_2$ at different temperatures and salt concentrations are small. The radius of the micelles remains constant with respect to salt concentration and becomes slightly smaller at higher temperatures. From these parameters, the average number of surfactants in a micelle ($\bar{N}$) can be determined. $\bar{N}_i$ in turn, allows the calculation of $\Delta F_{sc}$.

The free energies of scission are calculated based on eq 1 and plotted against temperature as shown in Figure 6. A linear relationship between $\Delta F_{sc}$ and temperature is observed at all salt concentrations. Note that the error bars depict the maximum expected inaccuracy as calculated from the error propagation based on the SANS counts. The enthalpy and entropy of scission are obtained through fits of $\Delta F_{sc}$ based on eq 1. They are summarized in Tables 1 and 2. $\Delta F_{sc}$ has only slight variation with temperature. The absolute values at different salt concentrations differ significantly. A decrease in both $\Delta S_{sc}$ and $\Delta H_{sc}$ with salt concentration is observed. As $T\Delta S_{sc}$ decreases more rapidly compared to $\Delta H_{sc}$, the overall $\Delta F_{sc}$ increases with increasing NaCl concentration as does the average contour length.

The average number of surfactant molecules per WLM, $\bar{N}$, is given as a function of salt concentration and temperature in Figure 7. As expected, $\bar{N} \propto L_2$ is smaller for higher temperatures and increases exponentially with increasing salt concentration since $\Delta F_{sc}$ is linear in $\phi_{w,NaCl}$ and eq 1 predicts an exponential dependence of $\bar{N}$ on $\Delta F_{sc}$. At low surfactant concentration, the contour length $L_2$ is the main factor governing the viscoelastic behavior. With these values of $\bar{N}$, $L_2$, and $R_t$, a surfactant head-group area of 50 Å² is calculated, in very good agreement with literature values for the very similar surfactant sodium dodecyl sulfate.

Table 1. Free Energy, Enthalpy, and Entropy of Scission of 0.2% Mixed Surfactant with Various Salt Concentrations at 15, 25, and 35 °C

<table>
<thead>
<tr>
<th>% NaCl (wt %)</th>
<th>T (°C)</th>
<th>$\Delta F_{sc}$ (kJ/mol)</th>
<th>$\Delta H_{sc}$ (kJ/mol)</th>
<th>$\Delta S_{sc}$ (J/(mol K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.01</td>
<td>15</td>
<td>62.1 ± 0.8</td>
<td>79 ± 3</td>
<td>60 ± 10</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>61.7 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>60.9 ± 1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.56</td>
<td>15</td>
<td>65.4 ± 1.2</td>
<td>74 ± 1</td>
<td>30 ± 4</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>65.1 ± 1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>64.8 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.01</td>
<td>15</td>
<td>66.8 ± 1.1</td>
<td>71 ± 2</td>
<td>16 ± 7</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>66.5 ± 1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>66.4 ± 0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.00</td>
<td>15</td>
<td>70.4 ± 1.5</td>
<td>60 ± 3</td>
<td>−38 ± 9</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>71.0 ± 2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>71.2 ± 3.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. $n_{sc}$ and $n_{br}/z$ of 0.2% Mixed Surfactant with Various Salt Concentrations at 15, 25, and 35 °C

<table>
<thead>
<tr>
<th>% NaCl</th>
<th>T (°C)</th>
<th>$n_{sc}$</th>
<th>$n_{br}/z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.01</td>
<td>15</td>
<td>11 ± 2</td>
<td>0.008 ± 0.002</td>
</tr>
<tr>
<td>3.56</td>
<td>15</td>
<td>26 ± 6</td>
<td></td>
</tr>
<tr>
<td>4.01</td>
<td>15</td>
<td>40 ± 8</td>
<td>0.6 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>80 ± 20</td>
<td>0.5 ± 0.4</td>
</tr>
<tr>
<td>3.01</td>
<td>25</td>
<td>8 ± 1</td>
<td></td>
</tr>
<tr>
<td>3.56</td>
<td>25</td>
<td>14 ± 2</td>
<td></td>
</tr>
<tr>
<td>4.01</td>
<td>25</td>
<td>18 ± 3</td>
<td>0.1 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>50 ± 20</td>
<td>0.5 ± 0.4</td>
</tr>
<tr>
<td>3.01</td>
<td>35</td>
<td>5 ± 1</td>
<td></td>
</tr>
<tr>
<td>3.56</td>
<td>35</td>
<td>10 ± 1</td>
<td></td>
</tr>
<tr>
<td>4.01</td>
<td>35</td>
<td>13 ± 1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>40 ± 10</td>
<td>0.5 ± 0.4</td>
</tr>
</tbody>
</table>

Figure 6. Free energy of scission $\Delta F_{sc}$ as a function of temperature at a constant surfactant weight fraction of 0.2% with 5% (□), 4.01% (△), 3.56% (■), and 3.01% (●) NaCl.

