

Inter-micellar interaction under hydrodynamic conditions

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Inter-micellar interaction is measured under defined hydrodynamic conditions using a rotating disk electrode (RDE).

The fluid dynamics of microheterogeneous solutions has received increasing attention recently with the stimulus being the increasing sophistication of design and use of supramolecular and self-assembled structures.¹ Although the microscopic behaviour of such systems is well characterised under quiescent conditions, a lack of understanding of microscopic processes under hydrodynamic conditions is a long-standing problem in physical chemistry. The earliest recognised self-assembled structures were micelles with their unusual rheological properties being known since the early days of micellar research. Optical and electrochemical techniques, applied under quiescent conditions,^{2,3} allow measurement of the micellar diffusion coefficient, average micellar radii and an interaction parameter describing the effect of interaction forces (coulombic, van der Waals and hydrodynamic) while rheology allows measurement of the macroscopic parameters of normal and tangential shear stress and changes in solution viscosity. An important problem in this research, which is considered a non-trivial experimental challenge,⁴ is exploring how micelles behave under hydrodynamic conditions, *i.e.* the inter-relationship between microscopic and macroscopic parameters under field flow conditions.⁴ Here, for the first time, the measurement of micellar transport dynamics and inter-micellar interaction under hydrodynamic conditions using the RDE are presented and compared to static measurements using cyclic voltammetry (CV).

CV and RDE voltammetry were carried out using a 7 mm Pt working electrode, a Pt gauze counter electrode and a Ag/AgCl reference electrode. The concentrations (c_s) of cetyltrimethylammonium chloride (CTAC) solutions were above the critical micelle concentration (cmc) of $8.0 \times 10^{-4} \text{ mol dm}^{-3}$; solutions contained $0.05 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ as supporting electrolyte. Equilibrium solutions of the electrochemical probe, ferrocene (Fc), were prepared from micellar solutions with stirring for 24 h. The Fc concentration was measured spectrophotometrically at 440 nm with $\epsilon = 0.93 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. Viscometry was carried out using a suspended level viscometer.

The CV half-wave potentials for Fc redox were a function of surfactant concentration, behaviour which has been interpreted previously.⁵ The anodic and cathodic peak potentials remained constant at constant [CTAC] with increasing potential sweep rate (v) up to 0.1 V s^{-1} , while peak-to-peak separations were *ca.* 60 mV at all surfactant concentrations. The anodic to cathodic peak current ratio was *ca.* 1.0 up to 0.10 V s^{-1} . These features indicate reversible one-electron transfer to an electroactive solution species. Peak currents increased linearly with $v^{1/2}$, having the intercept at the origin, indicating a diffusion-controlled process. As Fc is immobilised predominately in the micellar interior,⁵ diffusion coefficients calculated from this data, following correction for the finite aqueous concentration of Fc,⁶ represent micellar diffusion coefficients [$D_{m(\text{CV})}$] as given in Table 1. The micellar diffusion coefficients decreased

significantly with increasing surfactant concentration in agreement with reported data.⁶ RDE voltammetry for Fc oxidation in CTAC solutions resulted in well defined sigmoidally shaped curves as expected for diffusion-controlled processes. Plots of limiting currents i_{lim} vs. $\omega^{1/2}$ (ω = rotation speed in s^{-1}) were linear and passed through the origin, indicating a diffusion-controlled process. Micellar diffusion coefficients obtained from this data [$D_{m(\text{RDE})}$] are given in Table 1; again $D_{m(\text{RDE})}$ decreased with increasing surfactant concentration. It is evident that D_m values obtained by the static CV and hydrodynamic RDE techniques differ significantly under otherwise identical conditions and the difference is a function of surfactant concentration.

The effect of direct inter-micellar interaction processes on measured micellar diffusion coefficients has been reported and interpreted in terms of DLVO theory.^{7,8} Such behaviour can be described by an inter-micellar interaction parameter, f , using the linear function,⁸

$$D_m = D_m^0/[1 + f(c_s - \text{cmc})] \quad (1)$$

where D_m^0 is the diffusion coefficient in the absence of interaction. Plots of $1/D_m$ vs. c_s for CV and RDE data are shown in Fig. 1. These plots are linear suggesting inter-micellar interaction processes dictate the magnitude of the micellar diffusion coefficients.⁸ Extrapolation to cmc yields D_m^0 (Table 1). It is significant that D_m^0 is, within experimental error, identical for both techniques. Using the Einstein-Stokes relationship, the average hydrodynamic radii (R_h , Table 1) of

