

Voltammetry as a Tool for Monitoring Micellar Structural Evolution?

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Self-assembled systems such as micelles and liquid crystals are currently of interest as templates for the controlled formation of nanoscale structures. Knowledge of the mesophase structure, structural evolution, and interparticle interaction is of great importance in understanding the behavior of such systems especially for applications such as nanoreactors. Here, we compare the use of cyclic voltammetry, chronoamperometry, and the rotating disk electrode (RDE) for the determination of micellar hydrodynamic radii and show that only the steady-state RDE yields values directly comparable with nonelectrochemical techniques. The RDE is applied for the determination of cetyltrimethylammonium chloride micellar structure and observing micellar structural evolution as well as evaluating the usual intermicellar interactions. The results clearly show (a) the collapse of the micellar shear plane toward the hard-sphere surface with increasing electrolyte concentration, (b) the electrolyte-dependent spherical expansion of the micellar hard-spheres due to increasing aggregation (*N*) number, (c) the structural transition from spherical to rodlike micelles, and (d) micellar elongation. As well as structural evolution, the evolutionary changes in interaction processes are also observed, i.e. the transition from Coulombic interactions to excluded volume interaction. This paper describes in detail the voltammetric measurement of these processes and explicates the necessary experimental conditions for successful observation of micellar structural evolution.

Over the last two decades, the electrochemistry of electroactive probes has been studied using a variety of electrochemical techniques in microheterogeneous phases, in particular, in micellar and microemulsion systems.^{1–8} Principally, these studies

were concerned with the electrochemical behavior of the probe molecule in such unconventional media⁵ (e.g. electron-transfer kinetics and subsequent chemical reactions) and has been applied to useful reactions such the destruction of organohalide pollutants.⁶ Other studies have concentrated on the determination of critical micelle concentrations⁷ (cmc) or the partition of the electroactive probe (or the electrolytic product) between the microheterogeneous and aqueous phases.⁸ Recently, the use of lyotropic phases have been reported for the nanostructuring of electrode surfaces.⁹ Although only a few cases have been reported, it is apparent, for micellar systems at least, that detailed analysis of carefully obtained voltammetric data yields information concerning the micellar size as the hydrodynamic radius R_h^0 and also interparticle interaction as described by the interaction parameter, k_d .^{1–3}

It is well-known that micellar structure and the extent of intermicellar interactions are critically dependent on many variables including surfactant type and concentration, supporting electrolyte concentration and type, solution additives (e.g. salicylate), temperature, and shear conditions.¹⁰ Notwithstanding, it is generally assumed in voltammetric studies in micellar systems that intermicellar interaction does not affect the *i*–*V* behavior significantly;⁵ however, this has been shown not to be the case in recent studies.^{1–3}

It is well recognized that micelles, even very close to the critical micelle concentration, interact strongly, which results in attenuation of the measured micellar diffusion coefficient relative to that which would be observed at infinite dilution.¹¹ To account for this, it is usual to measure the micellar diffusion coefficient at a number of surfactant concentrations and apply the linear interaction theory¹¹ as given in (1), where D_s represents the measured (raw)

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

micellar self-diffusion coefficient, D_s^0 is the self-diffusion coefficient in the absence of interaction (i.e. at the cmc where $D_s = D_s^0$), and C_s is the surfactant concentration. With a knowledge of D_s^0 the micellar R_h^0 may be obtained using the Stokes–Einstein relation given in (2), where k_bT has its usual meaning and η_0 is the solution viscosity at infinite dilution.

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$$D_s^0 = \frac{k_b T}{6\pi\eta_0 R_h^0} \quad (2)$$

It is with such D_s data that micellar structure and interactions are usually probed;¹¹ therefore, as it is well-known that electrochemical techniques may be used to measure mass transport diffusion coefficients,¹² voltammetry provides a simple opportunity to probe micellar structure and interparticle interaction using appropriate micelle-immobilized electroactive probes. Although several reports detailing the voltammetric determination of micellar size and interaction have appeared,^{1–3} no systematic account of how voltammetry may be used to probe the structural features of micellar systems or structural evolution has been reported to date.

Traditionally, a variety of techniques are normally employed to study micellar diffusion as a function of experimental conditions. The usual techniques include dynamic and quasi-elastic light scattering,^{13,14} neutron scattering,¹⁵ tracer diffusion,¹⁶ and moving boundary measurements.¹⁷ With the exception of tracer diffusion, these techniques yield short-time mutual diffusion coefficients, D_m , which is localized diffusion under the influence of a concentration gradient. Usually, electrochemical techniques yield mutual diffusion coefficients, however, in electrochemical measurements on micellar systems incorporating a micelle-immobilized electroactive probe, self-diffusion coefficients (D_s) are obtained because a concentration gradient of micelles never exists at the electrode surface. In addition, electrochemical experiments yield long-time self-diffusion coefficients since the micellar displacement is much greater than the mean intermicellar spacing. A detailed discussion of mutual and self-diffusion coefficients may be found elsewhere.¹¹

Self-assembled systems such as micelles and liquid crystals are becoming important as they are being exploited as nanoreactors for the formation of templated nanostructures;^{9,18} therefore, the experimental study of structure and structural evolution in such nanoscale and mesoscale systems is currently of great interest.¹⁹ In this contribution, we demonstrate the use of simple voltammetric techniques in combination with ferrocene as an electroactive probe for the study of cationic cetyltrimethylammonium chloride (CTAC) micellar structural evolution and the study of intermicellar interaction. In particular, we describe the experimental approach necessary to obtain useful structural data from such measurements and speculate on the future application of appropriate electrochemical techniques in this area of research.

