

Electrolyte-Induced Structural Evolution of Triton X-100 Micelles

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The long-time self-diffusion coefficients of Triton X-100 micelles have been determined as a function of surfactant and electrolyte concentrations using rotating disk electrode voltammetry in conjunction with ferrocene acting as an electroactive probe. Micellar diffusion conforms to the linear interaction theory and yields micellar hydrodynamic radii values and interaction parameters as a function of electrolyte concentration. The interaction parameters varied from 3.4 to 3.6 over the electrolyte concentration range 0.01–0.8 mol dm⁻³ KCl, which is consistent with excluded volume interactions and indicated the absence of significant micellar shape changes with the addition of electrolyte. Micellar hydrodynamic radii varied linearly with respect to [KCl] from 4.22 to 6.21 nm, indicating the progressive evolutionary growth of the oblate micelles due to increasing aggregation number and “hydration”. The semimajor to semiminor axial ratio (*a/b*) increased from 2.0 to 3.5, indicating evolution to a more asymmetric structure. Micellar molecular weights increased from 77 700 to 326 000 over the electrolyte concentration range studied, which is predominantly due to water entrapment at the periphery of the self-assembled structures. Intrinsic viscosities were found to decrease from 6.09 to 4.61 cm³ g⁻¹, indicating a decrease in specific micellar volume, which may be attributed to ethylene oxide chain collapse due to dehydration. The decrease in micellar specific volume was found to correlate precisely with the electrolyte induced decrease of the cloud point.

Introduction

Micellar systems are of immense technological importance as flow field regulators, solubilizing agents, membrane mimetic compounds and recently as nanoreactors for enzymatic and chemical reactions.^{1–4} In general, the micellar structure (shape and size) strongly influences the behavior of such systems, and to this end, various strategies have been adopted to controllably attenuate micellar structure.⁵ For example, the addition of small molecules that interact with the micelles (e.g., simple electrolytes or salicylate) is known to induce micellar growth and shape changes.⁶ Also, the conditions used for many micellar applications, e.g., biopolymer (DNA,⁷ phospholipids⁸) processing, may induce structural changes; therefore the behavior of the surfactant system may depend critically on solution composition.

Triton X-100 ((*p*-(1,1,3,3-tetramethylbutyl)phenyl poly(ethylene glycol)) is a nonionic (*neutral*) surfactant and is one of the most frequently studied and exploited micellar system. Extensive studies have been carried out on this system to elucidate the micellar size and shape under various conditions in particular the effect of elevated temperature.^{9–11} Techniques such as quasi-elastic light scattering (QELS),¹⁰ light scattering (LS),⁹ small-angle X-ray scattering (SAXS),¹¹ NMR,¹⁰ and viscometry¹² have yielded substantial data on particle structure that suggests that the micellar shape is oblate ellipsoidal (disklike) with an axial ratio ≈ 2.0 at room temperature in the absence of electrolyte.^{13–15} With the exception of a few studies,^{5,12} the effect of electrolyte addition on Triton X-100 micellar structure has not been addressed. Phillies et al.⁵ have shown using QELS that the addition of NaCl induces micellar growth via aggregation number increases as well as increasing micellar hydration. Mandal et al.¹² using intrinsic viscosity data

postulated that the addition of Na₂SO₄ (at low concentrations) resulted in enhanced micellar hydration.

Recently, we have been successfully applying highly precise steady-state electrochemical techniques (the rotating disk electrode and microelectrodes) for the elucidation of cationic (cetyltrimethylammonium chloride (CTAC)) and reverse (AOT) micellar structure, structural evolution, and intermicellar interactions.^{16–18} Such measurements are based on determining the long-time self-diffusion coefficient of the micelles (*D_s*) with the aid of a micelle-immobilized electroactive probe. Ferrocene, due to its very low aqueous solubility, is used as the probe as it resides almost entirely within the hydrophobic core of the micelles and does not perturb the micellar structure; therefore, voltammetric responses give a direct and unambiguous measurement of micellar diffusion.

