



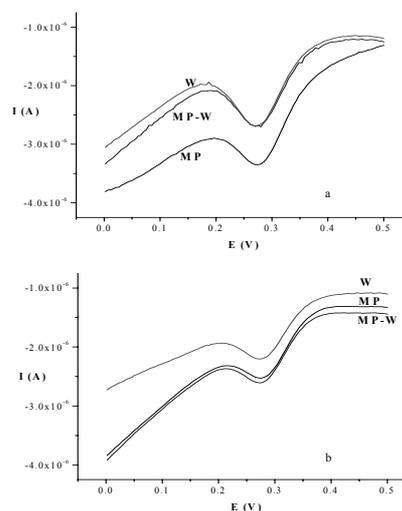
## HYDROPHILIC/LIPOPHILIC BALANCE INFLUENCE ON MIDDLE PHASE MICROEMULSION ELECTROCHEMISTRY

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The electrochemical behaviour in a “middle phase microemulsion” (MPME) of pentacyano(L)ferrate(III) complexes, where L is 4,4'-bipyridine and pyrazine, was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). A near reversible CV behaviour for both redox couples,  $[Fe(CN)_5L]^{2-}/[Fe(CN)_5L]^{3-}$  type, was found. The hydrophilicity-lipophilicity balance (HLB) of both coligand and of counteraction of the complex ion influences the “distribution” of the complex ion between the “microscopic aqueous phase” and the “water phase”. As a consequence, the height of the peak current in the “middle phase” is also influenced. Considering the Randles-Sevcik equation, besides the concentration, both the diffusion coefficients of the electroactive species and the active area of the working electrode positioned in the “middle phase” influence the value of the peak current. The paper figures of these contributions and warns of risks to calculate the working electrode active area immersed in “middle phase”, the electroactive species diffusion coefficient, and the electroactive species concentration without knowing exactly two of the three amounts.



### INTRODUCTION

The study of mixed-ligand cyanido-complexes is important because of their use in the synthesis of heterometallic complexes with applications such as room temperature magnets, photosensitizers, catalysts, magneto-optics properties,<sup>1,2</sup> etc. Pentacyanido complexes, with the general formula  $[Fe^{III}(CN)_5(L)]^{2-}$ , where L can be a neutral molecule ( $NH_3$ ,  $H_2O$ , pyridines, 4,4'-bipyridine, pyrazine, imidazoles,  $PPh_3$ ), or an anion ( $NCS^-$ ,  $NCS_2^-$ ,  $N_3^-$ ) have been studied.<sup>3-5</sup> The electrochemical behaviour of mixed ligand cyanido-complexes can be used to establish the

influence of the coligand upon the main electrochemical parameters. Middle phase microemulsion (MPME) electrochemistry of such complexes revealed interesting aspects of the redox reactions at the working electrode, the influence of the sixth ligand and of the counteraction.

Microemulsions (ME) are mixtures of two immiscible solvents stabilized by surfactants, brought into a single phase.<sup>6</sup> They are thermodynamically stable, macroscopically homogeneous, but microscopically heterogeneous. Due to their unique properties like capacity to solubilize both aqueous and oil-soluble compounds, large interfacial area, very low interfacial tension,<sup>7-9</sup> microemulsions have been

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the subject of extensive research over the last decades. They are of great scientific and technological importance, being used in various fields such as in enhanced oil recovery, separation, pharmaceuticals, cosmetics, food, agrochemicals, nanoparticle synthesis, in environmental remediation and detoxification, microporous media synthesis via microemulsion gel technique, in analytical applications, biotechnology, chemical engineering,<sup>10-17</sup> etc.

Microemulsions can be prepared by controlled addition of alkanols as cosurfactants (butanol, pentanol and hexanol) to emulsions in order to produce transparent solutions containing dispersions of water-in-oil (w/o, when the surfactant is strongly lipophilic) or oil-in-water (o/w, when the surfactant is strongly hydrophilic), in the nanometer or colloidal dispersion range (~100 nm). The miscibility of oil, water and amphiphile (surfactant plus cosurfactant) depends on the system composition. MEs morphology depends upon the surfactant properties and can be described by ternary and quaternary phase diagrams.

In the present work we used Winsor III type ME with three phases: middle phase microemulsion (MPME) (o/w plus w/o, called bicontinuous) in equilibrium with upper excess oil and lower excess water.<sup>18-22</sup> MEs consist of “microscopic aqueous phases or tubes” and “microscopic organic phases or tubes”, alternating on a microscopic scale, but each of the two phases being locally continuous. The structure of the ME depends on the appropriate balance between hydrophilicity and lipophilicity (HLB) of a surfactant in the system, moderated by cosurfactant and electrolyte (salt) concentration.<sup>23-25</sup> Microscopic aqueous and/or organic phases maintain the ionic conductivity of the MPME depending on the HLB of both electroactive species and indifferent of the electrolyte used. The dynamic network of “microscopic aqueous phases or tubes”, in direct contact with “microscopic organic phases or tubes”, generates a dynamic network of interfaces between two immiscible electrolyte solutions (ITIESs). This network is able to play a key role in the electrochemical behaviour of an electroactive species. As a consequence, on one hand, the geometric area of the working electrode (WE) positioned in the “middle phase” is in a dynamic random contact with both the microscopic aqueous and organic phase simultaneously. On the other hand, the interface

between these two microscopic phases from the middle phase is in fact ITIES (i.e., assembly of two double layers, one in “microscopic aqueous phases”, the other in “microscopic organic phase”, which plays an important role in the middle phase electrochemistry).

