Effects of Structure Variation on Solution Properties of Hydrotropes: Phenyl versus Cyclohexyl Chain Tips

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Supporting Information

ABSTRACT: The physicochemical behavior of the phenyl-n-alkanoate (PhenCx) and cyclohexyl-n-alkanoate (CyclohexCx) series has been investigated, supporting previous work on the understanding of hydrotropes (Hopkins Hatzopoulos, M.; Eastoe, J.; Dowding, P.J.; Rogers, S. E.; Heenan, R.; Dyer, R. Langmuir 2011, 27, 12346–12353). Electrical conductivity, surface tension, 1H NMR, and small-angle neutron scattering (SANS) were used to study adsorption and aggregation in terms of critical aggregation concentration (cac). The PhenCx series exhibited very similar d log(cac)/dn to n-alkylenzoates (CnBenz), exhibiting two branches of behavior, with a common inflection point at four linear carbons, whereas the CyclohexCx series showed no break point. Electrical conductivity and 1H NMR concentration scans indicate a difference in physicochemical behavior between higher and lower homologues in both the PhenCx and CyclohexCx series. Surface tension measurements with compounds belonging to either group gave typical Gibbs adsorption profiles, having d log(cac)/dn curves consistent with limiting headgroup areas in the region of (35–55 Å²) indicating monolayer formation. SANS profiles showed no evidence for aggregates below the electrical conductivity determined cac values, inferring an “on–off” mode of aggregation. Analyses of SANS profiles was consistent with charged ellipsoidal aggregates, persisting from lower through to higher homologues in both the PhenCx and CyclohexCx series.

INTRODUCTION

The physicochemical behavior of short chain organic salts has been the issue of much debate but of little scientific research in comparison to common surfactants. An array of these organic salts, commonly known as hydrotropes, has been observed to facilitate increased solubilization of insoluble organic compounds above a salt specific concentration. The broad class of hydrotropes encompasses a wide variety of types (anionic, cationic, neutral) and molecular structures, which has hampered any general overview of behavior. The point of contention has always been the mechanism of hydrotrope action and how they impart increased solubility of hydrophobic compounds. The formation of complexes between solute and hydrotrope and action as structure makers or breakers have been speculated before. On the other hand, association or aggregation of hydrotropes has been supported by a number of studies, being conclusively demonstrated by small-angle neutron scattering (SANS) experiments on common ionic hydrotropes. Having shown that hydrotropes aggregate, the mechanism of association is under debate. A gradual change in physicochemical properties is normally observed (e.g., electrical conductivity and dye solubilization), leading to the view that hydrotropes associate in a stepwise manner, rather than the “on–off” mechanism which is characteristic of surfactants. This is considered as a distinguishing feature of hydrotropes compared with classical surfactants. Balasubramanian and Srinivas proposed a distinction between hydrotropes and surfactants after examining a homologous series of n-alkylenzenesulfonates to find where hydrotropes “become” surfactants: a clear point of departure could not be identified. Recently, Hatzopoulos et al. studied aqueous solutions of the sodium n-alkylenzoate (CnBenz) series employing a range of techniques. Classical methods such as electrical conductivity and 1H NMR concentration scans showed that lower homologues exhibit gradual changes in behavior, generally observed previously for hydrotropes. However, when the alkyl tail consisted of four or more methylene (CH₂) groups, behavior characteristic of surfactants was observed. Surface tension measurements on the other hand produced typical Gibbs adsorption profiles throughout the homologous series, implying no distinction between the behavior for higher homologues and the lower “hydrotropic” members of the

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series. SANS data also concurred with this, all recorded profiles being consistent with charged ellipsoidal aggregates, suggesting that “hydrotropes” do not differ in their overall physicochemical properties to common surfactants. Scattering profiles also indicated that no aggregates formed below the cac, again characteristic of an “on—off” type of transition from a chaotic solution to an aggregate dispersion. A further point was that for such compounds not all carbon atoms in the molecule are thermodynamically equivalent, though still hydrophobic enough to drive aggregation.

