

Why Do Methylated and Unsubstituted Cyclodextrins Interact So Differently with Sodium Decanoate Micelles in Water?

Cristiano Andrade-Dias,[†] Sérgio Lima,[†] José J. C. Teixeira-Dias,^{*,‡} and José Teixeira[‡]

CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal, and Laboratoire Léon Brillouin (UMR12 CEA-CNRS), Saclay, France

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Small-angle neutron scattering is used to study the influence that methylated and unsubstituted cyclodextrins might have on sodium decanoate micelles in D₂O aqueous solution. When the concentration of the cyclodextrin is varied in a 200 mM sodium decanoate solution (CMC \approx 116 mM), it is found that methylated and unsubstituted cyclodextrins exhibit distinct behaviors. In particular, permethyl- α CD, dimethyl- β CD, and permethyl- β CD display linear increases of the specific surface area S/V obtained from the Porod equation with slopes following the degree of methylation of the cyclodextrins, whereas α CD and β CD present close S/V values which are approximately independent of the cyclodextrin concentration at least for the considered concentration range (from 5 mM up to 45 mM). When a cyclodextrin is added to the 200 mM perdeuterated sodium decanoate NaDec(d_{19}) solution in D₂O ($[CD]_0 = 30$ mM), methylated cyclodextrins show correlation peaks in the $I(Q)$ distributions, whereas α CD and β CD do not originate any correlation maximum. On the whole, the experimental results point to the adsorption of methylated cyclodextrins on the surface of the formed decanoate micelles and are consonant with the existence of an equilibrium between the molecules in aqueous solution and those adsorbed by the micelles. In turn, unsubstituted cyclodextrins are not adsorbed by the decanoate micelles and so are involved in a guest–host equilibrium with the decanoate ion in solution. As the cyclodextrin concentration increases, this equilibrium leads to the shifting of the multiple equilibria involving micelles of successive aggregation numbers toward those of smaller dimensions and to the decrease of the average intermicellar distance. It is suggested that methylated cyclodextrins should be more easily adsorbed on the electric double layer of the decanoate micelle–water interface than the unsubstituted cyclodextrins, as the former tend to sample the environment that is most energetically favorable, where the dielectric permittivity is lower than in bulk water and so is closer to those of the methylated cyclodextrins.

Introduction

Because of their hydrophilic–hydrophobic dual nature, surfactants can self-associate in water originating organized structures of different types and behaviors which result mainly from a balance between the hydrophobic attraction between the hydrocarbon chains and the headgroup hydrophilic repulsion.¹ The sizes and shapes of the aggregates are dependent on the structural characteristics of the amphiphile (the length and number of chains, the conformational flexibility of the hydrophobic moiety, the charge and dimension of the polar headgroup), and on medium variables (the amphiphile initial concentration, the solution pH and temperature, the electrolyte concentration).^{1–4}

The aggregation behavior of various salts of carboxylic acids in water and, in particular, of decanoate salts, illustrates most of the above-mentioned factors.^{5–16} For example, it has been shown by small-angle neutron scattering (SANS) that ammonium decanoate in D₂O solution originates spherical micelles.^{17,18} Analysis of ¹H NMR chemical shift variations of the methyl protons of sodium decanoate in D₂O solutions shows the occurrence of a critical micellar concentration (CMC) approximately equal to 116 mM, points to a narrow distribution of sizes about the mean aggregation number for decanoate ion

micelles and further suggests that, with an increase of temperature, the mobility of the decanoate ion chains in the micelles is improved and the methyl groups tend to spend more time near the micelle–water interfaces.¹⁹

Over the past two decades, the study of multicomponent systems has led to the design and preparation of supramolecular materials. In particular, cyclodextrins, doughnut-shaped cyclic oligomers formed by (α –1,4)-linked α -D-glucopyranose units, have played an important role in this context, as a result of the way they interact with other molecules by including molecules or molecular fragments in their internal cavities. In addition, various papers have reported that cyclodextrins influence micellization processes. For example, it has been previously suggested that hydroxypropylcyclodextrins (α , β , and γ) may lead to an increase in micelle size of a nonionic gemini surfactant and to a gradual transformation from spherical to rod-shaped aggregates.²⁰

