Growth and Hydration Of Triton X-100 Micelles In Monovalent Alkali Salts: A Light Scattering Study

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The purpose of this paper is to investigate the effect of various alkali-metal chloride electrolytes on the micellar formation process of Triton X-100. We have studied the micellar solutions by using static and dynamic light scattering. A combined analysis of the data obtained from both techniques has been carried out in the context of micellar structure and hydration. To examine the effect of the size and hydration of ions on the micellar growth, experiments with three different electrolytes (LiCl, NaCl, and CsCl) covering a wide range of ionic strength (0−2 M salt added) have been performed. It was found that both the ionic strength and the cation nature have a substantial effect on the micellar growth. The postulated growth mechanism consists of a progressive process involving both an increase in the micellar aggregation number accompanied with a rise of associated water which is nonspecifically bonded with the micelle. However, the amount of water molecules hydrogen bonded was found to decrease with the electrolyte addition. This mechanism is supported by the observed tendencies in both the partial specific volume and the cloud point of the surfactant for each added electrolyte.

Introduction

Micelles are formed by the self-aggregation of surfactant molecules in a dispersion medium. These micellar systems have a wide variety of scientific, engineering and technical uses. For example, the nonionic surfactant Triton X-100 is used in separation of protein from cell membranes[1,2] and DNA extraction,[3] and when mixed with phospholipids, it also produces effective substrates for studying enzymes of phospholipid metabolism.[4−6] Solubilization of lipidlike bodies by Triton X-100 through mixed micelle formation can be utilized in chemical and industrial work.[7−9] The effectiveness of such applications of micelles may depend on their size, shape, and composition as well as their effect on solution properties, e.g., viscosity.[10,11]

The conditions used for many micellar applications may induce structural changes. For example, the addition of electrolytes, alcohols, and amines that interact with the micelles is known to induce micellar growth and shape changes.[12−15] The behavior of the surfactant system may depend critically on medium.

In many surfactant processing steps, there will be a nonzero background electrolyte concentration, either deliberately added to the system to avoid polyelectrolyte effects or present as a remnant from the biological system being degraded. In the first case, the surfactants must perform their functions in the presence of electrolytes. Electrolytes are generally thought to salt out the surfactants and to destabilize surfactant-based suspensions, emulsions, and foams. Nonionic surfactants resist such adverse electrolyte effects better than the ionic ones.[16]

If the background electrolyte affects micelle properties, the behavior of nonionic detergents as extractants may depend on the solution ionic strength and composition via a perhaps-

unexpected path. It is therefore a wide potential interest to examine how background electrolytes may affect micelle properties.

In general, micellar growth is quite sensitive to the nature and concentration of electrolyte. The reasons for different growth rates for different electrolytes are, however, not fully understood. Although the structure of Triton X-100 micelles has been the subject of active interest, to our knowledge, relatively few studies reporting the effect of electrolyte on micellar structure have been reported.[11,17−19] We therefore have turned our attention to this system in an effort to observe the structural evolution of micelles in the presence of simple electrolytes as LiCl, NaCl, and CsCl.

The cloud point is a macroscopic property of nonionic micelles that can be used as an index for the effects of electrolytes on surfactant solutions. The ability of salts to alter the cloud point temperature has been extensively studied. However, correlations have not been established among the alterations in the structural properties and the changes in the cloud point of nonionic surfactants with electrolytes.

The present work is intended to be a step toward the study of the connection between micellar structural properties (size and hydration) and macroscopic properties such as the cloud point. In this context, we present a systematic study employing a variety of monovalent alkali salts and a representative nonionic surfactant, Triton X-100. We have used static and dynamic light scattering to get quantitative information on the micellar growth.

Experimental Section

Materials. All chemical used were of analytical grade quality. Doubly distilled water (Millipore) was used to prepare all solutions. The surfactant Triton X-100 (polyoxyethylene *p-t*-octylphenol) was obtained from Sigma (SigmaUltra, >99.6%), and it was used as supplied. All experiments were carried out with freshly prepared solutions.

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Density Measurements. The partial specific volume of micellar Triton X-100 was calculated from[19]

$$v = \frac{1}{\rho_0}\left(1 - \frac{d\rho_{01}}{dc}\right) \tag{1}$$

where c is the surfactant concentration in g/mL, and ρ_{01} and ρ_0 are the densities of sample solution and medium, respectively. The density values were measured with an Anton Paar DMA 58 density meter. This apparatus determines the density value by placing the sample in a U-shaped tube and measuring its period of oscillation. The instrument has an accuracy of $\pm 10^{-5}$ g/cm^3, and it was calibrated with air and water at 25 °C. The temperature was controlled within ± 0.01 °C.

The values so obtained are used to estimate the hydration factor, δ, from the hydrodynamic micellar diameter (d_H) calculated from the diffusion coefficient measured by dynamic light scattering and the unhydrated micellar diameter (d_0) obtained by static light scattering measurements:[19]

$$\delta = \left[\left(\frac{d_H}{d_0}\right)^3 - 1\right] v \rho_{water} \tag{2}$$

δ is expressed in grams of water associated with 1 g of dry micellar surfactant.

Cloud Point Measurements. The cloud points of Triton X-100 micellar solutions (10 g/L) were determined visually by noting the temperature at which the continuously heated solution suddenly became turbid. Heating was regulated to about 0.5 °C/min around the cloud point.