This work extends that of ref 8, shedding more light on these systems. It aims to probe the additive nature of hydrophobicity by investigating a analogous series of alkylbenzoates, being phenyl-\(n\)-alkanoates (PhenCx) or cyclohexyl-\(n\)-alkanoates (CyclohexCx). The generic structures are shown in the inset in Figure 1, where \(x\) is the number of linear carbons including the headgroup carbon. This structural switch reveals the change from cyclic aromatic to cyclic aliphatic chain tips, to explore the distinction between these different but related groups. Common commercial surfactants, like those from the Triton series, can be found in aromatic and reduced cyclohexyl forms; therefore it is of interest to isolate the effects of this general structural switch on physicochemical behavior. The phenyl ring is planar, and at 25 °C the cyclohexyl ring predominantly adopts a chair conformation.9 Even though these two groups

(phenyl vs cyclohexyl) differ by a mere five H atoms, as seen below, there are some quite surprising effects on solution properties.

## EXPERIMENTAL SECTION

**Materials.** All chemicals were purchased from Sigma Aldrich at the highest purity available. The sodium phenyl-\(n\)-alkanoates and cyclohexyl-\(n\)-alkanoates were synthesized from the parent acids. Sodium hydroxide was purchased from Fischer Scientific (97%). \(D_2O\) for NMR and SANS experiments was purchased from Aldrich (99.9%). EDTA tetrasodium salt, used in surface tension experiments, was also purchased from Aldrich (99.5%). Activated carbon was purchased from Lancaster and used as received.

**Methods.** Compounds were prepared according to ref 8. Sodium salts were generated by refluxing equimolar amounts of acid and \(NaOH\) for 8 h, in approximately 1.5 times the minimum amount of ethanol required to dissolve the acid. The hot solutions were passed over carbon black and the collected filtrate was allowed to boil while distilling excess ethanol. The solutions were then allowed to cool; the products were collected by filtration and washed with cold ethanol. The products were then dissolved in deionized water, any excess acid was extracted by shaking with distilled diethyl ether, and then the products were collected by evaporation of the aqueous phase. The powders were placed in a vacuum oven at 40 °C for 24 h over refreshed phosphorus pentoxide.

Electrical conductivities were determined using a Jenway model 4510 Conductivity/TDS meter with temperature controlled at 25 ± 0.1 °C (thermostatic water bath).

NMR proton shifts were measured using a Varian 400 MHz instrument at 25 °C, relative to HDO at 4.75 ppm.

Surface tension measurements were measured using the Wilhelmy plate method with a Krüss K100 instrument at 25 °C. Protocols for purification of the amphiphilic salts are given in the Supporting Information. Solutions were prepared with the necessary minimum amount of the chelating agent EDTA to sequester divalent ions introduced as impurities by \(NaOH\) in the preparation of the sodium salts (Supporting Information). All glassware was prewashed with 50% nitric acid and thoroughly rinsed with deionized water. The platinum plate was held over a blue flame until red hot after every measurement and then cooled to room temperature before every use.

Small-angle neutron scattering (SANS) was carried out on the D16 instrument at the Institute Laue Langevin (ILL). The wavelength at take off was 4.752 Å. A sample to detector distance of 900 mm was employed using three detector angles at 12°, 28°, and 44°, giving rise to a Q range of 0.01−1.2 Å\(^{-1}\). The sample changer was set at a 21° angle. Slits 1 were fully open at horizontally 15 mm and vertically 136 mm, whereas slits 2 (closest to the sample) were set at 5 mm horizontally and 8.8 mm vertically.

Additional measurements were made on the SANS2d instrument at ISIS at the Rutherford Laboratory. A simultaneous Q-range of 0.0045−0.75 Å\(^{-1}\) on the SANS2d instrument was achieved utilizing an incident wavelength range of 1.75−16.5 Å and employing an instrument set up of \(L_1=2 L_2=4\) m, with the 1 M2 detector offset vertically 150 mm and sideways 180 mm. The PhenCx series was measured on D16, as were CyclohexC1 and CyclohexC5. The compounds CyclohexC2−4 were measured on SANS2d.

The momentum transfer Q is defined as

\[
Q = \frac{4\pi \sin(\theta/2)}{\lambda}
\]

(1)

where \(\theta\) is the scattering angle and \(\lambda\) is the incident neutron wavelength.

D2O was used to prepare the solutions, providing the necessary contrast. Samples were contained in 2 mm path length Hellma fused silica cells. The SANS data were normalized for transmission and subtraction of the empty cell and solvent background.

