



ELECTROCHEMICAL BEHAVIOUR OF POTASSIUM HEXACYANOFERRATES (II) AND (III) IN MIDDLE PHASE MICROEMULSION

Daniela BALA, Petronia DASU and Constantin MIHAILCIUC*

Physical Chemistry Department, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta, Bucharest 030018, Roumania

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The electrochemical behaviour of both species belonging to $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple was investigated by using cyclic voltammetry (CV) technique and also differential pulse voltammetry (DPV) techniques in a “middle phase” formed between water and toluene, by using, beside the redox species, sodium dodecylsulfate as surfactant, 1-butanol as cosurfactant and sodium chloride as supporting electrolyte with the WE in “middle phase” but in two different three-electrode configurations, as well as in the water phase only in one three-electrode configuration. In each case expected reversible behaviour for both species was obtained. Diffusion coefficients were calculated. Different behaviour was found in “middle phase” for the two investigated electroactive species based on their different electric charge and their electric interaction with the negative (toward “microscopic aqueous phase”) electric charge of the interface between “microscopic aqueous phase” and “microscopic organic phase”.

INTRODUCTION

A microemulsion (ME)¹ has low viscosity and is very stable from thermodynamic viewpoint. It is formed spontaneously from a system containing water, organic solvent, surfactant and often cosurfactant in the presence of an adequate electrolyte. When the balance between hydrophilicity and lipophilicity of a surfactant in this system is suitable, the microemulsion has a bicontinuous structure, well known as “middle phase microemulsion” (MPME, Winsor III)²⁻⁵ which has a highly dynamic existence. In such systems the water phase and the organic phase form the so-called bicontinuous structure, consisting of “microscopic aqueous phases or tubes” and “microscopic organic phases or tubes”, the two different phases alternating on a microscopic scale but each of two being locally continuous. It is described as a network of water tubes in an oil matrix or a network of oil tubes in a water matrix. The ionic conductivity of the MPME

is maintained either by the continuous “microscopic aqueous phase” or by “microscopic organic phase”, at least one of them containing the indifferent electrolyte ions and the electroactive species depending on their hydrophilicity/lipophilicity balances (as to be solved in one or another “microscopic phase”). In the present work, it was chosen a MPME solution obtained⁶ from a system consisting of water, toluene, sodium dodecyl sulphate as surfactant, 1-butanol as cosurfactant and sodium chloride as supporting electrolyte. This system leads to three macroscopically separated phases (from the upper to the lower phase): a “toluene (organic) phase”, a “middle phase” and a “water (aqueous) phase” which is saline in fact, due to the used sodium chloride. If a redox species, such as ferricyanide or ferrocyanide, is added in an appropriate concentration in order not to modify the phase diagram of the system, the separation in the three macroscopic phases is observed. Finally, when the equilibrium of distribution is attained, the redox

* Corresponding author: cmpaul@gw-chimie.math.unibuc.ro

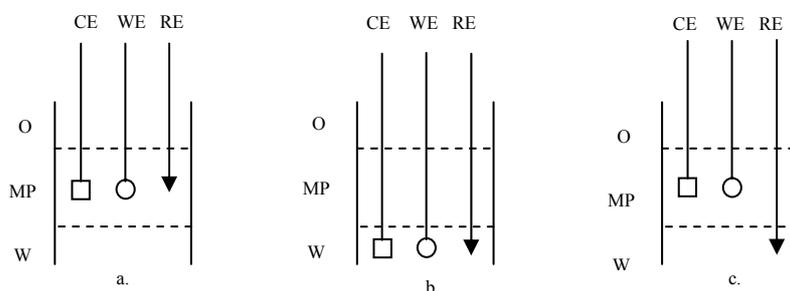
species can be found both in the “water phase” and in “microscopic aqueous phase” from the “middle phase” due to its solubility in the water existing inside the MPME. In this case the electrochemistry of a particular hexacyanoferrate may be studied even in the “middle phase”, even if this “middle phase” is highly dynamic and even if the surface of the working electrode is simultaneously in time but alternatively in space in direct contact with the “organic film” and with “aqueous film” (which constitute the “middle phase”) in a statistical fashion. The initial existing electroactive species in the system, ferricyanide or ferrocyanide, is chosen due to its simple, reversible electrochemistry, its high solubility in water and low solubility in toluene (the electroactive species is very hydrophilic). In addition, both redox forms are sufficiently soluble in water in contrast with other electrochemical probes such as cobalticenium ion/cobaltocene and ferricenium ion/ferrocene redox couples^{7,8} in which cases the cation is water soluble and the neutral form is oil soluble. We found that different cyclic voltammetry behaviours (as concern the direct peak currents) may be obtained, their features depending on the electric