It is usual to analyze micellar self-diffusion data using the linear interaction theory¹⁹ as given in eq 1,

$$D_s = D_s^0[1 - k_d(C_s - \text{cmc})] \quad (1)$$

where *D_s* represents the measured micellar self-diffusion coefficient, *D_s⁰* is the self-diffusion coefficient in the absence of interaction (i.e., at the critical micelle concentration (cmc) where *D_s* = *D_s⁰*), and *C_s* is the surfactant concentration. With a knowledge of *D_s⁰* the micellar hydrodynamic radius *R_h⁰* may be obtained using the Stokes–Einstein relation as given in (2),

$$D_s^0 = \frac{k_b T}{6\pi\eta_o R_h^0} \quad (2)$$

where *k_bT* has its usual meaning and *η_o* is the solution viscosity at infinite dilution.

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Although the structure of Triton X-100 micelles have been the subject of active interest, relatively few studies reporting the effect of electrolyte have been reported.⁵ Since a major application of Triton X-100 is biopolymer processing where background electrolytes are used to avoid polyelectrolyte effects, elucidating the effect of electrolyte on micellar structure is important. We therefore have turned our attention to this system in an effort to observe voltammetrically structural evolution in the presence of the simple electrolyte KCl. We will show that the micelles increase in size with increasing electrolyte concentration due to both increased N_{agg} and increased hydration and do not undergo dramatic structural transitions. From intrinsic viscosity data and R_h^0 measurements we have calculated the micellar molecular weights as a function of electrolyte concentration and also obtained micellar specific volumes. Significantly, the specific micellar volume decreases concurrently with micellar expansion, behavior attributed to EO chain dehydration.

Experimental Section

All voltammetric measurements were made at 298 K with a Sycopel AEW2 potentiostat using the three-electrode mode and an Oxford rotating disk electrode (RDE) assembly (Sycopel). The working electrode a 7 mm glassy carbon disk shrouded in epoxy, the auxiliary electrode was flamed Pt gauze while the reference electrode was the saturated Ag/AgCl electrode used in combination with a luggin capillary. The working electrode was polished with 0.015 μm alumina as an aqueous slurry prior to use and its electroactive surface area determined electrochemically using $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous solution of ferricyanide of known diffusion coefficient ($7.63 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). For RDE measurements, current–potential curves were recorded at a potential sweep-rate of 5 mV s^{-1} over the rotation speed (ω) range 2–12 Hz. Higher rotation speeds were avoided due to excessive foaming of the agitated surfactant solution although the expected current–rotation speed dependence was observed from 0.2 to 50 Hz.

Solution viscosity measurements were made at 298 K with a calibrated Brookfield DVI digital cone and plate viscometer under thermostatic conditions with deionized water as the reference.

All Triton X-100 (Aldrich) solutions were prepared from N_2 -purged Millipore deionized water ($18 \text{ M}\Omega^{-1}$) and stored under N_2 . Ferrocene (Fc, Aldrich) was dissolved in surfactant solutions by stirring overnight using a magnetic stirrer. Using previously reported aggregation numbers (N_{agg}),⁵ sufficient ferrocene was used to ensure that each micelle possessed at least one probe molecule.¹⁷ All solutions were prepared quantitatively.

Results and Discussion

Figure 1a–f shows current–potential curves for the oxidation of Fc (eq 3) in $0.167 \text{ mol dm}^{-3}$ Triton X-100 with $0.010 \text{ mol dm}^{-3}$ KCl at various electrode rotation rates.



