The characteristic curvature (Cc) of ionic surfactants assessed via Small-Angle X-ray Scattering (SAXS)

Zhuotao Leng¹, Edgar Acosta¹*

¹ University of Toronto, Department of Chemical Engineering and Applied Chemistry (200 College Street, Toronto, Ontario, M5S3E5)

* Corresponding author. Email: edgar.acosta@utoronto.ca

Abstract:

The characteristic curvature (Cc), within the Hydrophilic-Lipophilic Difference + Net (Hn) - Average (Ha) Curvature (HLD-NAC) framework, is the dimensionless net curvature, Hn·L (L is the surfactant’s tail length parameter), that a surfactant acquires at the characteristic condition (T=25°C, no added cosurfactants, oil with an equivalent alkane carbon number (EACN) of zero, and for ionic surfactants, a total salinity (S) of 1 g NaCl/100 mL). A recent article demonstrated the validity of the Cc concept, where Hn was assessed via oil and water solubilization radii. Here, we assess Hn from the characteristic length (ξ) obtained from the analysis of SAXS profiles of microemulsions produced at semi-characteristic conditions (characteristic condition, but varying S). The predicted relationship, -L·Hn_{semi-characteristic} = Cc_{bi} + bi·ln(S), was confirmed with the five ionic surfactants explored. The SAXS-assessed Cc (Cc = Cc_{bi}/bi) values are consistent with those obtained from solubilization studies and phase inversion scans. The Cc-SAXS method provides a way to assess the hydrophobicity of ionic surfactants directly, avoiding the bias that could be introduced by cosurfactants in phase inversion studies; and minimizing the impact of potential uncertainties in the surfactant volume-to-area ratio (v_s/a_s) required to calculate the solubilization radii in the solubilization method.

Keywords: microemulsion, anionic surfactant, cationic surfactant, extended surfactant, SAXS, HLD, NAC, curvature
1 Introduction

Understanding the hydrophobicity of a surfactant in a surfactant-oil-water (SOW) system is vitally important to predict the behavior of SOW systems and guide the formulation of microemulsions (µEs), emulsions, and related systems. The hydrophilic-lipophilic balance (HLB) is the best-known surfactant hydrophobicity parameter, which was introduced by Griffin in the late 1940s using an empirical scale based on emulsion stabilities obtained with various oils. Shinoda noted that, among other shortcomings, the HLB did not reflect the temperature-sensitivity and salt-sensitivity of most nonionic surfactants and proposed the phase inversion temperature (PIT) as an alternative centered in thermodynamics. The phase inversion of the surfactant refers to the change in surfactant partition from being primarily in water to being primarily in oil. The phase inversion reflects the difference in surfactant chemical potential in water and in oil.

The packing factor is another popular scale for surfactant hydrophobicity classification based on the geometry of the surfactant packing in micelles and other self-assembled structures. However, the packing factor has the limitation that the area per molecule of the surfactant used in the packing parameter calculation depends on the curvature of the system and, therefore, on the formulation conditions. Various advances have been made to implement a modified form of the packing parameter to predict SOW properties, but the connection between the packing parameter and formulation conditions is still incomplete.

In the 1970s and 80s, the study of µEs (SOW systems in thermodynamic equilibrium) for enhanced oil recovery led to the development of numerous studies and empirical correlations to determine what conditions led to the phase inversion point, where the interfacial tension (IFT) is minimum, and the oil recovery from reservoirs is facilitated. The most impactful of those empirical correlations is found in the PhD thesis of Salager, where the author introduced the expression

\[
\ln(S^*) = k \cdot \text{EACN} + f(A) - \sigma + \ldots
\]

The term \(S^*\) is the optimal salinity, or the salinity (in g NaCl/100 mL of aqueous phase) required to achieve the phase inversion point (PIP). EACN is the equivalent alkane carbon number and is determined experimentally from PIP data for most oils, but it is the number of carbon atoms in the linear chain of n-hexane to n-hexadecane oils. The term \(f(A)\) was meant as a placeholder function, mostly linear functions, representing the effect of the alcohol or cosurfactant added. The term \(\sigma\) was labeled as the surfactant parameter, but its physical significance was not fully stated, given that it could also be affected by other conditions that were...
not identified at the time. The S*, in many ways, was similar to the concept of PIT of Shinoda, but its explicit dependence on oil hydrophobicity (EACN) and the recognition that other factors could affect S*, such as the effect of alcohol or temperature in itself, made the formulation correlation of Salager a more comprehensive correlation than the PIT value. Salager’s team introduced many advances to the empirical correlation, including its expansion to nonionic surfactants. In the year 2000, Salager’s team introduced a publication confirming the thermodynamic significance of the formulation correlation for nonionic surfactants, by then re-labeled as HLD (Hydrophilic-Lipophilic Deviation, or Difference, as it is referred to here)\(^9\). The HLD equation for ionic surfactants in the absence of cosolvents is:

\[
HLD = \ln(S) - k \cdot \text{EACN} + \sigma - a_T \cdot (T-25^\circ\text{C}) \quad \text{Eq. 1}
\]

For nonionic surfactants, the HLD equation in the absence of cosolvents is:

\[
HLD = b \cdot S - k \cdot \text{EACN} + \sigma_n + c_T \cdot (T-25^\circ\text{C}) \quad \text{Eq. 2}
\]

The prefactors \(k\), \(a_T\), \(b\), and \(c_T\) are constants that depend on the selected surfactant.

According to the 2000 article, the HLD was found to represent the normalized difference in the chemical potential of the surfactant in oil (\(\mu_s^o\)) and water (\(\mu_s^w\)), \(\text{HLD} \sim (\mu_s^w - \mu_s^o)/RT\), where R is the universal gas constant, and T the temperature of the system\(^9\). This chemical potential interpretation of HLD was used in the Net-Average Curvature (NAC) model to assess the chemical potential “distance” to the net-zero curvature (phase inversion point) state, considered a critical state by the NAC model. The NAC uses critical scaling modeling to assess the net curvature (\(H_n\)) of the interface of \(\mu E\) systems and the average curvature (\(H_a\)) to track the size of \(\mu E\) domains\(^10\).

The NAC model describes the interface using two alternate states, one where oil is solubilized in spheres with solubilization radius \(R_o\), and the second where water is the solubilized phase with solubilization radius \(R_w\). Each solubilization radius can be calculated knowing the volume fraction of the solubilized phase (\(\varphi\)), the volume fraction of the surfactant (\(\varphi_s\)) and the surfactant volume to area ratio (\(v_s/a_s\)), such that \(R (R_o \text{ or } R_w) = 3(\varphi/\varphi_s)(v_s/a_s)\). The net curvature (\(H_n\)) is:

\[
H_n = \left( \frac{1}{R_o} - \frac{1}{R_w} \right) = -\frac{\text{HLD}}{L} \quad \text{Eq. 3}
\]

The average curvature (\(H_a\)) is:

\[
H_a = \left( \frac{1}{2} \right) \left( \frac{1}{R_o} + \frac{1}{R_w} \right) = \frac{1}{\xi} \quad \text{Eq. 4}
\]
For a given set of formulation conditions, the solubilization radii of oil and water (Ro, Rw) can be known by determining the phase volumes of the µE or by measuring the volume fractions of water, oil and surfactant in the µE via liquid chromatography or other means. In that case, one calculates the value of HLD from curvature using Eq. 3, such that \( \text{HLD}_{\text{curvature}} = -H_n\cdot L = -L(1/Ro - 1/Rw) \).