The FISH program was employed for data modeling.10 The scattering profile curve is broadly described by...
I(Q) \propto P(Q)S(Q) \tag{2}

where P(Q) is the form factor, which contains information about the size and shape of the aggregates, and S(Q) is the structure factor reporting on interactions. Here the ellipsoidal P(Q) model was used in final fits, in combination with a Hayter-Penfold charge repulsion S(Q). The ellipsoidal aspect ratio X is characterized by two principal radii R₁ and R₃

\[ X = R_3/R_1 \tag{3} \]

Other model parameters include the volume fraction φ, the Debye length κ⁻¹, and the effective radius of the charged micelle R₃(Q). An approximate value of κ⁻¹ value can be calculated by

\[ \kappa = \left( \frac{2FρI}{ε_0εRT} \right)^{1/2} \tag{4} \]

F is the Faraday constant, ρ is the solvent density, I is the ionic strength, ε₀ is the permittivity of free space, εᵢ is the solvent dielectric constant, R is the gas constant, and T is the temperature.

The first approaches to fitting used hydrophobic tail lengths calculated using the Tanford equation

\[ l_{\text{max}} = 1.5 + 1.265n \tag{5} \]

where \( l_{\text{max}} \) is the fully extended chain and n is the carbon number of the linear chain. It was assumed that a benzene ring ≈ 3.5 CH₂ in length. The micellar radii R₁ and R₃ were minimized in the final analyses.

### RESULTS AND DISCUSSION

**Electrical Conductivity.** Electrical conductivity was employed as a first estimation of the cac, and the values are shown in Table 1. When the cac values of compounds containing the same number of carbons are compared, it is readily appreciated that the higher homologues (x = 4 and 5) of the saturated compounds have significantly lower cac values to the corresponding aromatic. The opposite trend however is noted when comparing the lower homologues (x = 1–3). In both classes of compounds, the conductivity profiles showed a slightly curved behavior for the lower homologues, whereas the higher ones exhibited a clear break, which is readily identifiable as a critical point and is associated with reaching the cmc of common surfactants. Figure 1 presents two example cases of each category, illustrating examples of readily identifiable changes in behavior as a function of concentration in the higher homologue, but instead a gradual change in slope in the lower homologues.

A Klevens type analysis shows two behavioral modes for the phenyl-tipped alkanoates. Figure 1a shows that the phenyl-tipped series mirrors the behavior of the alkylbenzoates, examined in ref 8. The break in behavior seems to occur once more, at four linear carbons. Whereas the aromatic compounds appear to share similarities with each other with respect to the behavioral gradients and breaks, the cyclohexyl-tipped compounds appear different. The cac of the homologues, with the exception of the parent hydrotrope (CyclohexC1), fall on a straight line.

The regular dlog(cac)/dn \( \approx 0.285 \) is found for most of the homologous series, with the first member being a slight outlier, indicative of the similarity in hydrophobic contribution to the linear carbons by those of the cyclohexyl ring. The equations describing the regions of behavior are:

\[ C_{\text{nBenz}} \ log(cac) = -0.2866n + 0.4179 \tag{6} \]

\[ \text{PhenC}_x \ log(cac) = -0.2714n + 0.5626 \tag{7} \]

\[ \text{CyclohexC}_x \ log(cac) = -0.2867n + 0.0752 \tag{8} \]

These compare well to the Klevens equation (eq 9) for regular sodium alkanoates, which is gratifying, considering the difficulty in attaining precise cac values by conductivity for such compounds, where ionic strength is very high and the cac values are large.

\[ \text{linear alkanoates} \ log(cac) = -0.2832n + 1.5145 \tag{9} \]

Skauge andSplitzer measured CyclohexC1-CyclohexC4 by surface tension, reporting cac values in good agreement to those listed here for the higher homologues. Cyclohexanecarboxylate (CyclohexC1) data did not yield a plateau and hence for this compound was not reported. Interestingly the cac of sodium cyclohexanecarboxylate (CyclohexC2) was reported having a cac of 1 M. This is much higher than the value presented in this study and closer to the cac value of the parent hydrotrope reported here. Skauge and Splitzer measured a Klevens-like equation (eq 10) by adding all of the carbon atoms (ring carbons inclusive) to n, which gave a very similar gradient to the sodium alkanote Klevens equation (eq 9).