charge of the initial electroactive species used in experiments even if they are in the same initial concentration and similar in nature as it happens for ferricyanide and ferrocyanide (in addition, both of them, belonging to the same redox couple, participating to the same very fast electrode reaction).

EXPERIMENTAL

Apparatus: Electrochemical experiments were carried out using the potentiostat-galvanostat system AutoLab PGStat 12, controlled by GPES (General Purpose Electrochemical System) electrochemical interface for Windows (version 4.9.007). Three electrodes in one-compartment cell (10 mL) were used in all experiments. Platinum disk electrode served as a working electrode. All potentials were measured and given referred to Ag/AgCl/KCl (3M) used as reference electrode. The counter electrode was a platinum disk electrode too.

Measurements: All measurements were carried out at room temperature with no stirring and no inert gas purged. Three different positions (Scheme 1) of the three-electrode configuration were used: (a) all electrodes in “middle phase”, (b) all electrodes in “water phase” and (c) WE and CE in “middle phase” and the RE in “water phase”.



Scheme 1 – The three different positions of the electrodes used in measurements.

Chemicals: Toluene and 1-butanol (both from Sigma) were used without further purification, the water was doubly distilled. All other reagents $K_3[Fe(CN)_6]$ (Fluka / Sigma-Aldrich), $K_4[Fe(CN)_6]$ (Riedel-de Haën / Sigma-Aldrich), NaCl (Fluka), sodium dodecyl sulphate (Fluka) were also used without further purification and they all were analytical reagent grade. Before modification, the platinum electrode surface was polished with alumina (0.05 μm) slurry on a polishing pad, washed with distilled water and sonicated for 3 minutes in doubly distilled water.

RESULTS AND DISCUSSION

In Fig. 1a ($K_3[Fe(CN)_6]$) and 1b ($K_4[Fe(CN)_6]$) cyclic voltammetric behaviours in

the “middle phase”, for scan rates in the range from 10 to 100 mV/s, but only for scan rates 10, 30, 50, 70 and 90 mV/s are presented. One can notice a reversible behaviour of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple in both cases in the scan rate range investigated, even if the active surface exposed by the WE in the “middle phase” is randomly in contact with both “microscopic saline aqueous phase” and “microscopic no saline organic phase” and even if the hydrophilicity/hydrophobicity balance of its active surface can influence the contact with the “microscopic saline aqueous phase” and “microscopic no saline organic phase” in a dynamic way. In addition, even the nature of the

counteraction of the complex salt might play an important role by its own hydrophilicity/hydrophobicity balance which can decide or not its “repartition” at the interface between the “microscopic saline aqueous phase” and “microscopic no saline organic phase” inside the “middle phase”. As a result, the repartition of the electroactive species between the “water phase” and “microscopic aqueous phase” for a hydrophilic case or even in the “middle phase” between “microscopic aqueous phase” and “microscopic organic phase” is determined by the hydrophilicity/hydrophobicity balance.

Here, of course, the sodium chloride being water soluble helps the existence of the hexacyanoferrates in each aqueous parts of the three-phase system.

Plotting the corresponding cathodic peak current (Fig 2a) and anodic peak current (Fig 2b), respectively, for the corresponding cyclic voltammograms in Fig. 1a and 1b, respectively, versus the square root of the sweep rate one gets the straight lines in Fig. 2a and 2b, respectively, indicating a linear dependence upon $v^{1/2}$ of the peak currents in both cases, with very good correlation coefficients, R^2 being 0.9964 and 0.9934, respectively.