For all combinations of Triton X-100/KCl concentrations examined such curves were similarly sigmoidally shaped with well-defined limiting currents reflecting steady-state diffusion of micelle-immobilized ferrocene to the electrode surface. The current–voltage profiles exhibited typical nernstian behavior with slopes of $59 \pm 2 \text{ mV decade}^{-1}$, indicating the simple reversible electrochemistry of the electroactive probe in the micellar media as expected.²⁰

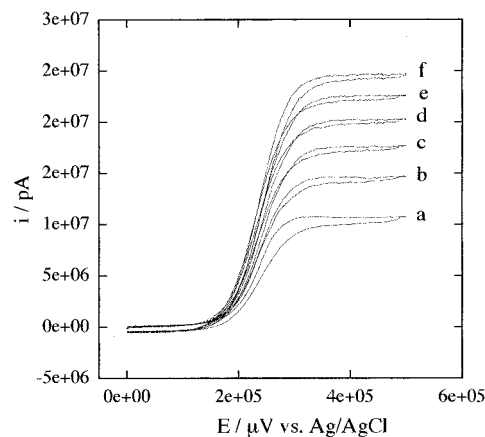


Figure 1. RDE voltammograms for the oxidation of $1.670 \times 10^{-3} \text{ mol dm}^{-3}$ ferrocene in $0.167 \text{ mol dm}^{-3}$ Triton X-100/ 0.01 mol dm^{-3} KCl solution at (a) 2, (b) 4, (c) 6, (d) 8, (e) 10, and (f) 12 Hz.

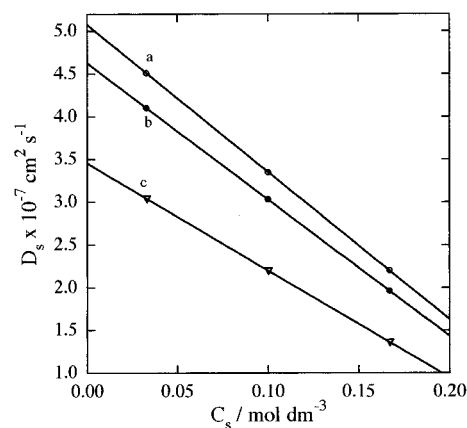


Figure 2. Plots of D_s vs C_s at (a) 0.01 mol dm^{-3} KCl, (b) 0.20 mol dm^{-3} KCl, and (c) 0.8 mol dm^{-3} KCl.

It is usual to analyze such limiting current (i_{Lim}) data using the Levich equation (eq 4), which yields the micellar long-time self-diffusion coefficient,

$$i_{\text{Lim}} = 1.554nFAD_s^{2/3}\nu^{-1/6}\omega^{1/2}c_{\infty} \quad (4)$$

where n is the number of electrons ($n = 1$), F is the Faraday constant, A is the electrode area, ν is the solution kinematic viscosity, ω is the electrode rotation rate (Hz), and c_{∞} is the concentration of electroactive probe immobilized within the micelle. Plots of i_{Lim} vs $\omega^{1/2}$ were linear and passed through the origin, indicating that the electrochemical process is under diffusional control.²⁰ Since the electroactive probe is predominantly immobilized within the micelle such data predominantly represent micellar diffusion. The current data are, however, corrected for the small finite aqueous phase solubility ($1.0 \times 10^{-8} \text{ mol cm}^{-3}$) of ferrocene.^{12,16,17} A detailed description of the data analysis for such measurements may be found elsewhere.¹⁷

We have determined D_s values at three different surfactant concentrations, 0.033, 0.100, and $0.167 \text{ mol dm}^{-3}$ over the electrolyte concentration range $0.01\text{--}0.8 \text{ mol dm}^{-3}$ KCl. Although distorted due to the iR drop effect, current–voltage traces obtained at $[\text{KCl}] < 0.01 \text{ mol dm}^{-3}$ yielded limiting currents identical (within experimental error) to 0.01 mol dm^{-3} ; therefore, lower KCl concentrations were not pursued in detail. In Figure 2, corrected D_s values are plotted as a function of surfactant concentration at several electrolyte concentrations. It is immediately obvious that these plots are strictly linear (r