The present work assesses the interactions between various unsubstituted (“native”) and methylated cyclodextrins and the micelles of sodium decanoate in D₂O solutions, using small angle neutron scattering. The sodium decanoate initial concentration (200 mM) is well above its critical micellar concentration in water (CMC = 116 mM)¹⁹ and the cyclodextrin concentration takes the values 5, 10, 15, 20, 30, and 45 mM. These concentrations correspond to a large excess of the decanoate monomer ions with respect to the cyclodextrin. In some of the SANS experiments, perdeuterated sodium decanoate was used

* To whom correspondence should be addressed. E-mail: teixeiradias@ua.pt. Tel: +351234370360. Fax: +351234370084.

[†] University of Aveiro.

[‡] Laboratoire Léon Brillouin.

in order to appreciably reduce the contrast, that is, the difference between the density of scattering lengths of micelles and water, and better discern the effect produced by adding a cyclodextrin. Varying the size and dimensions of the cyclodextrin and its degree of methylation may produce an effect on the interaction between the cyclodextrin and the micellar aggregates. We use α - and β -cyclodextrins (these have 6 and 7 glucopyranose units, respectively) and the following methylated cyclodextrins: permethyl- α -cyclodextrin, dimethyl- β -cyclodextrin, and permethyl- β -cyclodextrin.

Experimental Section

Materials. Sodium decanoate (NaDec, Sigma, 98%), D₂O (Aldrich, 99.9%), α -cyclodextrin (α CD, Fluka, 99%), heptakis (2,3,6-tri-O-methyl)- α -cyclodextrin (TRIMEA, Cyclolab, water content <5%), β -cyclodextrin (β CD, Fluka, 99%), (2,6-di-O-methyl)- β -cyclodextrin (DIMEB, Fluka, $\geq 98\%$), and heptakis (2,3,6-tri-O-methyl)- β -cyclodextrin (TRIMEB, Fluka, $\geq 98\%$) were used as received without further purification. Sodium decanoate-*d*₁₉ was prepared by dissolving 1 g of decanoic acid-*d*₁₉ (NaDec(*d*₁₉), Cambridge Isotope Laboratories, 98%) and 0.21 g of NaH (Aldrich, 60%, dispersion in mineral oil) into 20 mL of tetrahydrofuran (THF) (Riedel-DeHaen, $\geq 99.9\%$) under nitrogen atmosphere and vacuum. After stirring for several hours, 30 mL of THF was added. The resulting mixture was stirred for two additional hours and the THF was dried under vacuum. All the solutions used in this work were prepared following the general procedure mentioned elsewhere.^{21–23}

Method. SANS experiments were performed at the LLB, Saclay, France, using the PAXE small-angle neutron scattering facility. The incident neutron wavelength was $\lambda = 6 \text{ \AA}$ with a wavelength spread of $\Delta\lambda/\lambda = 10\%$. The sample–detector distance was 1 m, covering the range of the magnitude of the scattering vector from 0.0126 to 0.363 \AA^{-1} . Samples were contained in flat quartz cells with a path length of 1 mm. All measurements were made at room temperature of 25 °C. The two-dimensional intensity distributions were corrected for the background and the empty cell contributions, and then normalized to absolute intensities by a direct measurement of the intensity of the incident neutron beam.^{24,25} By integrating the normalized two-dimensional intensity distribution with respect to the azimuthal angle, one-dimensional scattering intensity distributions $I(Q)$ in the units of a differential cross section per unit volume of the sample (cm^{-1}) were obtained.

The occurrence of a correlation peak in $I(Q)$ is a manifestation of appreciable interactions between the micelles. The value Q_{max} at which the maximum of $I(Q)$ occurs enables us to determine the average distance between micelles from the equation $d = 2\pi/Q_{\text{max}}$.²⁶ This equation can also be used to define a molecular-level length scale resulting from the Q -range accessible in the SANS experiment. Q_{max} values were determined by fitting the $I(Q)$ curves near the maxima with second-order polynomials.