This HLD should, in principle, be the same as the HLD obtained from the empirical correlations in Eq. 1 or 2. Furthermore, if one applies the characteristic condition, \( T = 25^\circ\text{C}, \ S = 1 \ \text{g NaCl}/100 \ \text{mL} \) for ionic surfactants, \( \text{EACN} = 0 \), then from Eq. 1, \( \text{HLD}_{\text{correlation, characteristic}} = \sigma \). If the chemical potential interpretation of HLD holds for ionic surfactants, then \( \text{HLD}_{\text{curvature, characteristic}} = -L\cdot H_n \text{characteristic} \) should be the same as \( \text{HLD}_{\text{correlation, characteristic}} \). This interpretation led to the renaming of \( \sigma \) as the characteristic curvature or \( Cc \), where \( Cc = -L\cdot H_n \text{curvature, characteristic} = \sigma \).

The interpretation of \( \sigma \) as \( Cc \) was recently tested by Leng and Acosta using solubilization studies that evaluated Ro and Rw as a function of salinity (including \( S = 1 \ \text{gNaCl}/100 \ \text{mL} \)) at the semi-characteristic condition of \( T = 25^\circ\text{C} \) and \( \text{EACN} = 0 \) obtained by using a 50/50 (vol/vol) mixture of toluene and ethyl benzoate (TETB) as oil phase, and without cosurfactants or cosolvents. These solubilization studies revealed that for ionic surfactants, \( \text{HLD}_{\text{correlation}} \) had to be scaled by a term “bi” to reflect the changes in chemical potential properly. The new corrected term, \( \text{HLD}_{\text{bi}} = bi\cdot \text{HLD} \), was found to be equivalent to \( -L\cdot H_n \text{curvature} \). The new \( \text{HLD}_{\text{bi}} \) correlation equation is:

\[
\text{HLD}_{\text{bi}} = bi\cdot \ln(S) - k_{bi}\cdot \text{EACN} + C_{cbi} - a_{T_{bi}}(T-25^\circ\text{C}) \quad \text{Eq. 5}
\]

Considering that \( -L\cdot H_n \text{curvature} = \text{HLD}_{\text{bi}} = bi\cdot \text{HLD} \), then \( C_{cbi} = bi\cdot Cc \), or alternatively, \( Cc = C_{cbi}/bi \).

The solubilization studies of Leng and Acosta considered various salinities (not only \( S = 1 \)), setting \( T = 25^\circ\text{C} \) and \( \text{EACN} = 0 \). The researchers plotted \( -L\cdot H_n \text{curvature} = -L\cdot (1/Ro - 1/Rw) \) vs. \( \ln(S) \), where \( S \) is the total salinity of the system (added salt plus unbound electrolyte). This plot resulted in lines where the slope represented “bi”, and the intercept represented “\( C_{cbi} \)”, whereby \( Cc \) was assessed as \( C_{cbi}/bi \). Leng and Acosta found that the values of \( Cc \) determined via the solubilization method often match the \( Cc \) from phase behavior, considering a 20% uncertainty.

Although the \( Cc \)-solubilization method represents a step forward in determining the intrinsic hydrophobicity of surfactants, it is still an indirect assessment of a nanoscale curvature. A direct assessment of curvatures involves using small angle scattering of X-rays (SAXS) or a neutron beam (SANS) with wavelengths of similar size or smaller than the µE domains explored. This work aims to explore the use of SAXS in determining \( Cc \).
2 Small Angle Scattering and the Net-Average Curvature (NAC)

The first work that explored the connection between HLD-NAC and scattering techniques explored the prediction of average size ($\xi \sim 1/\text{Ha}$) of $\mu$E domains with the characteristic length ($\xi$) obtained from the Teubner-Strey model fitted to SANS profiles of bicontinuous $\mu$Es and the Porod radius of micellar and reverse micellar systems\textsuperscript{13}. In that work, the neutron scattering profiles were obtained using core scattering length density (SLD) contrast with deuterated solubilized phases and film contrast with deuterated external and solubilized phases. The second study that explored the SANS-NAC connection also involved the net curvature ($H_n$) by interpreting this term as the area-averaged curvature of $\mu$E domains in the form of cylinders with hemispherical caps\textsuperscript{14}. In that study, the SANS profiles for drop-type $\mu$Es were predicted considering the radius ($R_d$) and length ($L_d$) of the capped cylinders predicted by the HLD-NAC.

The two studies showing the connection between HLD-NAC and SANS profiles support the hypothesis that SAXS could be used to determine the $C_c$ of ionic surfactants. The reason to focus on SAXS, instead of SANS, is the greater accessibility to benchtop SAXS instrumentation than SANS nuclear reactor beamlines. There are two drawbacks to using benchtop SAXS over SANS: the lower energy flux of benchtop SAXS beams and the inability to implement film or core contrast in SAXS.

In general terms, the scattered intensity “$I$” detected at different scattering vectors “$q$” ($q = 4\pi \sin(\theta/2)/\lambda$, where $\theta$ is the scattering angle, and $\lambda$ is the wavelength of the beam) is often expressed as $I = C \cdot P(q) \cdot S(q)$, where $C$ is a term involving the concentration of colloidal domains (e.g., microemulsion drops), $P(q)$ is known as the form factor that considers the interactions of the beam with the electrons (for SAXS) or neutrons (for SANS) inside a single colloidal domain, and $S(q)$ is known as the structure factor that is often associated with the inter-particle interactions\textsuperscript{15}.

The analysis of SAXS profiles often follows one of two approaches, a dilute or a concentrated colloidal approach. In the dilute colloid approach, the separation between the colloidal domains is large enough that inter-particle interactions can be neglected, and one can assume $S(q) = 1$. In that case, the scattering profile is often fit using models of form factors, $P(q)$, derived for a given colloid shape (e.g., spheres, ellipsoids, etc.). The examination of SAXS profiles of dilute drop-type $\mu$Es or micellar solutions often requires the use of the core-shell ellipsoidal form factors that can reflect the fact that the electron density of the micelle core is different from the electron density of the
surfactant head groups (the shell) and different from the aqueous (solvent) phase electron density. The analysis of SAXS scattering profiles to obtain actual dimensions of µE environments is often met with skepticism because the electron density profile around the surfactant headgroup follows a Gaussian distribution and not a step function (slab model) often assumed in form factor models used to extract shape and dimensions.

In the concentrated colloidal approach, the inter-particle interactions dominate the scattering profile \( S(q) \neq 1 \). In those cases, one loses the ability to extract detailed shape information, but the available models give an idea of the volume-to-area ratio of the colloidal domains. One of the most reliable models used to analyze SAXS profiles of bicontinuous µE systems is the Teubner-Strey model. The Teubner-Strey (T-S) model is an empirical model of the form:

\[
I(q) = \frac{1}{a_2 + c_1 q^2 + c_2 q^4}
\]

where \( a_2 > 0, c_1 < 0, \) and \( c_2 > 0 \), and can be used to determine two length scales of the correlation or characteristic length \( (\xi) \) and the periodicity \( (d) \):

\[
\xi = \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{\frac{1}{2}} + \frac{1}{4} \left( \frac{c_1}{c_2} \right) \right]^{-\frac{1}{2}}
\]

\[
d = 2\pi \left[ \frac{1}{2} \left( \frac{a_2}{c_2} \right)^{\frac{1}{2}} - \frac{1}{4} \left( \frac{c_1}{c_2} \right) \right]^{-\frac{1}{2}}
\]

Given the robustness of the T-S model to fit µE scattering profiles, this model will be used as a default model to analyze the scattering profiles of the SOW systems considered in this work. However, as it will be shown later, not all SOW systems can be properly analyzed with the T-S model because this model assumes that the µE environments are interconnected, which is not true in all cases, especially for nearly spherical or ellipsoidal oil-swollen micelles under dilute conditions. For those cases, we will analyze the scattering profile using the core-shell ellipsoidal (EL) model programmed in SasView, whose equations and implementation method are shown in the supplementary information file.