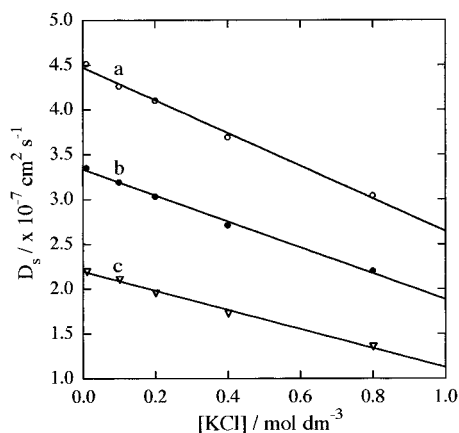


Figure 3. Plots of D_s vs $[KCl]$ at (a) $0.033 \text{ mol dm}^{-3}$, (b) $0.100 \text{ mol dm}^{-3}$, and (c) $0.167 \text{ mol dm}^{-3}$ Triton X-100.

> 0.999) with slightly different slopes and different intercepts. Phillies et al.⁵ found that at high surfactant concentration plots of D_m (mutual diffusion coefficient) vs C_s reached an almost constant minimum value. Since our measurements are conducted at significantly lower surfactant concentrations (by a factor of 10 approximately) we observe only the linear behavior similarly observed by Phillies et al.⁵ at low surfactant concentration. These observations demonstrate that the linear interaction theory holds, that the micelles are interacting (slope), and that the micellar hydrodynamic size is a strong function of electrolyte concentration (intercept). Phenomenologically these results reflect the behavior observed by Phillies et al.⁵ in NaCl electrolyte. Since solution kinematic viscosity is incorporated into eq 4, viscosity effects are therefore eliminated from the electrolyte-dependent effects observed here.

We have shown previously for cationic CTAC micelles that upon electrolyte-induced micellar sphere-to-rod structural transition (with subsequent micellar elongation) adherence to the linear interaction theory breaks down while plots of D_s vs $[KCl]$ (vide infra) exhibit a linear decrease in D_s followed by a precipitous decrease at high electrolyte concentration due to spherical micellar expansion and sphere-rod structural transition, respectively.¹⁷ That the linear interaction theory holds in the case of Triton X-100 at all electrolyte concentrations examined is significant, as it indicates that no dramatic micellar shape changes occur with increasing electrolyte concentration. This is further emphasized in Figure 3, where D_s values are plotted vs KCl concentration again show a strict linear relationship, indicating the monotonic increase in micellar size with increasing electrolyte concentration.

Interaction parameters may be obtained from the slopes of the plots in Figure 2; these values are given in Table 1. We¹⁷ and others¹² have shown previously that the intermicellar interaction parameters change significantly with increasing electrolyte concentration for charged micellar systems (i.e., Coulombic, screened Coulombic, and excluded volume interactions); however, here the interaction parameter change is small, i.e., from 3.4 to 3.6 over the electrolyte concentration range used. Such parameters describe the global effect of all interaction processes and also surfactant-concentration dependent changes in aggregation number if present. As we use relatively low concentrations of surfactant, [surfactant] dependent changes of N_{agg} are unlikely to affect the slope behavior measurably; therefore, the slope reflects intermicellar interaction processes. Since the self-assembled particles studied here are neutral, Coulombic and screened Coulombic interactions are absent. Also, several studies of Triton X-100 micelles using small-angle

neutron scattering have applied Baxter's sticky hard-sphere model to interpret scattering data in terms of direct sticky interaction (surface adhesion) due to a deep attractive potential energy well.^{21,22} However, in dilute surfactant solutions (i.e., $\leq 1 \text{ wt } \%$ as is the case here) the interparticle spacing is sufficient to effectively eliminate the effect of sticky interactions.^{21,22} We have shown elsewhere that sticky interaction of AOT reverse micelles in isooctane is manifested as enhanced R_h^0 values,¹⁸ it will be shown here that voltammetrically obtained R_h^0 values for Triton X-100 are identical to values obtained by QELS;⁵ therefore sticky encounters are sufficiently rare as not to affect D_s^0 measurements. Eliminating these possible interaction processes indicates that the observed behavior here is a slight increase in excluded volume interactions with increasing electrolyte concentration due to micellar expansion. These results indicate a simple monotonic micellar growth process occurs without dramatic micellar shape changes; it is generally recognized that Triton X-100 micelles undergo growth with increasing electrolyte concentration.^{5,12,14}

