



Concentration-dependent diffusion coefficients of *tert*-butylferrocene within dodecyltrimethylammonium chloride/brine liquid crystals

Jonathan E. Halls^{a,*}, Amal A. Altalhi^a, Fabiane C. de Abreu^{a,b}, Marília O.F. Goulart^b, Jay D. Wadhawan^{a,**}

^a Department of Chemistry, Hull University, Cottingham Road, Hull HU6 7RX, United Kingdom

^b Universidade Federal de Alagoas, Instituto de Química e Biotecnologia, Tabuleiro do Martins, 57072-970-Maceio, Alagoas, Brazil

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ABSTRACT

The title lyotropic liquid crystal is examined as a framework to investigate long-range charge transfer, using *tert*-butylferrocene (^tBuFc) as model hydrophobic system. It is found that the apparent one-dimensional diffusion coefficient depends on the ^tBuFc loading. It is suggested that an efficient relay mechanism for electron transfer is through the partitioning of the oxidised form between the two subphases, with inter-pseudophase reaction.

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1. Introduction

Electron transport chains are fundamental for a plethora of natural process, such as respiration and photosynthesis [1], and for relaying the effects of an external perturbation within a “plastic electronics” system (such as a biosensor or a dye-sensitised solar cell) to an output [2]. Electrochemical interrogation of such systems generally involves the chain “wired” to the electrode surface [3a], or has the electrode embedded within the system [3b]. Electron transport within such systems can then take place either through superexchange phenomena, or *via* carrier hopping, and provided counter ion transport is facile [4].

Herein, cyclic voltammetry (with timescale > 25 ms) is employed to deduce one-dimensional mutual diffusion coefficients of ^tBuFc (a well-known hydrophobic redox-switchable probe) randomly dispersed within three-dimensions inside the yoctolitre micelle ensembles of the optically isotropic discontinuous cubic phase (I₁) formed at 50 wt.% dodecyltrimethylammonium chloride (DOTAC) in brine [5]. This stiff and viscous phase (elastic modulus > 10 kPa [5b]) occurs at monomer concentrations between isotropic solution and H₁ phase, whenever the aggregation free energy outweighs entropic losses associated with micellar order, and when the solubility limit is reached before the conditions required for the formation of micellar “rods”; much of the reported structural characterisation of polycrystalline

samples of the I₁ phase of DOTAC/H₂O suggests that eight closed-aggregate prolate micelles (of axial ratio 2:1, each with a volume of 35.9 yL, and of “microviscosity” of 15–20 cP [5c]) comprise a unit cell based (of lattice parameter 86 Å for 43 wt.% DOTAC/H₂O [5a]) on the *Pm3n* structure [5d] (see Fig. 1), with six micelles restricted in rotation arranged with their symmetry axes perpendicular to the cubic direction, with two micelles free to rotate, and with an aggregation number of 89 ± 4 (for 50 wt.% DOTAC at 24.5 ± 0.3 °C, estimated under the assumption of an insignificant number of micelle fragments) obtained through time-resolved fluorescence measurements [5e, g, 6b]. The latter numbers only very slightly increase with surfactant concentration, indicating very low degrees of micellar-polydispersity, consistent with the near-spherical micellar shapes. Furthermore, NMR studies suggest that within these dynamic systems, the rotational tumbling of the micelles with monomer diffusion over the surface occurs with a correlation time [5f] of *ca.* 5 ns, and with slow monomer self-diffusion (*ca.* 5 × 10⁻¹³ m² s⁻¹ at 25 °C [5g]). Intermicellar exchange of solubilised species is thought to occur on the microsecond timescale through a micellar “fragmentation-coagulation” pathway – a “cubic motion” which enables the distribution of molecules or aggregates between different sites in the unit cell [6].

2. Experimental

All chemical reagents were purchased from Sigma-Aldrich or Strem. Water, of resistivity greater than 18.2 MΩ cm, was obtained from an Elgastat system (Vivendi, UK). The I₁ phase was prepared by adding a known mass of ^tBuFc to the solid surfactant and diluting with aqueous 0.1 M NaCl, with the mass ratio of the surfactant to aqueous electrolyte being 1:1. The mixture was heated in a water

* Correspondence to: J.E. Halls, Department of Chemistry, The University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom.