\[ \text{CyclohexC}_x \* \ log(cac) = -0.29n + 2.03 \tag{10} \]

As stated previously, the difference in intercept values of alkanoates, the compounds under study, arises from not including the hydrophobic effect of the ring moieties into the value of n in the form of nₑ. MacInnis et al. also investigated these cyclohexane-tipped alkanoates by ¹³C NMR and Na-NMR reporting cmc values in good agreement to those found in S and here. They also report a higher cme value for CyclohexC2 at 0.89 M by sodium chemical shift change and 1.02 M by ¹³C chemical shift change. A more detailed discussion on the discrepancies can be found in the Supporting Information.

Examining the hydrophobic contribution of the cyclic components of these compounds (Figure 2b), the benzene ring in both classes reaches limiting values (nₑ) of 3–4 when n has reached 4. It is appreciated that the saturated component, cyclohexane, imparts a higher hydrophobic contribution to the structures than the aromatic ring in either case. The stronger hydrophobic contribution of the cyclohexyl group appears constant at nₑ \( \approx 5 \) and hence higher than the aromatic analogues. The comparison of cyclohexyl to the phenyl ring hydrophobic contribution has been demonstrated recently in branched dodecylammonium bromide analogues containing these ring moieties with the cyclohexyl-tipped compounds possessing a lower cac to their phenyl-tipped analogues. As the compared compounds are identical in all structural aspects

Table 1. Critical Aggregation Concentration (cac) Values as Determined by Electrical Conductivity

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>PhenC₅</th>
<th>CyclohexC₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.17</td>
<td>0.88</td>
</tr>
<tr>
<td>5</td>
<td>0.31</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>0.37</td>
<td>0.18</td>
</tr>
<tr>
<td>3</td>
<td>0.39</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>0.48</td>
<td>0.60</td>
</tr>
<tr>
<td>1</td>
<td>0.48</td>
<td>0.97</td>
</tr>
</tbody>
</table>

*Data from ref 8.
Apart from the ring moieties, then it is reasonable to infer a higher hydrophobic contribution by the cyclohexyl than the phenyl ring.

An interesting point is that the aromatic ring in the parent hydrotröpe (sodium benzoate) has a higher hydrophobic contribution than its saturated counterpart (sodium cyclohexanecarboxylate). However when the second behavioral region is reached, it appears that the saturated ring has a higher contribution than the aromatic ring, in effect reversing the trend of the first behavioral branch with respect to the ring moiety. Though both governed by the hydrophobic effect, they are thermodynamically different. The break in the aromatic compounds can be seen as occurring due to a switchover in thermodynamic behavior. In the first behavioral branch it is the aromatic carbons that dominate the aggregation process, switching over to the saturated linear tails in the second branch. The saturated compounds however show no change.

This can be seen to result from the small difference between the cyclic saturated carbons and those belonging to the saturated linear tail, which may explain why the parent compounds show such difference in hydrophobic contributions across the three series. While sodium benzoate has a $n_{\text{eff}}$ of approximately 6.5 carbon atoms, sodium cyclohexanecarboxylate has a $n_{\text{eff}}$ of ~5 carbon atoms. This becomes an interesting point when considering that the cac approximately doubles, when the amphiphile “acquires” a double bond. The cac values of sodium cyclohexanecarboxylate and sodium benzoate do not compare directly, implying that aromaticity does play a role in promoting aggregation. The possibility of $\pi-\pi$ interactions has indeed been suggested in the past; however, the exact nature of this effect cannot be identified from the results of this study.

The electrical conductivity profiles of all compounds are similar with those of alkylbenzoates, in that lower homologues appear to lack clear breaks, whereas the higher homologues show a clear break in gradient. A Kleven type analysis of the PhenCx series supports the finding of a change in behavior at four linear carbons in line with the CnBenz series, which could be seen as the transition point from hydrotröpe to surfactants. The CyclohexCx series however reveals that the common Kleven behavior, encountered in linear alkanoes, is seen for all cyclohexyl-$n$-alkanoates, whose lower homologues possess cac values higher than those of the aromatic series; reinforcing the idea of a hydrophobic, thermodynamic balance at play, between saturated and unsaturated tail carbons.