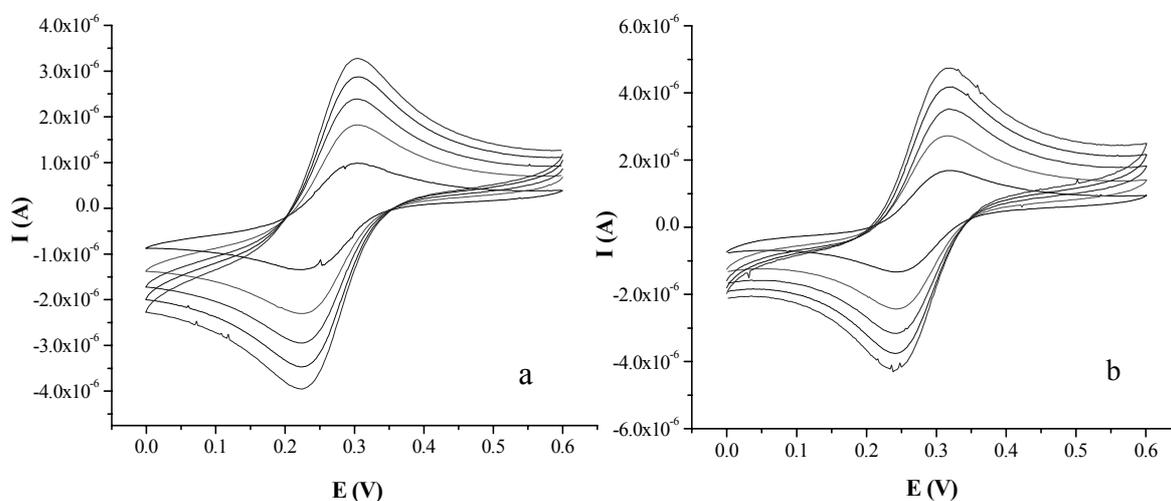


Fig. 1 – The cyclic voltammograms of $K_3[Fe(CN)_6]$ (a) and $K_4[Fe(CN)_6]$ (b) in “middle phase” at scan rates 10, 30, 50, 70 and 90 mV/s for 1 mM initial concentration in the initial aqueous solution.

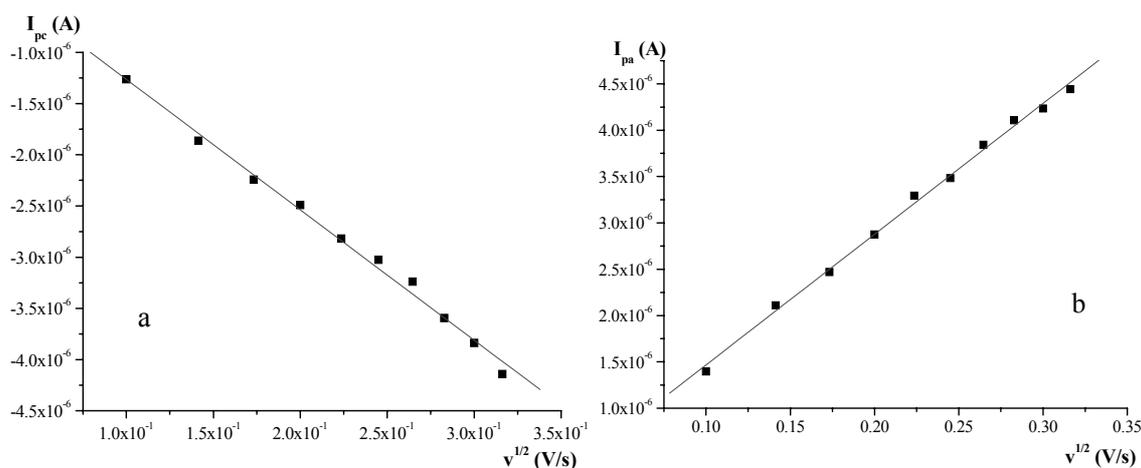


Fig. 2 – The dependences for the forward/direct peaks in the “middle phase” I_{pc} vs. $v^{1/2}$ for $K_3[Fe(CN)_6]$ (a) and I_{pa} vs. $v^{1/2}$ $K_4[Fe(CN)_6]$ (b) in “middle phase” at scan rates from 10 to 100 mV/s for 1 mM initial concentration referred to the initial aqueous solution.