In two previous papers, similar studies on the middle-phase electrochemistry of the  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  reversible redox couple (countercation  $\text{K}^+$ )<sup>25</sup> and of the pentacyano(L)ferrate(II) complexes (with L either 4,4'-bipyridine or ammonia, countercation  $\text{Na}^+$ )<sup>26</sup> were reported. One pointed out a difference in the response which depends upon the charge of the initial complex ion, either  $[\text{Fe}(\text{CN})_6]^{3-}$  or  $[\text{Fe}(\text{CN})_6]^{4-}$ , used in the CV experiment. The other one emphasized different behaviours strongly influenced by the nature of the coligand, both in the “middle phase” and in the “water phase”. In the current paper we studied the electrochemical behaviour, using cyclic voltammetry (CV) and differential pulse voltammetry (DPV), of two redox species belonging to the cyanoferrate (III) series:  $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]\cdot 3\text{H}_2\text{O}$  and  $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5(\text{pz})]\cdot 4\text{H}_2\text{O}$  in a middle phase microemulsion. Their synthesis, crystal structures and electrochemical data in acetonitrile were reported in a previous work.<sup>27</sup> Both redox compounds are sufficiently soluble in water. It is necessary that the redox species should be added in an appropriate concentration not to modify the position of the system in the phase diagram. When the distribution equilibrium is attained, the water soluble redox species can be found in the “water phase” and also in the “microscopic aqueous phase” of the “middle phase”. Therefore, the electrochemical behaviour of a particular cyanoferrate can be studied in the “middle phase”. Its response in MPME is strongly determined by the presence of the very hydrophobic countercation ( $[\text{P}(\text{C}_6\text{H}_5)_4]^+$ ). The aim of this work is to study the electrochemical response of two pentacyano(L)ferrate(III) complexes presumed to exhibit reversible kinetics which might be influenced by the coligand and the countercation. We found that both electroactive species containing a coligand (either 4,4'-bipyridine or pyrazine) are involved in near reversible electrode reactions at the Pt working electrode. Moreover, the half-wave and standard

electrode potentials are different depending on the electronic effects of the coligand. The arrangement of the surfactant molecules at the ITIES could influence the electrochemical responses of the negatively charged complex ion in the presence of a lipophilic counteranion. The shape of the cyclic voltammograms is also influenced by the electrochemical double layer of the numerous ITIESs existing in middle phase, by the counteranion of the complex ion, and by the coligand. A capacitive tail of the cyclic voltammograms could be noticed, especially due to the above mentioned first two factors.

## MATERIAL AND METHODS

**Apparatus:** Voltammetric measurements (cyclic voltammetry – CV and differential pulse voltammetry – DPV) were performed using the AutoLab PGStat 12 potentiostat-galvanostat system, 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: a platinum disk electrode (Metrohm, 3 mm in diameter) served as working electrode (WE), an appropriate counter electrode (CE) and a Ag/AgCl/KCl (3M) (Metrohm) reference electrode (RE). All experimental potentials were measured versus the reference electrode.

**Chemicals:** Toluene and 1-butanol (purchased from Sigma, A.R. grade) were used without further purification; the water used was double distilled. Sodium chloride (Fluka, A.R. grade) and sodium dodecylsulfate (SDS) (Fluka, A.R. grade) were also used without further purification. Electroactive reagents,  $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})] \cdot 3\text{H}_2\text{O}$  and  $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5(\text{pz})] \cdot 4\text{H}_2\text{O}$ , were received as a gift from the Inorganic Chemistry Department of the Faculty of Chemistry from the University of Bucharest. 1 mM solution of electroactive species in the initial volume of water was prepared. The surface of platinum electrode was polished with alumina slurry (0.05  $\mu\text{m}$ ) on a polishing pad, washed with distilled water and sonicated for 3 minutes in double distilled water, then again washed with double distilled water.

**Measurements:** All measurements were carried out at room temperature with no stirring and no inert gas purged. Three different arrangements of the three-electrode configuration were used: (1) all

electrodes in the “middle phase” (denoted as MP), (2) all electrodes in the “water phase” (denoted as W), and (3) WE and CE in the “middle phase” and the RE in the “water phase” (denoted as MP-W). A diagram of the experimental model is given in a previous paper.<sup>26</sup> The CV studies were accomplished at ten different scan rates (10-100 mV/s), in the potential range between 0.5 V (as starting potential) and 0.0 V (as switching potential). The DPV studies were performed in the same potential domain with a step potential (SP) of 5 mV (10 mV/s) or 10 mV (20 mV/s) and a modulation amplitude (MA) of 25 or 50 mV.

### Middle phase microemulsion and electroactive species:

The middle phase microemulsion studied in this paper was obtained after mixing, as previously described,<sup>28</sup> double-distilled water (19.3 mL), toluene (21.3 mL), sodium dodecyl sulfate (2.76 mmol) as surfactant, 1-butanol (21.6 mmol) as cosurfactant, and sodium chloride (1.1 mol/L) as supporting electrolyte. The electroactive species (taken as being 1 mM in the initial volume of water) was added to the reagents mentioned above, the mixture was sonicated for thorough mixing, then the system was allowed to reach the equilibrium. As a result a three-phase system was obtained. In the case of hydrophilic electroactive species, the ionic conductivity inside the middle phase is due to a continuous “microscopic aqueous phase” which contains the ions of the supporting electrolyte. The large positively charged counterion,  $[\text{P}(\text{C}_6\text{H}_5)_4]^+$ , very lipophilic, might be found either in the “microscopic organic phase” or at the ITIESs.