Surface Tension Measurements. All compounds exhibited surface tension behavior similar to that of common surfactants. Figure 3 illustrates the behavior of surface tension

$\gamma$ with activity (a) of PhenCx compounds with the $\gamma$ vs ln(a) plots exhibiting a smooth “pre-cac” tension decrease followed by a sharp break at the cac and a “post-cac” plateau. Data for PhenC3 were of poor quality, with low reproducibility, but broadly exhibiting similar features to the rest of the homologous series, as was for the carbon number equivalent C2Benz. Despite these difficulties, an approximate analysis still yields parameters in accord with the rest of the homologous series (Table 2). CyclohexCx compounds however do not

<table>
<thead>
<tr>
<th>PhenCx</th>
<th>activity (a)</th>
<th>$\gamma_{\text{cac}} \pm 0.01/(\text{mN/m})^2$</th>
<th>$\Gamma_{\text{cac}} \pm 0.1/(10^{-6} \text{ mol/m}^2)$</th>
<th>$A_{\text{cac}} \pm 10%/\text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.31</td>
<td>52.8</td>
<td>3.1</td>
<td>53.2</td>
</tr>
<tr>
<td>5</td>
<td>0.26</td>
<td>48.5</td>
<td>5.0</td>
<td>32.9</td>
</tr>
</tbody>
</table>
exhibit such inconsistencies (Figure 4) with all compounds behaving like typical surfactants even in the case of the parent

hydrotrope sodium cyclohexanecarboxylate with cac \( \approx 1 \) M. Only two of the PhenCx homologues are presented here due to the presence of impurities in the other compounds, despite being subjected to the same purification method. This can be expected, especially for the lower homologues, as their surface activity is quite low and hence even small amounts of impurities impart a big effect. As such, this is also a testament to the very high purity of the compounds that do exhibit a regular Gibbs isotherm.

For both classes of compounds, the limiting tension \( \gamma_{\text{cac}} \) shows a chain length dependence, decreasing with increasing \( n \), consistent with increased alkyl chain density lowering surface energy.\(^{20}\) The cac values as determined by tension measurements are in good agreement with those determined by electrical conductivity (Table 1). A slight decrease in “pre-cac” gradient with decreasing chain length is seen which was also observed for alkybenzoates.\(^{3} \) The pre-cac tensions were analyzed in terms of the Gibbs adsorption equation

\[
\Gamma = -\frac{1}{mRT} \frac{d\gamma}{\ln \alpha}
\]  

where \( \Gamma \) is the surface excess (mol m\(^{-2}\)), \( m \) is a constant associated with ion dissociation (see below), and \( R \) and \( T \) represent the gas constant and temperature. The activity coefficients were estimated using standard procedures.\(^{21} \)

Using a combination of surface tension and neutron reflectivity, a prefactor \( m = 2^{12-25} \) has been shown for ionic surfactants (<10 mM; in the presence of sufficient M\(^{12-} \) sequestrant EDTA). This value of \( m = 2 \) is taken to hold here despite the cacs being much higher than for conventional surfactants. The surface excesses \( \Gamma \) were determined by fitting quadratics to the pre-cac curves, the function and coefficients were used to generate local tangents and hence \( \Gamma \) vs \( c \) profiles. With the coefficients and the associated derivatives used to find the local tangents. Effective headgroup areas \( (A_{\text{hc}}) \) were estimated using eq 12

\[
A_{\text{hc}} = \frac{1}{\Gamma N}\n\]

where \( N_{A} \) is the Avogadro number.

The investigation of CyclohexC1-CyclohexC4 by surface tension by Skauge and Splitzler\(^{15} \) yielded slightly higher \( A_{\text{hc}} \) values, at around 60–65 Å\(^2\), though still comparable to the values ascertained in this study, and with a similar converging trend of values. The discrepancy in \( A_{\text{hc}} \) values could be attributed to the difference in solution preparation\(^{15} \) in that the stock solutions were prepared to pH \( \approx 10 \), whereas in this study the pH of the solution was not controlled.

