

Effect of NaCl on the Self-Aggregation of *n*-Octyl β -D-Thioglucoopyranoside in Aqueous Medium

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This report investigates the effect of sodium chloride (NaCl) on the micellization, surface activity, and the evolution in the shape and size of *n*-octyl β -D-thioglucoopyranoside (OTG) aggregates. By using surface tension measurements, information was obtained on both changes in the critical micelle concentration and adsorption behavior in the air-liquid interface with the electrolyte concentration. These data were used to obtain the thermodynamic properties of micellization along with the corresponding adsorption parameters in the air-liquid interface. From extended static and dynamic light scattering measurements, the micelle molecular weight, the mean aggregation number, and the second virial coefficient, the apparent diffusion coefficient and the mean hydrodynamic radius of micelles in a range of NaCl concentrations were obtained. The light scattering data have shown that when the surfactant concentration is lower to 4.5 g/L, only spherical micelles are formed. However, an increase in the surfactant concentration induces an increase in micellar size, suggesting a rodlike growth of the micelles. This deviation of micelle geometry from spherical to rodlike is supported both by the ratio between the hydrodynamic radius and the radius of gyration and by the angular dependence of light scattering. On the other hand, the studies performed in the presence of high NaCl concentration (0.2 and 0.5 M) provide strong support for the view that the micelles may overlap together to form an entangled network above certain crossover concentration.

Introduction

Alkylpolyglucosides (APGs) are a relatively new class of nonionic surfactants that can be prepared on the basis of renewable raw materials.^{1,2} These compounds are formed by an alkyl chain linked to a sugar residue, and this structure gives to the molecule a marked amphiphilic character. Whereas hydroxyl groups are responsible for the high solubility in water, an alkyl chain provides a suitable nonpolar environment. Therefore, as with other amphiphiles, APGs decrease the solution surface tension and undergo molecular association processes when their concentration overcomes a certain critical value, the so-called critical micelle concentration (cmc).³ APGs have properties such as high cmc, good solubilizing power, no denaturation of proteins, high solubility in water, and stability. These properties are very appreciated for the purpose of solubilization of the membrane of proteins, a field in which these surfactants are extensively used.⁴ In addition, the increased popularity of these products is motivated by the fact that they are nontoxic, biodegradable, and considered dermatologically safe. Therefore, these surfactants find extensive applications as liquid dishwashing agent, detergents, and personal care products, as well as hard surface cleaners, agrochemical, and for industrial and institutional cleaning.⁵ On the other hand, APGs show a number of advantageous properties when compared to the common alkyl polyglycol ether nonionic surfactants (*CiEj*). For instance, they have both stronger lipophobicity and hydrophobicity, and their temperature dependence on the solution properties is much less pronounced, do not show the clouding phenomenon when the temperature is raised.^{6,7} This behavior stems from the strength of the hydrogen bonds between the hydroxyl groups of the sugar group and water. As a consequence, the headgroup dehydration produced by the temperature increase is considerably less significant.²

In past years, a number of studies have been conducted to elucidate the behavior solution of different APG surfactants.^{3,8,17} Recently, we have also carried out investigations on the pure and mixed micellization of representative sugar-based surfactants.^{18,20} One of these studies was concerned with the effect of temperature on micellization, surface activity, and structure of *n*-octyl- β -D-thioglucoopyranoside (OTG).¹⁹ OTG is an APG surfactant that differs from the most popular *n*-octyl- β -D-glucopyranoside (OG) in which its hydrophilic group is linked by a thioether to the hydrophobic chain. This structural feature seems to be responsible for its different solution behavior as compared with OG.⁴ Moreover, recent investigations have pointed out the advantages of OTG against OG in several applications in the biomembrane field.^{4,21,22} In many of the applications mentioned above, it is frequently the presence of electrolyte in the medium, and these substances may induce changes in both intramicellar and intermicellar interactions.²³ It is well-known that, in the case of nonionic surfactants, these interactions are relatively weak; however, they can modify both structural and dynamic properties of micelles, determining the behavior of the surfactant in a certain application. One of the more important aspects refer to changes in the size and shape of the micelles induced by the presence of electrolytes, which can affect the effectiveness of surfactant in many applications in both chemical and industrial uses.^{24,25} For all, it is evident that the interest is in understanding how the electrolyte modifies the physicochemical properties of the nonionic surfactant solutions and, particularly, of those involving a sugar-based nonionic surfactant. In the present paper, we report an investigation on the effect of increasing NaCl concentrations on OTG Solutions at 25 °C. The study is focused on three fundamental aspects: surface activity, micelle formation, and micellar growth. With this purpose, we have used several experimental techniques. First of all, by using surface tension measurements, we have obtained the cmc values and the adsorption behavior in the air-liquid interface at different NaCl concentrations. The obtained cmc values were compared with those obtained by the well-established pyrene 1:3 ratio method. Subsequently, to gain information on the growth of OTG micelles upon NaCl addition, we have carried out a combined study of static and dynamic light scattering measurements.