## RESULTS AND DISCUSSION

### CV behaviour in the middle phase and in the water phase

Cyclic voltammetry of the  $[\text{Fe}(\text{CN})_5(\text{L})]^{2-}/[\text{Fe}(\text{CN})_5(\text{L})]^{3-}$  redox couple in the “middle phase”, in the potential range of 0.0V to 0.5V and scan rates from 10 to 100 mV/s (with 10 mV/s increment), indicated a quasi-reversible (very close to reversible) behaviour for both coligands (L) investigated (4,4'-bipyridine and pyrazine; Fig. 1a and 1b).

The “repartition” of the electroactive species at the interface between the microscopic aqueous and organic phases inside the “middle phase” can be

decided by the presence of the organic coligand as well as of the very large counteraction. The coligand (4,4'-bipyridine or pyrazine) is rather lipophilic than hydrophilic, of course, in different extent. The counteraction is also rather more lipophilic than hydrophilic.

As a result, the electrode reaction in the MP is modulated by the presence of the coligand and counteraction, both of them acting in conjunction and establishing the concentration level and controlling, in some extent, even the movement of the electroactive species inside the MP. The electrode reaction, consisting here in the exchange of an electron between the redox couple  $[\text{Fe}(\text{CN})_5(\text{L})]^{2-} / [\text{Fe}(\text{CN})_5(\text{L})]^{3-}$  and the WE surface is confined to that part of the electrode surface which is wet by the “microscopic aqueous phase” (this is the active area of the WE in “middle phase”). Even in the absence of a very hydrophobic ion generated by the indifferent electrolyte, the repartition of the electroactive species, even if hydrophilic in nature, should be influenced by the presence of a more lipophilic coligand.<sup>26</sup> As such, the electrochemical response

recorded in the “water phase”, is expected to be, more or less, similar in shape and position on the electrode potential axis to that recorded in the “middle phase”.

Attempts to record a CV response at the WE positioned in the “organic phase” failed, probably due to the preponderant hydrophilic character of each of the electroactive species and hence their very poor repartition in the “organic phase”. In spite of the existence of sodium chloride in the three-phase system, the lipophilic organic coligand and the large counteraction are those deciding the presence of the electroactive species especially in the MP, due to the intimate contact of the “microscopic aqueous phase” and the “microscopic organic phase” (namely, due to the presence of ITIESs). These theoretical considerations are supported by our CV experiments, as shown later.

There is a very good linear correlation between the peak cathodic currents and the square root of the scan rate,  $v^{1/2}$ , (Fig. 1a, 1b insets), with similar correlation coefficients  $R^2$ , for both complex ions (Table 1).

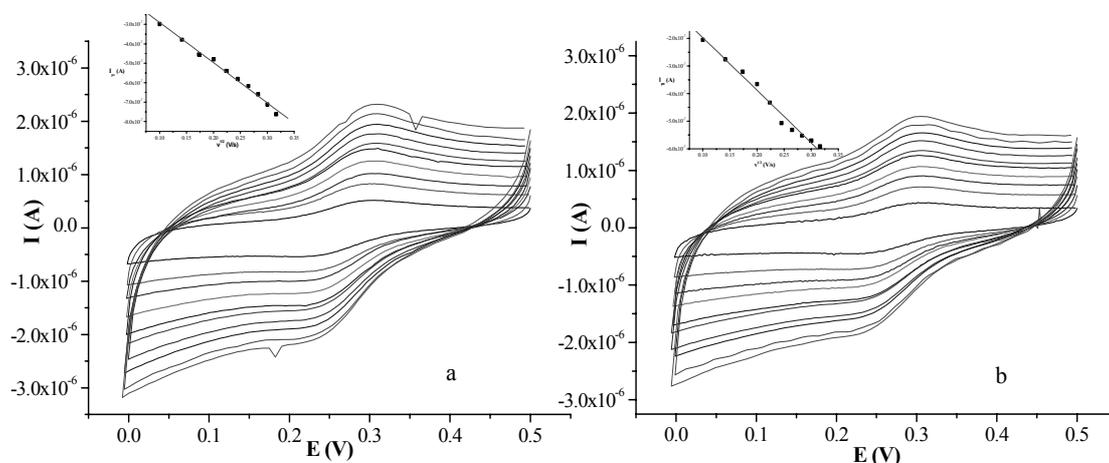


Fig. 1 – The cyclic voltammograms of 1 mM  $[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{2-}$  (a) and 1 mM  $[\text{Fe}(\text{CN})_5(\text{pz})]^{2-}$  (b), in MP at scan rates 10-100 mV/s. Insets:  $I_{pc}$  vs.  $v^{1/2}$ .