** Corresponding author.

E-mail addresses: j.e.halls@bath.ac.uk (J.E. Halls), j.wadhawan@hull.ac.uk (J.D. Wadhawan).

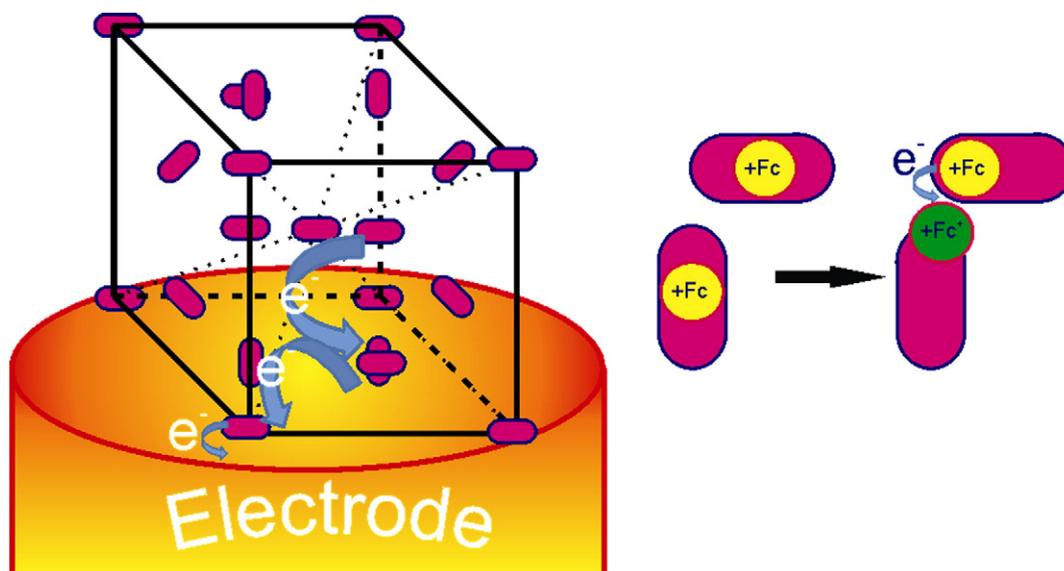


Fig. 1. Cartoon of the Pm3n structure with an example of bounded diffusion.

bath, with vigorous stirring under nitrogen to 90 °C to solubilise hydrophobic solutes within the micelles [7] and kept in the molten, isotropic micellar solution for at least 2 h, after which, slow cooling to room temperature enabled the formation of the polycrystalline I_1 phase (as in previous work [5]), of density 0.895 g cm^{-3} . As this phase is a single thermodynamic phase, all concentrations are reported in terms of moles per unit volume of I_1 phase. All electrochemical experiments were undertaken at $296 \pm 0.5 \text{ K}$, using a commercial potentiostat (AUTOLAB, PGSTAT30), utilising a 3.0 mm diameter glassy carbon working electrode, a sodium-saturated calomel reference electrode (SSCE) and a nickel spiral counter electrode. The working electrode was cleaned using carborundum paper of increasingly finer grades and then polished using an aqueous $0.3 \mu\text{m}$ alumina slurry. In all experiments, the working electrode was polished and carefully placed in different positions for every change in experimental parameter, so as to encompass any effects due to sample polycrystallinity. Note that since the I_1 phase is isotropic, no consideration was given to how the phase was aligned with the electrode.