The scattering length density of a molecule with i atoms can be calculated by the expression $\rho = (\delta N_A/M)\sum b_i$, where δ is the bulk density of the molecule, N_A is the Avogadro number, M its molecular weight, and b_i is the coherent neutron scattering length of nucleus i . The following bulk densities (g cm^{-3}) were used in the calculations for H₂O (0.997), D₂O (1.107), Dec[−](=CH₃(CH₂)₈COO[−]) (0.886), Dec[−](*d*₁₉) (0.984).²⁷ For the anhydrous forms of the cyclodextrins, α CD (1.34), β CD (1.22), DIMEB (1.24), TRIMEA (1.26), and TRIMEB (1.24), were directly obtained or deduced from the values reported for the cyclodextrin hydrates.²⁸

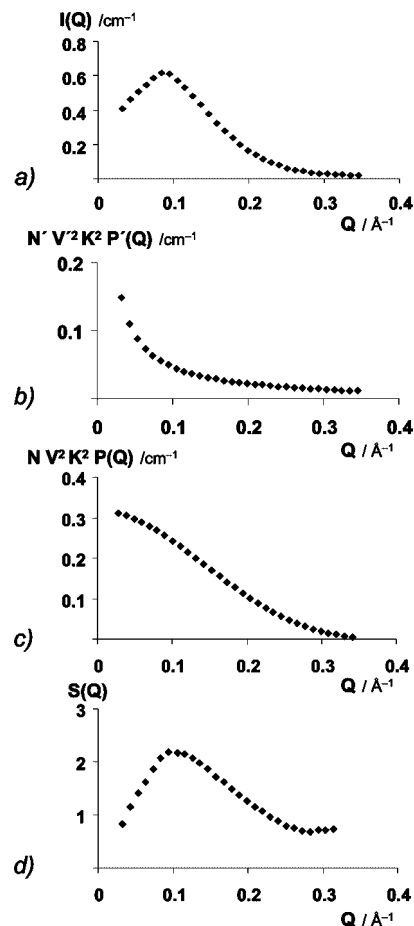


Figure 1. (a) Experimental scattered intensity vs Q for a 200 mM sodium decanoate solution in D₂O, at room temperature. The corresponding form and structure factors are shown below (see text): (b) $N^{-1} V^2 K^2 P'(Q)$, (c) $N V^2 K^2 P(Q)$, and (d) $S(Q)$.

Results and Discussion

The Sodium Decanoate Solution. The presence of charge in the decanoate ion headgroup plays an essential role in the emergence of the surfactant characteristics of sodium decanoate solutions. When the initial concentration of sodium decanoate, $[\text{NaDec}]_0$, increases gradually, it was shown by ¹H NMR chemical shifts plotted against concentration that the decanoate ions originate micellar aggregates, when $[\text{NaDec}]_0$ is above CMC $\approx 116 \text{ mM}$.¹⁹

Figure 1a shows the experimental scattered intensity versus Q for a 200 mM sodium decanoate solution in D₂O at room temperature. The observed correlation peak occurs at $Q_{\text{max}} = 0.0879 \text{ \AA}^{-1}$ which corresponds to the average intermicellar distance $d = 71.5 \text{ \AA}$. Since the aqueous solution is an isotropic medium, the micelles are regularly distributed in the medium. Hence, if one assumes a cubic arrangement, that is, each micelle having six next neighbors on the vertices of a regular octaeder (octaedic coordination), then it is possible to estimate the number density of micelles ($1/d^3 = 2.74 \times 10^{18} \text{ micelles cm}^{-3}$) and the average aggregation number of each micelle ($n_{\text{agg}} = 18.5$). In this calculation it was assumed that the concentration of decanoate molecules in the micelles is equal to $C_0 - \text{CMC} = 84 \text{ mM}$, where $C_0 = 200 \text{ mM}$ and $\text{CMC} = 116 \text{ mM}$.¹⁹