Figure 7. Average number of surfactants contained in a micelle versus NaCl weight fraction. The dashed lines follow eq 1 under the assumption that the scission energy is linear in salt concentration.
on scission decreases with increasing salt concentration, consistent with $\Delta H_{sc}$ previously reported for the pure SLE1S system. However, the overall moderate change in $\Delta H_{sc}$ between 3 and 5 wt % NaCl of about 25% is not compatible with the branch-stripping explanation given in the previous work. Although $\Delta H_{sc}$ decreases continuously in a linear manner, the branching sets in at 4 wt % NaCl as visible from $n_{br}$, average number of branch points per micelle, and $n_{br}/z$, number of branches per Kuhn unit, as shown in Table 2. Below this NaCl concentration, there is no reason to assume the presence of branches despite the large error bars for $n_{br}$. The fact that $\Delta H_{sc}$ decreases in the absence of branches rules out branch stripping as a competitive scission mechanism that causes the decrease in enthalpy of scission.

In a similar manner, the impact of branch points on the change in $\Delta S_{sc}$ can be ruled out. $\Delta S_{sc}$ decreases likewise continuously even in the absence of branches, reaching $\Delta S_{sc} \approx 0$ at about 4.2 wt % NaCl and becomes negative at a higher salt concentration. Accordingly, the more likely explanation is the increase in hydrophobic hydration at the end caps rather than the onset of branch stripping.

The hydrophobic hydration model has the advantage that it can explain both $\frac{\Delta S_{sc}}{\Delta H_{sc}}$ and the change in the scission enthalpy $\Delta H_{sc}$ without making additional assumptions on putative properties of branch points. The expected stabilization of the cylindrical WLM sections with more bound ions at higher salt level relative to end caps suffices as an explanation for both (see Figure 9). As indicated by both ion-cloud model and $^{23}$Na NMR results, which will be discussed below, addition of NaCl leads to the binding of more ions per surfactant molecule and a denser, energetically more stable packing of the cylindrical geometry. Stabilization of the cylindrical sections decreases the number of surfactants per end cap. Scission at high salt concentration leads accordingly to end caps with fewer surfactant molecules. The loosely packed end caps are more exposed to water, leading to more pronounced hydrophobic hydration, i.e., increasingly negative entropy $\Delta S_{sc}$. Alternatively, one may envision the hemispherical end caps at high salt concentration as swollen by radial displacement of surfactant molecules and penetration of water molecules, which would exhibit the same result. It can be said that hydrophobic hydration increases with increasing NaCl concentration at the end caps because this effect alone has been observed to lead to the trends of $\Delta H_{sc}$ and $\Delta S_{sc}$ with salt concentration.

The model outlined above necessarily requires the presence of two ion populations, bound and free, to explain the observed entropy changes. It has been shown that $^{23}$Na NMR spectroscopy is a useful technique in characterizing sodium mobility in various systems. Theoretically, the total sodium population (both restricted and unrestricted) is measured using SQ experiments, and DQF experiments filter out the signal from the unrestricted sodium ions and therefore are a direct measure of the “bound” sodium ions.

Measurements to assess the mobility of the sodium ion population have been performed. $^{23}$Na SQ and DQF spectra of mixed surfactant samples with increasing salt concentration are plotted in Figure 10. The peak with negative dips in the DQF
spectra is a typical feature indicating the presence of bound ions.\textsuperscript{44–46}

The molar concentration of Na\textsuperscript{+} was determined from the area under the peak of SQ spectra and normalized by the signal of the external reference. The obtained Na\textsuperscript{+} molar concentrations were converted to NaCl weight fractions (3.1, 3.6, 4.6, 4.8, and 5.4\%) show good agreement with the sample fabrication values (3.01, 3.56, 4.01, 4.5, and 5%). As expected, the samples in the presence and absence of surfactant at the same salt level have very similar \textsuperscript{23}Na SQ spectra, shown on the left of Figure 10, indicating that the presence of surfactant does not affect the acquirement of the Na\textsuperscript{+} resonance signal. The bound fraction of Na\textsuperscript{+} was determined by the ratio of the integration of the DQF signal to that of the SQ signal. Theoretically, if only free Na\textsuperscript{+} is present in the measured solution (pure salt solution), a flat line without a peak is expected for the DQF spectrum. However, due to high Na\textsuperscript{+} concentration, a small contribution was observed in the control samples (bottom right spectrum in Figure 10, average 12 $\pm$ 2\%), which was accounted for in the reported values.