Table 1

Regression equations and  $R^2$  for  $[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{2-}$  (A) and  $[\text{Fe}(\text{CN})_5(\text{pz})]^{2-}$  (B) in MP and W arrangements

	Regression equation for $I_{pc}$	$R^2$	SD
<b>A</b>	$I_{pc,MP} = -8.30 \cdot 10^{-8} - 2.07 \cdot 10^{-6} v^{1/2}$	0.9917	$1.42 \cdot 10^{-8}$
	$I_{pc,W} = 2.65 \cdot 10^{-7} - 2.52 \cdot 10^{-6} v^{1/2}$	0.9919	$1.71 \cdot 10^{-8}$
<b>B</b>	$I_{pc,MP} = -8.97 \cdot 10^{-9} - 1.89 \cdot 10^{-6} v^{1/2}$	0.9917	$1.29 \cdot 10^{-8}$
	$I_{pc,W} = -3.75 \cdot 10^{-7} - 1.53 \cdot 10^{-6} v^{1/2}$	0.9926	$9.91 \cdot 10^{-9}$

This leads to the conclusion that the two electroactive species participate in the electrode reaction as diffusional species, the electrode reactions being diffusion controlled. The anodic and cathodic peak current ratios,  $|I_{pa}/I_{pc}|$ , are less than unity for all the scan rates used (see Table 2 for the lowest and highest scan rate), meaning that the anodic peak current is smaller than the cathodic peak current. This finding is in contradiction with previously published data,<sup>26,27</sup> very likely due to the influence of the more lipophilic than hydrophilic balance of the  $[P(C_6H_5)_4]^+$  counteranion. In addition, this peak current ratio decreases with increasing scan rates as shown in Table 2. The two peak potentials, cathodic and anodic, seem to be in a very small degree variable irrespective of the scan rate used. For the 4,4'-bipyridine complex  $E_{pc} = 293 \text{ mV}$  (SD=0.00231) and  $E_{pa} = 235 \text{ mV}$  (SD=0.00375), and for the pyrazine complex:  $E_{pc} = 292 \text{ mV}$  (SD=0.00430) and  $E_{pa} = 239 \text{ mV}$  (SD=0.00429), respectively. The main parameters, such as peak potential separation and half-wave potential (see Table 2), are also relatively constant in the two studied cases: for  $[Fe(CN)_5(4,4'-bpy)]^{2-}$   $\Delta E_p \cong 58 \text{ mV}$  (SD=0.00474),  $E_{1/2} = 264 \text{ mV}$  (SD=2.02) and for  $[Fe(CN)_5(pz)]^{2-}$   $\Delta E_p \cong 52 \text{ mV}$  (SD=0.00704),  $E_{1/2} = 265 \text{ mV}$  (SD=2.46). The experimental peak separation is not too different from the theoretical value of 59 mV, and it might be influenced by the favourable lipophilic interaction of the coligand with the "microscopic organic phase" of the MP.

Table 2

Significant CV data for  $\Delta E_p$  (mV),  $E_{1/2}$  (mV) and  $|I_{pa}/I_{pc}|$  (at 10 and 100 mV/s) for  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  (A) and  $[Fe(CN)_5(pz)]^{2-}$  (B) in MP arrangement

v (mV/s)	$\Delta E_p$		$E_{1/2}$		$ I_{pa}/I_{pc} $	
	10	100	10	100	10	100
<b>A</b>	68	56	260	266	0.815	0.784
<b>B</b>	66	55	254	268	0.845	0.670

All these parameters, except the peak current ratio, indicate a good degree of reversibility of the electrode reaction at the WE operating in the MP for both compounds investigated.

The presence of different coligands in the two complex ions seems to play only a minor role in comparison with the influence of the large counterion, as can be noticed especially from the

values of the half-wave potential (see Tables 2 and 3) which are closer than in the case of  $Na^+$  as counteranion.<sup>28</sup> Regardless of its cathodic or anodic nature, the peak current obtained for the 4,4'-bipyridine complex (A) is greater than the one for the pyrazine complex (B). This result indicates a faster electrode reaction for complex ion A than for B, or a greater concentration of A the "microscopic aqueous phase" when compared to B.

### Comparison of the three-electrode arrangements

Experiments were performed for each complex ion (at 1 mM concentration relative to the initial water volume) by using the other two electrode configurations, i.e. all electrodes immersed in "water phase" (W) and, respectively, the working and counter-electrodes in the "middle phase" and the reference electrode in the "water phase" (MP-W), as opposed to the model in which all three electrodes were immersed in the "middle phase" (MP). Representative cyclic voltammograms recorded at a scan rate of 20 mV/s are shown in Fig. 2.

When the RE is displaced from the "middle phase" into the "water phase" no significant difference is observed in either the shape or the main electrochemical parameters of the voltammograms obtained for any of the two complex ions (Table 3).

Concerning the shape, a small capacitive influence of the "middle phase" structure and composition could be noticed, resulting in a larger area enclosed by the CV trace. The effect is more obvious for 4,4'-bpy than for pyrazine as coligand, as it is illustrated by the corresponding peak current ratios (Table 3).

The peak-to-peak separation and the half-peak potential in MP and MP-W arrangements are very similar as well as the direct (cathodic) peak currents ratios. It results that the position of the RE is not important.

The experimental values obtained for the peak potentials,  $E_{pc}$ , in the "middle phase", with the RE in the "middle phase" or in the "water phase", respectively, were 235 mV and 231 mV, respectively, for A, and 239 mV and 237 mV, respectively, for B. Surprisingly, when all three electrodes were placed inside the "water phase", a different behaviour was observed compared to that where the WE was positioned in the "middle phase". However, in this instance too, there was no significant difference in the behaviour of the complex ions investigated (Fig. 2, trace W). We found a larger  $|I_{pc,MP}/I_{pc,W}|$  peak current ratio for A than for B (Table 3).