The converging limiting adsorption parameters in both PhenCx and CyclohexCx series imply that adsorption is dictated by the ring moieties when the linear tail is short. The higher homologues show lower limiting surface tensions and headgroup area values, which are more typical of common surfactants. The reduction in \( \gamma_{\text{cac}} \) with \( n \) follows increased surface chain density\(^{26} \) longer alkyl chains pack more closely and have lower surface energies.

Pitt et al\(^{20} \) observed that compounds with similar cac values and headgroup areas but with different tail ends, exhibited limiting surface tensions following the trend of \( \text{CF}_3 < \text{CF}_2 < \text{CH}_3 < \text{CH}_2 < \text{phenyl} \). Similarly Nave et al.\(^{27} \) observed that phenyl-tipped Aerosol-OT analogues exhibited higher limiting surface tensions to that of regular \( \text{CH}_3 \)-tipped Aerosol-OT. These trends hold for this study as well, when analogues of similar cac values are compared.

In contrast to conductivity behavior (Figure 1), there does not appear to be any clear distinction between the air–water adsorption behavior of the compounds belonging to either behavioral branch of the Klevens plot. The results reveal that difficulties encountered for the lower homologues \( \text{C}_n\text{Benz} \) series are not a result of these compounds possessing physicochemical properties different to common surfactants and exclusive to “hydrotopes”; as the CyclohexCx series exhibited well-defined behavior for all homologues, with the lower ones possessing cac values considerably higher to the corresponding aromatic analogues. As such surface tension investigations in this study reiterate the conclusion\(^{8} \) that there does not appear to be a behavioral difference between “hydrotopes” and common surfactants.

A point of interest is that if the surface tension-determined cac of CyclohexC1 is used in the Klevens analysis for this series, then all \( \log(\text{cac}) \) values fall on the same line (eq 11) with similar to that obtained by electrical conductivity (eq 8).

\[
\log(\text{cac}) = -0.2875n + 0.0776
\]

This further emphasizes the thermodynamic similarity of the saturated cyclohexyl-ring carbons to the linear alkane carbons, as well as the difficulty in obtaining precise cac values at such low levels of hydrophobicity.

**NMR Proton Chemical Shift Measurements.** The difference in chemical shifts for the aromatic ring protons between the lowest concentration and those for higher concentrations, defined as \( \Delta \delta \) (ppm), was studied as a function

### Table 3. Parameters for the CyclohexCx Series, Derived from Surface Tension Measurements Using the Gibbs Equation in Terms of Activity

<table>
<thead>
<tr>
<th>CyclohexCx</th>
<th>( \alpha ) (( \gamma_{\text{cac}} ) ± 0.1/(mN m(^{-1}))</th>
<th>( \Gamma_{\text{cac}} ) ± 0.1/(10(^{-6}) mol m(^{-2}))</th>
<th>( A_{\text{hc}} ) ± 10%/Å(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.20</td>
<td>51.1</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>46.8</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>0.19</td>
<td>45.0</td>
<td>3.3</td>
</tr>
<tr>
<td>5</td>
<td>0.08</td>
<td>44.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>

The pH of the solution was not controlled.
of concentration. The behavior of the shift change with concentration is shown for all PhenCx homologues in Figure 5.

The value $\Delta \delta$ is approximately constant in the dilute region, with a change in behavior at values consistent with the cac as determined by electrical conductivity. The change in $\Delta \delta$ behavior comes from a change in the environment experienced by the protons. Lower homologues appear to go through a smooth transition in behavior with the $\Delta \delta$ vs $\log(c)$ being curved in the cac region. A sharper transition is only observed for the PhenC6 analogue, the highest homologue in the series studied. This $\Delta \delta$ vs $\log(c)$ behavior was also observed for the $n$-alkylbenzoate series with a definite presence of a clear break point in behavior appearing at the C5Benz and higher homologues. All PhenCx protons shifted with increasing concentration, which according to the reasoning found in indicates that the phenyl rings are embedded in the aggregates, in accord to the observations made by Martin et al. who employed the more sophisticated ROSEY $^1$H NMR experiment to determine the locus of the phenyl- and cyclohexyl-tipped DTAB analogues.

The figure for the behavior of the shift change of CyclohexCx series protons with concentration can be found in the Supporting Information. Again all protons shifted producing a plateau in the dilute region and this time a break in behavior for all homologues at values consistent with the cac values determined by electrical conductivity. A break point is observed for the highest homologue, CyclohexC5, whereas the smaller ones exhibit a smooth transition. Further still all protons shifted in the opposite direction to those of phenyl-$n$-alkanoate protons.