Light Scattering Measurements. Static and dynamic light scattering experiments were performed on a Malvern 4700 photon correlation spectroscopy (PCS) system using a 75 mW argon laser emitting vertically polarized light at a wavelength of 488 nm. All measurements were carried out at 25.0 ± 0.1 °C using a circulating water bath. By use of this PCS apparatus, the angular dependence of the scattering could be measured over the range 30−150°.

Cylindrical quartz cells of 10 mm diameter were used in all of the light scattering experiments. The cells were soaked in nitric acid, rinsed with distilled water, and finally rinsed with freshly distilled acetone before used. The surfactant solutions were filtered once through a 0.1 μm Millipore filter directly into the cell and sealed until use. This filtration removed any dust particles present because none of the solutions exhibited significant dissymmetry: the ratio of light scattered at the angles of 45° and 135° never exceeded 1.10 in any of the solutions. All measurements (the average scattered intensity and the intensity correlation function) were made at a scattering angle of $\theta = 90°$ after initial studies indicated that the micelles were too small to exhibit significant angular dependence of the scattered light within experimental error.

The intensity of scattered light was measured at least four times for each sample. The average error in these repeated measurements was approximately 2%. The autocorrelation function was obtained using a 256-channel photon correlator.

The diffusion coefficient was measured at least three times for each sample. The average error in these experiments was approximately 4%. To facilitate the light scattering measurements, we have performed these experiments for surfactant concentration ranging from 5 to 25 g/L. These surfactant concentrations are high enough to easily measure the micellar size.

The solvent viscosity values, used to evaluate the hydrodynamic radius, were measured at 25 °C with an Ubbelohde viscometer with flow times ranging from around 175−200 s. Times were collected with a digital stopwatch automatic system (Schott Geräte AVS 310) with an accuracy of ± 0.01 s.

The refractive index of samples was measured at 25.0 ± 0.1 °C using an Abbe-Refractometer (Shibuya). The refractive index increments (dn/dc) obtained were independent of cation nature, within the experimental error.

Theory

It is well-known that the mean intensity of the light scattered by a solution of macromolecules contains information on their molecular weight. On the other hand, the intensity of the scattered light continuously fluctuates around this mean value because of the Brownian movement of the macromolecules. Dynamic light scattering measurements make use of the fact that the time dependence of scattered light fluctuations can be related to the translational diffusion coefficient of the macromolecules. To quantify this time dependence, the autocorrelation function $G(\tau)$ is calculated from the product of two photon counts at time t and time $t + \tau$ such that $G(\tau) = \langle I(t)I(t + \tau)\rangle$. The normalized intensity autocorrelation function $g^{int}(\tau)$ is given by[20]

$$g^{int}(\tau) = \frac{\langle I(t)I(t + \tau)\rangle}{\langle I(t)I(t)\rangle} \tag{3}$$

The function $g^{int}(\tau)$ is related to the normalized field autocorrelation function $g^{field}(\tau)$ by the Siegert relationship[20]

$$g^{field}(\tau) = 1 + C|g^{int}(\tau)|^2 \tag{4}$$

where τ is the delay time and C is the Siegert constant, an experimental fitting parameter of the measuring device. Using the cumulant method[21] with a dilute dispersion of macromolecules, $g^{int}(\tau)$ becomes

$$g^{int}(\tau) = e^{-\Gamma\tau} \tag{5}$$

where the parameter Γ describes the diffusion of the particles under study. The so-called apparent diffusion coefficient (D_c) is related to Γ by

$$D_c = \frac{\Gamma}{q^2} \tag{6}$$

where q is the scattering vector.

The diffusion coefficient so measured by dynamic light scattering, which is concentration dependent, reflects the micelle diffusion as affected by the intermicellar interaction. At elevated micelle concentrations, these interactions are of two sorts: direct interaction (such as repulsive excluded volume effects and attractive van der Waals interactions) and hydrodynamic interactions (in which the motions of one particle are communicated to other particles via the flow of the solvent). For dilute solutions, the apparent diffusion coefficient varies linearly with the surfactant concentration[22,23]

$$D_c = D_0[1 + k_D(c - cmc)] \tag{7}$$

being D_0 the actual diffusion coefficient at infinite dilution, where the interactions are absent (i.e., at the cmc), k_D is a constant connected to the interparticle interaction potential, and c is the surfactant concentration. Once the D_0 value is determined, the micellar hydrodynamic radius R_H may be obtained

using the Stokes−Einstein relation as given in

$$D_0 = \frac{k_B T}{6\pi\eta_0 R_H} \tag{8}$$

where $k_B T$ is the thermal energy factor and η_0 is the solvent viscosity.