The peak currents ratios are, in some extent, different from unity. The peak separation, when extrapolating to zero scan rates, is also very close to the theoretical value of 59 mV. For the case when initially there is $[\text{Fe}(\text{CN})_6]^{3-}$ only $\Delta E_p \cong 0.067 \text{ V}$ and for the opposite case, initially $[\text{Fe}(\text{CN})_6]^{4-}$ only, $\Delta E_p \cong 0.066 \text{ V}$.

All these criteria indicate a very reversible electrochemical behaviour of the electrode reaction at the WE operating in MPME in both cases. For the cyclic voltammograms in Fig. 1a the ratio $|I_{pc} : I_{pa}| \cong 1.30$ while for those in Fig. 1b the ratio $|I_{pa} : I_{pc}| \cong 0.95$ or $|I_{pc} : I_{pa}| \cong 1.05$, (mean values). It results that in both cases the $I_{pc} > I_{pa}$ (for reversible or rapid electrode reactions this peak current ratios is very close to unity). It seems that inside the “microscopic aqueous phase” in the “middle-phase” the orientation of the surfactant molecules with its negative hydrophilic head inside the “microscopic aqueous phase” and the non-polar tail inside the “microscopic organic phase” helps the $[\text{Fe}(\text{CN})_6]^{4-}$ ions leading to a greater current than $[\text{Fe}(\text{CN})_6]^{3-}$ in both cases. The effect is by far more intense if $[\text{Fe}(\text{CN})_6]^{4-}$ ions are generated at the Pt electrodic interface in the direct scan than if they exist from the beginning, as can be seen from the ratios calculated above.

Taking into account the Randles-Sevcik equation for peak current, one may write that the peak ratio of direct peak current in MPME to direct peak current in water phase is given for a certain sweep rate by the following relationship:

$$\frac{(I_p)_{MP}}{(I_p)_W} = \frac{A_{MP}}{A_W} \sqrt{\frac{D_{MP}}{D_W}} \frac{c_{MP}}{c_W} \quad (1)$$

where A_{MP} and A_W are the areas of the WE in contact with “microscopic water phase” and with “water phase”, respectively, D_{MP} and D_W are the diffusion coefficients of the electroactive species in “microscopic water phase” and in “water phase”, respectively, and c_{MP} and c_W are the concentrations of the electroactive species in “microscopic water phase” and in “water phase”.

The “microscopic water phase” and the “water phase” being both aqueous in nature, one can make the assumptions that both the concentrations and diffusion coefficients of the electroactive species are the same in the two different phases. As the experimental results show, perhaps it is not true and at least one of two invoked quantities will be affected by the presence of the surfactant at the interface between the two immiscible electrolyte solutions in “middle phase”.

Considering the electrode reaction and the multicharged anion state of the two species of the redox couple, one can expect as these anions to be, in some extent, rejected from the electrode surface if the surfactant molecules form an adlayer on the electrode surface. Taking into account the cyclic voltammograms features discussed above, this effect seems to play no role. On the other hand, at the interface between the “microscopic saline aqueous phase” and “microscopic no saline organic phase”, the molecules of surfactant are oriented with their lipophilic chain in the “organic film” and with their hydrophilic functional group (negatively charged) in the “aqueous film”, so that the two complex ions are forced to move only inside the “aqueous films”, maybe in different bulk solutions depending on their electric charge. As a consequence, it is possible that the two diffusion coefficients of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ in “aqueous film” and in “water phase” to be very close.⁹ If there is a difference in diffusion it can be attributed to different diffusion model (not as simple as planar semi-infinite diffusion).