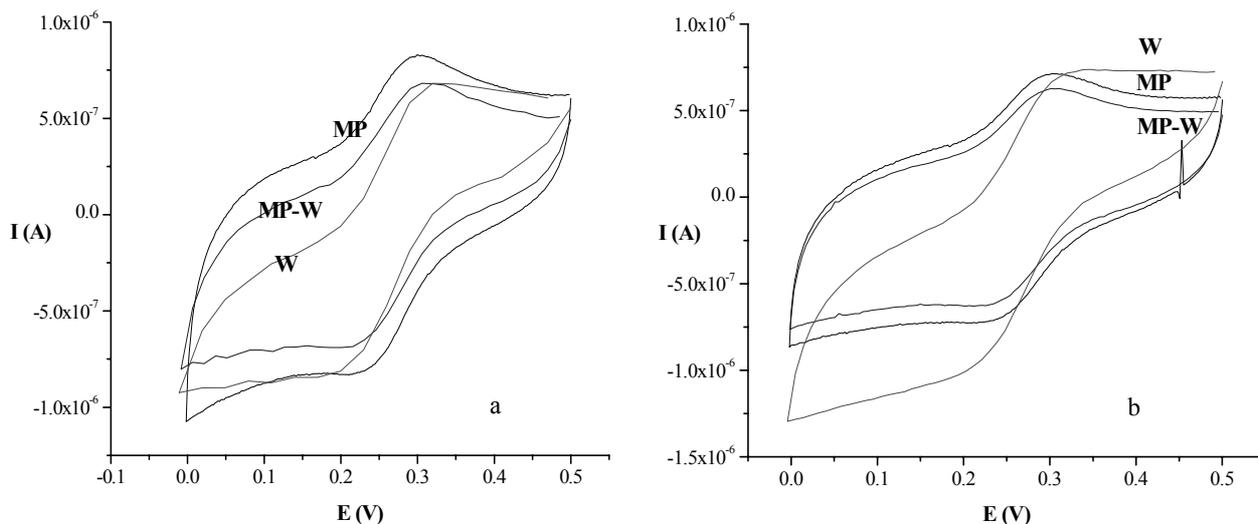


Fig. 2 – The cyclic voltammograms of 1 mM  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  (a) and 1 mM  $[Fe(CN)_5(pz)]^{2-}$  (b) in MP, W, and MP-W arrangements, at scan rate 20 mV/s.

Table 3

Significant CV data showing mean  $\Delta E_p$  (mV), mean  $E_{1/2}$  (mV),  $|I_{pc,MP}/I_{pc,W}|$  and  $|I_{pc,MP}/I_{pc,MP-W}|$  (at a scan rate of 20 mV/s) for  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  (A) and  $[Fe(CN)_5(pz)]^{2-}$  (B) with the electrodes in MP, W, and MP-W arrangements

	MP		MP-W		W		peak currents ratios	
	$\Delta E_p$	$E_{1/2}$	$\Delta E_p$	$E_{1/2}$	$\Delta E_p$	$E_{1/2}$	$ I_{pc,MP}/I_{pc,W} $	$ I_{pc,MP}/I_{pc,MP-W} $
<b>A</b>	58	264	62	262	118	258	0.57	0.94
<b>B</b>	52	265	57	266	88	255	0.43	1.00

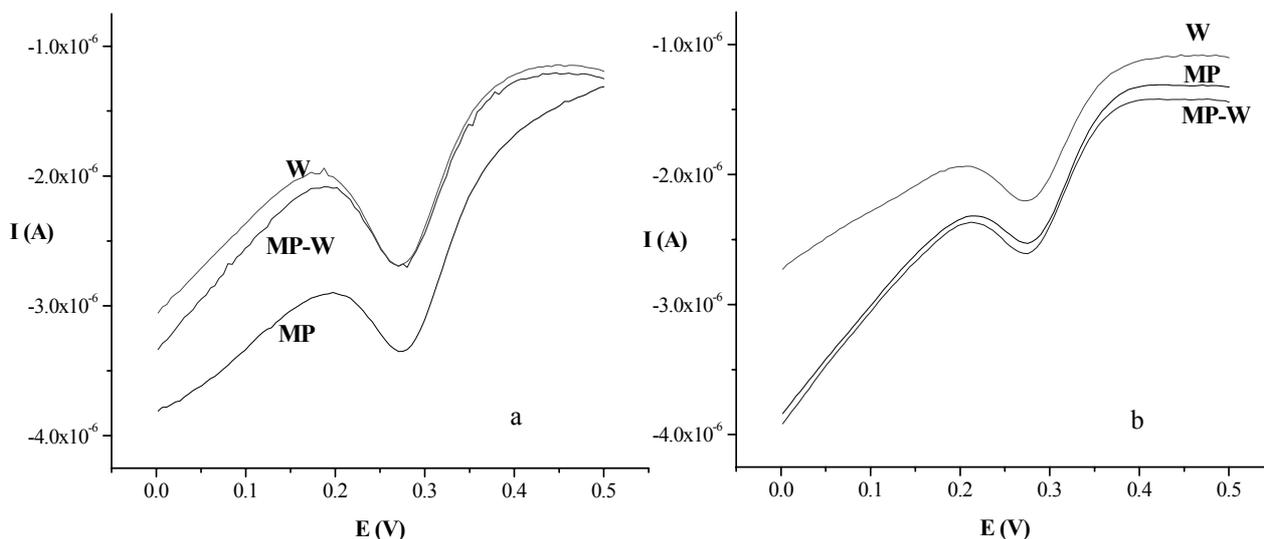


Fig. 3 – The DPV traces (SP= 5 mV, MA= 25 mV) of  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  (a) and  $[Fe(CN)_5(pz)]^{2-}$  (b) in MP, W, and MP-W arrangements at scan rate of 20 mV/s, and 1 mM concentration relative to the initial water volume.

Electrochemical data, in terms of peak potentials as well as peak currents, obtained from differential pulse voltammetry (Fig. 3) are in very

good agreement with those derived from the CV experiments.