Experimental Section

Materials. The samples of OTG and pyrene employed in this work were the same as those previously used.¹⁹ Because of their high

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purity, these compounds were used as received. Stock solutions of OTG were prepared in water, whereas that of pyrene was prepared in absolute ethanol. These solutions were stored at 4 °C. Working solutions were used immediately after preparation. Ultrapure water (resistivity ~18 MQ/cm) for the preparation of the solutions was obtained by passing deionized water through an ultrahigh quality polishing system (UHQ-PS, ELGA).

Surface Tension Measurements. The equilibrium surface tension measurements of aqueous solutions of OTG were carried out with a Sigma 701 (KSV) tensiometer by using the Du Nouy ring technique at a constant temperature (298.0(0.1 K). The ring was cleaned with distilled water and acetone and finally flamed. The surface tension measurements were automatically corrected by the software supplied by the manufacturer. Each series of measurements was started with a concentrated solution of surfactant, and successive diluted solutions were obtained by adding either pure water or salt solution to a jacketed vessel, in which temperature was maintained constant with a circulating water bath. After each dilution, the resultant surfactant solution was stabilized for at least 1 h before carrying out the measurement. The surface tension values were accurate within ± 0.1 mN m⁻¹.

Fluorescence Measurements. A SPEX FluoroMax-2 steady-state spectrofluorometer was used for the fluorescence experiments. This apparatus is fitted with a 150-W xenon lamp and equipped with a thermostated cell housing that allowed temperature control to ± 0.1 °C. All fluorescence measurements were recorded in the “S” mode with band-passes for excitation and emission of 1.05 nm. Fluorescence emission spectra of OTG solutions containing around 1 μ M pyrene were recorded between 360 and 500 nm by using an excitation wavelength of 335 nm. From these spectra, the intensities I_1 and I_3 were measured at the wavelengths corresponding to the first and third vibronic band located near 373 and 384 nm. The ratio I_1/I_3 is the so-called pyrene 1:3 ratio index. The cmc determination for each NaCl concentration was repeated at least two times. When we did not find an appropriate reproducibility, the experiment was repeated a third time.

Light Scattering Measurements. Light scattering measurements were carried out at 298 K with a Malvern System 4700 equipped with a 75-mW Ar ion laser emitting vertically polarized light at 488 nm as a light source. The sample temperature was stabilized by a thermostatic bath within ± 0.1 K. The sample cells were soaked in nitric acid, rinsed with distilled water, and finally rinsed with freshly distilled acetone before use. Surfactant solutions were filtered once through a

0.1 μ m Millipore filter directly into the cell and sealed until use. This operation removed any dust particles present.

Dynamic light scattering (DLS) was carried out to determine the apparent diffusion coefficient and associated apparent hydrodynamic radius of the micelles. By using the data treatment described in previous papers,^{24,25} we have obtained the so-called apparent diffusion coefficient (D_q) by

$$\text{EQ1}$$

where q is the scattering wave vector given by

$$\text{EQ2}$$

where θ is the scattering angle, n_0 is the solvent refractive index, and λ_0 is the wavelength of incident light in a vacuum. The diffusion coefficient was measured at least three times for each sample. The average error in these experiments was estimated at 4%. For small macromolecules, the diffusion coefficient is a function only of the concentration of the solution, and one can evaluate the hydrodynamic radius of micelles, R_h , from the Stokes-Einstein relation

$$\text{EQ3}$$

where $k_B T$ is the thermal energy factor and η_0 is the solvent viscosity. R_h coincides with the real hydrodynamic radius of the micelles only when they are spherical. In the case of rodlike micelles, we obtain from this equation an average equivalent sphere hydrodynamic radius, R_h , or apparent hydrodynamic radius.