The shift direction to lower ppm values has in the past been attributed to the protons experiencing a more apolar environment. Based on the results of Martin et al. where the cyclohexyl-ring was found to be embedded in the micelle, the parallel of the chemical shift axis to a hydrophobic scale can only be limited to aromatic compounds. It has been previously speculated that the change in direction of the proton chemical shift of the terminal CH$_3$- protons of surfactants is due to alkyl chain bending toward the aggregate palisade.

With respect to the mode of aggregation these $^1$H NMR studies provide an ambiguous picture as due to the existence of a distinction between the smooth transitions of the lower homologues and the sharp breaks observed for the higher homologues.

Small-Angle Neutron Scattering (SANS). SANS is a technique capable of directly probing the nature of amphiphile aggregates and other soft matter, unlike conventional techniques which offer indirect information. By the nature of the molecules in this work, results will be complementary to the earlier study on $n$-alkylbenzoates, which are structurally related.

Hydrotrope solutions in D$_2$O were prepared as multiples of the cac determined from conductivity measurements (Table 1), except for CyclohexC1 where the cac was that determined by surface tension. Figure 6 shows example SANS data for PhenC3 and CyclohexC5. For all compounds in this study, the scattering profiles are consistent with charged aggregates, features observed for anionic surfactants like SDS above the cmc. The intensity $I(Q)$ decreases with concentration to the point where it may not be detectable at $1 \times$ cac and below. Such behavior supports a surfactant-like “on-off” mode of aggregation crossing the cac (cmc) and is observed across the homologous series for both phenyl-$n$-alkanoate and cyclohexyl-$n$-alkanoate classes [see the Supporting Information].
Figure 7 shows scattering profiles of PhenCx and CyclohexCx D$_2$O solutions at 4 × cac, showing broadly common behavior across the series. Increasing chain length leads to increasing $I(Q)$, with $S(Q)$ also becoming more pronounced, suggesting stronger aggregate interactions. The data were fitted using the protocol and model described in the Experimental section, being consistent with charged ellipsoid aggregates at concentrations of 4 × cac (Table 4) and 2 × cac (Supporting Information).

The data and analyses show a persistent aggregation behavior across the homologous series: from the short chain homologues considered “true hydrotropes” to the longer chain homologues, considered closer to “true surfactants”, in both saturated cyclohexyl and aromatic phenyl classes.

When the scattering parameters in Table 4 and those reported in ref 8 are compared, it becomes apparent that for equal carbon number molecules aggregates follow the size order:

CyclohexCx > CnBenz > PhenCx

Table 4. Parameters Obtained by Fitting SANS Data to the Charged Ellipsoid Aggregate Model for PhenCx and CyclohexCx Homologous Series at 4 × cac

<table>
<thead>
<tr>
<th>PhenCx</th>
<th>$P(Q)$</th>
<th>$S(Q)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_g/\AA$</td>
<td>$X$</td>
<td>$k/\AA^{-1}$</td>
</tr>
<tr>
<td>5</td>
<td>7.9</td>
<td>2.2</td>
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<tr>
<td>4</td>
<td>6.7</td>
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<td>2.1</td>
</tr>
<tr>
<td>1$^a$</td>
<td>4.8</td>
<td>1.2</td>
</tr>
<tr>
<td>CyclohexC1</td>
<td>10.1</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>8.9</td>
<td>1.6</td>
</tr>
<tr>
<td>3</td>
<td>7.8</td>
<td>1.96</td>
</tr>
<tr>
<td>2</td>
<td>6.9</td>
<td>1.54</td>
</tr>
<tr>
<td>1$^b$</td>
<td>4.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

$^a$Parameters for C0Benz (sodium benzoate) at 4 × cac taken from ref 8. $^b$Parameters for CyclohexC1 (sodium cyclohexanecarboxylate) at 2 × cac. $R_g$ apparent radius in the $S(Q)$ model.

In the fitting procedure the Tanford equation (eq 5) was used as a first approximation to the length of the molecules. The aggregate sizes formed for phenyl-$n$-alkanoates were smaller than the predicted molecular length values, and for cyclohexyl-$n$-alkanoates to a lesser extent. For the latter, these discrepancies became smaller with longer molecules.