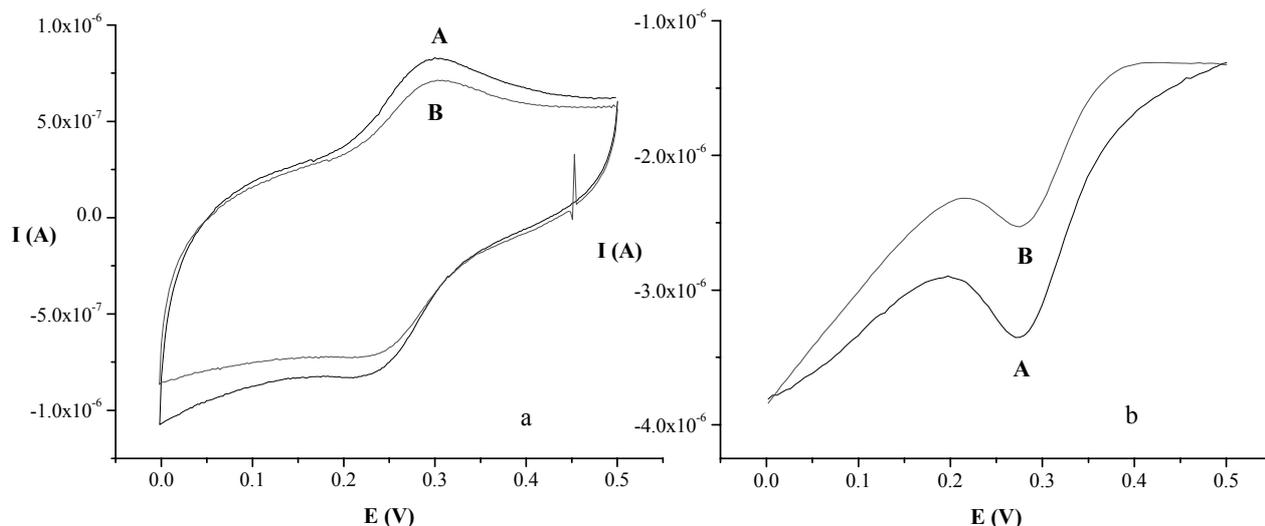


Fig. 4 – The cyclic voltammograms at 20 mV/s (a) and the differential pulse voltammograms with MA=25 mV and SP=5 mV (b) of 1 mM  $[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{2-}$  (A) and 1 mM  $[\text{Fe}(\text{CN})_5(\text{pz})]^{2-}$  (B) for MP arrangement.

### Influence of the coligand and of the counteraction

As mentioned earlier, for the same counteraction, the peak currents, regardless of their cathodic or anodic nature, were a little higher for the complex ion A than for B (see Fig. 4).

Irrespective of the coligand, the half-wave potential and the peak separation are the same in “middle phase” in the two positions of the RE. As concerning  $E_{1/2}$  it is also the same for all electrodes in “water phase” (see Table 3). Also the two peak ratios investigated are enough close one to each other as can be seen in Table 3. Briefly, the two coligands influence the electrochemical behaviour of the electroactive species in the same way.

As aforementioned (see Table 2), the peak current ratios,  $|I_{p,\text{reverse}}/I_{p,\text{direct}}|$ , are less than 1 but more than 0.5 for both complex ions studied in this paper. This result is not too similar to that found for the more common redox couple species (either  $[\text{Fe}(\text{CN})_6]^{3-}$  or  $[\text{Fe}(\text{CN})_6]^{4-}$ ), with  $\text{K}^+$  as counteraction.<sup>25</sup> It is, in some extent, different from the results found for  $[\text{Fe}(\text{CN})_5\text{L}]^{2-}$  species where the coligand L is either 4,4'-bpy or  $\text{NH}_3$ , with  $\text{Na}^+$  as counteraction,<sup>28</sup> where the same ratio is greater than but closer to 1. The different behaviour may be caused by the presence of the counteraction  $[\text{P}(\text{C}_6\text{H}_5)_4]^+$  instead of  $\text{Na}^+$  at

ITIESs. Lipophilic  $[\text{P}(\text{C}_6\text{H}_5)_4]^+$  can intervene in the repartition of the electroactive species. In each case the ratio  $|I_{pc}/I_{pa}|$  is greater than unity, the cathodic peak being increased comparing to the anodic peak.

In order to study the influence of the counteraction,  $\text{Na}^+$  or  $[\text{P}(\text{C}_6\text{H}_5)_4]^+$ , we generated the same redox couple  $[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{2-}/[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{3-}$  from different initial compounds  $\text{Na}_3[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]$  (A') and  $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})] \cdot 3\text{H}_2\text{O}$  (A), respectively, and recorded the cyclic voltammograms corresponding to these two instances (Fig. 5). The main electrochemical data generated by this experiment are shown in Table 4.

Our results indicate that both oxidation and reduction occur easier (the half-wave potential is smaller) when the counteraction is  $[\text{P}(\text{C}_6\text{H}_5)_4]^+$  in comparison with  $\text{Na}^+$ . The peak separation is closer to the theoretical value for a reversible electrode reaction when  $\text{Na}^+$  is the counteraction. The main electrochemical data are included in Table 4. Of course, the cathodic peak for A and the anodic peak for A' were considered as being the direct peak generated in the direct potential sweep (see Table 4). As expected, the repositioning of the RE has no considerable effect on the value of the peak current as long as the WE remains in the “middle phase”.