This work also introduces a third method of simplified analysis of the scattering profile, which we termed the transition or “TM” method. The transition method reflects the observation that at a
given “q_TR” the slope of the log(I) vs. log(q) curves change, and this q_TR reflects the area-to-volume ratio of µE domains, such that\textsuperscript{15}:

$$\xi \sim \frac{3}{q_{TR}}$$ \hspace{1cm} Eq. 9

The characteristic length (\(\xi\)) obtained after fitting SAXS profiles can be directly interpreted as the inverse of the average curvature of the SOW system (\(H_a \sim 1/\xi\) from Eq. 4). For the case of oil-swollen micellar systems with a continuous aqueous phase, one could assess the solubilization of oil (Ro) from \(\xi\) (from SAXS) using Eq. 4 such that: \(1/Ro = 2/\xi – 1/R_w\). In most micellar solutions, \(R_w \gg \xi\), which would lead to the approximation \(1/Ro \sim 2/\xi\). This approximation will not be used in this work, but it illustrates that the SAXS assessment of \(\xi\) reflects, almost directly, the solubilization radius used in the HLD-NAC model. At this point, the net curvature (Hn) and the HLD\textsubscript{curvature} could be calculated by introducing the \(\xi\)-assessed value of Ro into Eq. 3, such that:

$$H_{LD_{curvature}} = -L \times H_n = -2L \left(\frac{1}{\xi} - \frac{1}{R_w}\right)$$ \hspace{1cm} Eq. 10

One could go through a similar exercise for the case when water is the solubilized phase in reverse micelles. In that case, Ro is the radius of solubilization of the continuous phase, and the radius of the solubilized water, from Eq. 4, is \(1/R_w = 2/\xi – 1/Ro\). Introducing this expression into Eq. 3:

$$H_{LD_{curvature}} = -L \times H_n = 2L \left(\frac{1}{\xi} - \frac{1}{Ro}\right)$$ \hspace{1cm} Eq. 11

Eq. 10 and Eq. 11 enable obtaining HLD\textsubscript{curvature} almost directly from SAXS-fitted \(\xi\). In this work, we use this method to evaluate HLD\textsubscript{curvature}, at the “semi” characteristic conditions of \(T=25^\circ C\), EACN=0, and no added solvent or cosurfactant, but varying “S”. Given that previous work\textsuperscript{12} equated HLD\textsubscript{curvature} with HLD\textsubscript{bi}, then from Eq.5, HLD\textsubscript{curvature,semi-characteristic} = \(bi \cdot \ln(S) + Cc_{bi}\). Therefore, plotting HLD\textsubscript{curvature,semi-characteristic} vs. \(\ln(S)\) should produce straight lines with slope “bi” and intercept “Cc\textsubscript{bi}”. The Cc of the surfactant should then be Cc = Cc\textsubscript{bi}/bi. The SAXS-assessed Cc values are here compared with Cc values assessed from solubilization and phase inversion studies for three conventional anionic surfactants, an extended surfactant, and a cationic surfactant.
3 Materials and Methods

3.1 Materials.

Table 1 summarizes the surfactants used in this work, including their activity and the main NAC parameters. Table 2 summarizes the oils used in this work, their purities and EACN. Milli-Q water was used in this study, and the brine solutions were made from Sodium chloride (>99%) purchased from Sigma-Aldrich.

Table 1. Surfactants used in the study.

<table>
<thead>
<tr>
<th>Material (abbreviation)</th>
<th>% active</th>
<th>Lₐ (Å)</th>
<th>vₐ/aₛ</th>
<th>Source</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dihexyl sulfosuccinate (SDHS)</td>
<td>80%</td>
<td>11</td>
<td>6.4ᵇ</td>
<td>Colonial Chemical</td>
<td>Donated</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>98.5%</td>
<td>20</td>
<td>8.0ᵇ</td>
<td>Sigma-Aldrich</td>
<td>Purchased</td>
</tr>
<tr>
<td>Sodium bis(2-ethylhexyl) sulfosuccinate (AOT)</td>
<td>75%</td>
<td>11</td>
<td>6.7ᵇ</td>
<td>Cytec</td>
<td>Donated</td>
</tr>
<tr>
<td>Sodium tetrapropylene glycol (2-ethyl) octyl ether sulfate (C10PO₄S, ALFOTERRA® K3-4S)</td>
<td>32.5%</td>
<td>15</td>
<td>6.0⁹</td>
<td>Sasol</td>
<td>Donated</td>
</tr>
<tr>
<td>Benzethonium chloride (BCl)</td>
<td>≥98%</td>
<td>14ᵃ</td>
<td>11ᵈ</td>
<td>Sigma-Aldrich</td>
<td>Purchased</td>
</tr>
</tbody>
</table>

Notes: (a) length parameter estimated as 1.5·number of linear carbons·1.2 Å, as per Acosta et al.¹⁰; (b) Value estimated based on the molecular weight of the surfactant, assuming a density of 1 g/mL for the pure surfactant, and surfactant area per molecule (aₛ) obtained from the Rosen textbook²²; (c) Value obtained from the work of Choi²³; (d) Value estimated based on the molecular weight of the surfactant, assuming a density of 1 g/mL for the pure surfactant, and surfactant area per molecule (aₛ) obtained from the work of Cui et al.²⁴.

Table 2. Oils used in the study.

<table>
<thead>
<tr>
<th>Material/abbreviation</th>
<th>Purity</th>
<th>EACN</th>
<th>Source</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>&gt;99.0%</td>
<td>1ᵃ</td>
<td>Caledon laboratory chemicals</td>
<td>Purchased (ON, Canada)</td>
</tr>
<tr>
<td>Ethyl benzoate</td>
<td>&gt;99%</td>
<td>-1ᵇ</td>
<td>Sigma-Aldrich</td>
<td>Purchased (ON, Canada)</td>
</tr>
</tbody>
</table>

Notes: (a) Value of EACN reported by Baran et al.²⁵; (b) Value of EACN reported by Choi²³.

3.2 Methods

3.2.1 Phase behavior studies

Salinity scans were conducted in 7.4 mL flat-bottom glass test tubes. 3 mL of oil and aqueous phase were added to each test tube to perform a phase behavior scan. The aqueous phase was prepared by introducing the required distilled water, surfactant, and brine into the test tubes. The
oil phase was added to the test tubes, introducing 1.5 mL of toluene and 1.5 mL of ethyl benzoate (3 mL TEtB). The 50/50 volume ratio of these oils is known to produce an EACN of zero\textsuperscript{12}. Paraffin-lined caps were used to seal the test tubes to mitigate evaporation. These tubes were mixed by manually tumbling the test tubes 20 times (~ 1 head-over-heel tumble per second) until the solution was macroscopically well mixed, then mixed again using a LABQUAKE\textsuperscript{®} shaker at a rocking speed of 16.5 rpm for 6 hours. The test tubes were left to settle for 40 hours, followed by 20 minutes of centrifugation in a Cole-Parmer\textsuperscript{®} centrifuge at 2600 rpm. At this point, samples of the phase containing the surfactant (the aqueous phase for micellar systems or the oil phase for reverse micellar systems) were collected to perform the SAXS profile. One control sample containing only the surfactant and a selected brine was prepared for each set of phase scans.