Assuming that our system contains only two different phases, each of constant scattering length, ρ_{Dec} and ρ_{D2O} , and that the boundary between them is sharp, that is, has no measurable thickness, then the specific surface (interfacial) area, that is, the ratio S/V , can be determined from the Porod equation, $P(Q) =$

$2\pi K^2(S/V)Q^{-4}$, for values of Q much larger than the inverse of the smallest dimensions of the scattering particle. In this expression, K is the contrast ($K = \rho_{\text{Dec}} - \rho_{\text{D}_2\text{O}} = -6.12 \times 10^{10} \text{ cm}^{-2}$), S is the total area of the boundaries between the two phases and V is the total scattering volume.^{25,26,29} The value thus obtained for the specific surface area is $S/V = 1.07 \times 10^6 \text{ cm}^{-1}$. This value includes surface contributions not only from formed micelles, but also from decanoate monomers and oligomers, all contained in 1 cm^3 of sample.

In order to estimate the average surface area per decanoate molecule in the micelles, S_{mic} , S/V should be multiplied by the fraction of decanoate molecules in the micelles, x_{mic} ($= 84/200$), and subsequently divided by the total number of decanoate molecules in 1 cm^3 of sample, $S_{\text{mic}} = (S/V)x_{\text{mic}}/(1/d^3)$, yielding 88.7 \AA^2 . If it is further assumed that the decanoate micelles are spherical, then their radius is equal to 11.4 \AA . These two values can be easily reproduced by independent semiempirical estimates based on geometric and packing constraints,^{1,2} using an estimate for the volume contribution of the carboxylate ion.³⁰

If a model system of monodisperse spherical micelles in equilibrium with monomers is assumed, then the experimental $I(Q)$ distribution (Figure 1a) can be described by a sum of two terms, the first representing the scattering by sodium decanoate micelles, the second accounting for the scattering from decanoate monomers

$$I(Q) = NV^2K^2P(Q)S(Q) + N'V'^2K^2P'(Q) \quad (1)$$

In the second term of this expression, N' is the number density of isolated decanoate ions whose concentration is equal to the sodium decanoate CMC (116 mM), V' is the volume occupied by one decanoate molecule, K is the contrast, and $P'(Q)$ is the form factor of a cylinder ($P'(Q) = (\pi/(QL))\exp(-Q^2W^2/16)$).²⁵ This form factor represents the decanoate molecule with a fully extended (all-trans) hydrocarbon chain. $N'V'^2K^2P'(Q)$ is shown in Figure 1b for cylinders with length $L = 15 \text{ \AA}$ and diameter $W = 5 \text{ \AA}$.

In the first term of the above expression, N is the number density of spherical decanoate micelles with volume V , and $P(Q)$ is the form factor for spherical micelles ($P(Q) = \{3[\sin(QR) - QR \cos(QR)]/(QR)^3\}^2$).²⁵ $NV^2K^2P(Q)$ is shown in Figure 1c for $R = 11 \text{ \AA}$.

The structure factor $S(Q)$ expresses the spatial arrangement of the micelles in solution (a consequence of intermicellar interactions) and results from the interference of scattered waves by the micelles in solution. At large Q values, $S(Q)$ approaches 1. Hence, it does not appear explicitly in the second term of $I(Q)$. Solving the above $I(Q)$ expression for $S(Q)$, one obtains (Figure 1d)

$$S(Q) = (I(Q) - N'V'^2K^2P'(Q))/(NV^2K^2P(Q)) \quad (2)$$

In the Presence of Cyclodextrins. In order to assess the influence unsubstituted and methylated cyclodextrins might exert on sodium decanoate micelles, each cyclodextrin was added to the sodium decanoate solution. Figure 2 shows the $I(Q)$ curves for sodium decanoate solutions in the presence of β CD with defined concentrations (5, 10, 15, 20, 30, and 45 mM; the solution in the absence of cyclodextrin is also shown for comparison). As the β CD concentration increases, the correlation peaks decrease in intensity and become wider, pointing to the weakening of the intermicellar correlation and suggesting a larger micellar polydispersity. The latter manifests itself by the