In static light scattering experiments, we measure the scattered light from the surfactant solution, which depends both on the molecular weight of the micelles and intermicellar interactions. In these experiments, the Rayleigh ratio of the sample solutions is determined using toluene as a standard according to the relationship

$$R_\theta = \frac{I_\theta}{I_{tol}} R_{tol} \tag{9}$$

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. For R_{tol} at $\lambda = 488$ nm, a value of 31.6×10^{-4} m^{-1} was assumed.[24] In general, the difference in Rayleigh ratio between the micellar solution and the solvent solution in the absence of micelles, $\Delta R_\theta = R_\theta - R_\theta^0$, as determined by static light scattering is given by the expression

$$\Delta R_\theta = K(c - cmc) M_w P(q) S(q) \tag{10}$$

where M_w is the molecular mass of the micelles, $P(q)$ is the micelle form factor, $S(q)$ is the structure factor, and K is an optical constant given by

$$K = \frac{4\pi^2 n_0^2 (dn/dc)^2}{N_A \lambda_0^4} \tag{11}$$

where n_0 is the solvent refractive index, dn/dc is the refractive index increment of the sample solution, and λ_0 is the wavelength of incident light in a vacuum.

The particle form factor describes the intramicelle interference and essentially describes the angular dependence of the scattering intensity and is usually expressed in terms of the scattering wave vector, q. If the particle size is much smaller than the wavelength of light, as we expect for the micelles formed by TX-100 surfactant, then the scattering intensity shows generally a very low angle dependence, and the contribution of $P(q)$ can be neglected[25] (i.e., $P(q) = 1$).

On the other hand, the structure factor reflects the intermicellar interaction, and it is dependent on the interaction potential on the basis of the theory of simple liquid.[26] $S(q)$ value oscillates and is damped around unity as a function of q, being equal to unity when interactions are negligible. In this case, the intensity of scattered light can be directly related to the molecular weight of the micelles by[27,28]

$$\frac{K(c - cmc)}{\Delta R_\theta} = \frac{1}{M_w} \tag{12}$$

In this equation, c is the total surfactant concentration, but for all of the micellar solutions examined, $c \gg cmc$, so that the micelle concentration $c - cmc \approx c$. Experimentally, we determined M_w for each sample by measuring $Kc/\Delta R_\theta$ and applying eq 12.

This equation can be used in the case of a nonionic surfactant at relatively low surfactant concentrations where the interaction can be neglected. Triton X-100 micelles are not charged and, therefore, do not exhibit strong electrostatic interactions, and
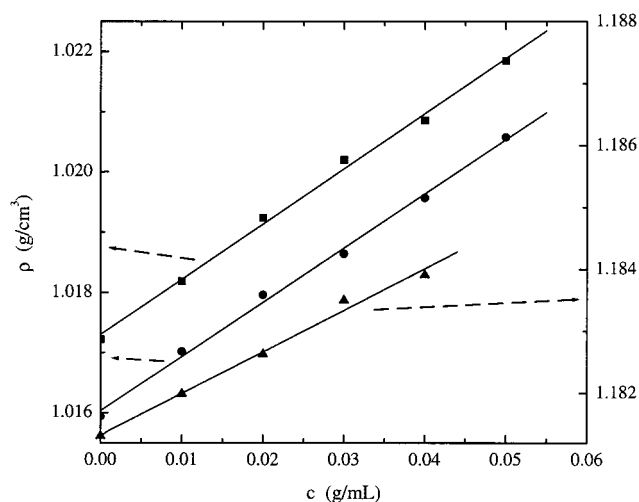
Figure 1. Density of Triton X-100 micellar solutions in (■) 0.5 M NaCl, (●) 1 M LiCl, and (▲) 1.5 M CsCl as a function of the surfactant concentration.

the surfactant concentration is low enough that repulsive, excluded-volume interactions, and attractive interactions can be neglected. Conversely, if the micelle size does not change with increasing surfactant concentration, as in the case of pure nonionic surfactant in aqueous solution,[23] the micelle size can be determined by extrapolating the static light scattering data to the cmc, where the intermicellar interactions are negligible.[29−31] The micelles can be seen as individual aggregates that are diffusing almost independently of each other. Note that in eq 10 the Rayleigh ratio depends on the scattering angle. However, in our systems ΔR_θ does not exhibit a strong angular dependence, and we can replace ΔR_θ with $\Delta R_{\theta=90}$.

Results and Discussion

Density Studies. The density of Triton X-100 solutions of varying concentrations was investigated as a function of electrolyte concentration. To study the cation influence, three salts have been used: LiCl, NaCl, and CsCl. Figure 1 corresponds to representative plots of density values as a function of surfactant concentration in the presence of 0.5 M NaCl, 1 M LiCl, and 1.5 M CsCl. As can be seen, a linear dependence was obtained (r > 0.99). A linear dependence was observed in the three media (LiCl, NaCl, and CsCl) for all electrolyte concentrations studied and over the entire range of Triton X-100 concentrations used. Partial specific volume of micellar Triton X-100 was calculated from eq 1 to ascertain a detailed picture of the micellar solution. For this purpose, linear regression analysis of the density data was used to estimate the slope ($d\rho_{01}/dc$ in eq 1). Table 1 lists the partial specific volume of the micellar surfactant so evaluated. The present v value in water agrees with the published values of 0.915[32] and 0.9135 mL/g.[19] Partial specific volume of Triton X-100 in water was marginally larger than in the presence of the electrolytes. On the other hand, the value of v decreases progressively with the addition of electrolyte, with this decrease being a function of the cation. Partial specific volume is a thermodynamic parameter that defines various intermolecular interactions;[33] that is, it is sensitive to hydrophobic and hydrophilic interactions involving solute and solvent. Because the partial specific volume of the micellar surfactant is affected by the electrolyte concentration and cation type, some change in the organization of the water molecules around the POE (polyoxyethyleneoxide) chains of the micelles could be revealed. It is important to emphasize