3.2.2 SAXS

Small-angle X-ray scattering experiments were conducted using an Anton-Paar SAXSpace instrument with X-ray generator ID 3003 of 1.5406 Å wavelength X-rays, equipped with a Mythen2 R 1K detector. The SOW samples were held by a 1mm quartz capillary cell, performing measurements at 25°C with 10 minutes of irradiation. The scattering curves were corrected and background subtracted via the SAXStreat and SAXSquant software, respectively. The treated data was then analyzed using the SasView software, employing either the T-S or the core-shell ellipsoidal model. The supplementary information file has more details about the parameters used in SasView to conduct the core-shell ellipsoidal fit and details about the implementation of the Teubner-Strey (TS) and the transition method (TM) in Excel.
4 Results and discussions

4.1 SAXS-based determination of Cc for alkyl sulfosuccinate surfactants

4.1.1 Sodium dihexyl sulfosuccinate (SDHS)

Figure 1 presents two example SAXS profiles for the 4% SDHS-toluene + ethyl benzoate (TEtB)-brine system. The top frame (a) presents a micellar system prepared with 1.5% NaCl, and the bottom frame (b) presents a reverse micellar system prepared with 4.5% NaCl. In both cases, the Teubner-Strey (dashed line) and the transition model (dotted line) can produce relatively accurate fits in the low-q region (<0.2 Å⁻¹ for frame (a) and < 0.1 Å⁻¹ for frame (b)). In this low-q region, the transition observed is often associated with the size of the µE domains. Other internal dimensions, for example, the thickness of the headgroup shell region, are reflected at higher q values, as illustrated in Figure 1a. The oil-free control shown in Figure 1a can be fitted using the core-shell ellipsoidal model programmed in SasView, as illustrated in Figure S1 in the supplementary information (SI) file. According to that fit, the SDHS micelle has a headgroup shell thickness of 3.2 Å and an equatorial radius of 11 Å, which is consistent with the value of the SDHS tail parameter L=11 Å listed in Table 1 for SDHS¹⁰,¹².

The Teubner-Strey fit in Figure 1a produced $\xi_{TS}=17$ Å. For the same system, the transition at low q was observed at $q_{TR} = 0.057$ Å⁻¹, from where $\xi_{TR}=3/q_{TR}=53$ Å. The characteristic length obtained from the core-shell ellipsoid (EL) analysis for 1.5% NaCl (Figure S1 in SI file) is $\xi_{EL}=32$ Å, which is in between $\xi_{TS}$ and $\xi_{TR}$. The system of 4% SDHS has been shown, in a previous SANS study¹³, to be dilute enough so that $S(q)\sim1$, which means that the ellipsoidal model (a form factor, $P(q)$, model) should provide a reasonable approximation for the 4% micelle and reverse micelle systems. The problem with using the ellipsoidal model is that it is not universally valid for all µE systems, especially when the micellar system forms bicontinuous µEs or interconnected micelles. The Teubner-Strey model is more suitable for bicontinuous or interconnected µE systems where, in addition to $\xi$ (indicating the sphere-equivalent volume to area ratio), there is a periodicity distance “d” between connection nodes. The transition model is inspired by Auvray’s observation that $q_{TR}$ can be used to calculate the sphere-equivalent radius in dilute and concentrated µE systems, suggesting that $3/q_{TR}$ could approximate the size of µE aggregates¹⁵. The difference between Auvray’s method of finding $q_{TR}$ and our method is that Auvray identified $q_{TR}$ as q where a
maximum peak is observed in Porod’s plot ($q^4 I$ vs. $q$), and we identified $q_{TR}$ as $q$ where “$n$” in the fitted expression $I = I_{TR} (q/q_{TR})^n$ changes. Auvray’s method for finding $q_{TR}$ works if “$n$” at $q > q_{TR}$ is $\sim -4$, characteristic of spherical micelles. The transition model is shape-independent but produces similar results to a modified Auvray’s approach where $q_{TR}$ is $q$ at the maximum in $I q^{-n_R}$ ($n_R$ is $n$ for $q > q_{TR}$) vs. $q$ plots.

![Figure 1](https://doi.org/10.26434/chemrxiv-2023-drq7n)

**Figure 1.** Example SAXS profiles for 4 wt% SDHS in the system of toluene + ethyl benzoate (TEtB, EACN=0) and brine at 25°C (semi-characteristic conditions). The system in frame (a) is a micellar system containing 1.5% NaCl, including the oil-free control (triangles). The system in frame (b) is a reverse micellar system produced with 4.5% NaCl.
The value of $n_R$ provides an idea of the shape of the $\mu E$ domains. If $n_R \sim -4$, then one has disconnected smooth spherical structures; $n_R \sim -3$ corresponds to “collapsed polymer structures”; $n_R \sim -2$ corresponds to Gaussian polymer chains or the presence of two-dimensional structures; $n_R \sim -1$ is associated with cylindrical structures. In Figure 1a, the micellar system has $n_R \sim -1$, but the reverse micellar system of Figure 1b has $n_R \sim -2.5$, which means that while the micellar system behaves as disconnected cylinders, the reverse micellar system might contain some level of interconnection between reverse micelles.

The values of $\xi_{TS}$, $\xi_{TR}$, and $\xi_{EL}$ were used in Eqs. 10 (for micellar systems) and 11 (for reverse micellar systems) to calculate $HLD_{\text{curvature}} = -L \cdot Hn$ for 4% SDHS-TEtB $\mu$Es prepared with varying levels of salts at 25°C (semi-characteristic conditions). For micellar systems, the solubilization radius of the continuous aqueous phase was calculated as $R_w = 3\cdot((1-\phi_s)/\phi_s)(v_s/a_s) = 3((1-0.04)/0.04)(6.4\text{Å}) = 461\text{Å}$. For the reverse micelle systems, a similar procedure was used, such that $R_o = 461\text{Å}$. Figure 2 presents the $HLD_{\text{curvature}}$ values obtained with $\xi_{TS}$ (squares), $\xi_{TR}$ (circles), and $\xi_{EL}$ (triangles) as a function of salinity. The $HLD_{\text{curvature}}$ from solubilization (crosses) in Figure 2 was obtained from our previous work on $C_c$ determination from TEtB solubilization. The $HLD_{\text{curvature}}$ from solubilization values and the ellipsoidal model values are consistent, except for the low salinity value ($S_{\text{added}} = 0.5\% \text{ NaCl}$). For micellar systems (negative $HLD_{\text{curvature}}$), the solubilization and ellipsoidal model values closely follow the trend obtained with the transition model, but the Teubner-Strey (TS) model produced $HLD_{\text{curvature}}$ values that were quite different from the other models. This difference could be explained by the fact that the $n_R$ exponent in all the micellar systems for 4% SDHS is $\sim -1$ (see Table S5 in the SI file), suggesting that the micelles are small, isolated cylinders, a configuration that is incompatible with the TS model. The TS model produces a reasonable trend for reverse micellar systems, which could be explained by $n_R \sim -2$ exponent found in reverse micelles (Table S5), suggesting interconnected aggregates akin to Gaussian polymer chains. The dataset identified as “correlation” in Figure 2 is composed of $HLD_{\text{curvature}}$ from $\xi_{TR}$ in micellar systems, and the average in $HLD_{\text{curvature}}$ obtained from $\xi_{TR}$ and $\xi_{TS}$ for reverse micellar systems (given that $\xi_{TS}$ is relevant for $n_R \sim -2$). The linear regression for the correlation dataset is compatible with the expected relationship $HLD_{\text{curvature,semi-characteristic}} = bi \cdot \ln(S) + C_{cbi}$. According to the regression in Figure 2, $bi = 1.00 \pm 0.06$, and $C_{cbi} = -0.89 \pm 0.05$ (the ± interval represents the 95% interval level), thus $C_{c_{\text{from SAXS}}} = C_{cbi}/bi = -0.89/1.00 = -0.89 \pm 0.06$. The 95% uncertainty interval for $bi$ and $C_{cbi}$ were obtained using the regression analysis tool in
EXCEL. The uncertainty for Cc was assessed as the standard deviation of 4 Cc extremes: $C_{c1} = C_{c_{bi_{max}/bi}}$, $C_{c2} = C_{c_{bi_{min}/bi}}$, $C_{c3} = C_{c_{bi}/b_{im_{in}}}$, $C_{c4} = C_{c_{bi}/b_{im_{ax}}}$.12