SANS is a direct report of the presence or absence of (commonly) H-domains in D$_2$O. Hence its capabilities extend in distinguishing between a gradual stepwise and sharp “on–off” mode of aggregation. The scattering profiles in this study are in line with the previous findings; an “on–off” aggregation mechanism is observed for a further two classes of organic salts. Despite the structural differences between CnBenz, PhenCx and CyclohexCx compounds, which are subtle, though significant, the profiles are consistent with charged ellipsoid structures in all cases. Previous studies by Triolo et al. demonstrated that a wide range of hydrotropes do associate in forms consistent with spherical aggregates near the cac and ellipsoid aggregates at higher concentrations. Pal et al. found that sodium butylbenzenesulfonate formed ellipsoid aggregates at approximately eight times the cac as determined by Balsubramanian et al.

CONCLUSIONS

The dilute aqueous phase properties of two classes of cyclic-tipped alkanoates have been investigated, with the results reinforcing the notion that hydrotropes with very different chemical structures exhibit similar solution, interfacial, and association properties as common surfactants. These findings support the observations made previously for the linear chain $n$-alkylbenzoate series.

Conductivity measurements with both classes of homologues, report a gradual physicochemical change with concentration, which would be consistent with a stepwise aggregation mechanism for the lower homologues, whereas a sharp break in behavior for higher homologues, more reminiscent of typical surfactant behavior. Kleven's analyses of the chain length dependence of critical aggregation (as in ref 8) show that phenyl-$n$-alkanoates exhibit a break in behavior at four linear carbons, in agreement with other observations with related compounds. Comparing compounds of equivalent carbon number, phenyl-$n$-alkanoates and $n$-alkylbenzoates have broadly similar cacs. Interestingly lower homologues of the...
cyclohexyl-n-alkanoate series are more hydrophilic than the equivalent n-alkylbenzoates and phenyl-n-alkanoates. However, this trend is inverted for higher homologues, with the cyclohexyl-n-alkanoates being the most hydrophobic of the three classes. The cyclohexyl-n-alkanoates appear to also parallel regular n-alkanoates from the first added −CH2− onward, behavior arising at much shorter chain length than for the aromatic series. These observations reinforce the concept of a thermodynamic balance between ring carbons and linear carbons. Aromatic carbons appear to dominate the aggregation behavior up to a certain value of n, after which the linear −CH2− groups take over. Cyclohexyl, −CH2−, being saturated, is closer in nature to the linear tail −CH2− carbons, hence the break in behavior occurs at a much shorter chain length. Surface tension measurements do not exhibit such a distinction in behavior, with homologues belonging to either dlog(cac)/d

branches of the Klevens plot, exhibiting typical Gibbs adsorption branches.

NMR experiments are consistent with lower homologues gradually forming ill-defined structures, whereas higher homologues present a more abrupt change more typical of classical surfactants.

SANS profiles on the other hand show clear transitions from apparently nonstructured solutions, then giving clear evidence for the presence of aggregates above a certain concentration. With previous reports on related compounds, these additives appear to form ellipsoid-shaped aggregates.

This work reiterates the notion that physicochemical behavior of “hydrotropes” is very similar to that of regular surfactants. Further still, amplifying recent work with surfactant ionic liquids (SAILs), it is demonstrated that not all carbons are thermodynamically equal, even though they are hydrophobic enough to drive aggregation and interfacial phenomena. This is now clearly emphasized here, seen in the distinctly different behavior of saturated cyclic versus aromatic cyclic amphiphiles, as well as for the CHn/CH2 groups in surfactant anions and organic counterions in SAILs. A point not debated often enough is the degree of hydrophobicity of “unusual” carbons; hence, distinguishing between surfactants and nonsurfactant amphiphiles on the basis of hydrophobic moiety atomic arrangements should be revisited. This aspect of surfactant/hydrotrope chemical structure—function relationships deserves further attention for providing a deeper understanding about molecules.

ASSOCIATED CONTENT

Supporting Information Additional details of hydrotrope solution properties, surface tensions, NMR, and neutron scattering data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes The authors declare no competing financial interest.

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