POTASSIUM HEXACYANOFERATE(III) CYCLIC VOLTAMMETRY IN “MIDDLE PHASE”

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abstract: The complex $K_3\left[Fe(CN)_6\right]$ was investigated by using cyclic voltammetry (CV) technique in a “middle phase” formed between water, toluene, sodium dodecylsulfate and 1-butanol in the presence of sodium chloride, that allows to get information about electrochemical mechanism of redox behaviour of the compound during cyclic voltammetry experiment.

1. 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 electrolyte which is mandatory for electrochemical studies. 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 is highly dynamic. In such systems the water phase and the organic phase form the so-called bicontinuous structure, the two different phases alternating on a microscopic scale. In the present work, it was chosen a MPME solution obtained [6] from a system consisting of water, toluene, sodium dodecyl sulfate as surfactant, 1-butanol as cosurfactant and sodium chloride as 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 “saline (water) phase”. If a redox species, such as $K_3[Fe(CN)_6]$, is added in an appropriate concentration in the initial aqueous solution of preparation, after the separation in the three macroscopic phases, no effect is observed on the phase diagram of the system. Finally, when the equilibrium of distribution is attained, the redox species can be found both in the “saline phase” and in “middle phase” due to its solubility in the water that forms the “saline films”. In this case the electrochemistry of $K_3[Fe(CN)_6]$ 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 alternatively in direct contact with the “organic film” and with “aqueous film” (which constitute the “middle phase”). The electroactive species

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$K_3[Fe(CN)_6]$ is chosen due to its simple, reversible electrochemistry, its high solubility in water and low solubility in toluene (it is very hydrophilic). In addition, both $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are soluble in water in contrast with other electrochemical probes such as cobalticenium ion/cobaltocene and ferricenium ion/ferrocen redox couples [7] in which cases the cation is water soluble and the neutral form is oil soluble.

2. Experimental Part

2.1. Apparatus

The electrochemical measurements were performed using a Volta Lab^{TM} 32 system, having an IMT102 electrochemical interface and a DEA 332 33V/2A potentiostat model. A three-electrode single-compartment electrochemical cell was used. The working electrode was a platinum disc of 2 mm diameter, in contrast it was used even a microelectrode of Pt [8] , the reference electrode was in fact a pseudo-reference electrode of Ag wire (all the electrode potentials quoted in this paper refer to this reference electrode) and the counter electrode was a platinum wire long enough. All measurements were carried out at room temperature.

2.2. Reagents

Toluene and 1-butanol (both from Sigma) were used without further purification, the water was double distilled. All other reagents ($K_3[Fe(CN)_6]$ (Sigma), NaCl (Fluka), sodium dodecyl sulphate (Fluka)) were also used without further purification and they all were analytical reagent grade.

2.3. Preparation of "middle phase"

Microemulsions were prepared as indicated [9], the typical content of the three phase system being: water (4.68 g), toluene (4.625 g), NaCl (0.30 g), sodium dodecyl sulfate (0.199 g), 1-butanol (0.396 g) and $K_3[Fe(CN)_6]$ (0.00154 g). The electroactive species was introduced by using 1 mM $K_3[Fe(CN)_6]$ aqueous solution the preparation procedure as water phase.

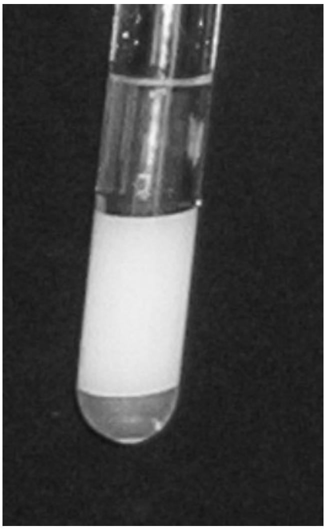

Fig. 1 *Visual aspect of the three-phasemicroemulsion consisting of "toluene phase", "middle phase" and "saline phase" with* $K_3Fe(CN)_6$*. content. The "middle phase" is the "bicontinuous microemulsion"*

3. Results and discussions

In Fig. 2 is presented the $K_3[Fe(CN)_6]$ cyclic voltammetric behaviour in the "middle phase" at several different scan rates. One can notice a reversible behaviour of the $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$ redox system even if an increasing peak appears with increasing scan rate. The cause is probably due to the existence of the “organic film” inside the “middle phase”; the organic film does not contain indifferent electrolyte and, as a consequence, the ohmic drop could play an active role during the CV experiments. On the other hand, in the “middle phase” the surface exposed by the working electrode toward electrode reaction is less than the surface which the same working electrode should expose in the “aqueous phase” at the same concentration of the electroactive species. It is also possible that the surfactant adlayer on the electrode surface would influence the electrode reaction. Of course, the diffusion itself in the aqueous films from the “middle phase” differs, in some extent, from the usual diffusion for a disk electrode in an “aqueous phase”; so that a different model for diffusion in these films could be necessary.

