THE ELECTROCHEMICAL REDOX PROCESSES IN THE LYOTROPIC LIQUID CRYSTALS

T. Uhlířová[1], J. Reiter[1], J. R. Owen[2]

[1] Institute of Inorganic Chemistry, Academy of Sciences, 250 68 Řež near Prague, Czech Republic
[2] Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom

Corresponding author: J. Reiter (reiter@iic.cas.cz)
Phone: +420 266 172 198, Fax: +420 220 941 502

Introduction

Recently, template synthesis of several nanostructured metals and oxides from the lyotropic liquid crystals (LLCs) were reported [1-3]. The present work describes electrochemical measurements of ion transport processes in lyotropic liquid crystals using two highly reversible redox systems, $[Fe(CN)_6]^{3-}$/ $[Fe(CN)_6]^{4-}$ and ferrocene (Fc) / ferricinium (Fc^+):

$$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^- \qquad (a)$$

$$Fc \rightarrow Fc^+ + e^- \qquad (b)$$

Variations in the solvent, giving solvation changes of both reduced and oxidised forms are generally expected to yield changes in the thermodynamics and kinetics of electron-transfer reactions [4-5] and changes of half-wave potentials. Electrochemical redox reaction of the $[Fe(CN)_6]^{3-/4-}$ and ferrocene – ferricinium couples is diffusion controlled and can be termed electrochemically ‘reversible’ or ‘Nernstian’ under the experimental conditions mentioned below [4-6]. Generally, the peak-to-peak separation value (ΔE_P) can be used to determine the deviation of the redox processes from the theoretical Nernstian behaviour. The main difference between the $[Fe(CN)_6]^{3-/4-}$ and Fc-Fc^+ couples is in extremely low solubility of ferrocene in water (ca. 10^{-5} $mol.dm^{-3}$) compared with the oxidised form, e.g. Fc^+ BF_4^- salts [8]. That means, that the ferrocene molecules are located predominantly in the non-polar phase of the LLC, and that the reagent may transfer to the aqueous phase once oxidised.

Experimental

The liquid crystalline phase was prepared by mixing an non-ionic surfactant Brij 56 (Fluka) with 1M KCl (Suprapur, Merck) solution in water in a 50:50 wt. % ratio. The LLC formation was performed at ca. 50 °C, when the surfactant is melted. After careful homogenisation the LLC was slowly cooled to 22-25 °C to form the liquid hexagonal crystalline phase (cit. [7]). In the case of the $[Fe(CN)_6]^{3-/4-}$ redox system, 5.10^{-3} M solutions of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (both Lachema, Czech Republic) in 1M KCl were used for the LLC preparation. In the case of non-polar ferrocene, a weighed amount of ferrocene (Sigma-Aldrich) was slowly dissolved in melted Brij 56 at 50°C and than mixed with 1M KCl water solution. In both cases polarised light microscopy was used to confirm the presence of the hexagonal after addition of the redox reagents and KCl.

Potentiogalvanostats PGSTAT 10 and 30 (Eco Chemie, The Netherlands) were used for electrochemical measurements including FRA-2 (Frequency Response Analyser) module used for impedance measurement. The measurements were performed using a glassy carbon electrode (GC, diameter 3 mm, BASi, United Kingdom) and platinum microdisk electrode (diameter 20 μm, Eco Chemie, The Netherlands). All potentials in text were measured vs. aqueous SCE. Experiments with the microdisk electrode were performed in a Faraday cage.

Results and Discussion

Fig. 1 presents the cyclic voltammogram of the Brij 56-water hexagonal phase on a platinum electrode. The experiment showed a potential window, from ca. -1.1 to +0.8 V vs. SCE, for the LLC phase containing KCl supporting electrolyte. The impedance measurements showed a reasonable ionic conductivity for the LLC, ca.19.8 $mS.cm^{-1}$ at 22 °C. For comparison, the conductivity of 1M KCl at 22 °C is 106 $mS.cm^{-1}$.