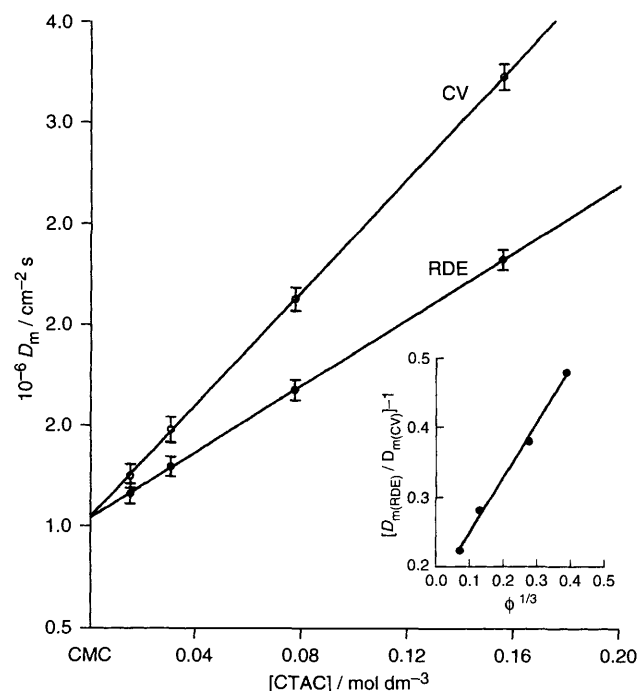


Fig. 1 Plots of $1/D_m$ vs. c_s for CV and RDE measurements and inset $\{[D_{m(\text{RDE})}/D_{m(\text{CV})}] - 1\}$ vs. $\phi^{1/3}$

the micelles at zero interaction for both static and hydrodynamic measurements are identical and consistent with previously published values for quaternary alkylammonium surfactants.⁹ This suggests that the micellar shape and size are similar under both static and hydrodynamic conditions and are unaffected by the moderate shear forces at the RDE. This, in turn, indicates that the difference between CV and RDE measured diffusion coefficients is related to differences between inter-particle interaction under static and hydrodynamic conditions. The interaction parameters obtained from the slopes were $f = 13.5 \pm 0.2 \text{ dm}^3 \text{ mol}^{-1}$ for CV and $7.9 \pm 0.2 \text{ dm}^3 \text{ mol}^{-1}$ for RDE. The CV value is consistent with the value of $16.0 \text{ dm}^3 \text{ mol}^{-1}$ reported previously.³ The lower value for the RDE measurements indicates that under hydrodynamic conditions the effect of inter-micellar interaction on micellar mobility is less pronounced than under static conditions.

It is known that hydrodynamic interaction (*i.e.* particle motion coupling *via* viscous shear waves) in microheterogeneous solutions affects particle mobility.^{10,11} To analyse the hydrodynamic effect of the RDE measurements we use the general form of the linear diffusion equation to the first virial coefficient;⁸

$$D_{m(\text{RDE})} = D_{m(\text{CV})} [1 + k_h \phi] \quad (2)$$

where we define k_h as a hydrodynamic interaction parameter and ϕ is micellar volume fraction; $\{[D_{m(\text{RDE})}/D_{m(\text{CV})}] - 1\}$ was found to be proportional to $\phi^{1/3}$ giving k_h to this order as 8.0 ± 0.04 (Fig. 1 inset). As the inter-particle separation $l \approx 2 R_h/\phi^{1/3}$,

Table 1 Micellar transport parameters

[CTAC]/ mol dm ⁻³	10 ⁻⁷ $D_{m(\text{CV})}^a$ / cm ² s ⁻¹	10 ⁻⁷ $D_{m(\text{RDE})}^a$ / cm ² s ⁻¹
0.016	8.0	8.6
0.032	6.8	7.7
0.078	4.7	6.0
0.156	3.1	4.3
$c_S \rightarrow \text{cmc}$	$D_m^0 = 9.5 \pm 0.2$ ($R_h = 2.5 \pm 0.3 \text{ nm}$)	$D_m^0 = 9.6 \pm 0.2$ ($R_h = 2.6 \pm 0.3 \text{ nm}$)

^a ± 0.1 .

this implies that the extent of hydrodynamically induced particle coupling interaction is an inverse function of particle separation.

These results suggest that hydrodynamic electrochemical techniques may be useful for studying micellar transport dynamics, micellar sizes, inter-particle and hydrodynamic interaction processes under well defined hydrodynamic conditions, such measurements are not possible with conventional techniques. Rheological measurements of microheterogeneous solutions have shown the importance of interaction forces on rheological behaviour,¹ a major uncertainty however is the inability to experimentally distinguish between shear induced processes such as micellar growth and changes in particle interaction processes.⁴

Significantly, hydrodynamic electrochemical techniques operate under conditions suitable for rheological measurements which introduces the possibility of simultaneous measurements of microscopic and macroscopic parameters and may provide a powerful experimental tool for understanding the hydrodynamic behaviour of microheterogeneous solutions on the microscopic scale.

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