Let us consider for each electroactive species identical diffusion coefficients in both aqueous parts of the system and also equal concentrations which can be taken as 1 mM (the water and toluene are reciprocally/mutually insoluble). In this case the complete equation is transformed into the following one, which is the simplest possible:

$$\frac{(I_p)_{MP}}{(I_p)_W} = \frac{A_{MP}}{A_W} \quad (2)$$

showing that, from the ratio of the direct peak currents, one can estimate the ratio of the area exposed by the WE to the electrode reaction in each phase, and, subsequently, the area of the WE exposed to the electrode reaction in the MPME.

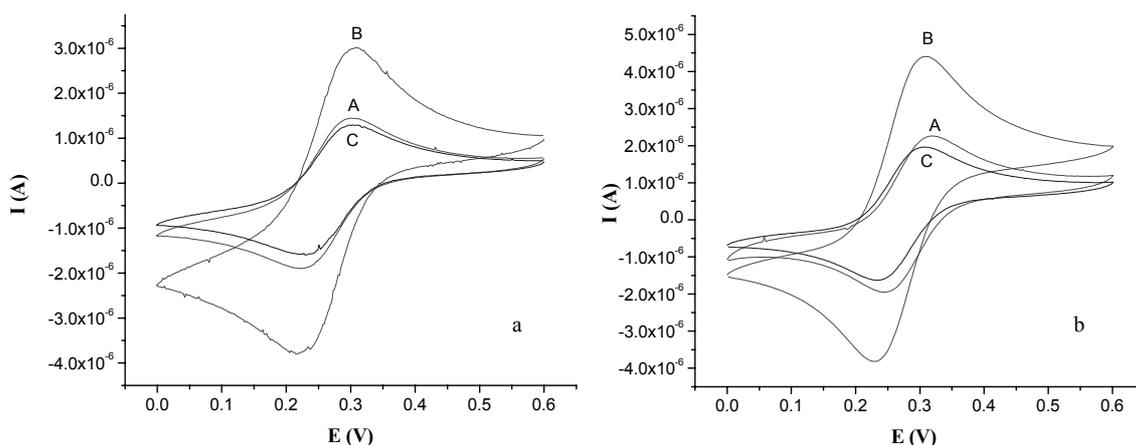


Fig. 3 – The cyclic voltammograms of $K_3[Fe(CN)_6]$ (a) and of $K_4[Fe(CN)_6]$ (b) with all electrodes in “middle phase” (A), with all electrodes in “saline phase” (B) and with WE and CE in “middle phase” and RE in “saline phase” (C) at $v=20$ mV/s for 1 mM initial concentration in the initial aqueous solution.

A comparison between voltammograms having all electrodes in “middle phase” and all electrodes in “water phase” (see Fig. 3a and 3b) will allow to estimate the fraction of the area of the WE which is the stage of the electrode reaction. The ratio of $(I_p)_{MP}$ to $(I_p)_W$ for 20 mV/s scan rate is $\frac{(I_{pc})_{MP}}{(I_{pc})_W} \cong 0.46$ for the case of $[Fe(CN)_6]^{3-}$ as

initial electroactive species and $\frac{(I_{pa})_{MP}}{(I_{pa})_W} \cong 0.51$ for

the case of $[Fe(CN)_6]^{4-}$ as initial electroactive species so that one can calculate the fraction of the active WE area which is the stage of the electrode reaction.

It follows that in the case of $[Fe(CN)_6]^{3-}$, as the initial electroactive probe, 46% of Pt surface is confined to the electrode reaction and, as a consequence, 46% of this active surface is in the contact with “microscopic water phase” and 54% with “microscopic toluene phase” when the WE is positioned inside the “middle phase”. In the case of $[Fe(CN)_6]^{4-}$, as initial electroactive probe, 51% of the Pt surface is dedicated to the electrode reaction and, as a consequence, 51% of this active surface is in the contact with “microscopic water phase” and 49% of the active surface is in contact with the “microscopic toluene phase” when the WE is positioned inside the “middle phase”. So, taking into account the fact that both “toluene phase” and “water phase” have almost equal volume and, supplementary, the above results

obtained from the peaks ratios, in both cases, one may conclude that “microscopic organic phase” and “microscopic aqueous phase” have also, more or less, the same volume. As a consequence, around 50%, statistically speaking, of WE surface is the stage of the electrode reaction.