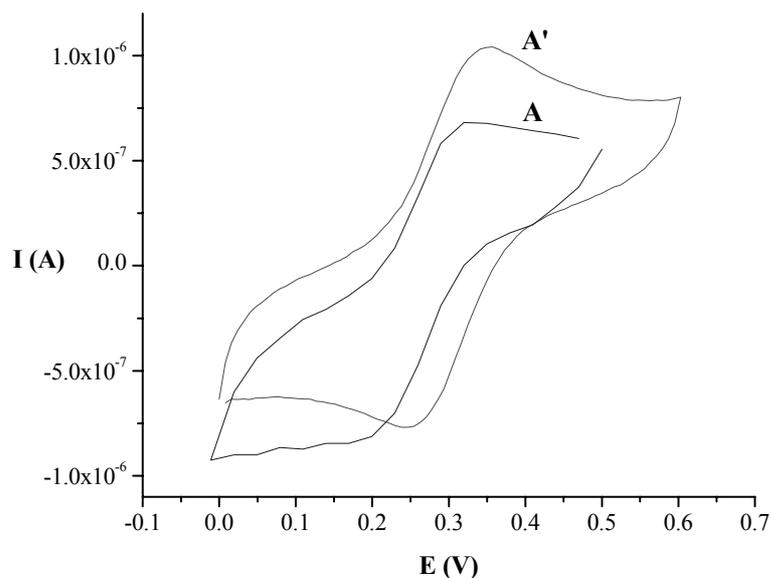


Fig. 5 – The cyclic voltammograms of  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  and  $[P(C_6H_5)_4]^+$  as countercation (A) and of  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  and  $Na^+$  as countercation (A') at scan rate 20 mV/s of 1 mM referred to initial water volume.

Table 4

Significant CV data showing  $E_{pc}$  (mV),  $E_{pa}$  (mV),  $\Delta E_p$  (mV), and  $E_{1/2}$  (mV) in MP arrangement, together with  $|I_{p,MP}/I_{p,W}|$  and  $|I_{p,MP}/I_{p,MP-W}|$  for  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  with the counterion either  $[P(C_6H_5)_4]^+$  (A) or  $Na^+$  (A') (at a scan rate of 20 mV/s)

	MP				peak currents ratios	
	$E_{pc}$	$E_{pa}$	$\Delta E_p$	$E_{1/2}$	$ I_{p,MP}/I_{p,W} $	$ I_{p,MP}/I_{p,MP-W} $
A	232	290	58	264	0.57	0.94
A'	258	338	80	298	0.94	0.97

Considering the peak ratio,  $|I_{p,direct,MP}/I_{p,direct,W}|$ , of the direct peak in MP to the direct peak in W (see Table 4), one can notice that for  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  the ratio is very close to unity when the counterion is  $Na^+$  and very close to 0.5 when the counterion is  $[P(C_6H_5)_4]^+$ . In the former case the influence of the coligand seems to be opposite to that of the lipophilic counterion. The peak currents ratio is very similar to that reported<sup>27</sup> for more common hexacyanoferrates (III) and (II) respectively. On the contrary, in the latter case the influence of the coligand seems to be decisive compared to that of the hydrophilic counterion, the cathodic electrode reaction being favoured in MP-arrangement compared to W-arrangement of the WE. The same conclusion is valid for  $[Fe(CN)_5(pz)]^{2-}$  when the counterion is  $[P(C_6H_5)_4]^+$  (see Table 3).

In addition, the peak potentials are not considerably shifted either (Table 3 and results from previous papers).<sup>25,26</sup> It can be also concluded that, regardless of the positioning of the three-electrode system in the “middle phase” or in the “aqueous phase”, the counterion HLB has a major effect. The small hydrophilic  $Na^+$  ion leads to almost equal peak currents both in MP and in W (as expected), while for the large lipophilic  $[P(C_6H_5)_4]^+$  the peak current in MP is almost half of that in W. As it can be seen, the HLB of the counterion acts on the degree of reversibility of the electrode reaction itself.

#### Using the Randles-Sevcik equation

Applying the well-known Randles-Sevcik equation for the peak current in “middle phase” and in the “water phase”, it results that:

$$\frac{(I_p)_{MP}}{(I_p)_W} = \frac{A_{MP}}{A_W} \frac{D_{MP}^{1/2} c_{MP}}{D_W^{1/2} c_W} \quad (1)$$

where  $A$  is the active area of the working electrode,  $D$  is the diffusion coefficient and  $c$  the concentration of the electroactive species. In another form:

$$\frac{A_{MP}}{A_W} \frac{D_{MP}^{1/2} c_{MP}}{D_W^{1/2} c_W} = \frac{b_{MP}}{b_W} \quad (2)$$

where  $b_{MP}$  and  $b_W$  are the slopes of the plots  $I_{pa}$  vs.  $v^{1/2}$  in the "middle phase" and in the "water phase", respectively. From Eq. (2) and the slopes tabulated in Table 1, it results that  $\frac{A_{MP}}{A_W} \frac{D_{MP}^{1/2} c_{MP}}{D_W^{1/2} c_W}$

is 0.82 for the  $[Fe(CN)_5(4,4'-bpy)]^{2-} / [Fe(CN)_5(4,4'-bpy)]^{3-}$  and 1.24 for the  $[Fe(CN)_5(pz)]^{2-} / [Fe(CN)_5(pz)]^{3-}$  redox couple. Considering the case of common hexacyanoferrates (II) and (III), where the most intense studied MPME with 1 mM electroactive probe corresponds to a point in the "phase diagram", more or less, identical with the point of the three-phase system without electroactive probe, and the visual observation of equal volumes of "toluene phase" and "water phase", one can approximate that the WE area in direct contact with "microscopic aqueous phase" is half of the active area of the WE. Therefore, for both complex ions studied in this paper  $A_{MP} D_{MP}^{1/2} c_{MP} > 0.5 A_W D_W^{1/2} c_W$ . This result may be specialized by using some simplifying assumptions.