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TABLE 1: Partial Specific Volumes of Triton X-100 Micelles as a Function of Nature and Concentration of Electrolyte

| salt	[salt] (M)	v (mL/g)
no salt	0.0	0.914
LiCl	0.5	0.902
	1.0	0.896
	1.5	0.887
	2.0	0.870
CsCl	0.5	0.878
	1.0	0.800
	1.5	0.790
	2.0	0.787
NaCl	0.5	0.892
	1.0	0.887
	1.5	0.858
	2.0	0.854

that the information obtained from partial specific volume about the micellar hydration is entirely thermodynamic, not hydrodynamic, in nature. It is expected that density measurements depend on the water molecules that have a significant thermodynamic interaction with surfactant molecules via hydrogen bonds. It is well-known that micellar water structure can be disrupt by electrolytes. Some salts (such as LiCl, CsCl, and NaCl), in which cations are extensively hydrated, provoke micellar dehydration. The observed decrease in the partial specific volume with electrolyte could be due to a gradual dehydration of the hydrophilic outer mantle of the micelle. This dehydration is related to an increase in molecular motion by the POE chain that permits a micellar growth by inserting surfactant molecules in the micelles. Considering this, the micelles become more compact with increasing electrolyte concentration although significant micellar expansion occurs concurrently. Similar conclusions were derived by Charlton and Doherty[18] in their study on the effect of KCl on the TX100 micelles by using intrinsic viscosity measurements.

Light Scattering Studies. The static light scattering depends on the scattering angle, the solution refractive index increment, and the osmotic compressibility. For sufficiently dilute solutions, the scattering intensity is directly proportional to the particle size. A large increase in the intensity of scattered light would, therefore, indicate an increase in the micellar aggregation number. In Figure 2 parts a−c, the excess scattering ratios for Triton X-100 solutions at an angle of 90° (ΔR_{90}) are displayed versus surfactant concentration in the presence of electrolytes. The curves are for LiCl, CsCl, and NaCl added solutions, respectively. These electrolytes have the same anion but a different cation. These measurements were performed in pure water and at salt concentration of 0.5, 1, 1.5, and 2 M. The dashed line in Figure 2c corresponds to experimental data for Triton X-100 micelles in the absence of electrolyte.

In all cases, the ΔR_{90} values increase with electrolyte concentration for the same surfactant concentration. This increase in the scattered light could be indicative of micelle size growth with the electrolyte addition. The rate of intensity increase with respect to the salt concentration is higher for NaCl than for CsCl, and it is higher for CsCl than for LiCl.

Quantitative information about micellar growth has been obtained from eq 12 by calculating the molecular mass and the aggregation number of micelles. As it can be seen in Figure 2 parts a−c, the ΔR_{90} values are directly proportional to Triton X-100 concentration. These results indicate that the micellar interactions are negligible (the second virial coefficient is practically zero) and that the micellar molecular weights are essentially independent of surfactant concentration in the present range. Table 2 lists the micellar molecular weight (M_{w}) and the
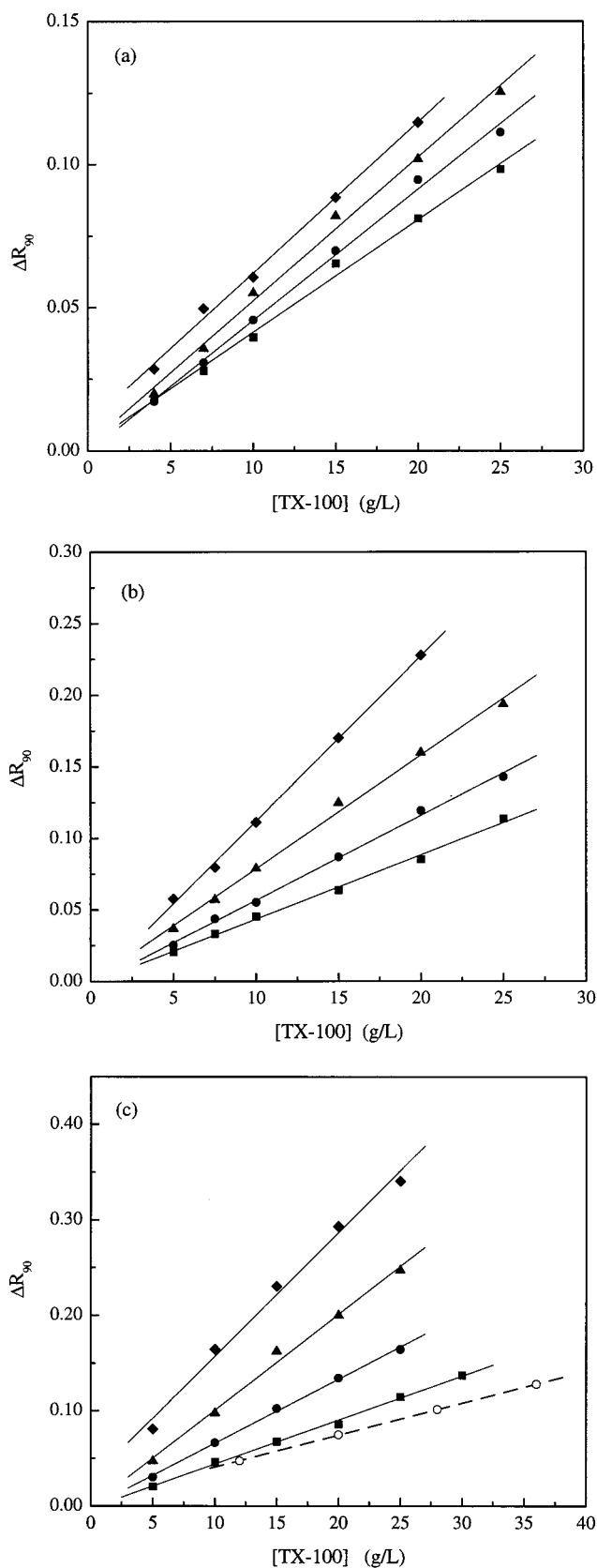
Figure 2. Excess scattering ratios (ΔR_{90}) versus micellar concentration as a function of electrolyte concentration for LiCl (a), CsCl (b), and NaCl (c). Symbols correspond to (■) 0.5, (●) 1, (▲) 1.5, and (◆) 2 M. The dashed line in Figure 2c corresponds to Triton X-100 micelles in the absence of electrolyte.