Figure 11 shows the dependence of the bound fraction (DFQ) of Na\textsuperscript{+} (red circles and left axis) as a function of the overall weight percent Na\textsuperscript{+} (SQ). The bound fraction (DFQ) of Na\textsuperscript{+} is the number of bound Na\textsuperscript{+} divided by the number of all Na\textsuperscript{+} in the system. Based on the ion-cloud theory,\textsuperscript{33} this value should remain constant with increasing salt concentration. The bound fractions (DFQ) of Na\textsuperscript{+} remained roughly unchanged with increasing salt level in the measured samples, as shown in Figure 11. The number of bound Na\textsuperscript{+} per surfactant (green open squares and right axis), also plotted in Figure 11, increases from about 40 (3.01% NaCl) to about 80 (5% NaCl). The counterion association and related theories are often studied under relatively low salt-to-surfactant ratios or even in the absence of salt where the degree of counterion binding is limited by the charge of the micelles. In these cases, the number of counterions per surfactant is lower than 1.\textsuperscript{50,51}

The ion-cloud model, developed from the mathematical result of SANS measurements for samples with high salt-to-surfactant ratios,\textsuperscript{33} is based on the assumption that ion binding to the micelle cannot saturate, that is, the charge of the bound counterions can exceed the charge of the surfactants to a great extent. The counterion concentration in the ion-cloud model scales with the increasing salt concentration. The relatively
constant bond fraction of Na\(^+\) with increasing NaCl concentration and the high ratio of bound Na\(^+\) to surfactant as measured by NMR are in agreement with the ion-cloud model developed based on SANS measurements.\(^3\) Further improvement of the ion-cloud model is necessary for better understanding of this special ion behavior and the related thermodynamic impact on micellar systems. The data also suggest the presence of at least two types of sodium ions differing with respect to their mobility, as postulated by the proposed hypothesis. These are preliminary results from a first series of DQF \(^{23}\)Na NMR measurements on a surfactant caps. The occurrence of negative values of \(\Delta \)Na indicates the presence of excess bound ions. From a structural perspective, ascription of the observed \(\Delta H_{\text{sc}}/\Delta S_{\text{sc}}\) to an increase in hydrophobic hydration at the end caps is the simplest explanation. It would imply that the breakage of WLMs is dominated by the scission of the cylindrical part leading to the formation of two end caps. This occurs in the absence as well as in the presence of branches under the observed experimental conditions.

The SANS model as well as the thermodynamic model employed in this study are surely simplified and of an approximate nature. It is a bit surprising that these simple models yield plausible results. As a continuation of the results presented in ref 13, the applied SANS approach has proven a robust method capable of obtaining verifiable results. For further improvement, a more accurate determination of the scattered intensity \(I(q)\) at low \(q\) values would be required. The scattered intensity in the low-\(q\) region contains information on the WLM contour length. Accordingly, more accurate data at a lower \(q\) will provide more accurate values for the number of subunits \(z\) and the branch content \(n_{\text{br}}\). This would allow testing of more complex theoretical models.

**CONCLUSIONS**

WLM scission energies \(\Delta F_{\text{sc}}\) have been determined for a mixed surfactant system consisting of SLE1S and CAPB at various temperatures and salt concentrations using SANS and a structural model that allows determination of contour lengths and radii. The enthalpy and entropy of scission were determined by linear fits of \(\Delta F_{\text{sc}}\) as functions of temperature. The energies \(\Delta H_{\text{sc}}\) and \(\Delta S_{\text{sc}}\) decrease with increasing salt concentration. At salt concentrations above 4 wt % of NaCl, \(\Delta S_{\text{sc}}\) adopts negative values. The positive values of \(\Delta S_{\text{sc}}\) can be understood in terms of bound or associated ions, which are released upon scission and formation of hemispherical end caps. The occurrence of negative values of \(\Delta S_{\text{sc}}\) can be explained through a model involving increased hydrophobic hydration of the end caps at high salt concentrations. This hypothesis can explain the decrease in both \(\Delta H_{\text{sc}}\) and \(\Delta S_{\text{sc}}\).

Initial \(^{23}\)Na NMR measurements indicate the presence of immobilized as well as mobile ions, as hypothesized in the previously proposed ion-cloud model. Approaching the WLM system from a structural point of view using SANS in combination with the hybrid wormlike chain scattering function has proven a fruitful method that allows formulation and scrutiny of model-based expectations.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b02930.

Micellar size parameters (Table S1); scattering profiles and fits of studied samples at 15, 25, and 35 °C (Figures S1–S3); scattering profiles of micelles with different geometries (Figure S4) (**PDF**)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: gbeaucage@gmail.com.*

**ORCID**

Karsten Vogtt: 0000-0003-3206-1070

Gregory Beaucage: 0000-0002-6632-0889

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was funded by P&G. The work relied on the expertise and assistance of Yuri Melnichenko at GP-SANS, ORNL. A portion of this research used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

**REFERENCES**