3. Results and Discussion

Initial experiments were undertaken using 50 wt.% DOTAC with 50 wt.% aqueous 0.1 M NaCl with a variable amount of added ${}^t\text{BuFc}$. Brine was included in order to reduce Ohmic losses in addition to minimising electrical migration of the cationic micelles, and was kept in a low weight fraction in the aqueous electrolyte ($\sim 6 \times 10^{-3}$), so that I_1 phase formation is possible (for salt fractions < 0.03) [8]. The addition of this quantity of lyotropic salt is thought to decrease the mutual solubility between the surfactant and water, changing the degree of ion adsorption in the micellar electrical double layer, and assumed insignificant change in the viscosity of the phase. It has been observed that brine addition induces only a slight reduction of the effective surface area of each surfactant molecule, with small increase in the micellar aggregation number [8], not least since only cationic surfactant chlorides are thought to form the I_1 phase owing to the larger degree of dissociation compared with other halides [8c]. All liquid crystals prepared appeared dark (at low ${}^t\text{BuFc}$ loadings $< 2.6 \text{ mM}$) when viewed through crossed-polarisers, but exhibited radiance at higher loadings, suggesting hexagonal phase (H_1) formation [8], and we observed that very high loadings (ca. 150 mg ${}^t\text{BuFc}$ in 10 g DOTAC/10 g aqueous 0.1 M NaCl) formed two phase systems, where a small amount of the orange oil did not solubilise, even after prolonged periods of keeping the

system in the molten state. Such loadings correspond to occupancies of greater than one ${}^t\text{BuFc}$ molecule-per-micelle; we propose that saturation of the lyotropic liquid crystal occurs when the complete micellar occupancy is in unity [8]. This seems reasonable considering the solubilisation of each ${}^t\text{BuFc}$ (of assumed spherical radius [9] 3.9 \AA) within the liquid-like hydrophobic micellar core would cause, at most, a micellar swelling [8] (assuming no mixing) of ca. 0.8%. Accordingly, all experiments reported herein were undertaken at fractional loadings less than approximately 1/2 molecule per micelle ($< 8 \text{ mM}$), and we focus quantitative analysis primarily on low concentration ($< 2.6 \text{ mM}$) data.

Fig. 2A illustrates typical cyclic voltammograms observed for the one-electron oxidation of ${}^t\text{BuFc}$ within this I_1 phase. There is a slight loss in signal intensity upon consecutive scans, indicating that the position of the product (${}^t\text{BuFc}^+$) within the micelles is not identical with neutral precursor, as expected. Similar behaviour was observed when dexamethylferrocene or vitamin K_1 was employed as the redox species; in the case of N -methylphenothiazine as the hydrophobic solute, dramatic signal decreases on redox cycling were observed, suggesting that the oxidised form escapes from the micelles [10]. Nevertheless, the waves exhibit characteristics of both fast heterogeneous electron transfer kinetics ($E_p^{\text{Ox}} - E_p^{\text{Ox}} = 70 \text{ mV}$) across the timescales probed, suggesting fast counter ion movements. The voltammograms are also consistent with semi-infinite diffusion-control; use of the Randles–Sevcik equation,

$$i_p = 0.4463 F S c_0 \sqrt{D} \sqrt{\frac{Fv}{RT}} \quad (1)$$

in which the symbols retain their usual meanings, enables the deduction of the apparent diffusion coefficient (D) as a function of the analyte loading. Given that the phase is spatially heterogeneous – the electrode “sees” both surfactant and aqueous pseudophases, all analyses employed an effective area (S') given by the ratio of the volume of the micelles to that of a unit cell: $S' = \frac{8 \times 35.9}{8.6^3} S = 0.452 S$, (Fig. 2B), where it is appreciated that the diffusion coefficient is proportional to the loading at low concentrations ($< 2.6 \text{ mM}$), tailing off to a value reported for the micelle monomer self-diffusion at 8 mM (0.4 molecules-per-micelle). Increasing the concentration further caused a plateau which dropped when the system phase separated.