EXPERIMENTAL SECTION

General Considerations and Solution Preparation. Since probing micellar structure essentially involves measuring the

micellar diffusion coefficient,¹¹ care must be taken to eliminate conditions leading to inadvertent variations in D_s . In particular, the parameters (1) solution temperature variations, (2) active electrode area variation, and (3) buildup of the water-soluble ferrocenium in the aqueous phase all lead to irreproducible voltammetric data. Therefore, all measurements were made under strict thermostatic conditions with large sample volumes (e.g. $\geq 500 \text{ cm}^3$) using electrodes with electrochemically measured electroactive surface areas (with ferricyanide in 1.00 mol dm^{-3} KCl at 298 K). Although obvious, all mass and volume measurements must be made quantitatively to ensure reproducible results.

All CTAC (Aldrich) solutions were prepared from N_2 -purged Millipore deionized water and stored under N_2 ; prior purging is necessary to avoid foaming of the surfactant solution and to prevent O_2 oxidation of ferrocene (especially at elevated temperatures). Ferrocene (Fc, Aldrich) was dissolved in surfactant solutions by stirring overnight using a magnetic stirrer.

Voltammetry and Viscometry Measurements. All voltammetric measurements were made with a BAS CV-50W potentiostat using the three-electrode mode and an Oxford rotating disk electrode (RDE) assembly (Sycopel). The working electrode was a 7 mm glassy carbon disk shrouded in epoxy, and 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 $0.015 \mu\text{m}$ alumina as an aqueous slurry prior to use and its electroactive surface area determined electrochemically using ferricyanide. For RDE measurements, current–potential curves were recorded at a potential sweep rate of 5 mV s^{-1} over the rotation speed (ω) range 2–20 Hz; higher rotation speeds were avoided due to excessive foaming of the agitated surfactant solution although the expected current–rotation speed dependence was observed up to 50 Hz. Cyclic voltammetry (CV) was carried out with potential sweep rates up to 0.50 V s^{-1} using the same system but with a stationary electrode while using iR compensation. Chronoamperometric measurements were made using potential steps across the Fc/Fc^+ potential window from -0.2 to 0.6 V vs Ag/AgCl with a 3 mm diameter glassy carbon electrode (BAS) prepared in the manner already described.

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

RESULTS AND DISCUSSION

Preamble. Ferrocene was chosen as the electroactive probe because of its usually cited features, i.e. simple, stable, and reversible electrochemistry; however, more importantly, its very low solubility in H_2O ($1 \times 10^{-8} \text{ mol cm}^{-3}$) means that the probe molecules reside almost entirely inside the micellar structure and therefore its diffusion-controlled current *predominately* reflects the mobility of the micelles. Notwithstanding the near ideal attributes of ferrocene, the effect of the finite aqueous solubility of the probe in the aqueous phase must be considered since its diffusion coefficient is ca. 1 order of magnitude greater than micellar diffusion.^{3,7} Broadly speaking, there are two schools of thought regarding the correction procedure; first, shifts in half-wave potential have been attributed to changes in probe distribution

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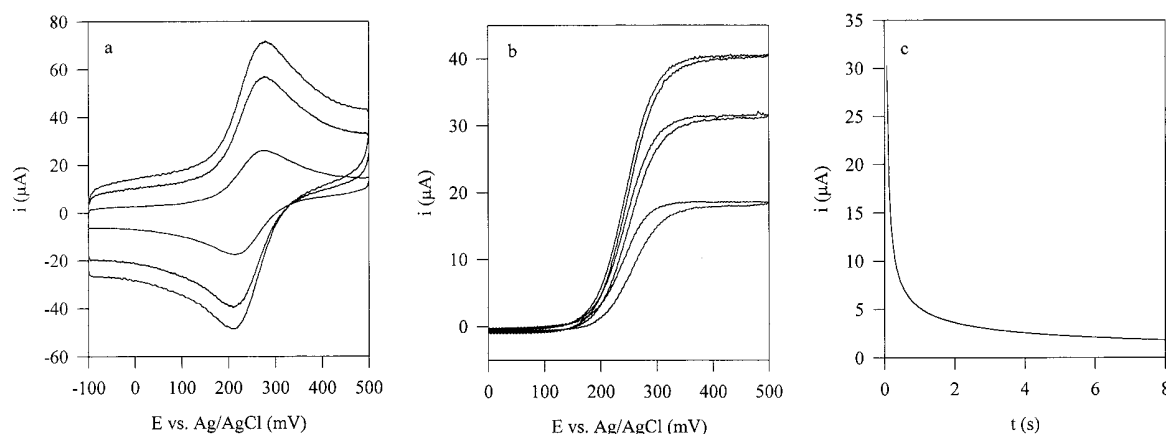


Figure 1. (a) Cyclic voltammograms of ferrocene redox at 20, 80, and 120 mV s⁻¹, (b) RDE voltammograms for Fc oxidation obtained at 5 mV s⁻¹ with electrode rotation speeds of 2, 6, and 10 s⁻¹, and (c) i - t response for Fc oxidation. All solutions contained 0.1563 mol dm⁻³ CTAC, 0.100 mol dm⁻³ KCl, and 1.563×10^{-3} mol dm⁻³ Fc.

between the aqueous phase and the micellar phase.^{20,21} The alternative approach, first detailed by Mandal,³ involves simple numerical correction for the finite aqueous solubility of the probe. Neither approach may be considered ideal; i.e., the first approach does not take account of a significant surfactant adsorption or liquid junction potential changes both of which may considerable effect changes of $E_{1/2}$ and, also, the approach assumes that the oxidized form of the probe partitions fully into the aqueous phase. To this end, in an early paper, Zana and Mackay²² questioned the use of $E_{1/2}$ values as being entirely indicative of probe partitioning. The second approach is also limited by the assumption that the aqueous phase concentration of probe is constant at all surfactant/electrolyte concentrations.