The apparent diffusion coefficient may contain contributions from both rotational and translational motion. To obtain the pure translational diffusion coefficient (D_0), it is necessary to extrapolate the apparent diffusion coefficient D_q to a zero scattering wave vector. For a rodlike micelle, this extrapolation may be expressed by²⁶

$$\text{EQ4}$$

The parameter C , which represents the contribution of internal motions to the apparent diffusion coefficient, provides a measure of flexibility in the case of chainlike structures. For rods, C has a theoretical value of 0.033. As chain flexibility increases, C passes through a maximum value of 0.2-0.3 and then reaches a theoretical limit of 0.17 for a random coil structure.²⁷

Static light scattering (SLS) data provide information on the average molecular weight of the micelles, M_w , and the second virial coefficient, B_2 . The second virial coefficient gives a direct measure of the thermodynamic quality of the solution. Thermodynamic quality is defined as good when solute-solvent interactions are preferred over solute-solute interactions ($B_2 > 0$) and poor when solute-solute interactions are favored over solute-solvent interactions ($B_2 < 0$).^{28,29}

According to the Rayleigh-Gans-Debye theory, the scattered intensity of light from a dilute solution of weakly interacting particles with dimensions that are small compared with the wavelength of the incident light (i.e., diameter $< \lambda/20$) may be approximated by:

$$\text{EQ5}$$

where c is the total surfactant concentration, cmc is the critical micelle concentration, M_w is the micelle molecular weight, $P(q)$ is the particle form factor, and K is an optical constant given by:

$$\text{EQ6}$$

Here, dn/dc is the refractive index increment of the micellar solution. The refractive index values of the solvent and micellar solutions were measured by using a digital Abbe refractometer (WYA-1S). The refractive index increment was determined by fitting n as a

linear function of the surfactant concentration. The particle form factor at small scattering angles can be approximated by:

$$\text{EQ7}$$

regardless of micelle shape, where R_g is the radius of gyration of micelles. If micelles are polydisperse, M_w is their weight-average molecular weight and R_g is their some-higher-order-average radius of gyration. If the scattering angle is extrapolated to zero or if there is no angular dependence of light scattering (i.e., when the particle size is much smaller than the wavelength of light), the value of $P(q)$ is unity.

The excess scattering ratio of the micelles is given by $\Delta R\theta$, which represents the difference in the Rayleigh ratio between the micellar solution and the solvent solution in the absence of micelles, $AR_e = R_e - R_0$. On the other hand, the Rayleigh ratio of the sample solution is determined by using toluene as a standard according to the relationship:

$$\text{EQ8}$$

where I_θ and I_{tol} are the scattered intensity of the sample solution and the toluene, respectively, and R_{tol} is the Rayleigh ratio of toluene. This value was assumed to be $31.6 \times 10^{-4} \text{ m}^{-1}$ at 488 nm. The intensity of scattered light was measured at least four times for each sample. The average error in these repeated measurements was approximately 2%.

Results and Discussion

Micellization and Adsorption Properties. The cmc values and the adsorption parameters of OTG at different NaCl concentrations were obtained by measuring the surface tension of OTG micellar solutions as a function of the surfactant concentration. The surface

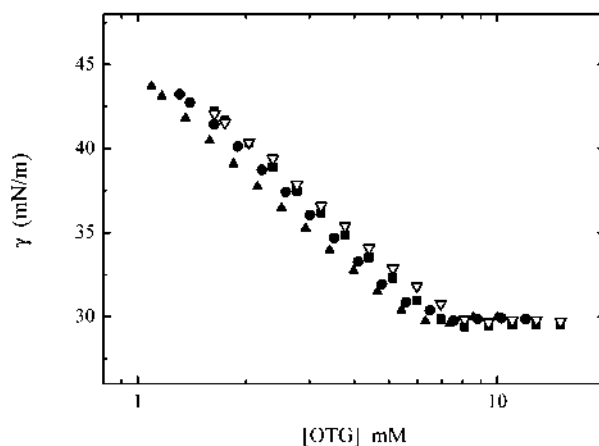


Figure 1. Surface tension isotherms of OTG at different electrolyte concentrations: (3) 0 M, (9) 0.1 M, (b) 0.2 M, (2) 0.5 M.

tension curves as a function of the OTG concentration are shown in Figure 1. From these plots, it is seen that the surface tension values decrease as the surfactant concentration increase, reaching marked break points, which were taken as the cmc values. The obtained cmc values are listed in Table 1. Also, the cmc values were obtained by the well-established pyrene 1:3 ratio method.³⁰ Figure 2 shows the variations of the pyrene 1:3 ratio with the total concentration of OTG for various NaCl concentrations. In all cases, it is observed that the pyrene 1:3 ratio parameter shows a typical sigmoidal decrease as the surfactant concentration increases. From plots in Figure 2, the cmcs were obtained by using the data treatment previously described.³¹ The cmc values obtained by this last method are also listed in Table 1. It is observed that the pyrene 1:3 ratio method provides cmc values systematically higher than those obtained by surface tension measurements. This is an expected result because the use of methods based on molecular probes requires the formation of aggregates where that molecule can be incorporated. From the data in Table 1, it is observed that the cmc of OTG decreases as the NaCl concentration increases. The most accepted explanation of this trend is given in the context of the “salting out” effect.³² In this sense, it has been suggested³² that the decrease in cmc for nonionic surfactants with electrolyte addition is related to the work required to disrupt the structure of the aqueous solvent by the insertion of a surfactant molecule. Because the added salt acts to enhance the water structure, the introduction of the monomeric surfactant molecule will require an additional amount of work to overcome that added structural energy. As a consequence, it decreases the solubility of the surfactant and the cmc is reduced. Furthermore, a second contribution to the reduction of the cmc can be considered. Note that the decrease of the headgroup size with increasing NaCl concentration can result in less repulsive headgroup/headgroup interactions, which might be also behind the observed decrease of the cmc. This fact is also reflected by the standard free energy of micelle formation per mole of monomer, ΔG_{mic}^0 (see Table 1), which in the case of a nonionic surfactant, is given by³³