Figure 2. HLD curvature calculated from the characteristic length ξ obtained from SAXS profiles analyzed using the Teuber-Strey (TS, $\xi_{TS}$, squares) model, the transition model (TM, $\xi_{TR} = \frac{3}{q_{TR}}$, circles), and the core-shell ellipsoid model (EL, $\xi_{EL}$, triangles) as a function of the logarithm of the total salinity (including added salt and unbound counterion). The HLD curvature from solubilization was obtained from Leng and Acosta12 with the permission of Wiley. The correlation points were taken as the HLD curvature from $\xi_{TR}$ for micellar systems and the average between HLD curvature from $\xi_{TR}$ and $\xi_{TS}$ for reverse micellar systems. The system consists of 4% SDHS in TETB at 25°C and varying salinities (semi-characteristic conditions).
4.1.2 Sodium dioctyl sulfosuccinate (Aerosol OT or AOT)

Figure 3 presents an example SAXS profile for a 4% AOT-TEtB-brine system (circles) reverse micellar system prepared with 1% NaCl. Figure 3 also presents an oil-free control (triangles) of 4% AOT micelles in 1% NaCl brine. Figure S3 in the SI file presents the ellipsoidal core-shell fit of the control system considering a headgroup shell thickness of 3.2 Å (same as SDHS) and an equatorial radius of 11.5 Å, consistent with AOT’s tail parameter L=11Å listed in Table 1.

Figure 3. Example scattering profile for 4 wt% AOT in TEtB (EACN=0) and brine at 25°C (semi-characteristic conditions). The system is a reverse micellar system produced with 1.0% NaCl. The control system is an oil-free (triangles) micellar system at 1.0% NaCl.

The value of \( n_R = -2.3 \) obtained with the transition model fit in Figure 3 for the reverse micellar system at 1.0% NaCl was characteristic of \( n_R \approx -2 \) obtained for all the salinities explored (0.2 to 4% NaCl of added salinity, see Table S6), therefore, based on the observations with the SDHS system, one could expect the TS model to be relevant for these systems.

Figure 4 presents the \( \text{HLD}_\text{curvature} \) values calculated using Eq. 11 for reverse micellar systems with \( R_0 = 3((1-\phi_s)/\phi_s)(v_s/a_s) = 3((1-0.04)/0.04)(6.7\text{Å}) = 482 \text{ Å} \) and \( \xi_{TS} \) (squares), \( \xi_{TR} \) (circles), and \( \xi_{EL} \) (triangles) obtained from fits of the SAXS profiles at different salinities (see SI file for fits and detailed set of fitting parameters). Similar to the SDHS system, the trend obtained in Figure 4 with the core-shell ellipsoidal fit is close to the \( \text{HLD}_\text{curvature} \) obtained via solubilization. For the reverse
micellar systems shown in Figure 4, the TS model over-estimates HLD\textsubscript{curvature} (i.e., under-estimates \(\xi\)), and the transition model under-estimates HLD\textsubscript{curvature} (i.e., over-estimates \(\xi\)), but the correlation set (an average in HLD\textsubscript{curvature} obtained from \(\xi_{\text{TS}}\) and \(\xi_{\text{TR}}\)) is consistent with the ellipsoidal and the solubilization HLD\textsubscript{curvature}. The correlation dataset did not include added salinities less than 1\% NaCl because we suspect the plateau in the HLD\textsubscript{curvature} obtained with the ellipsoids analysis for negative \(\ln(S)\) values suggests that it is likely that those systems did not reach the necessary equilibrium solubilization. In our previous work, AOT systems were the most difficult ones to analyze, likely because of the formation of metastable systems that did not reflect the equilibrium solubilization\textsuperscript{12}. In that case, the assessment of suspicious data was based on the expected in HLD\textsubscript{curvature} vs. \(\ln(S)\). Based on the water solubilization obtained by Rabie and Vera\textsuperscript{27,28}, turned into HLD\textsubscript{curvature}, the expected slope for the correlation line in Figure 4 should be around 0.35. The regression line for the correlation dataset has a slope of 0.32, close to the expected value.

\[
y = 0.3173x + 1.1582 \\
R^2 = 0.9515
\]

Figure 4. HLD\textsubscript{curvature} calculated from the TS model (\(\xi_{\text{TS}}\), squares), the transition model (\(\xi_{\text{TR}}\textsuperscript{*}=3/q_{\text{TR}}\), circles), and the core-shell ellipsoid model (\(\xi_{\text{EL}}\), triangles) as a function of the logarithm of the total salinity (added salt + unbound counterion). The HLD\textsubscript{curvature} from solubilization was obtained from Leng and Acosta\textsuperscript{12} with the permission of Wiley. The correlation points represent the average HLD\textsubscript{curvature} obtained from \(\xi_{\text{TR}}\) and \(\xi_{\text{TS}}\) for these reverse micellar systems. The system consists of 4\% AOT in TEtB at 25\textdegree C and varying salinities (semi-characteristic conditions).
Based on the regression line for the correlation dataset in Figure 4, bi = 0.32±0.2, Cbi= 1.2±0.2, and Cc = 1.2/0.32 = 3.7±5.4. The reported “±” uncertainties were calculated as explained for the case of SDHS. The large uncertainty in the calculated value of Cc reflects the relatively large uncertainty in the value of bi. Among all the surfactants reported in this work and our previous work\textsuperscript{12}, AOT is the system that requires further investigation to understand the role of potentially metastable systems on the assessed curvature. Another point that deserves further attention is the explanation as to why bi~ 0.32 for AOT while bi~1 for SDHS, given that these two surfactants are very similar. The electrostatic curvature model (ECM), introduced in our previous work to explain the origin of the term “bi”, indicates that “bi” is larger for ionic surfactants that can accommodate smaller packing parameters at low salinities\textsuperscript{12}. This ability to reach low packing parameters is often associated with short surfactant tail length and a large area per molecule. While SDHS and AOT both have small tail lengths (~10 Å), and high surface areas (~100Å\textsuperscript{2}/molecule, according to the literature\textsuperscript{22}), the ethyl branches in AOT hinder the arrangement of the surfactant into the cone-like structures required to achieve low packing parameters.