aggregation number (N_{agg}) calculated from the slopes values (obtained by linear regression, $r > 0.99$).

TABLE 2: Structural Parameters for Triton X-100 Micelles as a Function of Nature and Concentration of Electrolyte

salt	[salt] (M)	$D_0 \times 10^7$ (cm^2/s)	R_H (nm)	M_w (Da)	N_{agg}	R_0 (nm)	δ	a_0 (Å^2)
no salt	0.0	6.63	3.7	65 500	105	2.9	0.98	100.7
LiCl	0.5	5.98	4.8	84 600	135	3.1	2.45	89.5
	1.0	5.43	5.4	98 300	157	3.3	3.03	87.2
	1.5	4.96	5.7	107 000	171	3.4	3.29	85.0
	2.0			112 000	179	3.4		81.2
CsCl	0.5	6.04	4.2	96 100	154	3.2	1.11	83.6
	1.0	4.82	5.3	126 000	202	3.4	2.23	71.9
	1.5	4.39	5.9	167 000	267	3.7	2.41	64.4
	2.0	3.66	7.1	240 000	384	4.2	3.01	57.7
NaCl	0.5	6.02	4.1	99 000	158	3.3	0.82	86.6
	1.0	4.57	5.1	144 000	230	3.7	1.44	74.8
	1.5	3.72	6.0	210 000	336	4.1	1.83	62.9
	2.0	2.62	8.0	270 000	432	4.5	3.94	58.9

From M_w data, the dry micellar volume, V_0, can be obtained by the relationship

$$V_0 = \frac{\upsilon M_w}{N_A} \tag{13}$$

If the partial specific volume, υ, is known and, hence, assuming a spherical geometry, the dry micellar radius, R_0, can be derived. It is well recognized that Triton X-100 micelles are quasispherical.[34,35] The R_0 values are given in Table 2 where it can be seen that the micelle radius becomes larger with increasing electrolyte concentration. For surfactant solution in the presence of LiCl, the unhydrated micellar radius practically does not increase. This increase is more significant for solutions with NaCl or CsCl.

Previously reported values of Triton X-100 micellar molecular weight in water were in the range of 63 000−98 000,[36−39] so our value is in good agreement with them.

In the solutions with electrolyte, both R_0 and N_{agg} are larger than their values for salt-free solution. On the other hand, these results show that micellar growth is dependent on the cation nature. The micellar molecular weight of Triton X-100 in water was increased by a factor of 1.71, 3.66, and 4.12 by 2 M LiCl, CsCl, and NaCl, respectively. The difference in the effect of the three salts is commensurate with the difference in their salting-out capacity as will be shown in the next section by the corresponding cloud point depressions.

The formation of micelles from a surfactant solution is the result of the competition of different opposing forces, namely, in the case of nonionic surfactant, the attractive hydrophobic interaction of the hydrocarbon chain units and the repulsive force between adjacent headgroups arising from steric repulsion. The geometry of the micelle is expected to depend on the volume and the critical chain length of the tail and on the optimal headgroup area. The latter parameter is a measure of those opposing forces together and depends on the hydration of the POE segments. A progressive dehydration occurs when the salt is added to the nonionic surfactant solution. This dehydration results in a smaller effective headgroup area and hence in a change in the micellar size; that is, a higher electrolyte concentration induces a higher micellar growth.

In accordance with this possible explanation, the micellar growth with electrolyte should depend on the cation nature, as observed in Table 2. Because of the different size and hydration of cations, they modify the intramicellar interactions in a dissimilar way and, consequently, the micellar growth.