Considering now the peak potentials, they practically do not move with increasing sweep rate. As concern the cathodic peak in the case of $[Fe(CN)_6]^{3-}$, as initial electroactive probe, its position is $(E_{pc})_{MP} = 0.225$ V, $(E_{pc})_W = 0.225$ V and $(E_{pc})_{MP-W} = 0.231$ V and the anodic peak potential in the case of $[Fe(CN)_6]^{4-}$, as initial electroactive probe, is $(E_{pa})_{MP} = 0.315$ V, $(E_{pa})_W = 0.303$ V and $(E_{pa})_{MP-W} = 0.303$ V, respectively.

Considering the peak separation, $\Delta E_p = E_{pa} - E_{pc}$, the following results were obtained: $(\Delta E_p)_{MP} = 71$ mV, $(\Delta E_p)_W = 73$ mV and $(\Delta E_p)_{MP-W} = 69$ mV for $[Fe(CN)_6]^{3-}$, as initial electroactive probe, and $(\Delta E_p)_{MP} = 69$ mV, $(\Delta E_p)_W = 69$ mV and $(\Delta E_p)_{MP-W} = 69$ mV for $[Fe(CN)_6]^{4-}$ as initial electroactive probe. So they are essentially the same irrespective of the three-electrode configuration arrangement in “middle phase”, in “water phase” or with WE and Pt in “middle phase” and RE in “water phase”.

More or less, the same cyclic voltammograms (comparing A with C in Fig. 3a and 3b) were

recorded for both cases, even if the RE was moved from “the middle phase” into the “water phase”. A little decrease of both anodic and cathodic peak currents can be observed, perhaps due to the intervention of a small ohmic drop (the current lines pass across the “microscopic organic phase”

$$\frac{(I_{pc})_{MP}(I_{pa})_W}{(I_{pc})_W(I_{pa})_{MP}} = \frac{(A_{[Fe(CN)_6]^{3-}})_{MP}(A_{[Fe(CN)_6]^{4-}})_W}{(A_{[Fe(CN)_6]^{3-}})_W(A_{[Fe(CN)_6]^{4-}})_{MP}} \sqrt{\frac{(D_{[Fe(CN)_6]^{3-}})_{MP}(D_{[Fe(CN)_6]^{4-}})_W}{(D_{[Fe(CN)_6]^{3-}})_W(D_{[Fe(CN)_6]^{4-}})_{MP}}} \frac{(c_{[Fe(CN)_6]^{3-}})_{MP}(c_{[Fe(CN)_6]^{4-}})_W}{(c_{[Fe(CN)_6]^{3-}})_W(c_{[Fe(CN)_6]^{4-}})_{MP}} \quad (3)$$

As has been demonstrated, the addition of $[Fe(CN)_6]^{3-}$ and/or $[Fe(CN)_6]^{4-}$ to the typical three phase system described above, does not change the position of the system in the phase diagram.¹⁰

As a consequence, one can assume that in both studied cases, the WE exposes only around half of its active surface for electrode reaction occurrence so that the term consisting of areas in Eq. (3) becomes unity. Considering again that aqueous mature of the “water phase” and “microscopic aqueous phase” determines a constant of repartition equal to unity for electroactive species, it results that the term in concentrations is also unity. Using the values of diffusion coefficients obtained with all three electrodes in “water phase”

$$D_{[Fe(CN)_6]^{3-}} = 1.70 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} \quad \text{and}$$

$$D_{[Fe(CN)_6]^{4-}} = 1.61 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1},$$

one obtains the value for their ratio in “water phase” which is 1.056, so that the above Eq. (3) turns into:

parts and a little bit smaller overvoltage remains to be used for driving electrode reaction).