Despite the relatively high uncertainties in bi and Cc for AOT, the SAXS method delivered an assessed Cc = +3.7 that is relatively close to that obtained via solubilization studies\textsuperscript{12}, Cc = +3.5, but higher than the Cc value reported from phase behavior studies\textsuperscript{11} Cc = +2.5, obtained with mixtures of AOT with SDHS as reference surfactant. It is worth pointing out that obtaining a Cc from phase behavior studies in mixtures of a reference and a test surfactant assumes that the HLD constants (k, a\textsubscript{T} in Eq. 1) are the same. Given the difference in “bi” values for SDHS and AOT, the assumptions used to obtain the Cc from phase behavior for AOT might need to be revisited.

4.2 SAXS-based determination of Cc for alkyl sulfate surfactants

4.2.1 Sodium dodecyl sulfate (SDS)

Figure 5 presents an example SAXS profile for a 4% SDS-TEtB-brine (circles) micellar system prepared with 0.5% NaCl. Figure 5 also presents an oil-free control (triangles) of 4% SDS micelles in 0.5% NaCl brine. Figure S5 in the SI file presents the ellipsoidal core-shell fit of the control system considering a headgroup shell thickness of 1.1 Å and an equatorial radius of 16.4 Å, which is smaller than SDS’s tail parameter L=20 Å listed in Table 1, but it is close to the equatorial radius of 17.8 Å reported by Pozza and Bonneté obtained via Synchrotron SAXS\textsuperscript{29}. The same article reports a shell thickness of 4.85 Å, which was obtained considering a scattering length density.
(SLD) for the SDS headgroup of $13.28 \times 10^{-6}$ Å$^{-2}$, which is substantially smaller than the SLD = $22 \times 10^{-6}$ Å$^{-2}$ used in this work for the sulfate headgroup. The SLD of the headgroup was obtained using the SLD calculator in SasView, entered as “SO4Na”, and with a density of 2.6 g/cm$^3$ (typical of sodium sulfate). While using smaller SLDs for the headgroup yields larger shell thickness, the reality is that the main features of the scattering profile that we are interested in (around $q_{TR}$) are not substantially affected by the scattering features of the shell, as illustrated in Figure 5. Furthermore, as a comparison, the oil-free SDS control was re-analyzed using SLD = $13.3 \times 10^{-6}$ Å$^{-2}$ for the shell (we already used similar SLDs for the micelle core and the solvent as those used by Pozza and Bonneté’s) and we obtained an equatorial radius of 16.3Å and a shell thickness of 3.2Å, which further supports that the difference in shell SLD affects, primarily, the thickness of the shell and only slightly the dimensions of the core.

Figure 5. Example scattering profile for 4 wt% SDS in TEtB (EACN=0) and brine at 25°C (semi-characteristic conditions). The system is a micellar system produced with 0.5% NaCl. The control system is an oil-free (triangles) micellar system at 0.5% NaCl.
The value of $n_R = -1.3$ obtained with the transition model fit in Figure 5 for the micellar SDS system at 0.5% NaCl suggests that these micelles are closer to being cylindrical and isolated. Furthermore, as determined for the SDHS system, when $n_R \sim -1$, one should expect the TS model to be unsuitable for assessing the size of the $\mu$E domains.

Figure 6 presents HLD_{curvature} obtained with Eq. 10 (micellar systems), $R_w = 3((1-0.04)/0.04)(8\text{Å})= 576 \text{ Å}$ and $\xi_{TS}$ (squares), $\xi_{TR}$ (circles), and $\xi_{EL}$ (triangles) obtained from SAXS fits (see Table S7 in SI file for the fitting parameters). The core-shell ellipsoidal HLD_{curvature} is almost constant throughout the salinity scan. The HLD_{curvature} from solubilization and from the transition model are consistent, even within the positive $\ln(S)$ range. Given that $n_R \sim -1$ for these SDS micellar systems, the correlation data set was taken from the transition data alone. This $n_R \sim -1$ value helps explain why the HLD_{curvature} from $\xi_{TS}$ differs from all the other methods.

Figure 6. HLD_{curvature} calculated from the TS model ($\xi_{TS}$, squares), the transition model ($\xi_{TR} = 3/q_{TR}$, circles), and the core-shell ellipsoid model ($\xi_{EL}$, triangles) as a function of the logarithm of the total salinity (added salt + unbound counterion). The HLD_{curvature} from solubilization was obtained from Leng and Acosta\textsuperscript{12} with the permission of Wiley. The correlation dataset used HLD_{curvature} calculated from $\xi_{TR}$, given that $\xi_{TS}$ is unsuitable ($n_R \sim 1$) for this micellar system. The system consists of 4% SDS in TETB at 25°C and varying salinities (semi-characteristic conditions).
The regression analysis for the correlation dataset in Figure 6 produced a $b_i = 0.39 \pm 0.09$, $C_{c_{bi}} = -1.07 \pm 0.07$, and $C_c = -1.07/0.39 = -2.7 \pm 0.6$. This SAXS-assessed value of $C_c$ is very close to the solubilization-assessed value of -2.6 in our previous work$^{12}$ and still relatively close to the $C_c$ of -2.3 from phase behavior studies$^{11}$. Much like the previous reservation regarding the comparison with phase behavior $C_c$ for AOT, the phase behavior $C_c$ for SDS was obtained using mixtures of SDHS and SDS, which do not have the same “$b_i$” or “$k$” values. The fact that two independent methods (SAXS and solubilization), that do not use mixtures with a reference surfactant, produce similar $C_c$ values points to $C_c \sim -2.6$ as the most accurate value for the $C_c$ of SDS.

4.2.2 Sodium tetrapropylene glycol (2-ethyl) octyl ether sulfate (C10PO4S)

The inclusion of the extended surfactant (surfactants with intermediate polypropylene glycol or PO block) C10PO4S among the surfactants considered was motivated by three reasons; first, there have been only three previous studies, that we could find, on SAXS of extended surfactants$^{30–32}$; second that none of these studies used the core-shell ellipsoidal model to interpret the size of these micelles and the effect that the propylene glycol group might have on the radius of the empty micelle (and the tail parameter $L$); and finally that the $C_c$ of C10PO4S has been determined from phase behavior without the need for mixtures with a reference surfactant.

Figure 7 presents an example SAXS profile for a 4% C10PO4S-TEtB-brine system (circles) micellar system prepared with 1.5% NaCl. Figure 7 also presents an oil-free control (triangles) of 4% C10PO4S micelles in 1.5% NaCl. Figure S7 in the SI file presents the ellipsoidal core-shell fit of the control system that produced a headgroup shell thickness of 1.3 Å and an equatorial radius of 19.3 Å, which is larger than C10PO4S’s tail parameter $L= 15$ Å listed in Table 1. Using a Guinier analysis of the SAXS profile of a system of 5% C10PO4S containing 1.25% ethyl caprate as solubilized oil, Choi and Acosta found that these systems formed cylinders with a radius of 13 Å$^{31}$. The parameter $L$ for C10PO4S was estimated based on the length of 8 linear carbons in the surfactant tail group (see molecular structure in Figure 7), that assuming a C-C bond length of about 1.5 Å, it should total a length of 12.5 Å. ($L\sim1.2$-tail length ~ 15Å). The radius of 19.3 Å obtained from the ellipsoidal analysis makes sense considering that the length occupied by the four propylene glycol groups should be added to the 12.5 Å calculated for the hydrocarbon length. The four polypropylene glycol groups must exist in a coiled structure for them to contribute only around 7 Å, given that each propylene glycol has a length of ~ 4.5Å considering 3 linear bonds in
each PO group. The coiled structure of polypropylene glycol groups has been previously discussed in the literature. 