$$\text{EQ9}$$

x_{cmc} being the mole fraction of surfactant at the cmc, R the gas constant, and T the absolute temperature. Data in Table 1 show that the free energy of micellization is negative and becomes more negative as the electrolyte concentration increases, indicating that the micellar formation becomes more favorable in the presence of increasing NaCl concentrations.

TABLE 1: Effect of NaCl Addition on Micellization and Adsorption Parameters of OTG at 25 °C^a

[NaCl] (M)	cmc ^a (mM)	- ^A γ _{mic} (kJ/mol)	Γ _{max} -10 ³ (mmol/m ²)	A _{min} Å ² /molecule	Π _{cmc} (mN/m)	- ^A G ⁰ _{ds} (kJ/mol)
0	7.86 (8.70)	21.96	3.16	52.54	42.27	35.34
0.1	7.09 (7.61)	22.21	3.49	47.57	42.47	34.38
0.2	6.37	22.48	3.41	48.69	42.63	34.98
0.5	5.59 (7.00)	22.76	3.38	49.12	43.44	35.61

^a Within parentheses are the cmc values as obtained by the pyrene 1:3 ratio method.

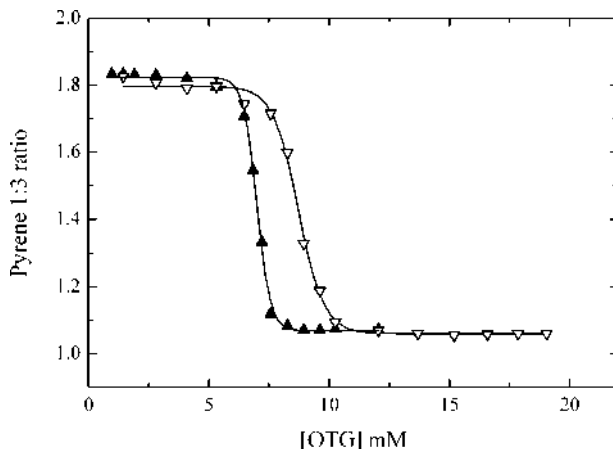


Figure 2. Plot of pyrene 1:3 ratio vs concentration of OTG at two different NaCl concentrations: (3) 0 M, (2) 0.5 M.

On the other hand, from the plots of surface tension versus logarithm of the surfactant concentration (Figure 1), we have also

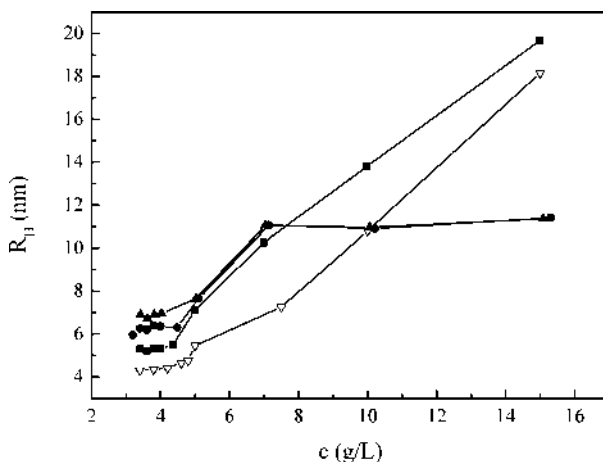


Figure 3. Apparent hydrodynamic radius, R_h , of OTG micelles as a function of surfactant concentration at different NaCl concentrations: (3) 0 M, (9) 0.1 M, (b) 0.2 M, (2) 0.5 M.