Taking again into account Randles-Sevcik equation and considering the Eq. (1) for both $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ ions one has, for a given sweep rate, the following relationship:

$$\frac{(I_{pc})_{MP}(I_{pa})_W}{(I_{pc})_W(I_{pa})_{MP}} = 0.973 \sqrt{\frac{(D_{[Fe(CN)_6]^{3-}})_{MP}}{(D_{[Fe(CN)_6]^{4-}})_{MP}}} \quad (4)$$

So we can calculate the ratio of diffusion coefficients in MPME at a sweep rate of 20 mV/s (for example) which is 0.869, a value which is in fact very different from that obtained in “water phase” which is 1.056.

The cyclic voltammograms in Fig. 4a are consistent with the idea that in “microscopic aqueous phase” the $[Fe(CN)_6]^{4-}$ ions lead to an increased response when comparing with $[Fe(CN)_6]^{3-}$ (the concentration of each species being 1 mM on the whole). The results are supported by the DPV study too $I_{pc} = -3.354 \cdot 10^{-6}$ A and $I_{pc} = 4.113 \cdot 10^{-6}$ A (see Fig. 4b).

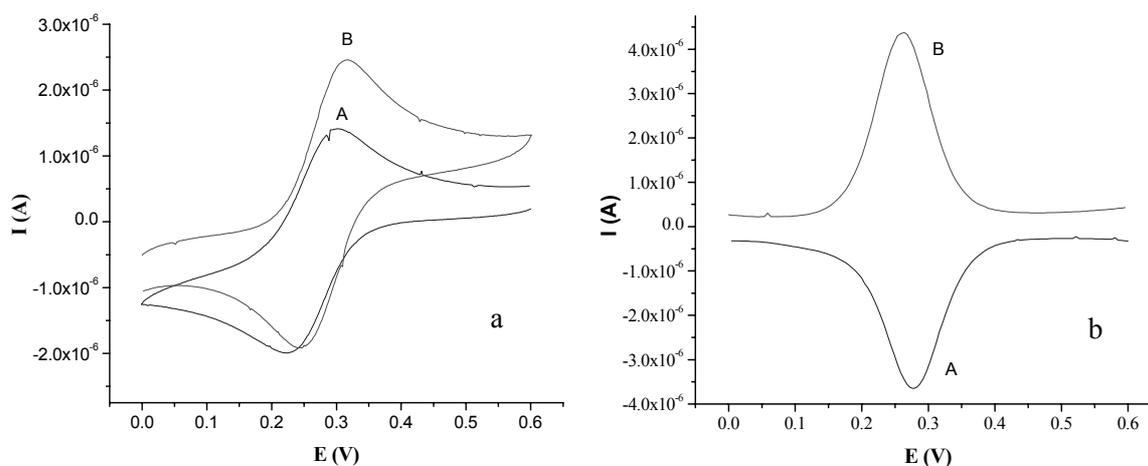


Fig. 4 – The cyclic voltammograms at 20 mV/s (a) and the differential pulse voltammograms with MA=25 mV and SP=5 mV (b) of $K_3[Fe(CN)_6]$ (A) and of $K_4[Fe(CN)_6]$ (B) with all electrodes in “middle phase”, for 1 mM initial concentration in the initial aqueous solution.

As one can see, the ratio $\frac{(D_{[\text{Fe}(\text{CN})_6]^{3-}})_W}{(D_{[\text{Fe}(\text{CN})_6]^{4-}})_W} = 1.056$ in “water phase” and 0.869 in “microscopic aqueous phase”. This means that in “water phase” $[\text{Fe}(\text{CN})_6]^{3-}$ ions have a little larger diffusion coefficient but in “microscopic aqueous phase” from “middle phase” on the contrary the $[\text{Fe}(\text{CN})_6]^{4-}$ ions have a larger diffusion coefficient. The value of the diffusion coefficients of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, determined from the slopes of I_{pc} vs. $v^{1/2}$ for $K_3[\text{Fe}(\text{CN})_6]$ and I_{pa} vs. $v^{1/2}$ $K_4[\text{Fe}(\text{CN})_6]$ in MPME, on the entire range of sweep rates used, are $D_{[\text{Fe}(\text{CN})_6]^{3-}} = 1.80 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ and $D_{[\text{Fe}(\text{CN})_6]^{4-}} = 2.21 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ if considering equal areas as stage of electrode reactions, in each case. Their ratio is $\frac{(D_{[\text{Fe}(\text{CN})_6]^{3-}})_{MP}}{(D_{[\text{Fe}(\text{CN})_6]^{4-}})_{MP}} = 0.815$. So