Figure 7. Example scattering profile for 4 wt% C10PO4S in TEtB (EACN=0) and brine at 25°C (semi-characteristic conditions). The system is a micellar system produced with 1.5% NaCl. The control system is an oil-free (triangles) micellar system at 1.5% NaCl.

While the right-side exponent, \( n_R = -1.7 \), is not -2 in Figure 7, the model fit summary table (Table S8 in the SI file) for C10PO4S shows that the exponent \( n_R \) is close to -2 or more negative for most of the salinities considered, suggesting that the Teubner-Strey fit is relevant for these micellar systems. Figure 8 presents the HLD\textsubscript{curvature} obtained with Eq. 10 (micellar systems), \( R_w = 3((1-0.04)/0.04)(6\text{Å}) = 432 \text{Å} \) and \( \xi_{TS} \) (squares), \( \xi_{TR} \) (circles), and \( \xi_{EL} \) (triangles) obtained from SAXS fits (see Table S8 in the SI file for the fitting parameters). When \( \ln(S) \) is positive, the core-shell ellipsoidal HLD\textsubscript{curvature} is consistent with the TS model and the solubilization-based HLD\textsubscript{curvature}; however, at negative \( \ln(S) \), the ellipsoidal model reaches a nearly constant HLD\textsubscript{curvature}. A closer look at Figures 2 and 6 reveals that, at low or no added salinity (\( \ln(S) \ll 0 \)), the ellipsoidal model tends to produce HLD\textsubscript{curvature} values that are less negative than the rest of the models, which is also evident in Figure 8. The inset in Figure 8 compares the SAXS profiles obtained with the ellipsoidal model for 0% added NaCl in C10PO4S+TEtB and the control of 1.5% NaCl in C10PO4S, illustrating how the two profiles (each reproducing their respective experimental profiles) are very
similar to each other. This observation suggests that at low or no added salinity, the dimensions of the micelles obtained via the ellipsoidal model are dominated by the surfactant tail group and not the solubilized oil. The assessed $\xi_{\text{EL}}$ from the ellipsoidal model at 0% added NaCl is 27.1 Å, which is roughly $\sim 1.4$ times the radius of the surfactant micelle (19.3 Å). The ellipsoidal model starts to approach the solubilization curvature, and the correlation dataset, when the added salinity is 1% NaCl ($\ln(S_{\text{total}}) = +0.13$), at which point $\xi_{\text{EL}} = 36$ Å, nearly twice the radius of the surfactant-only micelle. This observation suggests that HLD curvature from $\xi_{\text{EL}}$ is not reliable for micelles if $\xi_{\text{EL}}$ is smaller than the equatorial diameter of the surfactant-only ellipsoid, as this HLD curvature would be primarily influenced by the surfactant tail and not the oil solubilized. Based on this criterion, one needs to disregard HLD curvature from $\xi_{\text{EL}}$ for $\ln(S) = -0.4$ for SDHS in Figure 2 and all the HLD curvature from $\xi_{\text{EL}}$ in Figure 6 (explaining why the ellipsoidal curvature was nearly constant in Figure 6).

Figure 8. HLD curvature from the TS model ($\xi_{\text{TS}}$, squares), the transition model ($\xi_{\text{TR}} = 3/q_{\text{TR}}$, circles), and the core-shell ellipsoid model ($\xi_{\text{EL}}$, triangles) as a function of the logarithm of the total salinity (added salt + unbound counterion). The HLD curvature from solubilization was obtained from Leng and Acosta$^{12}$ with the permission of Wiley. The correlation represents the average of $\xi_{\text{TR}}$- and $\xi_{\text{TS}}$-HLD curvature values. The system consists of 4% C10PO4S in TEtB at 25°C and varying salinities (semi-characteristic conditions). The inset shows the core-shell ellipsoid SAXS profile for 0% NaCl C10PO4S-TEtB and the 1.5% NaCl C10PO4S control.
The correlation dataset in Figure 8 represents the average HLD_{ curvature } from \( \xi_{ TR } \) and \( \xi_{ TS } \), whose linear regression produced \( b_i = 0.40 \pm 0.05 \), \( C_{ cb } = -0.69 \pm 0.05 \), and \( C_c = -0.69/0.40 = -1.7 \pm 0.2 \). This SAXS-assessed value of \( C_c \) is very close to the solubilization-assessed \( C_c \) of -1.65 from our previous work^{12} and relatively close to the phase behavior \( C_c \) of -2.1 from a previous study that did not use mixtures with a reference surfactant^{32}.

### 4.3 SAXS-based determination of \( C_c \) for benzethonium chloride (BCl)

The inclusion of benzethonium chloride among the surfactants studied in this work was motivated by three reasons; first, BCl is the only cationic surfactant included in this work; second, BCl is one of the few cationic surfactants where the phase behavior \( C_c \) has been determined without the aid of cosurfactants or cosolvents; and third, BCl is commonly used in disinfecting formulations and sanitizers.

Figure 9 presents an example SAXS profile for a 4% BCl-TEtB-brine system (circles) micellar system prepared with 0.2% NaCl. Figure 9 also presents an oil-free control (triangles) of 4% BCl micelles in 0.2% NaCl. The SAXS profile for the oil-free BCl control was not analyzed using the ellipsoidal model for two reasons, first that the signal was too noisy to have well-defined features, and second the uncertainty in assigning a well-defined headgroup. While we have highlighted the quaternary ammonium group for BCl in Figure 9, the only previous BCl-SAXS study found in the literature suggests that the phenyl group, the ethoxy groups, and bound water form a headgroup environment that has a different electron distribution from other well-defined quaternary cationic surfactants^{34}. One other important feature in Figure 9 is that the right-side exponent of the transition fit is \( n_R = -2 \), suggesting that the Teubner-Strey model is still relevant for these systems; however, as indicated in the fit summary in Table S9, the system prepared with 0.1% NaCl (ln(S) = -1.36) has an \( n_R = -1.43 \).

Figure 10 presents HLD_{ curvature } obtained with Eq. 10 (micellar systems), \( R_w = 3((1-0.04)/0.04)(11\text{Å}) = 792 \text{Å}, \xi_{ TS } \) (squares) and \( \xi_{ TR } \) (circles) obtained from SAXS fits (see SI file for fits and fitting parameters). The correlation dataset in Figure 10 represents the average HLD_{ curvature } from \( \xi_{ TR } \) and \( \xi_{ TS } \) (except for ln(S) = -1.36) whose linear regression produced \( b_i = 0.29 \pm 0.11 \), \( C_{ cb } = -0.08 \pm 0.07 \), and \( C_c = -0.08/0.29 = -0.28 \pm 0.23 \). This SAXS-assessed \( C_c \) is almost the same as the phase behavior \( C_c \) of -0.34 from our previous work^{12} and close to the solubilization-assessed \( C_c \) of +0.05 in the same reference.
Figure 9. Example scattering profiles for 4 wt% BCl in TEtB (EACN=0) and brine at 25°C (semi-characteristic conditions). The system is a micellar system produced with 0.2% NaCl. The control system is an oil-free (triangles) micellar system containing 0.2% NaCl.