Here, we adopt the second approach by assuming a saturated concentration of ferrocene in the aqueous phase under all conditions. It will be shown below that the solubility-corrected D_s values are almost identical with $E_{1/2}$ -corrected values. A further validation of the simple correction is that it yields micellar hydrodynamic *radii* directly comparable with the known dimensions of CTAC micelles based upon published aggregation numbers and hydration parameters at different electrolyte concentration (vide infra) as well as with independently obtained nonelectrochemical methods. For this reason, all current measurements are corrected for the finite aqueous solubility of ferrocene (1.0×10^{-8} mol cm⁻³) as described previously.³ CTAC was chosen because it has been extensively characterized using a range of techniques therefore aiding in the interpretation of voltammetric responses and self-diffusion coefficient data.

Which Technique? One striking feature of voltammetrically measured micellar self-diffusion coefficients which we have observed is the dramatic variation evident between different electrochemical techniques. Apart from our initial observations,^{1,2} no study comparing different voltammetric techniques for D_s measurements per se has been reported although it is usual to assume any voltammetric technique is applicable.⁵ Here, we use CV, the RDE, and chronoamperometry to determine D_s under otherwise identical experimental conditions making use of the

following well-known expressions¹² (3–5) in the expectation of

$$i(t) = \frac{nFAD_s^{1/2}C_\infty}{\pi^{1/2}t^{1/2}} \quad (\text{CA}) \quad (3)$$

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

$$i_p = 0.4463nFA\left(\frac{nF}{RT}\right)^{1/2}D_s^{1/2}C_\infty\nu^{1/2} \quad (\text{CV}) \quad (5)$$

obtaining identical D_s values⁵ (within experimental error), where n is the number of electrons, F is the Faraday constant, A is the active electrode area, C_∞ is the probe concentration, T is the absolute temperature, R is the gas constant, t is time after the potential step, ν is the solution kinematic viscosity, v is the potential sweep rate, ω is the electrode rotation speed, and i_p , i_{lim} , and $i(t)$ are the CV peak current, the RDE limiting current, and the current at time t in CA, respectively. The nature of the free-probe correction may be discounted here from explaining the intertechnique variation since the correction is applied equally to each procedure and therefore the relative differences will remain constant notwithstanding the absolute magnitudes of D_s are different. In addition, we have used all three techniques to determine the diffusion coefficient of ferricyanide in 1.00 mol dm⁻³ KCl and have found identical and expected results; therefore, we may also eliminate erroneous experimentation from accounting for the significant discrepancies observed in micellar systems.

Figure 1a–c shows cyclic voltammograms, RDE voltammograms, and chronoamperometric responses for the Fc/Fc⁺ couple under various conditions in CTAC/KCl solution. Importantly, each micelle contained on average at least (and usually) one probe molecule (vide infra). At first sight, the electrochemical responses observed in each case are entirely consistent with a one-electron reversible redox couple; i.e., for CV, ΔE_p is 58 ± 2 mV while i_p vs $\nu^{1/2}$ is perfectly linear. For RDE, Nernstian plots reveal slopes of 58 ± 2 mV decade⁻¹ while plots of i_{lim} vs $\omega^{1/2}$ are linear up to 50 Hz. The CA responses were found to conform to the predicted $i(t)-t^{-1/2}$ relationship as expected although at time scales greater than 2 s, which indicated a large cell time constant, RC_{dl} , where

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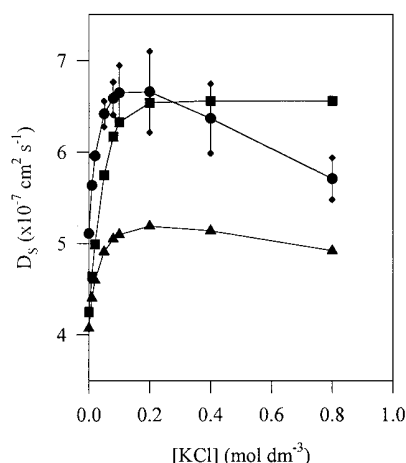


Figure 2. Plots of D_s vs $[KCl]$ with D_s values obtained using the RDE (▲), CV (■), and CA (●).

R is the uncompensated solution resistance and C_{dl} is the electrode double layer capacitance. As R is negligible in most systems examined (i.e. contain appreciable amounts of electrolyte), this is probably due to potential-dependent adsorption/desorption of surfactant on the glassy carbon electrode surface (note the significant capacitance current in the CVs and RDE hysteresis). For all three techniques capacitance current contributions were removed by using the standard procedures i.e. linear extrapolation from the electroinactive region (CV, RDE) or by measuring the capacitance current in the absence of probe and subsequent subtraction.²³ Saveant et al. has, however, pointed out that this procedure may lead to erroneous results in systems exhibiting large capacitance currents using transient techniques.²⁴

Translating the electrochemical responses into micellar self-diffusion coefficients using eqs 3–5 reveals unusual behavior which is depicted in Figure 2. For both CA and CV, D_s values are approximately equal and are consistently higher than those found by RDE. In addition, significant experimental error (between repeat experiments) is clearly evident for CA while RDE and CV measurements were obtained with significantly higher precision, i.e. typically $\pm 0.05 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

Applying the linear interaction theory to the (precise) CV-derived D_s data shows nonlinear behavior (Figure 3a,b) suggesting nonconformity to the theory as applied to experimental data obtained using other techniques.¹¹ However, plots of $1/D_s$ vs C_s exhibit linear behavior in a similar manner as observed previously by Zana et al.²² (polarography), Mandal³ (CV), and ourselves^{1,2} (CV/RDE). This reciprocal form of analysis has been used to linearly extrapolate to the cmc to obtain D_s^0 and R_h^0 values.^{1–3} Analyzing the reciprocal CV data here to obtain R_h^0 values yields micellar dimensions in the range 2.18–4.17 nm, which is unreasonable since at $[KCl] \geq 0.05 \text{ mol dm}^{-3}$ $R_h^0 \leq R_{HS}$ (where R_{HS} is the minimum micellar hard-sphere radius based on molecular volume considerations²⁵ (vide infra)); i.e., the micelles appear to be smaller than physically possible. Considering that the linear interaction theory is not obeyed and that the R_h^0 values are