From the intercepts in Figure 2, D_s^0 values may be obtained (Table 1), which are also plotted vs $[KCl]$ in Figure 4a. It is evident that D_s^0 decreases linearly with increasing electrolyte concentration as expected from the behavior exhibited in Figure 3. Using relation 3 the micellar hydrodynamic radii, assuming a spherical model, are obtained (Table 1) and are also plotted vs $[KCl]$ in Figure 4b. Data obtained using QELS by Phillies et al.⁵ (spherical model assumed) are also plotted. These plots demonstrate the increase in micellar size and also the simple evolutionary micellar growth unaccompanied by dramatic electrolyte-induced micellar structural changes. The agreement with the QELS data is useful as it indicates that the voltammetric measurements of D_s^0 and therefore R_h^0 are accurate and comparable with other techniques. It also indicates that the effect of KCl and NaCl on Triton X-100 micellar structure is very similar.

It is well recognized that Triton X-100 micelles are quasi-spherical;^{11,13,15} for example, a study by Wright et al.²³ showed that Triton X-100 micelles exhibit electric birefringence and by definition an isotropic sphere would show no such effect therefore, an oblate (quasi-spherical) or prolate ellipsoidal shape was indicated. It is generally accepted that the prolate ellipsoid model does not fit micellar hydration values;^{12,14} therefore Triton X-100 are considered to be oblate structures defined by an axial ratio a/b ($a = c \neq b$). The magnitude of R_h^0 values (i.e., 4.22–6.21 nm) is informative as it not only indicates relatively small micelles exist but also indicates the lack of dramatic structural changes and micellar elongation processes (i.e., prolate formation), which supports the absence of dramatic changes in intermicellar interaction parameters. Consequently, the structural evolution observed here may be interpreted as the progressive growth of an oblate ellipsoid due to the addition of electrolyte.

Intrinsic viscosity ($[\eta]$) measurements of micellar systems have been used extensively to study particle structure (i.e., Simha parameters) and specific micellar volumes.^{10,12–14} For Triton X-100 micelles, eq 5 has been used in variable temperature studies to assess the shape parameter (ν) and the degree of hydration, δ ,

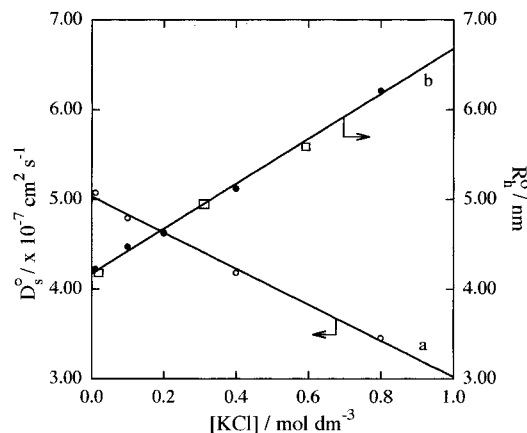
$$[\eta] = \nu(V_T + \delta V_w) \quad (5)$$

where V_T and V_w are the specific volumes of Triton X-100 ($0.91 \text{ cm}^3 \text{ g}^{-1}$) and water ($1.0 \text{ cm}^3 \text{ g}^{-1}$), respectively. A problem arises as estimation of either ν or δ depends on a prior knowledge of the other. Mandal et al.¹² has tackled this problem by using relative conductivity measurements (solution conductivity in the

TABLE 1: Transport and Structural Parameters for Triton X-100 Micelles as a Function of [KCl]