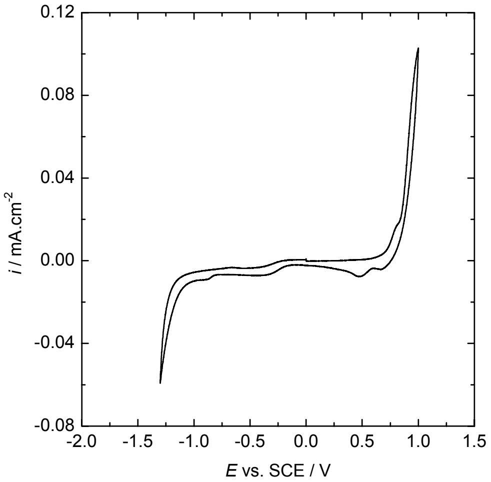
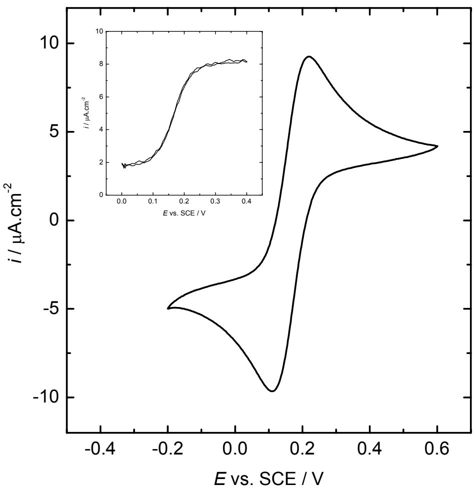


Fig. 1 *Cyclic voltammogram of Brij 56 – 1M KCl in water (50:50 wt. %) on the platinum electrode (1 mm diameter; 5* $mV.s^{-1}$ *scan rate).*

Fig. 2 shows the cyclic voltammogram of the $[Fe(CN)_6]^{3-/4-}$ redox couple measured on the GC electrode or platinum microdisc electrode. Fig. 3 shows similar voltammograms of the Fc/Fc^+ redox couple. In both cases, reversible behaviour was observed.



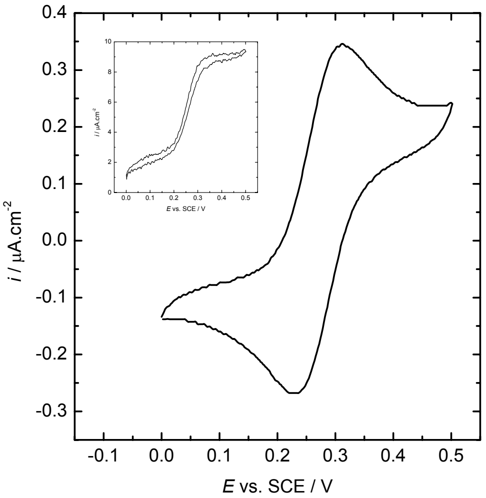


Fig. 2 *(left) Cyclic voltammogram of* $[Fe(CN)_6]^{3-/4-}$ *redox couple in the LLC medium on GC large area electrode (inserted: measurement on the platinum microdisk electrode. Probe concentration* $2.88 \, . \, 10^{-3}$ *M; scan rate* $5 \, . \, 10^{-4}$ $V.s^{-1}$*).*

Fig. 3 *(right) Cyclic voltammogram of ferrocene in the LLC medium on GC large area electrode (inserted: measurement on the platinum microdisk electrode, probe concentration* $6.7 \, . \, 10^{-4}$ *M; scan rate* $5 \, . \, 10^{-4}$ $V.s^{-1}$*).*

The Randles-Ševčík equation was used to interpret results of GC electrode measurements:

$$i_P = (2.69 \, . \, 10^5) \, n^{3/2} A \, D_0^{1/2} \, v^{1/2} \, c \, , \qquad (1)$$

where i_P is peak current (A), n number of transferred electrons, A area of the working electrode (cm^2), D_0 apparent diffusion coefficient ($cm^2.s^{-1}$), v scan rate ($V.s^{-1}$) and c concentration of the species ($mol.cm^{-3}$). The constant $2.69 \, . \, 10^5$ is calculated for a measurement temperature of 25 °C.

For the experiment with the microdisk electrode, the expression used to interpret the steady-state limiting current was :

$$I_\ell = 4 \, n \, F \, D_0 \, c \, r \, , \qquad (2)$$

where I_ℓ is the limiting current (A), c is the reactant concentration ($mol.cm^{-3}$), F is Faraday constant, r electrode radius (cm) and D the diffusion coefficient ($cm^2.s^{-1}$).