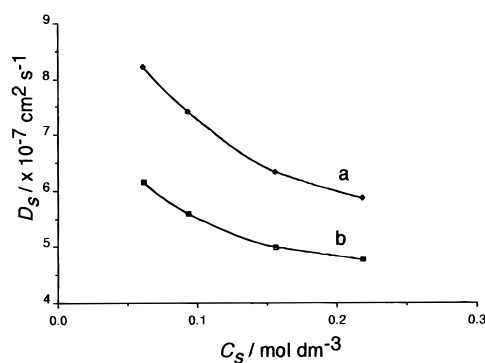


Figure 3. Plots of D_s vs C_s derived from CV data at (a) 0.10 mol dm^{-3} KCl and (b) 0.02 mol dm^{-3} KCl.

unreasonably low suggests that this technique yields diffusion coefficient data not wholly representative of freely diffusing and interacting micellar particles.

For CA-derived D_s data, the adherence to the linear interaction theory was difficult to ascertain due to the large experimental error, especially at low surfactant concentrations. However, D_s data appeared to conform to eq 1 at high surfactant concentrations. Extrapolation of plots of D_s vs C_s yielding D_s^0 values (using the high concentration region) gave values of R_h^0 typically 30% lower than can be expected from molecular volume considerations.²⁵ This, and the imprecise nature of the CA measurements, again suggests that this technique is not useful for detecting subtle changes in micellar size and shape. Rusling et al.²⁶ also criticized CA for the difficulty in obtaining accurate background capacitance current correction. All attempts to reduce the error associated with the CA measurements proved fruitless in this study.

Extracting R_h^0 values from the RDE data yields micellar radii in the range 2.73–3.32 nm (vide infra) which are consistent with the known dimensions of CTAC micelles in KCl electrolyte i.e. $\approx 2.9 \text{ nm}$ ²⁷ and also with molecular volume considerations.²⁵ Since the values for R_h^0 obtained here correspond directly with other techniques, the validity of using the simple free-probe correction seems justified.

The data presented clearly indicate that using different electrochemical techniques yields different D_s values; this behavior is already apparent in the literature for CV and RDE measurement for CTAB micelles ($B = \text{Br}^-$, ferrocene probe in the presence of 0.1 mol dm^{-3} NaCl) where Rusling²⁶ found $D_s = 1.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and Georges and Desmetre²⁰ reported a value of $0.67 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ obtained using the RDE. It is also interesting to note that Georges and Desmetre²⁰ used a free-probe correction based on $E_{1/2}$ changes whereas our approach, involving ferrocene solubility in the aqueous phase, yields an almost identical (and similarly “low”) value of $0.62 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (at 0.1 mol dm^{-3} KCl), again suggesting that the effect of free-probe correction is suitably accounted for here and that, irrespective of whichever approach, RDE yields lower diffusion coefficients.

It is generally assumed⁵ that the mass transport coefficients obtained by different experimental techniques are the same; this

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is, however, not the case.¹¹ Electrochemical experiments on micellar systems yield long-time self-diffusion coefficients whereas, for example, QELS experiments yield short-time mutual diffusion coefficients. Only at the limit of infinite dilution (i.e. at zero interaction) do self- and mutual-diffusion coefficients become comparable; therefore, in the absence of extrapolation to the cmc, direct comparison of variously obtained D_s values can be misleading. For example Rusling et al.²⁶ studied sodium dodecylsulfate (SDS) micelles (by CV/CA in 0.1 mol dm⁻³ NaCl, 0.1 mol dm⁻³ SDS with methyl viologen probe) and reported a D_s value of 1.4×10^{-6} cm² s⁻¹ which was compared to a mutual diffusion coefficient (D_m) value of 1.4×10^{-6} cm² s⁻¹ obtained under identical conditions using QELS.¹⁵ Superficially, the comparison is excellent; however, since D_m increases with increasing surfactant concentration (cf. Figure 4 in ref 15) and electrochemically obtained D_s values decrease with increasing surfactant concentration, departure from 0.1 mol dm⁻³ SDS would yield relatively higher D_m /lower D_s values at higher surfactant concentration and vice versa at lower surfactant concentrations. Obviously, large discrepancies would be observed where $C_s \neq 0.1$ mol dm⁻³. That these values coincide at appreciable surfactant concentration (0.1 M) suggests that the electrochemically measured D_s , if it were extrapolated to D_s^0 , would be significantly larger (i.e. yield lower R_h^0) than the D_s^0 obtained by QELS. Qualitatively at least, this agrees with the "low" D_s values, which we (and others²⁰) have observed with the RDE compared to CV/CA, and is in agreement with other nonelectrochemical methods (e.g. QELS). This example emphasizes the danger in utilizing single surfactant concentration studies for comparison purposes although the D_s values may be accurately determined electrochemically. Similarly, determination of micellar *radii* using a single surfactant concentration and ignoring the effect of interaction²⁷ is also inappropriate.

The evidence presented here and that already in the literature²⁰ indicates that the RDE yields "different" (lower in magnitude) micellar diffusion coefficients compared with CV or CA and also that the RDE yields values for R_h^0 which are directly comparable with know independently measured and calculated values. Although there is a plethora of CV studies on micellar systems, there is a corresponding dearth of reports detailing extrapolation to the cmc; therefore, it is difficult to determine (from the literature at least) if the observed behavior here is specifically characteristic of the system under investigation or a general phenomenon. However, we also find consistently higher D_s values using CV/CA compared to RDE with the nonionic surfactant Triton X-100 suggesting that the behavior is general in nature. (Triton X-100 results will appear separately.) The reason for the enhanced D_s (and ultimately smaller R_h^0) values from CA and CV (although the experiments were carried out under rigorously controlled and therefore identical conditions) relative to the RDE values is unclear. Certainly, the free-probe correction procedure appears appropriate because (a) it yields the expected R_h^0 values and (b) it compares favorably with the $E_{1/2}$ -based procedure (notwithstanding its limitations) as indicated above. At this stage we can only speculate as to the phenomenological basis for the apparent discrepancies between techniques, e.g. anisotropic diffusion, forced hydrodynamics, surface preconcentration, Dahms–Ruff type electron self-exchange behavior, the existence of two diffusional regimes, or errors in capacitance background current correction.