[KCl]/mol dm ⁻³	10 ⁷ <i>D</i> _s ⁰ /cm ² s ⁻¹	<i>R</i> _h ⁰ /nm	<i>k</i> _d /mol ⁻¹ dm ³	[<i>η</i>]/cm ³ g ⁻¹	<i>a</i> /nm	<i>b</i> ^c /nm	<i>a</i> / <i>b</i>	<i>ν</i>	<i>V</i> _m /cm ³ g ⁻¹	<i>δ</i>	10 ⁻³ <i>M</i> _{wt}	<i>N</i> _{agg}	<i>N</i> _{H₂O}
0.01	5.07	4.22	3.38	6.09	5.28	2.70	1.96	2.83	2.15	1.24	77.7	80	19
0.10	4.79	4.47	3.34	5.91	5.75	2.70	2.13	2.93	2.02	1.11	95.3	89	25
0.20	4.63	4.62	3.45	5.73	6.04	2.70	2.24	3.00	1.91	1.00	108.3	99	26
0.40	4.18	5.12	3.50	5.35	7.05	2.70	2.61	3.23	1.66	0.75	157.8	121	38
0.80	3.45	6.21	3.63	4.61	9.42	2.70	3.49	3.76	1.23	0.32	326.8	131	104

^a Error $\pm 0.06 \times 10^{-7}$ cm² s⁻¹. ^b Error ± 0.05 nm. ^c The *b* semiminor axis is assumed to stay constant.

**Figure 4.** Plots of (a) D_s^0 and (b) R_h^0 vs [KCl]. Phillies' data are plotted in (b) as open squares.

absence and presence of micellar obstructants) to determine δ and subsequently obtained ν values. Unfortunately, since high electrolyte concentrations are used here relative conductivity measurements are not feasible. However, Robson et al.¹⁴ have reported that, for Triton X-100, the hydrophobic molecular core contributes ≈ 1.0 nm to the semi axis *b* whereas the hydrated ethylene oxide hydrophilic chain (meander geometry) contributes 1.7 nm, giving a total semiminor axis dimension of 2.7 nm. Since, the semiminor axis is usually relatively constant for oblate ellipsoidal structures and corresponds to the molecular dimensions of the monomer, using the relation for a sphere of equal volume for an oblate ellipsoid ($(a^2b)^{1/3}$) with $b = 2.7$ nm, we can approximate the semimajor axis dimension *a* and hence the *a*/*b* ratio. Knowing *a*/*b*, the approximate shape parameter may be obtained using available data.²⁴ These values are given in Table 1 where it is obvious that the shape becomes more asymmetric with increasing electrolyte concentration. At low electrolyte concentrations, $\nu \approx 2$, as expected from previous studies,^{13,15} which indicates that the assumption of $b \approx 2.7$ nm is justifiable. It should be noted that for a 0.3 nm error in *b*, a corresponding 9% error occurs in ν .

Because the intrinsic viscosity is decreasing and the shape parameter is increasing, the term ($V_T + \delta V_w$) in eq 5 (which is the specific micellar volume V_m) is decreasing. V_m values are given in Table 1 along with the apparent hydration parameters (δ). As it is expected that the specific micellar volume will increase due to hydration (eq 5) with the addition of electrolyte, these results indicate a significant decrease in specific micellar volume due to apparent micellar dehydration, contrary to the expected behavior, i.e., increased water content (vide infra). We have also used Vand's²⁵ approach to determine the specific micellar volume and have obtained similar results. The hydration parameters at low electrolyte concentration are, however, in good agreement with values for an oblate ellipsoidal Triton X-100 micelles where $\delta \approx 1.0$.¹⁴ Birdi^{13,26} has reported hydration values of 1.3 obtained using molecular weight and intrinsic viscosity data, which is in good agreement with the value obtained here. Again, assuming a maximum error of 0.3

nm in *b*, a corresponding maximum error in V_m is $<10\%$ and therefore the unexpected behavior observed cannot be explained by error alone. Considering this, and also that the shape and δ parameters (at low electrolyte concentration at least) are reasonable, these results indicate that the micelles become more compact with increasing electrolyte concentration although significant micellar expansion occurs concurrently.