Taking in account the closeness to unity ratio between the volumes of the "water phase" and "organic phase", before and after the formation of the "three-phase system", one can assume that the surface area of the WE in contact with "microscopic aqueous phase" and the surface area of the WE in contact with "microscopic organic phase" are close enough to half of the entire WE surface area. In fact, in the phase diagram<sup>29,30</sup> there is only a slight shift of the point denoting the three-phase system. As such, the electrode reaction is confined to about one half of the WE surface. On the contrary, in the "water phase" the entire WE surface is the stage of the electrode reaction.

With this assumption ( $2A_{MP} = A_W$ ), the Eq. (1) leads to:

$$\frac{(I_p)_{MP}}{(I_p)_W} = \frac{1}{2} \frac{D_{MP}^{1/2} c_{MP}}{D_W^{1/2} c_W} \quad (1')$$

and Eq. (2) becomes:

$$\frac{1}{2} \frac{D_{MP}^{1/2} c_{MP}}{D_W^{1/2} c_W} = \frac{b_{MP}}{b_W} \quad (2')$$

for the same sweep rate or by using the slopes from Table 1. In this case  $\frac{D_{MP}^{1/2} c_{MP}}{D_W^{1/2} c_W}$  equals 1.64 for  $[Fe(CN)_5(4,4'-bpy)]^{2-} / [Fe(CN)_5(4,4'-bpy)]^{3-}$  and 2.47 for  $[Fe(CN)_5(pz)]^{2-} / [Fe(CN)_5(pz)]^{3-}$ . Since  $D_{MP}^{1/2} c_{MP} > D_W^{1/2} c_W$ , either one or both parameters,  $D$  and  $c$ , in the "middle phase" have to be larger than in the "water phase".

(i) So, equal diffusion coefficients (valid assumption for water as solvent) result in an increase of the electroactive species concentration in the "middle phase", compared to the "water phase". Obviously, this accumulation/concentration is favoured by the presence of 4,4'-bipyridine or pyrazine as ligand in the complex. The concentration ratios are now 1.64 for  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  and 2.47 for  $[Fe(CN)_5(pz)]^{2-}$ .

(ii) If the concentrations are the same in the two phases, then the diffusion coefficient in the "middle phase" is larger than in the "water phase". The diffusion coefficient ratios are now 2.70 for  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  and 6.10 for  $[Fe(CN)_5(pz)]^{2-}$ .

## CONCLUSIONS

The two redox species we studied in this paper displayed near reversible electrochemistry both in the "middle phase" and in the "water phase". The CV revealed a predominant distribution of  $[Fe(CN)_5(4,4'-bpy)]^{2-}$  and  $[Fe(CN)_5(pz)]^{2-}$  ions in the "microscopic aqueous phase" compared to the "water phase", due to the presence of 4,4'-bipyridine or pyrazine as lipophilic coligands and of the lipophilic  $[P(C_6H_5)_4]^+$  as counterion. Besides other contributions, the lipophilic counteraction intervenes in the distribution of the electroactive species between the two aqueous phases. Only expression of the type  $A_\varphi D_\varphi^{1/2} c_\varphi$  ( $\varphi$  denoting the phase to which the electroactive species belongs), or their ratio, can be estimated by using the Randles-Sevcik equations. Therefore,

this paper raises a question regarding the possibility of estimating the diffusion coefficients or the surface area of the working electrode in direct contact with one or the other of the “microscopic phases”. Using appropriate assumptions, one may predict the distribution of an electroactive aqueous species between the “microscopic aqueous phase” and “water phase”, or the value of its diffusion coefficient in the “middle phase” in comparison with that in the “water phase”. From their half-wave potentials, it can be concluded results that  $[\text{Fe}(\text{CN})_5(\text{pz})]^{2-}$  is a somehow stronger oxidant than  $[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{2-}$ . The influence of the large lipophilic counteraction  $[\text{P}(\text{C}_6\text{H}_5)_4]^+$ , compared to that of the small  $\text{Na}^+$ ,<sup>26</sup> was evidenced by the electrochemistry of both  $[\text{Fe}(\text{CN})_5\text{L}]^{2-}/[\text{Fe}(\text{CN})_5\text{L}]^{3-}$  redox couples. Thus, the decrease of the anodic peak currents of the reduced forms  $[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{3-}$  and  $[\text{Fe}(\text{CN})_5(\text{pz})]^{3-}$  versus the cathodic peak currents of the oxidized forms  $[\text{Fe}(\text{CN})_5(4,4'\text{-bpy})]^{2-}$  and  $[\text{Fe}(\text{CN})_5(\text{pz})]^{2-}$ ,<sup>27</sup> when the WE is positioned in “middle phase”, could be caused by the intervention of both the surfactant anion and counteraction at the ITIES appeared between the “microscopic aqueous phase” and the “microscopic organic phase”. Owing to the Bruggemann geometric factor,<sup>31</sup> the presence of the “microscopic organic phase”, that could be considered as a microporous system, leads to an enhanced trajectory pathway which is able to account for the geometric constraints in this bicontinuous “middle phase” system.

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