TABLE 2: Structural Parameters of OTG Micelles as a Function of Electrolyte Concentration, as Obtained in the Dilute Region

[NaCl] (M)	M_w (Da)	N_{agg}	$B_2 \times 10^8$ (mol m g ⁻²)	R_h^0 (nm)	R_{EFF} (nm)
0	35040	114	-1.46	3.5	12.1
0.1	44410	144	-1.19	5.1	13.2
0.2	59521	193	-0.82	5.6	14.2
0.5	165611	537	-0.20	6.2	17.6

obtained the adsorption parameters of the surfactant in the air-liquid interface. The surfactant surface excess concentration, Γ_{max} , which represents a measurement of the effectiveness of the adsorption of the surfactant, can be determined for dilute solutions by the Gibbs equation³³

$$EQ10$$

where γ is the corrected surface tension, and c is the surfactant concentration. The minimum area occupied by the surfactant molecule at the air-liquid interface, A_{min} , was then determined by the equation

$$EQ11$$

where N_A is Avogadro's number. Finally, the standard free energy of adsorption, ΔG_{ads}^0 , was determined by using the equation^{33,34}

$$\text{EQ12}$$

where the standard state for the surface phase is defined as a hypothetical surface covered with a monolayer of surfactant at its closest packing but at a surface pressure equal to zero,^{33,34} and where Π_{cmc} stands for the surface pressure, that is

$$\text{EQ13}$$

γ_0 and γ_{cmc} being the surface tension of the system solvent and of the micellar solution at the cmc, respectively. The values obtained for these parameters are summarized in Table 1. From the data in Table 1, it can be seen that only a small increase of Γ_{max} occurs in NaCl 0.1 M and then decreases slightly with the electrolyte concentration. The increase of Γ_{max} on the addition of NaCl can be related to the dehydration of the hydrophilic group induced by the presence of the electrolyte. The further reduction is probably due to the negative surface excess (increase of the surface tension) of the solvent system produced by the addition of NaCl. As expected, A_{min} shows a reverse trend upon NaCl addition. In general, from the obtained A_{min} values ($52.54 \text{ \AA}^3/\text{molecule}$ or less), it can be concluded that the hydrophobic chains adsorbed at the air-liquid interface are not in close-packed arrangement normal to the interface at saturation adsorption.³³ The surface pressure, Π_{cmc} , shows a slight increase, which is mainly controlled by the increase of γ_0 with the electrolyte concentration, as discussed above. Finally, it is observed that the standard free energy of adsorption, ΔG_{ads}^0 , is negative in all the cases but undergoes small variations with the presence of NaCl. In relation to this parameter, the more relevant aspect is that ΔG_{ads}^0 values are more negative than their corresponding ΔG_{mic}^0 values, indicating that the adsorption of the surfactant in the air-liquid interface is a more favorable process than the micellar formation, this situation being almost unaffected by the presence of NaCl.

Size and Structure of the Aggregates. In Figure 3, the apparent hydrodynamic radius of OTG micelles versus surfactant concentration without electrolyte and at various NaCl concentrations are plotted (0.1, 0.2, and 0.5 M NaCl). As can be seen, the results showed a well-pronounced transition in the micelle size at a certain surfactant concentration. At surfactant concentrations lower than this transition surfactant concentration (around 4.5 g/L), the micelle size presents a weak dependence on surfactant concentration. In this region of low surfactant concentration, micelles are small, and it is plausible to suppose that they have a spherical shape. After the break point in the curve is observed a strong concentration dependence of the micelle size, which rapidly increases. The data indicate a significant micellar growth with the corresponding change in the micelle shape from sphere to rodlike. The free diffusion coefficients were obtained by extrapolation of the data at infinite dilution ($c = 0$) in the dilute region. The hydrodynamic radius at infinite dilution, R_h^0 , as obtained by eq 3, is listed in Table 2, where it is noteworthy that the hydrodynamic radius of OTG micelles is dependent on salt concentration.

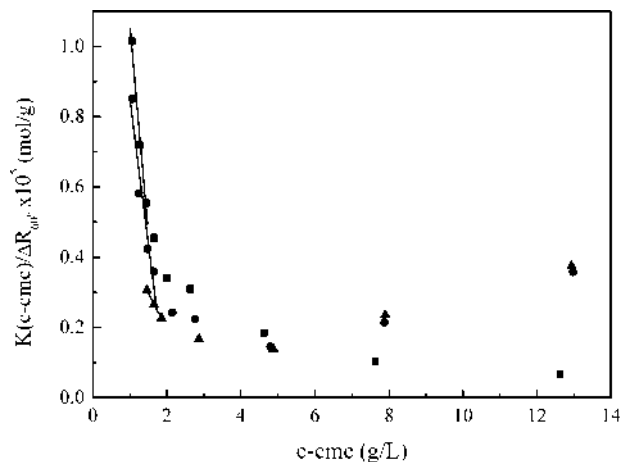


Figure 4. Debye plots for OTG solutions at various NaCl concentrations: (a) 0.1 M, (b) 0.2 M, (c) 0.5 M. Light scattering at 60° direction.