It is useful to estimate the micellar molecular weight (M_{wt}) using the following relation:

$$R_h^0 = \left(\frac{3[\eta]M_{wt}}{10\pi N_A} \right)^{1/3} \quad (6)$$

where N_A is Avogadro's number. The values are given in Table 1 where it can be seen that the micellar molecular weight increases dramatically with the addition of electrolyte. Previously reported values in the absence of electrolyte were in the range 63 000–98 000, and up to 150 000 with small amounts of electrolyte.^{11,14} Brown et al.¹⁰ reported a value of 69 000 at 298 K (static light scattering); therefore the values reported here appear to be in good agreement with light scattering, SAXS, and ultracentrifugation methods. It is also apparent from the literature^{10,11,14} that addition of electrolytes results in a significant increase in micellar molecular weight, e.g., in the presence of 0.50 mol dm⁻³ NaCl, $M_{wt} = 150\,000$,²⁶ behavior in agreement with the trend observed here.

The total molecular weight of the micelles is comprised of contributions from both the surfactant and water (both bound to the EO groups and unbound). Phillies et al. have reported N_{agg} values as a function of NaCl concentration. Because we have observed almost identical values for R_h^0 in the presence of KCl, we have interpolated these data to obtain N_{agg} values for Triton X-100 in KCl, which are given in Table 1, where the electrolyte dependence is immediately obvious. Using the N_{agg} values and the total molecular weight allows an estimation total number of water molecules associated with the micelles (bound by hydrogen bonding and unbound) expressed per surfactant molecule (N_{H_2O}), which are also given in Table 1. At 0.01 mol dm⁻³ KCl 19 water molecules per chain are evident, which agrees with the belief that each EO group requires two H₂O molecules for hydration²⁷ since on average each chain possesses 9.5 EO units. This is in excellent agreement with SAXS data where 20 D₂O molecules per chain were determined for an average of 10 EO units per chain.^{21,22} Hydration numbers for Triton X-100 have been reported in the range 20–50;^{9,13,21,28,29} so the data presented at <0.8 mol dm⁻³ KCl here are in good agreement with previously reported values.

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 bound to the EO chains.⁵ Calculating the weight percent of H₂O of the total weight of micelles reveals the extent of hydration of the micelles (Table 1). The particles possess 36% H₂O at 0.01 mol dm⁻³ KCl, which increases to 75% H₂O at 0.8 mol dm⁻³ KCl, indicating that the significant growth is predominantly due to water uptake by the micelles.

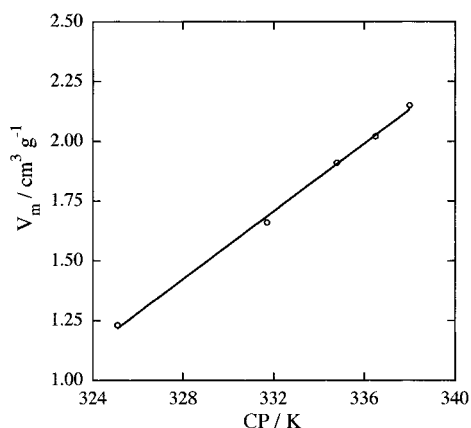


Figure 5. Plot of specific micellar volume, V_m , vs cloud point, CP, as a function of [KCl].