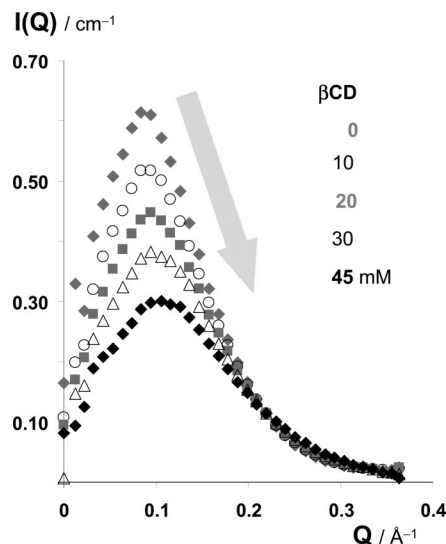


Figure 2. Experimental scattered intensity vs Q for a 200 mM sodium decanoate solution in D_2O at room temperature with various concentrations of β CD (0, 10, 20, 30, and 45 mM).

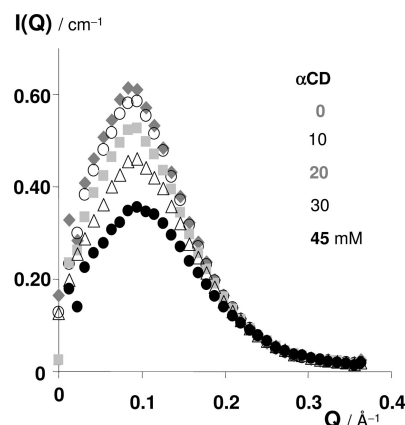


Figure 3. Experimental scattered intensity vs Q for a 200 mM sodium decanoate solution in D_2O at room temperature with various concentrations of α CD (0, 10, 20, 30, and 45 mM).

increase of the width of the correlation peak, with the increase of $[\beta\text{CD}]_0$, an effect which was also observed for α CD, particularly, when $[\alpha\text{CD}]_0 = 45 \text{ mM}$ (Figure 3). A closer observation of the broadening of the correlation peaks shows that it occurs mainly on the large Q wings, favoring aggregates with smaller aggregation numbers and increasing the number density of micelles, thus contributing to the decrease of the average distance between them.

Let us now consider in Figure 4 the $I(Q)$ curves for sodium decanoate solutions in the presence of permethyl- β CD, that is, TRIMEB, added in different concentrations (5, 10, 15, 20, 30, and 45 mM; the solution in the absence of cyclodextrin is shown for comparison). As $[\text{TRIMEB}]_0$ increases, the Q_{max} values increase and the correlation peaks increase in intensity, suggesting that the correlation between different micelles becomes stronger. For $Q > 0.2 \text{ \AA}^{-1}$, $I(Q)$ is sensitive to the variation of $[\text{TRIMEB}]_0$, unlike what was observed for β CD.

The above distinctive trends of β CD and TRIMEB have been also confirmed by α CD, which behaved like β CD, and by DIMEB and TRIMEA, which exhibited trends similar to TRIMEB (the $I(Q)$ distributions for DIMEB and TRIMEA, as functions of the cyclodextrin concentration, are not shown). In particular, the observed variation of the Q_{max} values enables to estimate the average distance between micelles and plot this

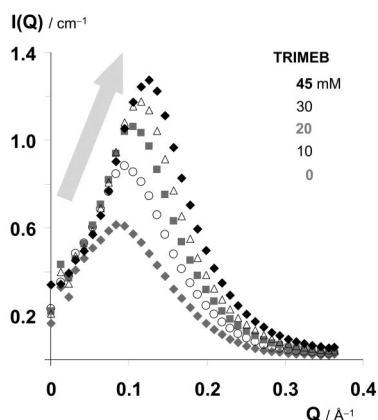


Figure 4. Experimental scattered intensity vs Q for a 200 mM sodium decanoate solution in D_2O at room temperature with various concentrations of TRIMEB (0, 10, 20, 30, and 45 mM).