Recently, anisotropic diffusion behavior in solution-phase liquid crystals has been observed;^{29–31} however, no evidence exists in the literature to suggest that CTAC liquid crystal structures are formed in solution or on electrodes. Although it is likely that CTAC is adsorbed at the electrode surface, AC impedance measurements carried out here suggests that no significant CTAC aggregation occurs on the carbon electrode until extreme potentials, i.e. $> \pm 1$ V vs Ag/AgCl, although evidence of aggregate formation has been reported at silver electrodes.³² In any case, if anisotropic diffusion was responsible, we believe it should affect all techniques examined similarly. Also, since i_{lim} vs $\omega^{1/2}$ is strictly linear from 0.2 to 50 Hz, forced hydrodynamics is unlikely to be responsible for the differences although we thought this may be the case initially.² The other experimental difference between CV/CA and RDE is the steady-state nature of the RDE responses relative to the transient responses obtained from CV/CA. With CV and CA, it is possible that preconcentration of the electroactive material occurs at the electrode surface within a surfactant-rich layer,³³ which may give rise to enhanced transient currents. Dahms–Ruff type electron self-exchange behavior³⁴ may be discounted due to the relatively low concentrations of probe being used. The possibility of the existence of two diffusion regimes³⁵ (i.e. fast/slow) at organized electrode surfaces due to interfacial solution structuring has been proposed. Essentially, with the transient techniques the fast regime may be dominant whereas with the steady-state technique the slow regime may be more pronounced. The final possible explanation for the enhanced transient currents is error in capacitance current correction although the procedures adopted here (both manual and software correction were used) are widely used albeit for simple diffusing molecular entities.²³ Significant capacitance currents were observed, even at high electrolyte concentration (e.g. 190 μ F cm⁻² at 0.80 mol dm⁻³ KCl/0.1563 mol dm⁻³ CTAC). Although at this stage we are unable to account for the discrepancies between RDE and CV/CA, the steady-state technique effectively eliminates errors due to (a) capacitance current background correction, i.e. very low capacitance currents (i_{Cdl}) observed, highest $i_{Cdl} = 0.9 \mu$ A cm⁻² at 0.1563 mol dm⁻³ CTAC/0.80 mol dm⁻³ KCl, and (b) the possibility of surface preconcentration. In any case, from our extensive experiments, and from the results available in the literature,²⁰ only steady-state measurements yield D_s values which ultimately give R_h^0 values directly comparable with independently obtained data using nonvoltammetric techniques.²⁷ Subsequent D_s and R_h^0 data presented here will therefore be derived from RDE results almost exclusively.

How Much Probe To Use? An important question to address in these measurements is, how much probe to use? In this area it is usual to use a [probe]:[micelle] ratio of 1 (based on known aggregation numbers). However, it is known that ferrocene solubilization conforms to the Poisson distribution,^{8,20} which

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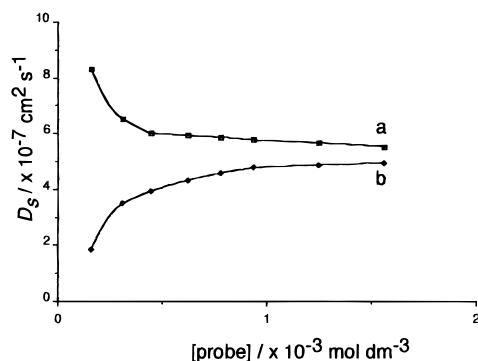


Figure 4. (a) Plot of raw D_s vs $[Fc]$ obtained at $0.80 \text{ mol dm}^{-3} \text{ KCl} / 0.1563 \text{ mol dm}^{-3} \text{ CTAC}$ and (b) plot of corrected D_s vs $[Fc]$ under the same conditions.

indicates that the presence of a probe molecule within a micelle will not affect further solubilization; therefore, multiple-occupancy is possible even if $[\text{probe}]:[\text{micelle}] < 1$. Unfortunately, there is some contradiction in the literature concerning the effect of probe concentration; for example, both Gorges et al.²⁰ and Chokshi et al.³⁶ have stated that micellar diffusion coefficients and $E_{1/2}$ are independent of probe concentration (as expected for a nonpartitioning or nearly nonpartitioning probe²²) whereas Rusling et al.²⁶ have observed a probe-concentration dependence on D_s . In Rusling's work, D_s was found to decrease with increasing probe concentration and the behavior was satisfactorily interpreted in terms of multisite binding equilibria. In Georges et al.'s work, a saturated concentration of ferrocene was used (in $0.11 \text{ mol dm}^{-3} \text{ CTAB} / 0.1 \text{ mol dm}^{-3} \text{ NaCl}$); therefore, $[\text{probe}]:[\text{micelle}] > 1$. Close inspection of Figures 5 and 6 in ref 26 reveals that at $[\text{probe}]:[\text{micelle}] > 1$ D_s remains reasonably constant, i.e., reaches an asymptotic value $\pm 0.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, and is behavior which our data concurs with.