We have shown that the micelles grow significantly with increasing electrolyte concentration predominantly due to increasing water content of the micelles and to a lesser extent to increasing N_{agg} . We have also shown that the specific volume decreases with increasing electrolyte concentration, which is unexpected since increasing hydration should increase the specific micellar volume according to eq 5. To understand these apparently conflicting results, it is necessary to consider the types of water associated with the micellar particles. First, water bound to the EO chains and second unbound water present in the free volume of the particles and rugose surface.^{5,21,22} It is recognized from cloud point measurements³⁰ that addition of certain electrolytes to Triton X-100 results in a lowering of the cloud point (CP) (i.e., “salting out” where the system exhibits a lower consolute point). Using the CP shift for Cl^- of -16.5 K mol^{-1} ,³⁰ CPs can be estimated at each electrolyte concentration, which obviously reveals a salting out process where CP decreased from 338 to 325 K over the electrolyte range studied. It is interesting to note that (a) CPs are independent of electrolyte concentration³¹ below $0.01 \text{ mol dm}^{-3} \text{ Cl}^-$, which supports the voltammetric observation that D_s is independent of [KCl] at low electrolyte concentrations, and (b) the effect of Na^+ and K^+ on CPs is almost identical³⁰ (i.e., for K^+ the CP shift is ca. 1 K less negative than that for Na^+ ; therefore the agreement with Phillies et al.’s data (in NaCl) and ours is not surprising).

The CP shifts may be explained in terms of changes in localized water structure due to attenuated hydrogen bonding. For KCl the anion acts to enhance water structure, i.e., promote the formation of “flickering” water clusters,³⁰



which lowers the concentration of molecular H_2O free for hydrogen bonding (i.e., solvating) to the EO groups of the surfactant, therefore causing dehydration and contraction of the hydrophilic chains, which, in turn, is manifest by the reduction in specific volume as observed here. It is interesting to plot the specific micellar volume V_m vs CP, as shown in Figure 5, where a linear relationship is observed, suggesting that the electrolyte progressively dehydrates the hydrophilic periphery, as expected for a salting out electrolyte.

Phenomenologically, the results presented reveal a picture of a dimensionally stable hydrophobic micellar core ($r \approx 1.0 \text{ nm}$) surrounded by a progressively collapsing hydrophilic periphery. The location of the significant quantities of H_2O is, however, uncertain. Phillies et al.⁵ have postulated that the micellar periphery may be diffuse in nature, therefore accom-

modating relatively large quantities of water; however, the apparent decrease in specific micellar volume suggests that EO chain collapse occurs, which will inevitably lead to a more compact outer structure and therefore less free volume to accommodate unbound H_2O . As significant quantities of water are entrapped by the micelles at elevated salt concentrations, we speculate that the micellar surface may become increasingly rugose due the collapsing surface, which, in turn, leads to the physical entrapment of H_2O that diffuses with the particle. The highly convoluted surface of Triton X-100 micelles has been demonstrated by SAXS.¹¹ This view is reasonable because (a) EO chain dehydration results in increased structural disorder^{32,33} and (b) at increased electrolyte concentrations water cluster formation is favored and, therefore, relatively large “icebergs” of water may be associated with the micelles, which may extend to considerable distances from the micellar hard-sphere surface.

Conclusions

The data presented here conform closely with those reported by Phillies et al.,⁵ which indicate a progressive micellar growth with increasing KCl concentration. The growth is due to both increasing N_{agg} and increased entrapped water, the latter accounting for the majority of growth. By using intrinsic viscosity measurements, the specific micellar volume was shown to decrease progressively with the addition of electrolyte concurrent with micellar expansion. Because increasing hydration of the micelles (assuming all other parameters are equal) should result in an increase in specific micellar volume, these results suggest that electrolyte causes compaction of the micellar particles. Since it is well-known that certain electrolytes disrupt EO-bound H_2O , leading to chain dehydration and contraction, these results indicate that addition of electrolyte results in EO chain collapse. Since the measurement of R_h^0 is hydrodynamic rather than thermodynamic (i.e., sensitive to entrapped water), the result suggests that the micellar particle surface may become increasingly convoluted and therefore entraps increasing quantities of water, possibly as clusters, with increasing ionic strength.

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