The peaks of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox couple in “middle phase” were smaller and larger than those recorded in the “saline phase” at a concentration of 0.5 mM (one suppose that the initial 1 mM concentration of $K_3[Fe(CN)_6]$ in the preparation solution is distributed between the “saline films” from the “middle phase” and “saline phase” under the control of coefficient of diffusion/repartition equal to unity).

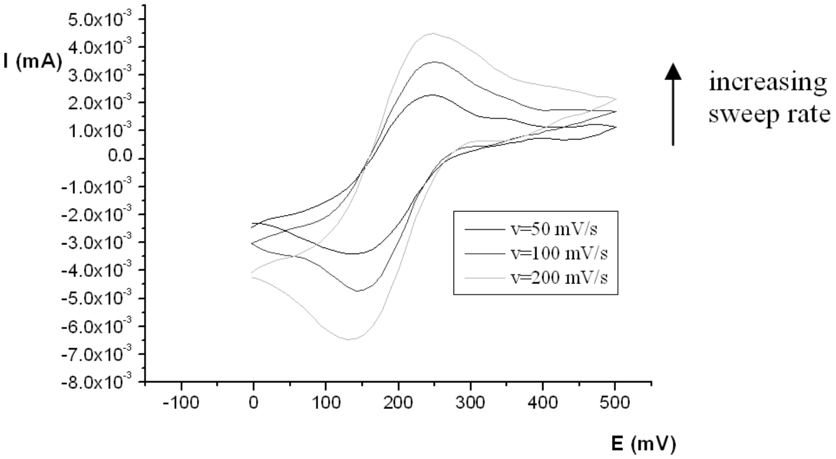

Fig. 2 *The cyclic voltammograms of* $K_3[Fe(CN)_6]$ *in “middle phase” at several different scan rates at v=50, 100 and 200 mV/s for 1 mM* $K_3[Fe(CN)_6]$ *in the initial aqueous solution.*

In Fig. 3 are presented the plots of the peak currents versus the square root of the scan rate; there is a linear dependence in both cases indicating a diffusion control of the electrode reaction at the working electrode from the “middle phase”.

The cathodic peak shifts negatively and the anodic peak positively, the peak separation increasing with the increasing scan rate. The average cathodic peak potential is 141 mV and the anodic peak potentials is 246 mV and the average separation peak is 104 mV.

Considering the electrode reaction and the multicharged anion state of the two species of the redox couple, one can expect these anions to be, in some extent, rejected from the electrode surface if the surfactant molecules form an adlayer on the electrode surface. On the other hand, at the interface between the “toluene film” and “saline film” the molecules of surfactant are oriented with their lipophilic chain in the “toluene film” and with their hydrophilic functional group (negatively charged) in the “saline film”, so that the two anionic electroactive species are forced to move only inside the “saline films”. As a consequence, it is possible that the two diffusion coefficients of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ in “saline films” and in “saline phase” to be very close [10]. If there is a difference in diffusion, it can be attributed to different diffusion model (not as simple as planar semi-infinite diffusion).