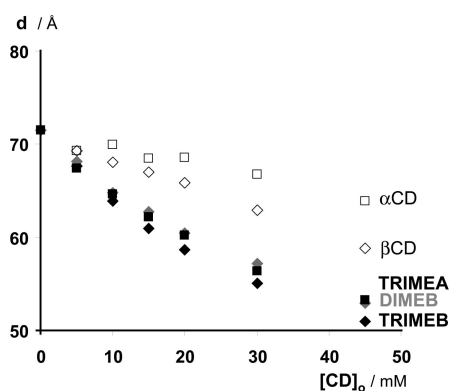


Figure 5. The average distance between micelles d obtained from Q_{\max} values (see text), as a function of the cyclodextrin concentration (0, 5, 10, 15, 20, 30, and 45 mM), for α CD, β CD, DIMEB, TRIMEA, and TRIMEB.

distance as a function of the cyclodextrin concentration for all considered cyclodextrins (Figure 5). While d decreases as $[CD]_0$ increases, for all the cyclodextrins, the methylated cyclodextrins exhibit larger negative slopes with closer variations, as compared with the unsubstituted cyclodextrins. We will come back to the interpretation of these variations after discussing the S/V results.

Figure 6 shows the specific surface area values for all the cyclodextrins considered in this work, as functions of the cyclodextrin concentration. From this plot, a clear distinction between methylated and unsubstituted cyclodextrins emerges; while the former display linear increases of S/V with correlation coefficients larger than 0.996 and slopes increasing in the order DIMEB < TRIMEA < TRIMEB, the latter present close S/V values which are approximately independent of the cyclodextrin concentration, at least for the considered concentration range. The order of increase of the S/V slopes for the methylated cyclodextrins follows the total number of methyl groups per cyclodextrin molecule, namely, 14 for DIMEB, 18 for TRIMEA, 21 for TRIMEB.

The linear S/V versus $[mCD]_0$ dependences (mCD stands for methylated cyclodextrin, in this work, DIMEB, TRIMEA, or TRIMEB) correspond to constant slopes, that is, to constant values of $\Delta(S/V)/\Delta[mCD]_0$. Since the sample volume appears both in the numerator and the denominator of these quantities, it can be canceled, and the $\Delta(S/V)/\Delta[mCD]_0$ slopes converted without any additional assumption into the rates of variation of the surface area per methylated cyclodextrin molecule, $\Delta S/\Delta mCD$, yielding 571 \AA^2 for DIMEB, 703 \AA^2 for TRIMEA, and

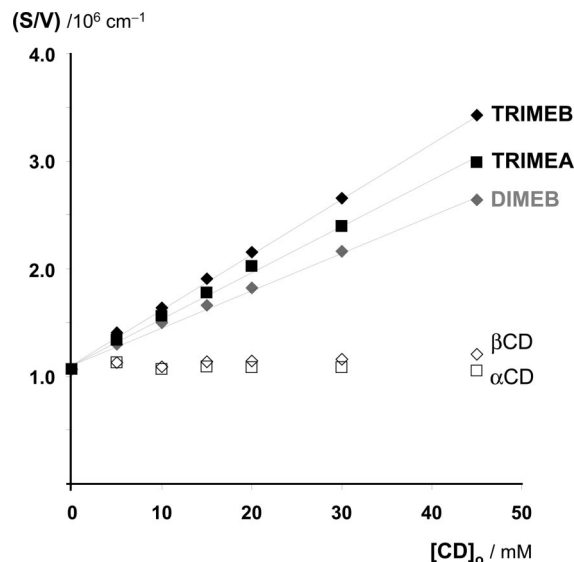


Figure 6. The specific surface area (S/V) as a function of the cyclodextrin concentration (0, 5, 10, 15, 20, 30, and 45 mM), for α CD, β CD, DIMEB, TRIMEA, and TRIMEB.