On the other hand, as can be seen from Figure 3, two different patterns may be deduced in the nonspherical shape region. First, for 0 and 0.1 M NaCl, R_h values monotonically increase with OTG concentration, with the micellar size bigger in the presence of 0.1 M NaCl. This result is similar to those reported previously for ionic surfactant micelles in electrolyte solutions by different authors.³⁵⁻³⁷ However, dynamic light scattering measurements performed in 0.2 and 0.5 M NaCl show that R_h increases initially and then is practically constant for surfactant concentration higher than 7 g/L (for both electrolyte concentrations). By analogy with solutions of semiflexible polymers, the surfactant concentration where the apparent hydrodynamic radius is constant may be identified as an “overlap threshold concentration”, c^* , between a dilute and semidilute regime.³⁸ According to this model, the micelles can be seen as individual aggregates that are diffusing almost independently of each other below c^* in the dilute region. Above c^* , in the semidilute region, micelle growth has progressed to an extent that the micelles start to overlap together and become entangled. The network so formed has an average mesh size ξ , called the correlation length, which is the average length between two points of entanglements.³⁹ This correlation length dominates the dynamic light scattering rather than the size of individual micelles. The overlap or entanglement of rodlike micelles was first evidenced by Hoffmann et al.⁴⁰

The static light scattering behavior of the surfactant solution in the presence of NaCl is represented as plots of $K(c - \text{cmc})/AR_{90}$ against $c - \text{cmc}$ (the so-called Debye plot) in Figure 4. As can be seen, the results show a strong initial decrease with increasing surfactant concentration and then leveling off at high concentrations for 0.1 M NaCl. For 0.2 and 0.5 M NaCl solutions, the Debye plots decrease sharply, pass a minimum, and then increase with increasing micelle concentrations. Similar results have been obtained by Imae for heptaoxyethylene alkyl ethers.⁴¹ As with dynamic light scattering, the strong increase in the Debye plots above the minimum value originates from the overlap of rodlike micelles. The surfactant concentration where the minimum occurs (7 g/L) is the crossover concentration c^* from dilute to semidilute regions. For all electrolyte concentrations, an apparent linearity is observed in the range of low surfactant concentration (where spherical micelles are present). We may infer that the micelle growth is promoted by the increase in micelle concentration above a certain value. From this point, the micelles associate into larger micelles (rodlike shape), and the results deviate downward from a straight line.⁴² Linear regression analysis of the initial part of the data in Figure 4 (assuming that $P(6) = 1$) was used to estimate the micellar molecular weight of OTG micelles in the respective electrolyte concentration, and hence we obtained the corresponding mean micellar aggregation number values. On the other hand, the second virial coefficient can be obtained from the slope of linear regression. The whole set of data is collected in Table 2. As seen in the previous section, the values of cmc decrease when the concentration of NaCl grows, indicating that the increase of the ionic strength favors the formation of the micelle. From Table 2, it can be seen that the molecular weight of the micelle grows with the concentration of added NaCl, and consequently the aggregation number, as was observed by other surfactants.^{43,44}

Virial coefficients reflect deviations from ideality due to the existence of intermolecular interactions. The second virial coefficients obtained from the fit of the experimental data are negative (see Table 2). The fact that B_2 values are small and negative indicates that the micelle—micelle interactions are favored over the micelle—solvent ones. In addition, the B_2 values are less negative with increasing the electrolyte concentration, suggesting that interactions between micelles become less attractive.

On the other hand, the second virial coefficient for macromolecules of any architecture can be expressed in terms of a sphere volume (the so-called effective volume, V_{EFF}) that is equivalent to a hard, homogeneous sphere. The value of the effective volume accounts for the micelle interactions, and its value for particles interacting as hard spheres is equal to the actual micelle volume (V_s). In contrast, V_{EFF} could be substantially different from V_s if long-range interactions are present. V_{EFF} can be expressed through the second virial coefficient⁴⁵

EQ14

Further, from V_{EFF} , we estimated the effective radius of micelles (R_{EFF}) as a function of electrolyte concentration. The calculated values are presented in Table 2. We find that R_{EFF} as determined by static light scattering is higher than the free hydrodynamic radius R_h^0 , which is due to the long-range interaction between the OTG micelles. Some authors suggest that a negative virial coefficient could be a consequence of the increase in micellar size with surfactant concentration.^{46,47}