Consideration of mass transport of ${}^t\text{BuFc}$ within the system would suggest mechanisms similar to that in solids (exchange, ring, interstitial, interstitialcy, crowdion, vacancy, divalency, relaxation, dislocation pipe, grain boundary or surface mechanisms) [11]. However,

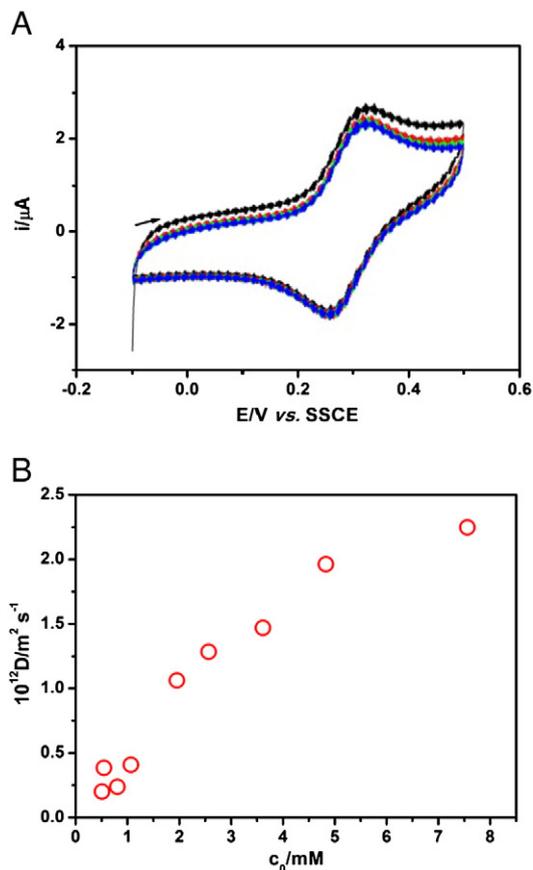


Fig. 2. (A) Typical cyclic voltammograms (0.1 V s^{-1}) for the oxidation of 7.6 mM ${}^t\text{BuFc}$ within the title system. (B) Variation of the area-corrected diffusion coefficient with ${}^t\text{BuFc}$ loading; note that the concentration scale ranges from 0.03 to 0.4 ${}^t\text{BuFc}$ molecules-per-micelle.

assuming the electrode/electric field does not perturb the structure of the material, only the exchange/ring routes appear possible as a means of physical translation, through the context of the fragmentation-coagulation mechanism; although this is on-going at all times, it leads to net mass transport only when there is an unoccupied micelle next to an occupied micelle [6]. Furthermore, as for supramolecular systems with *irreversibly attached* redox functionalities, there is a possibility for carrier hopping as a competing route [12], so that in the kinetic limit that the physical displacement rate constant (k_{ex}) is smaller than that for hopping (k_{hop}), percolation behaviour is observed since the process is governed by the exact distribution of redox sites within the system *and* their interconnectivity. In the opposite limit ($k_{\text{ex}} > k_{\text{hop}}$, the “mean-field” condition), reorganisation of the molecular distribution is fast, so that there is no “memory-effect”. There is another consideration within the present system which involves the partitioning of the product species from surfactant to aqueous subphases, which would allow for a route for inter-subphase electron transfer [10], and would allow for mean-field conditions to operate, and can be approximated by the notion of “bounded diffusion”, corresponding to some physical displacement of otherwise lattice-anchored molecules [12, Eq. (16)]. Thus, considering D_p as the diffusion coefficient for physical diffusion, and D_e as the hopping/bounded diffusion coefficient, we may write, assuming correlation factors of unity [11]:

$$D = P_0 D_p + (1 - P_0) D_e \quad (2)$$

where P_0 is the probability that a micelle is unoccupied. For very low (“rare event”) concentrations ($< 2.6 \text{ mM}$, corresponding to $P_0 > 0.9$),

we observed $< 0.5\%$ error in approximating P_0 by the Poisson distribution: $P_0 = e^{-\bar{x}}$ where \bar{x} is the mean number of ${}^t\text{BuFc}$ molecules-per-micelle [10]; assuming an aggregation number of 90, we found $\bar{x} = (0.0528 \pm 0.0003)c_0$. This formulation, though approximate, enables ensemble properties to be encompassed within the analysis [12]; for ease, since \bar{x} is small, we approximate through linearization of the exponent: $P_0 \approx 1 - \bar{x}$; $(1 - P_0) \approx \bar{x}$.