Figure 4a shows raw D_s (from RDE and uncorrected for free $[\text{probe}]$) vs $[Fc]$. It is obvious that raw D_s values decrease with increasing probe concentration in a fashion similar to that observed by Rusling,²⁶ which may be interpreted in terms of multiple binding equilibria. It is worth noting that the values obtained when $[\text{probe}]:[\text{micelle}] > 1$ (at $> 1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Fc}$) are effectively constant ($\pm 0.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) suggesting that when, on average, each micelle possesses at least one probe, the mass transport diffusion coefficients are effectively indifferent to probe concentration, which agrees with previous findings²⁶ although the magnitude of D_s is lower with RDE. All measurement made here in attempting to study micellar structure and structural evolution were made with $[\text{probe}]:[\text{micelle}] \geq 1$; therefore, errors due to probe partitioning at low probe concentrations may be effectively eliminated. This is further supported by $E_{1/2}$ data where it was observed that $E_{1/2} = 0.236 \pm 1 \text{ mV}$ vs Ag/AgCl at $[\text{probe}]:[\text{micelle}] \geq 0.66$ suggesting that probe partitioning remains measurably unaltered at high probe concentrations (i.e. as the probe concentration approaches the micellar concentration).

Figure 4b shows free-probe corrected D_s values as a function of probe concentration where the dependence behavior is the opposite to that observed for uncorrected D_s data. Since the $E_{1/2}$ -

based correction gives essentially the same results,²⁰ similar behavior will be observed irrespective of the correction procedure. The corrected (and uncorrected) data indicate that, at high probe concentration, D_s is effectively independent of probe concentration. For strongly bound probes, D_s is expected to be independent of $[\text{probe}]$;²² therefore, the corrected (and uncorrected) data indicate that the probe is strongly bound at high probe concentrations. Also, increasing $[Fc]$ such that each micelle possessed up to four probe molecules does not attenuate D_s beyond the limiting value; therefore, the presence of the probe does not attenuate the structure of the micelle significantly, i.e. measurably. In addition, the exact number of probe molecules per micelle need not be known precisely other than it must be one or more with simply the actual bulk concentration of probe being used in all calculations. Previously reported aggregation numbers for CTAC micellization in KCl solutions facilitated this analysis.³⁷

An entirely accurate correction procedure would produce D_s values independent of probe concentration; obviously, in Figure 4b D_s increases with $[Fc]$ before reaching concentration independence. It is likely that the correction procedure overcorrects for the free probe concentration at low probe concentrations whereas it yields the predicted behavior at high probe concentrations (which are used here); therefore, the correction procedure again seems reasonable at high probe concentrations. To estimate the extent of overcorrection at low probe concentration, extrapolation of the linear portion of Figure 4b yields a $D_{s(\text{extrapolated})}$ value of $3.75 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$; knowing that uncorrected $D_s = (D_f f_f + D_b f_b)$ ²⁶ and that $D_{s(\text{uncorrected})} - D_{s(\text{extrapolated})} = D_f f_f$, f_f and f_b may be estimated at low probe concentration (where D_f is the diffusion coefficient of free probe, f_f is the fraction of free probe, D_b is the diffusion coefficient of bound probe, and f_b is the fraction of bound probe). At $[Fc] = 0.159 \text{ mol dm}^{-3}$, $f_f = 0.04$ and $f_b = 0.96$ as compared to 0.06 and 0.94 using ferrocene solubility. At high probe concentration (i.e. $[\text{probe}]:[\text{micelle}] \geq 1$), and assuming that the free probe concentration cannot exceed the saturation concentration, f_f is ≤ 0.01 ; therefore, the maximum discrepancy which may be expected from erroneous free probe correction is $1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. This cannot be attributed to the significant intertechnique variations.

What Is the Effect of Electrolyte (KCl) Concentration on Micellar D_s ? Armed with the knowledge that RDE voltammetry could yield precise micellar D_s values, provided that rigorous control of experimental conditions could be achieved, introduces the opportunity to probe micellar structure via variations in D_s . Figure 5a–c shows D_s values as a function of $[\text{KCl}]$ at three CTAC concentrations. An initial increase in the micellar diffusion coefficient is clearly evident for each $[\text{CTAC}]$; this is usually attributed to a reduction in electrostatic drag due to neutralization of the micellar double layer, i.e. shear-plane collapse.¹⁶ This is followed by an almost linear decrease in D_s up to $0.80 \text{ mol dm}^{-3} \text{ KCl}$ which may be attributed to electrolyte-dependent micellar growth.¹⁶ At electrolyte concentrations beyond 1.0 mol dm^{-3} a precipitous decrease in D_s is evident. Such dramatic behavior corresponds to the transition from spherical to rod-shaped micelles followed by electrolyte dependent micellar elongation.²⁷ The D_s results presented here are entirely consistent with the known behavior of CTAC micelles in simple electrolyte solution;^{16,27} therefore, we

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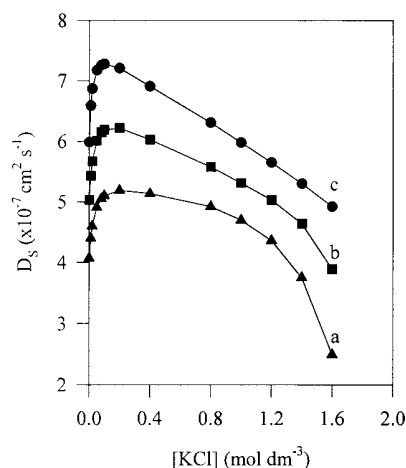


Figure 5. Plots of D_s vs $[KCl]$ at (a) 0.1563, (b) 0.0938, and (c) 0.0313 mol dm⁻³ CTAC.