Figure 10. HLD\textsubscript{curvature} from the TS model ($\xi_{\text{TS}}$, squares) and the transition model ($\xi_{\text{TR}}=3/q_{\text{TR}}$, circles) as a function of the logarithm of the total salinity (added salt + unbound counterion). The HLD\textsubscript{curvature} from solubilization was obtained from Leng and Acosta\cite{12} with the permission of Wiley. The correlation represents the average of $\xi_{\text{TR}}$- and $\xi_{\text{TS}}$- HLD\textsubscript{curvature} values. The system consists of 4% BCl in TEtB at 25°C and varying salinities (semi-characteristic conditions).
4.4 SAXS- vs. solubilization- and phase behavior- Cc values

Figure 11 Compares the Cc values obtained from SAXS, solubilization and phase behavior studies for the five surfactants considered in this work, along with their calculated (for SAXS and solubilization) and expected uncertainties noted as error bars. The expected uncertainties for the phase behavior Cc were obtained as the maximum between ±0.2 and 25% of the absolute Cc value, as proposed by Zarate et al. Except for the solubilization Cc for AOT, all other uncertainty intervals overlap, meaning that the reported Cc values are consistent among the different methodologies. While the AOT case deserves further investigation, including reducing the uncertainty for SAXS-Cc, the reality is that the Cc for AOT was obtained using SDHS as a reference and assuming that all the HLD constants for SDHS apply to AOT. The SAXS- and solubilization-Cc for AOT and all other surfactants are very close to each other, which lends further support that the use of the characteristic curvature concept produces consistent Cc values even when using completely different methods to assess HLD curvature.

Figure 11. SAXS-assessed characteristic curvature (Cc) for the surfactants considered in this work and its comparison with solubilization- and phase behavior-assessed Cc. The phase behavior Cc for SDHS was taken from Baran et al.; for AOT and SDS from Acosta et al.; for C10PO4S from Choi et al.; and for BCl from the HLD-NAC fit of Leng and Acosta. The solubilization Cc was obtained from Leng and Acosta.
There are two important advantages of the SAXS method over the solubilization method, first is that the SAXS method does not require specialized method development for each surfactant (the solubilization requires confirming/adapting the chromatography), and the second is that the SAXS method is more direct and less input dependent. The solubilization method must calculate Ro and Rw using the v/s/aₘ ratio. For SAXS, only the continuous phase solubilization radius needs v/s/aₘ, and for most cases, this radius is so large, compared to ξ, that it only plays a minor role in HLD-curvature. The other input required for the SAXS method is the tail length parameter, L, which has a direct proportional effect in Ccᵦ and bi, but in the ratio Ccᵦ/bi that effect cancels out, making the assessed Cc value impervious to uncertainties in the value of L. After evaluating various uncertainty input scenarios (calculations not shown), the assumed parameter that can have a more serious implication in the value of Cc is the fraction of unbound counterion (fₑᵤ). When the added salt level is very low or zero, the salinity (S) only contains the unbound counterion, and this can produce extreme ln(S) deviations, which is an issue relevant to SAXS-Cc and solubilization-Cc. To minimize potential uncertainties, it is best to aim for salinity scans with 0.5% or more added NaCl. For most of the surfactants used in this work, 0.5% added NaCl corresponds to ln(S) ~ -0.3, considering a 30% unbound counterion. If one observes Figures 4, 6 and 8, the HLD-curvature values from ξₜₛ (square symbols) display odd deviations in the linear trend around ln(S)< -0.3, supporting the recommendation that salinity scans should be conducted with more than 0.5% NaCl.

The obvious disadvantage of the SAXS method is the access to the benchtop instrumentation and the interpretation/fit of the SAXS profile, which is not a trivial endeavor. Benchtop SAXS instrumentation is becoming more common in academic and industrial facilities, and it is more accessible than neutron facilities for SANS or synchrotron SAXS facilities. Regarding the interpretation limitation, the supplementary spreadsheet of this work contains an Excel™ example fitting for the Teubner-Strey and the transition model. The SI file has complementary notes on recommended practices for conducting these fits.
5 Conclusions and recommendations

This work aimed to explore the use of SAXS in determining Cc using the concept of characteristic curvature. At the heart of this method is the use of the HLD\text{curvature} equations, that for micellar systems is $HLD_{\text{curvature}} = -2L(1/\xi - 1/R_w)$, where the tail length parameter “L” is estimated as 1.2 times the length of the straight alkyl chain of the surfactant. For micellar systems, the solubilization radius of the continuous aqueous phase (Rw) is calculated considering the $v_s/a_s$ ratio and the surfactant volume fraction.

The characteristic length ($\xi$) was assessed from the SAXS profile using three methods, a core-shell ellipsoidal fit (to produce $\xi_{EL}$), the Teubner-Strey (TS) fit (for $\xi_{TS}$) and a new transition model (for $\xi_{TR}$). The value of $\xi_{EL}$ was highly influenced by the surfactant tail in micellar systems, especially when $\xi_{EL}$ was smaller than twice the equatorial radius of the oil-free micelles; however, for reverse micelles, $\xi_{EL}$ produced the most accurate values of HLD\text{curvature}, consistent with the values obtained via water solubilization. The new transition model fits the power law $(I/I_{TR}) = (q/q_{TR})^n$ around the value of q ($q_{TR}$) where the exponent “n” changes substantially between the left ($n_L$) and the right ($n_R$) side of the transition point in the low q range; assessing $\xi_{TR} = 3/q_{TR}$. Overall, $\xi_{TR}$ produced HLD\text{curvature} values that were often consistent with solubilization HLD\text{curvature}, especially in micellar systems. The TS model was unsuitable for disconnected micellar systems, as indicated by $n_R \sim -1$, which is understandable given that this model was developed for bicontinuous $\mu$Es.

A correlation data set of HLD\text{curvature} vs. $\ln(S)$ was obtained with HLD\text{curvature} calculated from $\xi_{TR}$ or the average in HLD\text{curvature} from $\xi_{TR}$ and $\xi_{TS}$ for the cases when the TS model was suitable. This correlation data followed the linear trend predicted by the HLD$_{bi}$-NAC, that for the conditions of EACN=0 (toluene + ethylbenzoate), at 25°C and in the absence of cosurfactants with varying salt levels (semi-characteristic conditions) was $HLD_{bi} = HLD_{\text{curvature}} = bi\cdot \ln(S) + Cc_{bi}$. The characteristic curvature was assessed as $Cc = Cc_{bi}/bi$, resulting in Cc values that were often indistinguishable from the values obtained from solubilization and phase behavior studies.

While there are aspects that require further consideration, for example, the role of metastable phases, the benchtop SAXS method for Cc determination opens the opportunity for an almost direct assessment of Cc, without using reference surfactants or cosolvents, and where the input information of $v_s/a_s$ and L has a minor influence in the final Cc value.
Credit author statement

Zhuotao Leng: Conceptualization, Software, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing Original Draft, Writing- review and Editing, Visualization. Edgar Acosta: Conceptualization, Development of the transition model, Software, Formal analysis, Data Curation, Writing and Editing, Visualization, Supervision, Funding acquisition.

Conflict of interest/Ethics Statement

The authors declare that they have no conflict of interest.

Data availability Statement

The source data can be made available upon email request to the corresponding author.

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