The platinum microdisk electrode was also used for the potential step experiment (see Fig. 4).

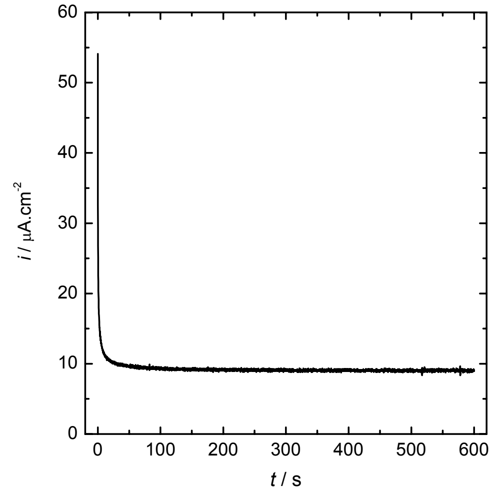


Fig. 4 *i - t response of the ferrocene oxidation – chronoamperometric measurement of the LLC with 1.64 . 10^{-3} M ferrocene (20 µm platinum microdisk electrode, E_{WE} = 0.4 V vs. SCE, t = 600 s)*

Results of the electrochemical investigation of both redox systems are summarised in Table 1.

Table 1 *Summarised electrochemical data for the investigation of the $[Fe(CN)_6]^{3-/4-}$ and Fc/Fc^+ redox couples in Brij 56-water (50:50 wt.%) lyotropic liquid crystals (GC working electrode, 5 . 10^{-4} V.s^{-1} scan rate). D_0^1 values were obtained by using eq. (1), while D_0^2 were calculated from eq. (2) and D_0^3 from chronoamperometry.*

Redox system		$[Fe(CN)_6]^{3-/4-}$	Fc/Fc^+
E_P(OX)	[V]	0.211 ± 0.005	0.305 ± 0.007
E_P(RED)	[V]	0.115 ± 0.005	0.235 ± 0.007
$E_{1/2}$	[V]	0.163 ± 0.005	0.270 ± 0.007
ΔE_P	[V]	0.096	0.070
$D_0(OX)^1$	[cm^2.s^{-1}]	3.7 . 10^{-7}	2.2 . 10^{-8}
$D_0(RED)^1$	[cm^2.s^{-1}]	2.8 . 10^{-7}	2.4 . 10^{-8}
$D_0(OX)^2$	[cm^2.s^{-1}]	1.7 . 10^{-8}	3.0 . 10^{-8}
$D_0(RED)^2$	[cm^2.s^{-1}]	1.7 . 10^{-8}	3.0 . 10^{-8}
$D_0(RED)^3$	[cm^2.s^{-1}]	–	4.6 . 10^{-8}

Values for the apparent diffusion coefficients are remarkably different for the two techniques in the case of the $[Fe(CN)_6]^{3-/4-}$ redox couple (see Table 1). Values calculated using Randles-Ševčík equation are ca. one order lower than those obtained during the measurements with a microdisk electrode. This effect was not observed in the case of LLC with ferrocene, when the D_0 values of both reduced and oxidised form are corresponding with each other.

Baur and Wightman determined the apparent diffusion coefficient of $[Fe(CN)_6]^{3-}$ anion in an aqueous solution to be 7.2 . 10^{-6} cm^2.s^{-1} at 25 °C (cit. [9]).

The results are quite erratic, possibly indicating instability of the orientation of the LLC at the interface with the electrolyte. At present, the diffusion coefficients are apparently one or two orders of magnitude less than in aqueous solution, but accurate values await a more careful study.

Conclusions

The electrochemical redox processes of $[Fe(CN)_6]^{3-/4-}$ and ferrocene were studied in the medium of the lyotropic liquid crystals Brij 56-water. Both redox systems were described from the qualitative point of view and also the apparent diffusion coefficients were estimated.
Further experiments with the microdisk electrodes and other ferrocene-based complexes will follow.

Acknowledgements

This work was supported by the Academy of Sciences (Open Science Project and Research Plan AV0Z40320502) and Ministry of Education (project MSMT LC523).

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