Table 1. Micellar Structural and Interaction Parameters as a Function of Electrolyte Concentration

$[KCl]$ (mol dm ⁻³)	k_d (dm ³ mol ⁻¹)	r^2 (corr coeff)	D_s^0 ($\times 10^{-7}$ cm ² s ⁻¹)	R_h^0 (nm)
0.00	2.50	1.0000	6.45	3.32
0.01	2.46	0.9994	7.11	3.01
0.02	2.45	0.9995	7.42	2.89
0.05	2.34	0.9998	7.74	2.77
0.08	2.26	0.9999	7.81	2.74
0.10	2.23	1.0000	7.83	2.73
0.20	2.09	0.9999	7.72	2.77
0.40	1.93	0.9999	7.35	2.91
0.80	1.67	0.9996	6.65	3.22
1.00	1.63	0.9996	6.29	3.40
1.20	1.73	0.9987	5.98	
1.40	2.16	0.9963	5.73	
1.60	3.48	0.9962	5.59	

can be confident that our measurements reflect actual structural changes within the micellar system. This is significant since electrochemistry provides a simple and straightforward method to examine micellar structure through D_s measurements.

Adherence to the Linear Interaction Theory? It was shown above that CV-derived D_s data did not conform to the linear interaction theory although analysis of D_s^{-1} yielded linear plots. However, for RDE-derived D_s data, the linear interaction theory is obeyed directly up to the sphere-to-rod transition point (1.2 mol dm⁻³ KCl); this is evident by the slopes (i.e. interaction parameters) and correlation coefficients (r) shown in Table 1. However, above 1.2 mol dm⁻³ KCl the linear interaction theory begins to break down (i.e. $r < 0.9990$); therefore, k_d are apparent values only (obtained by simple linear regression) but they are useful for demonstrative purposes and are also given in Table 1. Values for the interaction parameter k_d are plotted vs $[KCl]$ (up to 0.8 mol dm⁻³ KCl) in Figure 6a. It is evident that there is a smooth exponential-type decrease in k_d with electrolyte concentration up to 0.8 mol dm⁻³ KCl indicating decreased Coulombic interaction due to electrostatic screening,¹⁶ as expected for charged particles such as micelles. We have shown elsewhere³⁸ that the interaction parameters obtained from RDE measurements correlate with

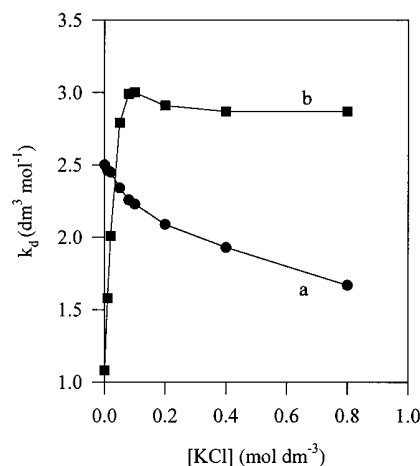


Figure 6. Plots of k_d vs. $[KCl]$ obtained using (a) the RDE and (b) cyclic voltammetry.

calculated Coulombic interaction potentials for charged macroionic species at various electrolyte concentrations. Above 1.0 mol dm⁻³ KCl (Table 1), the point where sphere-to-rod transition occurs, k_d values increase rapidly reflecting the electrolyte-dependent micellar elongation process and a changeover to excluded volume interactions.³⁹ These results are entirely in accordance with physicochemical processes occurring in the micellar/electrolyte system,^{16,27} therefore, RDE voltammetry gives also useful insight into the intermicellar interaction processes.

Examination of the slope behavior (although nonlinear) for CV-derived D_s data in Figure 3a,b suggests that there is less interaction at lower electrolyte concentrations than at higher electrolyte concentrations. This is entirely unreasonable since at low electrolyte concentrations the particles are relatively small (no elongation) and their surface charge generates significant Coulombic interaction potentials. Also plotted, in Figure 6b, are the interaction parameters obtained from CV data (from D_s^{-1} vs C_s), where the data show wholly different behavior compared to the RDE data. In addition, interaction parameters derived for CV data do not correlate with calculated Coulombic interaction energies contrary to the RDE-derived data. The reason for this is totally unclear; however, it was stated above that the CV-derived D_s data do not appear to be wholly representative of freely diffusing and interacting micelles, and this observation seems to confirm that observation. What these results do indicate is that CV-derived interaction parameters must be interpreted with caution since they do not reflect known behavior in a simple fashion whereas the RDE gives direct access to intermicellar interactions.

Micellar Structural Evolution? The D_s^0 values (intercepts) at each KCl concentration and their corresponding R_h^0 values are also given in Table 1 but up to 1.0 mol dm⁻³ KCl only since the assumptions governing the use of eqs 2 and 4 specify spherical particles which is not the case.²⁷ Plotting R_h^0 values vs $[KCl]$ over the region 0.0–0.8 mol dm⁻³ KCl (Figure 7a) clearly indicates that the micellar size (R_h^0) is a function of KCl concentration. There is an initial decrease in R_h^0 up to 0.10 mol dm⁻³ KCl which is followed by a linear increase in R_h^0 ; therefore, the micelles appear to be getting smaller and subsequently larger with the addition of electrolyte. It is useful to compare this behavior with

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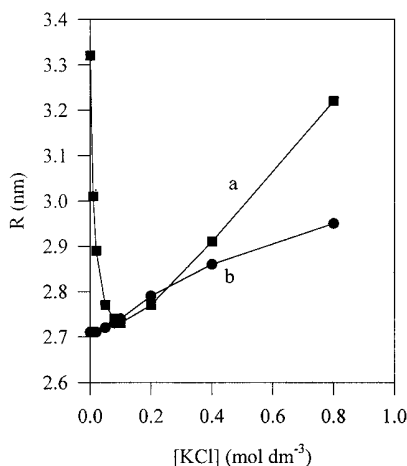


Figure 7. Plots of (a) R_h^0 and (b) R_{HS} vs [KCl].