both diffusion coefficients seem to be increased in “microscopic aqueous phase” by the intervention of the negatively charged walls of the “microscopic aqueous tubes” network from the oil matrix. The explanation could be connected to the electric charge of two ions and their interaction with the negative barrier of charge (provided by $-\text{SO}_3^-$ groups of surfactant) existing at the interface between water and microscopic tubes. This negatively charged wall repels more $[\text{Fe}(\text{CN})_6]^{4-}$ ions than $[\text{Fe}(\text{CN})_6]^{3-}$ and two consequences appear: 1. this aqueous tube containing $[\text{Fe}(\text{CN})_6]^{4-}$ expands in comparison with tube containing $[\text{Fe}(\text{CN})_6]^{3-}$ ions and 2. the more repulsive interaction exerted on $[\text{Fe}(\text{CN})_6]^{4-}$ ions obliges them to move a little faster than $[\text{Fe}(\text{CN})_6]^{3-}$ ions.

The first conclusion is supported by the active area of WE confined to the electrode reaction which is 51% for $[\text{Fe}(\text{CN})_6]^{4-}$ in comparison with 46% for $[\text{Fe}(\text{CN})_6]^{3-}$ and the second, by the enhanced cathodic peak currents (as is obvious

from comparing $|I_{pc} : I_{pa}| \cong 1.30$ with $|I_{pa} : I_{pc}| \cong 0.95$).

The polarization of the interface between the two microscopic phases helps $[\text{Fe}(\text{CN})_6]^{4-}$ to move faster to Pt electrode than $[\text{Fe}(\text{CN})_6]^{3-}$ due to its greater electric charge by forcing $[\text{Fe}(\text{CN})_6]^{4-}$ ions to occupy a smaller volume inside the “microscopic water phase” than $[\text{Fe}(\text{CN})_6]^{3-}$ ions (coulombic repulsive forces are to be considered). So, even small, a supplementary anodic contribution to the anodic current, due to the diffusional $[\text{Fe}(\text{CN})_6]^{4-}$, could be considered. On the other hand, taking into account the distribution itself of $[\text{Fe}(\text{CN})_6]^{4-}$ ions between the “water phase” and the “microscopic water phase”, the same repulsive electric forces could be invoked so that it is possible as $[\text{Fe}(\text{CN})_6]^{4-}$ ionic concentration in “microscopic water phase” to be smaller than in “water phase”. This is the reason for moving all these electrodes inside the “water phase” having as goal to see if the cyclic voltammograms of two electroactive species are in agreement with this supposition.

CONCLUSIONS

The electrochemistry of redox couple $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in MPME is reversible and the electrode reaction occurs on about half of the active surface of the WE. But there is a difference between the two investigated cases: when starting with $[\text{Fe}(\text{CN})_6]^{3-}$ ions the area used is roughly 46% and when starting with $[\text{Fe}(\text{CN})_6]^{4-}$ ions is 51%.

The electrochemical behaviour is, in some extent, dependent of the magnitude of electric charge of the electroactive species: 1. the first direct anodic peak for $[\text{Fe}(\text{CN})_6]^{4-}$ ions is higher than the first direct cathodic peak for $[\text{Fe}(\text{CN})_6]^{3-}$ ions, obviously for the same initial concentration of the electroactive species and for the same sweep rate, and 2. the ratio of the diffusion coefficients of $[\text{Fe}(\text{CN})_6]^{3-}$ ions and $[\text{Fe}(\text{CN})_6]^{4-}$ ions is less in MPME than in “water phase”.

The diffusion coefficients in MPME are, more or less, equal for entire range of sweep rates used and a little larger than in “water phase”, perhaps due to the way in which the molecules of surfactant are distributed at the interface between the “microscopic water phase” and “microscopic toluene phase” in “middle phase”.

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