The hydrated sizes of the Cs^+, Na^+, and Li^+ ions are 3.3, 3.6, and 3.8 Å, respectively.[40] The fact that the bare sizes of

Cs^+, Na^+, and Li^+ are 1.69, 0.95, and 0.68 Å, respectively, shows that the smaller ions are more hydrated than the larger ones. We expected that, the higher the lyotropic number of the cation, the greater the effect on the micellar growth is. In other words, Na^+ is expected to have more effects than Cs^+ (as observed in Table 2). However, we expected Li^+ to have more effects than Na^+, which was not observed. However, Schott et al.[41] suggested that Li^+ probably forms complexes with Triton X-100 molecules and it cannot compete with ether groups for water of hydration. Owing to their large number of ether groups, the surfactants probably act as polydentate ligands, displacing water of hydration from the cations. Only Na^+ and Cs^+ do not form stable adducts with ethers, and therefore, they dehydrate the surfactant molecules.[42]

Opposite with our results, Aswall et al.[43] have observed a different trend on the micellar growth by electrolyte using the ionic surfactant sodium dodecyl sulfate. These authors have shown that the aggregation number of the ionic surfactant increase as the hydration of the cation decreases. For ionic surfactants, the electrostatic repulsion between ionic groups in the micelle play an important role in the micelle formation process. When the electrolyte is added to the ionic micellar solution, it has a tendency to neutralize the charge of the micelle. Different studies suggest[44] that less hydrated cations bind more effectively to negative micelles reducing the effective headgroup. In short, the effect of electrolyte on the micellar growth depends on the interactions between the surfactant monomers in the micelle.

We have shown that the number of monomers in the micelle increases in the presence of electrolyte. On the other hand, it is well-known that in the case of nonionic surfactant micelles the outer hydrophilic region consists of the POE shell plus the water of hydration. This hydrated POE mantle, which takes up the major part of the total micellar volume, could be altered with the presence of electrolytes in the medium. Therefore, the micellar growth can be due to an increase in the aggregation number and/or an increase in the micellar hydration. To evaluate both contributions, we have performed dynamic light scattering measurements to yields the value of the micelle hydrodynamic radius. This parameter has two contributions: first the dry micellar radius and second the water molecules which travel with the micelle as it diffuses.

If the surface of a micelle is highly rugose, then a large amount of water will be physically entrained by the moving micelle, even though the water molecules do not have a significant thermodynamic linking with surfactant molecules.[11,17,18] Therefore the extent of micellar hydration evaluated by dynamic light scattering is entirely hydrodynamic. It will be the water linked to surfactant molecules by hydrogen bonds plus the water physically entrapped in the micelle.

Figure 3 parts a−c shows the electrolyte dependence of the translational diffusion coefficient of Triton X-100 in the presence of LiCl, CsCl, and NaCl, respectively. It was not possible to obtain the data for 2 M LiCl solution.

The dashed line in Figure 3c corresponds to surfactant solutions without electrolyte. The micelle diffusion coefficients were in the range of $1.5 \times 10^{-7} - 6.8 \times 10^{-7}$ cm^2/s, and it depends on the electrolyte concentration and cation type. As a general rule for the three studied salts, it is quite clear that the micelle diffusion coefficient decreases with increasing electrolyte concentration for the same surfactant concentration. This change in D_c can be interpreted as arising from changes in the size of the Triton X-100 micelles (as expected from static light measurements). Measurements of D_c of Triton X-100 in water

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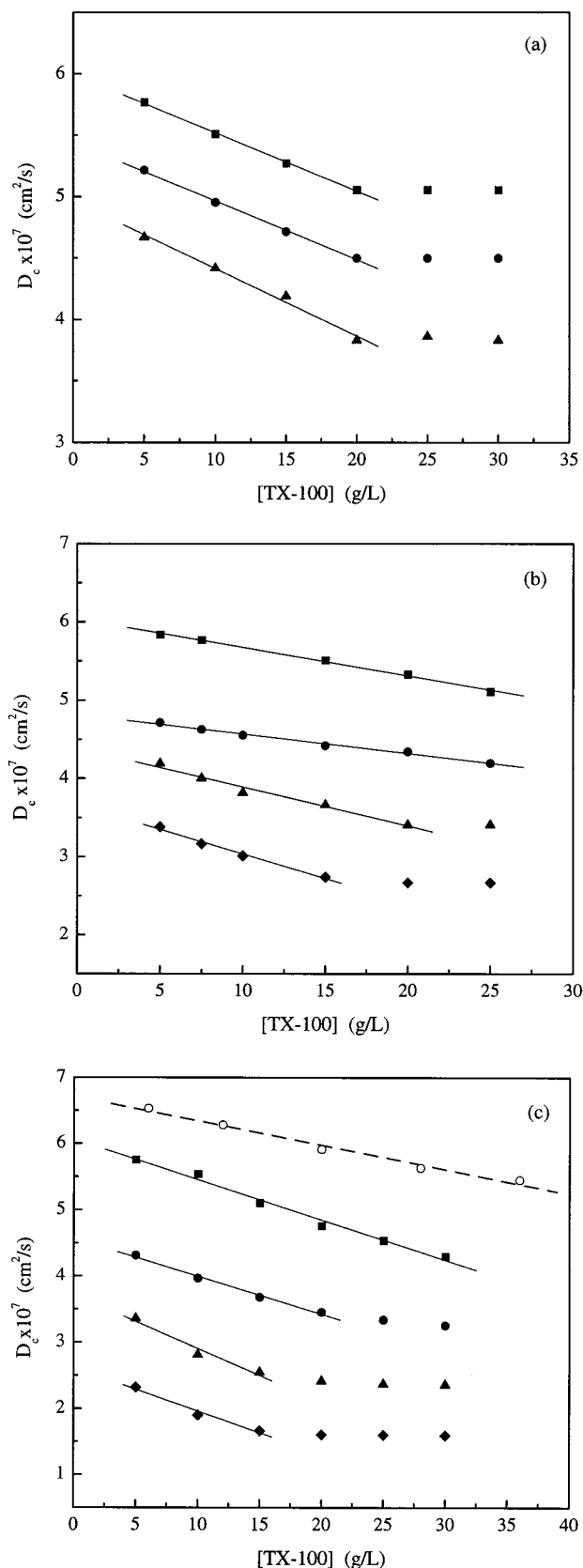
Figure 3. Plots of the micelle diffusion coefficient (D_c) versus micellar concentration as a function of the electrolyte concentration for LiCl (a), CsCl (b), and NaCl (c). Symbols correspond to (■) 0.5, (●) 1, (▲) 1.5, and (◆) 2 M.