the micellar hard-sphere radius, R_{HS} , (Figure 7b), which may be calculated from the micellar volume, V_m , using expression 6,²⁵

$$V_m = N[V_{CH_3} + nV_{CH_2} + V_{HG} + \omega_{HG}V_S + (1 - \delta)(V_{Cl} + \omega_{Cl}V_S)] \quad (6)$$

where V_{CH_3} and V_{CH_2} are the volumes of these groups, n is the number of CH_2 groups in the hydrocarbon chain, V_{HG} is the volume of the headgroup, V_{Cl} is the volume of Cl^- , δ is the degree of dissociation, V_S is the volume of H_2O , ω is the degree of hydration, and N is the aggregation number; these values are reported elsewhere.^{37,40} It is clear that the micellar R_h^0 decreases while the calculated R_{HS} values increase with increasing KCl concentration until they become coincident at 0.1 mol dm^{-3} KCl. The increase in R_{HS} may be attributed to an electrolyte-induced increase in N ,^{37,40} whereas the decrease in R_h^0 represents a decrease in the actual hydrodynamic size of the micellar particles. We have shown elsewhere⁴¹ that the initial decrease in R_h^0 is due to collapse of the micellar shear-plane toward the micellar hard-sphere surface. Considering these data, it is evident that we have observed, voltammetrically, the structural evolution of the micellar particles, i.e. an initial collapse of the micellar shear plane followed by the linear spherical expansion of the micelle due to increasing aggregation number and, at high electrolyte concentration, the transition from sphere- to rod-shaped micelles with subsequent micellar elongation (i.e. precipitous decrease in D_s). These processes are shown pictorially in Figure 8.

CONCLUSIONS

The primary purpose of this manuscript is to explicate the necessary experimental conditions to investigate micellar structure, structure evolution, and interaction using simple voltammetric techniques. It was shown that CA yielded D_s values which conform to the linear interaction theory (albeit only at high surfactant concentration); unfortunately, due to the low precision of the data and the fact that extrapolation to the cmc yields unreasonably low R_h^0 values, this technique appears inappropri-

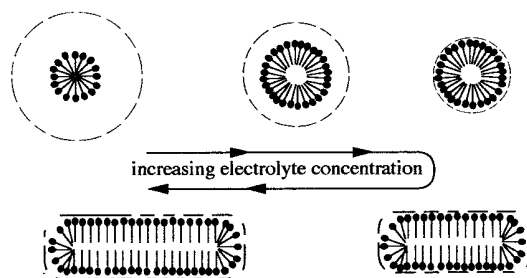


Figure 8. Simple (not to scale) schematic representation of the structural evolution of CTAC micelles with the addition of simple KCl electrolyte where --- represent the micellar shear plane.

ate for such studies. CV data did not conform to the linear interaction theory; however, reciprocal analysis was found to linearize the data although, again, micellar R_h^0 values were unreasonably low. In addition, CV interaction parameters did not correlate to the calculated interparticle Coulombic potential. These observations lead us to the conclusion that CV-derived D_s values do not represent purely freely diffusing and interacting micellar particles; therefore, this technique also appears inappropriate for micellar structural and interparticle interaction analysis.

The RDE data yielded consistently lower D_s values compared with CA/CV, which is consistent with previous observations in the literature. The reason for the enhanced currents is, as yet, unknown but a number of possibilities have been proposed. Anisotropic diffusion, forced hydrodynamics, and Dahms–Rhuff self-exchange are unlikely to be responsible; therefore, we consider that the difficulties with accurate background correction and the possibility of surface preconcentration of electroactive probe or the existence of two diffusional regimes may be responsible. Essentially, RDE eliminates problems with background correction and surface preconcentration.

For the RDE-derived D_s data, the linear interaction theory was strictly obeyed and yielded micellar R_h^0 values directly comparable with values obtained independently using nonelectrochemical techniques and with calculated values from molecular volumes/aggregation numbers. In addition, RDE interaction parameters correlated with calculated Coulombic interaction potentials. Since we observe wholly expected behavior from the RDE data, we conclude that D_s data represent freely diffusing and interacting micellar particles and therefore this technique is appropriate for micellar structural and interparticle interaction analysis.

The question posed in the title may therefore answered affirmatively although with the proviso that the correct technique must be adopted. The key aspects of the RDE technique is that, first, it does not rely on any assumptions about the extent and nature of interaction processes or the extend of polydispersity and, second, highly precise and accurate (i.e. reflects known dimensions) measurements of long-time self-diffusion coefficients may be made easily and unambiguously under steady-state conditions. We have observed the collapse of the micellar shear plane toward the hard-sphere surface, the electrolyte-dependent linear spherical expansion of the micellar particles, and, at high electrolyte concentration, the transition from spherical to rodlike structures and structural elongation. We have also shown the evolutionary transition from Coulombic interaction to excluded volume interactions as a function of electrolyte concentration.

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Although the actual voltammetric measurements described here are trivial to effect, we have demonstrated that every aspect of the electrochemical measurement process must be carefully considered and controlled to acquire data which, although accurate per se, may be subsequently analyzed for micellar structural information. An important conclusion from this work, and which is well-known in the micellar field, is that a single voltammetric measurement or a limited number of measurements of diffusion coefficients of micellar particles do not reflect an accurate view of the micellar system and its complex structural evolution.

Nanoscale and mesoscale supramolecular assemblies are becoming important for a diversity of applications, e.g. nanoreactors. Understanding of their structure and structural evolution processes is of paramount importance in designing systems to effect desired phenomenon and also in understanding their

physical behavior. The results presented here demonstrates that voltammetric techniques, judiciously chosen under appropriate conditions, may be used as analytical tools for the structural characterization of micellar and possibly other evolving self-assembled systems. Significantly, such techniques may be harnessed for monitoring evolutionary processes in self-assembled systems in real-time.

ACKNOWLEDGMENT

A. P. D. thanks The Royal Society for a University Fellowship, and I.D.C. thanks the EPSRC for a studentship.

Received for review April 6, 1999. Accepted November 19, 1999.

AC990354C