The effect of salt on the micellization of ethylene oxide-based nonionic surfactants is primarily controlled by the polarizability of the ions.^{48,49} These effects are mainly ascribed to the change in water structure due to interactions between inorganic salt and water.⁵⁰ OTG molecule carries a rigid but strongly hydrated headgroup. Structure makers are salts such as NaCl, which lead to an increase in the self-hydration of water through hydrogen bonding. The presence of salt in the medium leads to a removal of water molecules associated with the polar headgroups at the micellar interface. Formally, this corresponds to the breaking of intermolecular hydrogen bonds. This loss of solvate molecules is likely to reduce the effective headgroup size.⁵¹ A volume decrease of the polar part of the surfactant molecule will lead to a decreased stability of a spherical, but a stabilization of a planar, arrangement of the surfactant molecule.⁵² A reduction of curvature, i.e., a tendency toward a more planar arrangement will, of course, favor association and the subsequent growth of micelles. This leads to the formation of rodlike micelles. With increasing salt and surfactant concentration, the rodlike micelles grow in length. At high electrolyte concentration, the micelles overlap together and become an entangled mesh in which the identities of individual micelles are lost.³⁹

To gain more insight into the growth of micelles from globular to rodlike structures, we have investigated the angular dependence of light scattering. The presence of longer micelles with increasing surfactant concentration at 0.1 M NaCl is indicated by the emergence of angular-dependent scattering. Figure 5 shows the angular dependence of light scattering from OTG solutions at 10 g/L and 15 g/L in the presence of 0.1 M NaCl. As can be seen, the reciprocal angular envelope of light

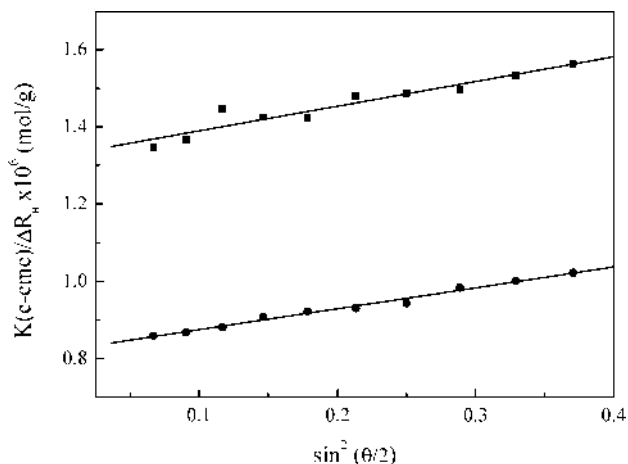


Figure 5. Angular dependence of light scattering from OTG solutions in the presence of 0.1 M NaCl: (a) 10 g/L (b), 15 g/L.

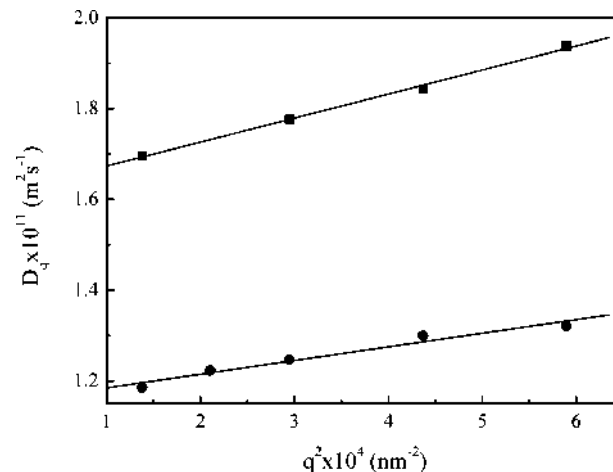


Figure 6. Angular dependence of apparent diffusion coefficient of OTG micelles in the presence of 0.1 M NaCl: (a) 10 g/L (b), 15 g/L.

TABLE 3: Characteristics of OTG Rodlike Micelles as a Function of Surfactant Concentration in 0.1 M NaCl

c (g/L)	$M_w \times 10^{-5}$ (Da)	N_{agg}	R_g (nm)	R_h (nm)	p
10	7.5	2432	35	14	2.5
15	12	3891	43	19	2.3

scattering linearly increases with increasing $\sin^2(\theta/2)$. OTG is unlikely to form large rodlike micelles at a surfactant concentration lower than 4.5 g/L because no angular dependence was observed in light scattering, corresponding to small spherical micelles. According to eqs 5 and 7, the intercept of the curve gives the reciprocal of the weight-average molecular weight, M_w , of the micelle at a given surfactant concentration, assuming that B_2 is negligible. From the value of the finite slope, we can evaluate the radius of gyration, R_g (see Table 3). It is important to notice that, in order to derive the exact value of these parameters, we have to take account of the contribution of the second virial coefficient B_2 . However, for micelles with large molecular weight, the contribution of the second virial coefficient can be neglected without introducing a large error. This assumption has been used by several authors.^{38,53,56} From data in Table 3, it is noteworthy that the mean aggregation number is too high to be accommodated to a spherical micelle. At these surfactant concentrations, rodlike micelles would be formed. Thus, the OTG surfactant forms spherical micelles at the critical micelle concentration, but they associate into rodlike micelles as the micelle concentration is increased.