were restricted to a concentration range in which D_c was a linear function of the surfactant concentration. In the case of electrolyte

solutions, a maximum concentration of Triton X-100 of 25 or 30 g/L was employed.

From Figure 3 parts a−c, it is observed that D_c shows a weak dependence on the surfactant concentration as expected for neutral surfactants where the intermicellar interactions are negligible. A general trend observed in these figures is the existence of two regions: first, a surfactant concentration range, where the diffusion coefficient depends linearly with Triton X-100 content, and a second region, above a certain surfactant concentration where D_c ceases to be linear in c. This last trend suggests micellar growth at elevated surfactant concentrations. Therefore, we have restricted our study to the concentration range where the experimental results are well described by eq 7.

Linear regression analysis of the data was used to estimate the intercepts at $c \rightarrow 0$ to evaluate the diffusion coefficient at infinite dilution, D_0. From the value of D_0, the hydrodynamic radius R_H was calculated according to eq 8 for each electrolyte concentration (see Table 2). From the data, we can see that the hydrodynamic radius of micelles become larger with increasing electrolyte concentration. This micellar growth is due to an increase in the aggregation number, as static light scattering results showed, and an increase in the water content in the micelle. By comparison of dry and hydrated micelle radii, we observed that the significant growth of micelles with electrolyte is predominantly due to increasing water content in the micelles and to a lesser extent of increasing the aggregation number. For example, the volume percentage of water of the total volume of Triton X-100 micelles in the presence of 0.5 M CsCl is around 56%, which increases to 80% at 2M CsCl. From Table 2, it is also clear that this effect of electrolyte on micellar water content is a function of cation type.

We have estimated micellar hydration as the difference between the hydrodynamic and the dehydrated micellar volumes according to eq 2. The computed values are listed in Table 2. The hydration factor values δ in electrolyte solutions are significantly higher than the corresponding value in water. This result suggests that surfactant micelles are more hydrated in the presence of electrolyte, increasing the hydration with the salt concentration.

In the previous section, we have shown that the partial specific volume decreases with electrolyte concentration probably because of micellar dehydration. This suggested dehydration of POE segments can also be inferred from the surface area per headgroup, a_0. The a_0 values presented in Table 2 were determined from the dry radius and the aggregation number by assuming a spherical geometry. This parameter is an important structural parameter that plays a decisive role in the geometric or packing properties of micelles, controlling the magnitude of steric repulsions between the heads.[45] As it can be seen in Table 2, the surface area per headgroup of Triton X-100 micelles decreases with the presence of electrolyte. This behavior suggests micellar dehydration provoked by the existence of cations in the surfactant solutions.

The dynamic light scattering studies indicate that the micelles are more hydrated when there is electrolyte in the surfactant solution (δ data), whereas both the partial specific volume and the surface area per headgroup prompt micellar dehydration (v and a_0 data). To understand these apparently conflicting results, it is necessary to consider the types of water associated with the micellar particles. The nonionic micelles incorporate water through two mechanisms: first the water bound to the ether groups by hydrogen bonding, which contributes hydration proper, and second the osmotic flux and mechanical entrapment
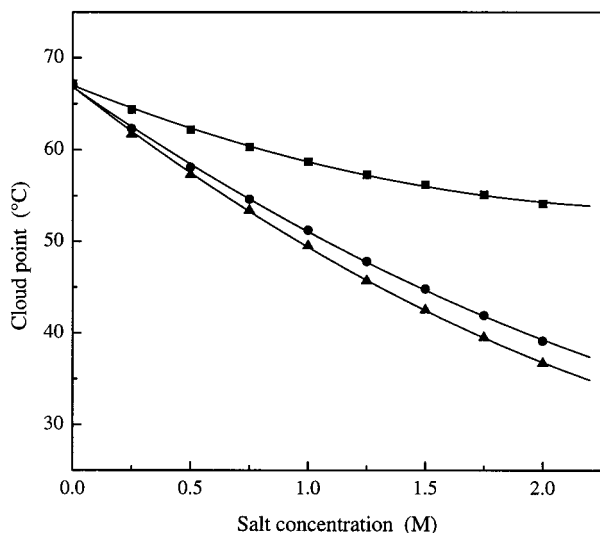
Figure 4. Cloud point of TX-100 solution as a function of the concentration of the added electrolyte (■) LiCl, (●) CsCl, and (▲) NaCl.

of aqueous media within the mesh of hydrated POE chains that comprise the outer shell of the micelles. Increasing the electrolyte concentration is seen to increase the water content of the micelles, which at elevated electrolyte concentrations may be considered predominantly "entrapped" rather than linked to the POE chains by hydrogen bonding.[11] Electrolyte disrupts ether-bound water, leading to chain dehydration and contraction of the hydrophilic chains, which is manifest by the reduction in partial specific volume as observed here. Water entrapping is therefore possible in the network of the many flexible headgroups on the outer mantle of the micelles. Therefore, as suggested by Charlton and Doherty,[18] the addition of electrolyte induces the POE chains to collapse. We speculate that the micellar surface may become increasingly rugose because of the collapsing surface, which, in turn, leads to the physical entrapment of water that diffuses with the particle.