858 \AA^2 for TRIMEB. These values correspond to approximately 9, 11, and 14%, respectively, of the surface area of a spherical micelle, whose radius is the sum of the radius of a core of decanoate anions (11.4 \AA) plus the width of a second layer of methylated cyclodextrin molecules surrounding the micelle (10.9 \AA). Interestingly, the volume of this outer layer is $n_{\text{agg}} (= 18.5)$ times the volume of a cylinder whose height is 10.9 \AA (this is the approximate height of truncated cones containing DIMEB, TRIMEA, and TRIMEB molecules) and whose diameter is 15.9 \AA (the approximate outer widths of DIMEB and TRIMEB are 15.3 \AA , and that of TRIMEA is 13.7 \AA).

In the absence of cyclodextrin, the concentration of micelles in the 200 mM sodium decanoate solution is approximately $4.5 \text{ mM} (= 84/18.5)$. Hence, when $[TRIMEB]_0 = 45 \text{ mM}$, it can be expected that a maximum of 54% of the total volume available in a second layer of the micelles can be occupied by TRIMEB molecules ($0.54 \times 18.5 \approx 45/4.5$), and the average intermicellar distance is expected to decrease, as observed (see Figure 5).

A constant value of $\Delta S/\Delta mCD$ implies that ΔS per mCD molecule has a defined value. In turn, this is consonant with the occurrence of an equilibrium between the mCD molecules in aqueous solution and those adsorbed by the micelle, $mCD_{\text{aq}} \rightleftharpoons mCD_{\text{ad}}$. On the other hand, α CD and β CD present S/V values which are approximately independent of the cyclodextrin concentration at least for the considered concentration range. This behavior suggests that the unsubstituted cyclodextrins are not adsorbed on the surface of the decanoate micelles.

Compared with unsubstituted cyclodextrins, the methylated cyclodextrins have very different physical and complexation properties.^{28,31,32} Among these are the distorted conformations associated with the strong tilt of the axes of one or two glucopyranose units which, in turn, reduces the guest access to the cavities and the available space for inclusion. While these characteristics have been reported for the solid state, it is admissible that the methylated cyclodextrins, once adsorbed on the surface of the decanoate micelles, might behave in a way similar to that of the solid, and so are not included by a decanoate ion guest. In turn, the unsubstituted cyclodextrins are not adsorbed on the surface of the micelles, but are involved in a guest–host inclusion equilibrium with the decanoate anions in solution.

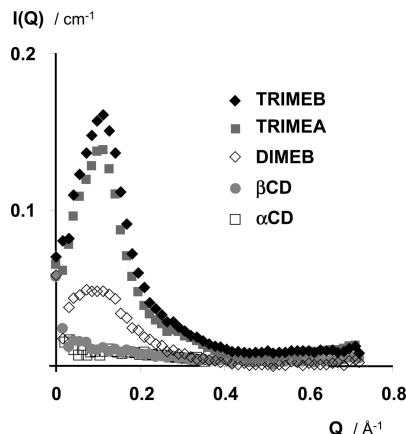


Figure 7. $I(Q)$ for a 200 mM perdeuterated sodium decanoate solution in D_2O at room temperature in the presence of a cyclodextrin ($[CD]_0 = 30$ mM).

TABLE 1

	$K = \rho - \rho(D_2O) / 10^{10} \text{ cm}^{-2}$
Dec ⁻	-6.12
Dec ⁻ (d ₁₉)	0.05
αCD	-4.77
βCD	-4.91
DIMEB	-5.17
TRIMEA	-5.26
TRIMEB	-5.28

An amphiphilic molecule acting like a guest or as a monomer in a micelle has distinct mean lifetimes. The mean lifetime of an amphiphile in a small micelle (typically, 10^{-5} – 10^{-3} s)¹ is orders of magnitude longer than the mean lifetime of the same molecule as a small guest in a cyclodextrin cavity (typically, 10^{-8} – 10^{-7} s).^{33–35} However, both mean lifetimes are very short, indicating that none of the inclusion and micellar aggregation equilibria can be ignored. This applies to the unsubstituted cyclodextrins which are not adsorbed by the decanoate micelles and so are involved in a guest–host equilibrium with the decanoate ion in solution. This equilibrium leads to the shifting of the multiple equilibria involving micelles of successive aggregation numbers toward those of smaller dimensions, as suggested by the observed increase in the width of the correlation peaks of βCD and αCD in their large Q wings, when the cyclodextrin concentration increases (Figures 2 and 3). As a result, the average distance between micelles decreases, as observed (Figure 5).