The magnitude of R_g gives important information about particle shape. Particles of different shape with identical M_w values have different R_g values. The ratio R_g/R_h (denoted as p) is a micelle structure-dependent parameter, which usually varies from 0.775 for spherical micelles to $p > 2$ for rodlike aggregates (a complete set of p values and equations according to specific structures was presented by Burchard).⁵⁷ The values obtained in the present work are 2.5 for 10 g/L and 2.3 for 15 g/L, suggesting that the micelles derive from spherical geometry to rodlike. Scaling relationships can provide useful information on the conformation and flexibility of micelles. The scaling relationship between the molecular weight of micelles and the radius of gyration is sensitive to micelle shape³⁹

EQ15

A double logarithmic plot of R_g versus the molecular weight of micelles presents an exponent $n = 0.44$. A value of 0.5 is characteristic of a random coil structure, whereas rigid and thin rods are expected to give an exponent close to unity.³⁹ The apparent diffusion coefficient of OTG micelles measured at 10 and 15 g/L in 0.1 M NaCl evidence some angular dependence (see Figure 6). Again, these results are consistent with the presence of larger micelles with increasing surfactant concentration. The structure-sensitive parameter C (see eq 4) has been calculated from the slope of the straight line and using the value of the radius of gyration obtained from static light scattering (Table 3). This parameter indicates the flexibility in the elongated micelles and is a measurement of the deviation of the apparent diffusion coefficient from the pure translational coefficient as a consequence of rotations and internal motions. For both surfactant concentrations, the C value obtained was 0.13. This value is found to approach the value predicted for random coil structure (0.17), and it is in concordance with the exponent n obtained with the scaling relationship between the molecular weight of the micelles and the radius of gyration.

The apparent diffusion coefficient measured in 0.2 and 0.5 M NaCl is independent of scattering angle. If the idea that rodlike micelles entangle together and form a network at higher electrolyte concentration is correct, this fact could reflect increasing chain entanglement, which causes a reduction in the distance between chain overlap points.³⁷ The solutions of rodlike micelles can be divided into two regions, that is, dilute and semidilute regions. For the dilute solutions, the micelles isolate without any contact with one another. However, when the surfactant concentration is increased, the rodlike micelles formed in 0.2 and 0.5 M NaCl may overlap together above certain crossover concentration c^* (semidilute region). By comparison of Figures 3 and 4, it is observed that correspondence between positions of the minima in static light scattering (identified with c^*) and the constant value of the hydrodynamic radius is good.

Conclusions

Surface tension and light scattering measurements were performed on *n*-octyl α -D-thioglucopyranoside aqueous solutions in the presence of NaCl of different concentrations. From the surface tension isotherms, we have obtained information on both micellization and surface properties of the surfactant. The cmc values of OTG decreases as the NaCl concentration decreases. The adsorption data in the air-liquid interface showed that the adsorption of the surfactant occurs spontaneously and becomes more favorable in the presence of increasing NaCl concentrations. Thermodynamic analysis of data indicates that the adsorption of the surfactant in the air-liquid interface is a more favorable process than the micellar formation, this situation being almost unaffected by the presence of salt.

From static and dynamic light scattering measurements, we have demonstrated that OTG micelles undergo a process of growth in the presence of electrolyte (NaCl). By using dynamic light scattering, we have determined the apparent hydrodynamic radius of micelles. There is a rather abrupt change in micellar size when the surfactant concentration is higher than 4.5 g/L, which can be attributed to a sphere-to-rod transition. The micelles are spherical at low surfactant concentration where no angular dependence of light scattering was observed, but they become rodlike at high surfactant concentration. The mean aggregation number and the second osmotic virial coefficient of the spherical micelles were determined from static light scattering measurements. The results obtained indicated that the mean aggregation number increases with increasing the electrolyte concentration, whereas the virial coefficient decreases in absolute value, probably due to a decrease in attractive interactions between OTG micelles and solvent. The scaling relationship between R_g and M_w , at least in 0.1 M NaCl, indicated that the micelles prefer to adopt a random coil structure. This result is in line with the obtained values of the structure-sensitive parameter (C).

On the other hand, for high NaCl concentrations (0.2 and 0.5 M), we have observed that the Debye plots exhibit minimum values around the overlap threshold concentration, above which micelles probably entangle together. For these electrolyte concentrations, the observed constancy in the hydrodynamic radius for surfactant concentration higher than this crossover concentration is consistent with the presence of micellar entangled networks.

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