Another tentative explanation for the increase of δ is the following. Because the micelles are larger in high electrolyte concentration, they are probably more asymmetrical than at low electrolyte concentration where the micelles are smaller.[46] Because a sphere has the smallest surface area for a given volume, a change to a less symmetrical micellar shape results in an increased area per micellar ethylene oxide unit on the surface of the hydrocarbon core. Such increase in the area facilitates the osmotic influx of aqueous medium into the micellar shell, thereby increasing the hydrodynamic volume of the micelle and δ.

Cloud Point Results. One of the most characteristic features of nonionic surfactants is that a liquid–liquid phase separation occurs when the temperature rises above a certain value. The temperature at which the incipient phase separation takes place is called the cloud point. It is widely assumed that the phase separation is due to the reduction of the intermicellar repulsion, as a result of the dehydration of the oxyethylene groups as the temperature is increased. Because we observed that the addition of electrolytes produces a remarkable alteration in the hydration layer of micelles, it seems interesting to evaluate and to analyze its influence on the cloud point of the Triton X-100 micellar solutions.

Figure 4 shows the cloud point of surfactant solutions in the presence of LiCl, CsCl, and NaCl as a function of electrolyte concentration. From this figure, it is quite clear that these salts

decrease the cloud point of Triton X-100 (salting-out behavior). The effect seems to be greater with NaCl than with CsCl and LiCl.

The salting-out capacity of these electrolytes is due to the elevated hydration of the respective cations. The cloud point shifts may be explained in terms of changes in localized water structure because of attenuated hydrogen bonding. Cations decrease the concentration of single water molecules that are capable of forming hydrogen bonds with the ether groups. These water molecules are barriers for micellar interactions. Once they move out at higher temperature, the micelle-micelle interaction becomes easier. This is why the cloud point is seen to lower temperature. The cation Na^+ is more hydrated than the cation Cs^+, and for this reason, the cloud point of the surfactant solution is lower in the presence of NaCl electrolyte than in the CsCl medium. As previously mentioned the cation Li^+, which is the most hydrated of the studied cations, can complex the ether oxygen being the cloud point shifts the lowest.

The fact that the larger electrolyte concentration creates a greater reduction in the cloud point of the surfactant seems contradictory with the effect of the added electrolyte in the hydration parameter, δ. However, it is apparent that the observed tendency in Figure 4 could be explained in relation to the water amount linked to the micelle via hydrogen bonding.

The light scattering studies have shown that the micellar water content increases with electrolyte concentration. At higher electrolyte concentration the main percentage of water is physically entrapped in the micelle. As the number of water molecules thermodynamically linked to micelle structure decreases with the electrolyte, the cloud point shift is highest at elevated salt concentration. Therefore, it is not surprising that the Triton X-100 micelles had larger δ values in the presence of salt additives than in water.

A correlation between micelle structural properties and the cloud point of surfactant solution could be proposed. The cloud point is a micellar macroscopic property related to the water bound via hydrogen bonding. The addition of salting-out electrolyte to surfactant solution causes a 2-fold effect: (i) a reduction in bound water, as corroborated by both the decrease of partial specific volume of micelles and surface area per headgroup, and (ii) an increase of mechanically trapped water. The micellar dehydration permits the growth of micelles that depends on the cation dehydration capacity. In the presence of NaCl, the micelles are bigger than in the presence of CsCl or LiCl, as those surfactant solutions present the lowest cloud point values.

Conclusions

Light scattering and density measurements of Triton X-100 micellar solutions with varying concentrations of LiCl, CsCl, and NaCl have been discussed. These salts have a strong effect on the micellar solution of Triton X-100. The results show a micellar growth due to both increasing aggregation number and increased entrapped water, the latter accounting for the majority of the growth. This entrapped water is nonspecifically associated with the micellar POE mantle. It is seen that micellar growth strongly depends on the cation hydration, except for Li^+ which apparently forms complexes with Triton X-100 molecules. We have found that the more hydrated the cation is the larger the growth of the micelles is. The partial specific volume of micelles and the cloud point studies suggest that the amount of hydrogen-bonded water to the micelle decreases with increasing electrolyte concentration. The cation present in the surfactant solution disrupts the water structure around the micelles, leading to

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dehydration and contraction. This reduction in the water content linked via hydrogen bonding to micelles provokes a shift of the cloud point to lower temperatures as the electrolyte concentration increases. We believe that the data reported here provide important new insights, from a fundamental point of view, upon the effect of salts on the micelle formation in Triton X-100 solutions and in general for nonionic surfactants.

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