The Perdeuterated Sodium Decanoate Solution. In order to further confirm that the methylated cyclodextrins, unlike the unsubstituted ones, adsorb on the surface of decanoate ion micelles, each cyclodextrin was added to a 200 mM perdeuterated sodium decanoate (NaDec(d₁₉)) solution in D_2O . Figure 7 shows the $I(Q)$ curves, when $[CD]_0 = 30$ mM. As it is immediately clear, there is a striking difference between the methylated and unsubstituted cyclodextrins; whereas the former show correlation peaks, the latter do not exhibit any correlation maximum.

The contrast values for αCD and βCD, that is, the scattering length density differences with respect to the D_2O solvent, are 78 and 80% of the corresponding value for the decanoate ion (Table 1). Hence, the absence of a correlation peak for the sodium perdeuterated decanoate solution in the presence of unsubstituted cyclodextrins cannot result from a fortuitous contrast match; it is rather a clear indication that the native cyclodextrins are not adsorbed on the surface of the decanoate micelles.

Molecules that can function like spectroscopic probes, when they are located at a micelle–water interface in the charge free region of the electric double layer occupied by water molecules, report an environment which is neither completely waterlike nor completely hydrocarbon-like.³ While an exact description of the micelle–water interface is difficult if not impossible, it is possible to relate its electric characteristics to an apparent dielectric permittivity of the solvent in that region. For example, the effective permittivity of sodium decyl sulfate micelles (SDS micelles) in ethanol–water or in dioxane–water mixtures has been found to lie between 50 and 55.³ More recently, the dielectric permittivity of interfacial water at mica–water interfaces has been directly measured using atomic force microscopy, yielding a profile that starts, at the interface, with ϵ_r , the relative permittivity or dielectric constant,¹ equal to 4 (liquid paraffin has $\epsilon_r = 4.8$), and increases up to $\epsilon_r = 80$ at about 100 Å from the surface ($\epsilon_r = 88$ for liquid water at 0 °C). These results suggest that the water dipoles in the charge free region of the electric double layer are strongly aligned, hence forming a medium whose dielectric constant is lower than in bulk water.³⁶

These findings bear on the results of the present work, as they enable us to understand why do methylated cyclodextrins adsorb more easily on the electric double layer of the decanoate micelle–water interface than the unsubstituted cyclodextrins. In doing so, the methylated cyclodextrins sample more favorable environments, that is, environments with lower chemical potentials, where the dielectric constants are lower than in bulk water and so are closer to those of these cyclodextrins. Considering the concentration of the decanoate monomers in solution, $[NaDec]_{mon} = 116$ mM, the length of the double layer (Debye length, $1/\kappa$) is approximately 9 Å,^{1,3} a value which compares reasonably with the height of a methylated cyclodextrin (≈ 11 Å). Once the methylated cyclodextrins are adsorbed on the surface of perdeuterated decanoate micelles, they originate correlation scattering peaks and micelles become “visible” by SANS (the outer layer of cyclodextrin produces a strong contrast with the D_2O solvent; see Table 1). This interpretation is further supported by the fact that DIMEB originates a broader and weaker correlation peak than TRIMEB. In fact, an increase in the degree of methylation of the cyclodextrin molecules when passing from DIMEB to TRIMEB leads to a decrease in their dielectric constants, allowing TRIMEB molecules to better sample the sodium decanoate micelle–water interfacial regions than DIMEB molecules.

Conclusion

Methylated and unsubstituted cyclodextrins have very different physical and complexation properties. The present work considers the interaction between cyclodextrins and sodium decanoate micelles in water and concludes that the former are adsorbed on the surface of decanoate ion micelles to an extent that follows the degree of methylation of the adsorbed cyclodextrin molecules. It is suggested that this peculiar behavior is driven by the affinity of methylated cyclodextrins to the electric double layer region of the sodium decanoate micelles, due to the low dielectric permittivity of this region.

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