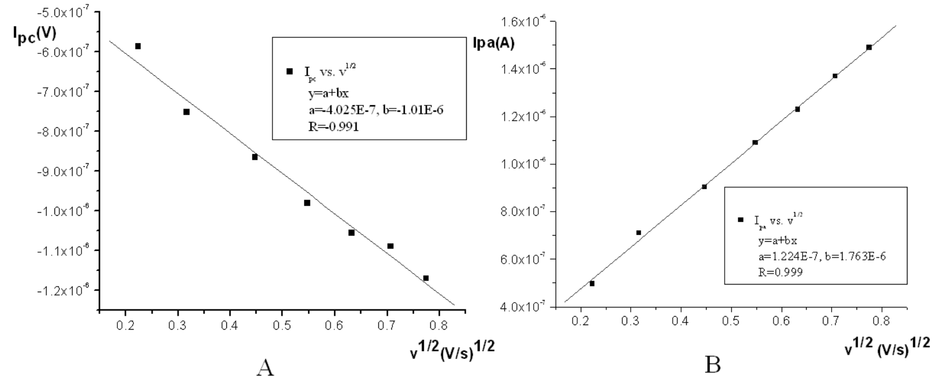

Fig. 3 *The dependences* I_{pc} *vs.* $v^{1/2}$ *(A) and* I_{pa} *vs.* $v^{1/2}$ *(B s for 1 mM* $K_3\left[Fe(CN)_6\right]$ *in the initial aqueous solution (scan rates 50, 100, 200, 300, 400, 500 mV/s).*

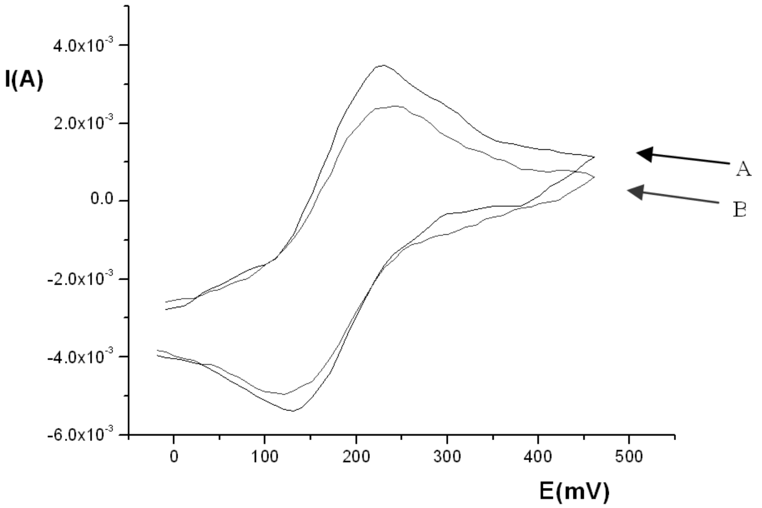

Fig. 4 *Comparison between two cyclic voltammograms obtained: with all electrodes in “middle phase” (A) and with WE in “middle phase” and RE and CE in “saline phase” (B) at v=100 mV/s for 1 mM* $K_3[Fe(CN)_6]$ *in the initial aqueous solution of preparation.*

In Fig. 4 two cyclic voltammograms are presented. The first of them, the cyclic voltammogram A, is performed with all electrodes in the “middle phase” (the electrodes are in direct contact with the “saline films”) of the equilibrated three-phase system, the second, the cyclic voltammogram B, is performed with the WE in “middle phase” and the RE and CE in “saline phase”.

The cathodic peak potential is shifted in the negative direction ($E_{pc,A} = 141\,mV$, $E_{pc,B} = 137\,mV$), the anodic peak potential in the positive direction ($E_{pa,A} = 246\,mV$, $E_{pa,B} = 251\,mV$) and the peak potential separation ($\Delta E_p = E_{pa} - E_{pc}$) being ($\Delta E_{p,A} = 105\,mV$, $\Delta E_{p,B} = 109\,mV$). The small increase in the peak separation, $\Delta E_{p,B} - \Delta E_{p,A} = 4\,mV$, reflects a small increase in the ohmic drop when the RE and CE are placed inside the “saline phase” but the WE remains in “middle phase”. On the other hand the cathodic and anodic peak currents decrease in the same order A>B reflecting the effect of placement of RE and CE inside the “saline phase”.

The peak current of the $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ in “middle phase” was approximately 11.5% (for the cathodic peak) and respectively 20.5% (for the anodic peak) smaller than the corresponding ones observed in “saline phase” and the peak is also larger. This difference can be assigned to the effective magnitude of the working electrode surface available for electrode reaction only at the direct contact of the electrode surface with the “saline films” from “middle phase” in comparison with its magnitude when the WE is placed in “saline phase”.

4. Conclusions

One may conclude that the electrochemistry of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ in “middle phase” could be observed due to the main fact that the “middle phase” containing both “saline films” and “toluene films” allows the occurrence of the electrode reaction in “middle phase”. This electrochemistry of electroactive species in MPME depends upon the way in which the MPME is organised, the balance between the hydrophilicity and lipophilicity of the surfactant and cosurfactant used, the structure of the “middle phase” and, of course, the nature of the electrode used.

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