Thus, we estimate D_p as $8.6 \pm 2.5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ from a plot of $\frac{D}{P_0}$ vs. c_0 in the limit $c_0 \rightarrow 0$. Pleasingly, this suggests micellar fragmentation-coagulation occurs within $\sim \frac{(2r_m)^2}{6D_p} = 35 \text{ } \mu\text{s}$, as anticipated [5c,f], affording [12, Eq. (6)], $k_{\text{ex}} = 12(2r_m)D_p L = 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, where r_m is the spherical micelle radius (2.13 nm) [5c] and L is Avogadro’s number. Comparison with the rate constant for bounded motion, obtained from a plot of $D_e = \left(\frac{D - D_p P_0}{1 - P_0}\right)$ vs. c_0 for $P_0 > 0.9$ affords [12, Eq. (23)] $k_{\text{hop}} = \frac{6D_e}{\{(2r_m)^2 + 3r_m^2\}} = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, implying the predominance of percolation effects at low concentrations ($< 2.6 \text{ mM}$), as expected. This value is about one order of magnitude larger than ferrocene-self-exchange kinetics in *homogeneous solvents* [9]; such apparent rate enhancement derived from the confinement of redox sites is not unknown [3], but may represent the occurrence of a smaller reorganisation energy, or error in approximating partitioning and inter-subphase electron transfer *via* a bounded diffusion harmonic model.

To unravel whether partitioning of ${}^t\text{BuFc}^+$ occurs between the two pseudophases, we sought to estimate the interaction potential energy (w) between the electron-exchanging redox species (${}^t\text{BuFc}$ and ${}^t\text{BuFc}^+$) *via* D_e , based on a regular solution model [13, Eqs. (4) and (18) in 13b]:

$$\frac{D_e}{D_e^{\text{ideal}}} = 1 - 2\alpha P_0(1 - P_0) \quad (3)$$

where D_e^{ideal} may be estimated from the data at low loadings: $D_e^{\text{ideal}} = 5.4 \pm 1.6 \times 10^{-12} c_0$, and the interaction parameter, $\alpha = \frac{zw}{RT}$ in which $z = 2$ (the number of nearest neighbours in the $Pm3n$ structure); our data conformed to $\frac{D_e}{D_e^{\text{ideal}}} = 1.2 - 4.9P_0(1 - P_0)$, Pearson’s product-moment correlation coefficient of 0.95, suggesting an interaction energy on the order of the thermal energy in the system, $w \sim 3 \text{ kJ mol}^{-1}$, a positive value indicating that “repulsive” interactions between ${}^t\text{BuFc}$ and ${}^t\text{BuFc}^+$ pairs occur – ${}^t\text{BuFc}$ and ${}^t\text{BuFc}^+$ are *incompletely miscible* within the studied system, even at low loadings. This result is in agreement with our earlier notion [10] that differential partitioning of the two halves of a redox couple between aqueous and surfactant subphases may empower an alternative route for long-range electron transfer. In this manner, the attenuation coefficient for long-range electron transfer, typically [4] *ca.* $1 \text{ } \text{Å}^{-1}$ for these systems, is not prohibitively large.

4. Conclusions

Concentration-dependent diffusion coefficients of ${}^t\text{BuFc}$ in the I_1 phase of the title system, extracted using voltammetry, appear to occur as a result of the partitioning of the oxidised form (${}^t\text{BuFc}$) between surfactant and aqueous subphases in a thermally activated process, which we have treated in terms of bounded diffusion: the redox species basculates between water-soluble ${}^t\text{BuFc}^+$ and water-insoluble ${}^t\text{BuFc}$ through inter-subphase electron transfer. We have treated this as though it is a self-exchange process; strictly, it is *not*, as the molecular environments of the two forms are not identical – they are in *different* pseudophases. Nevertheless, noting the very high viscosity of the I_1 phase, it is remarkable that this process allows charge diffusion to occur *faster* than in polymeric systems [3a], or even redox-active room temperature ionic liquids [14].

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