

Electrochemical behavior of $K_4Fe(CN)_6$ in $[bmim]PF_6/$ TX-100/ H_2O based microemulsions

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Abstract The electrochemical behavior of potassium ferrocyanide $[K_4Fe(CN)_6]$ at Pt/ionic liquid (IL) microemulsion interfaces was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). $H_2O/$ TX-100/ $bmimPF_6$ was used to prepare three IL microemulsions: water in 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) (W/IL), bicontinuous (WIL) and $bmimPF_6$ in water (IL/W). The results show that the IL microemulsion systems have relatively narrower potential windows compared with the pure IL system. The redox potential gap is about 100 mV in the pure water and the three IL microemulsions. The redox potentials of $K_4Fe(CN)_6/K_3Fe(CN)_6$ and the redox peak currents decrease in the order pure water, IL/W, WIL, W/IL. Furthermore, the peak currents increase linearly with the square root of the scan rate, while the diffusion coefficient increased in the order W/IL, WIL, IL/W. The Nyquist plots obtained in the WIL and IL/W systems show capacitive resistance arcs at high frequencies and 45° straight lines at low frequencies, implying that the electrochemical reactions are controlled by charge transfer and diffusion steps. For the W/IL system there is only a 45° straight line in the Nyquist plot, indicating that diffusion is the controlling step at all frequencies.

Keywords Ionic liquid microemulsions · Cyclic voltammetry · Electrochemical impedance spectroscopy · Electrochemical behavior · Potassium ferrocyanide

1 Introduction

Room temperature ionic liquids (ILs) have low melting points ($<100^\circ C$) and consist solely of ions [1]. They have many attractive properties such as high thermal stability [2], low volatility [3], co-solvent miscibility, wide electrochemical potential window [4–6], and unique solubility [7]. ILs have been extensively employed in organic synthesis [8], catalysis [8, 9], separation technology [10, 11], electrochemical reactions [12], and novel electrolytes for batteries [13]. However, they have limited applications in electrochemistry because of their higher viscosity, lower electric conductivity, weaker solubility for organic and inorganic compounds, and stronger surface activity compared with traditional solvents. To overcome these problems, a few approaches have been used to modify traditional ILs, one of which is to create microemulsions using surfactants.

Microemulsions are isotropic and thermodynamically stable mixtures of two immiscible solvents stabilised by an amphiphilic surfactant [14]. They have wide applications in separation science, reaction engineering, environmental science, and materials science. Reverse microemulsions (water-in-oil) have been successfully applied to prepare nanoscale materials including metals [15, 16], organic conductive polymers [17], and metal and nonmetal compound materials [18]. However, reverse microemulsions with oil as the continuous phase, are unsuitable for application in electrochemistry on account of their low electrical conductivity. Our recent study showed that the conductivity of reverse microemulsions can be increased by three orders of magnitude by changing the pH of the water cells [19]. Besides, Au and Ni nano-sized deposits were successfully prepared in an electrochemical system constructed by a reverse microemulsion and an electronic conductor phase.

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It is interesting to use hydrophobic ILs instead of conventional organic solvents to prepare IL microemulsions, which may possess some unexpected advantages in applications due to the unique properties of ILs. Eastos et al. [20] reported the preparation, structure performance and applications of IL microemulsions. Han Buxin's group [21] successfully prepared three types of IL microemulsions (W/IL, WIL and IL/W). Subsequently nano-sized porous silicon was prepared by using IL microemulsion [22]. The phases, microstructure and influence of water in [bmim]BF₄/TX-100/toluene have been investigated [23–25]. The response of solvatochromic probes and the aggregation behavior of several common surfactants in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide have also been studied [26].

IL microemulsion systems are different from conventional systems as they can be used as ionic conductor phase to construct electrochemical systems. Moreover, electrode/IL microemulsion systems have their own characteristics when compared with electrode/IL and electrode/water systems. In this work, [bmim]PF₆/TX-100/H₂O microemulsions were prepared, and the electrochemical behavior of K₄Fe(CN)₆ in different IL microemulsions was investigated.

2 Experimental

2.1 Reagents

[bmim]PF₆ (purity 97%) was purchased from Hang Zhou Kemo Chemistry Co. of China. K₄Fe(CN)₆ and ethanol were produced by Tian Jin Damao Chemical Reagent Factory. TX-100 was obtained from Chemistry Reagent Co. of National Medicine Group. Hydrochloric acid was attained from Zhu Zhou Chemical Industry Graduate School. All reagents were analytical grade and were used without further purification.

2.2 Preparation of IL microemulsions

IL microemulsions were prepared according to the literature [21]. The components of the three different IL microemulsions were as follows: 0.5 mL K₄Fe(CN)₆ water solution, 0.5 mL IL and 3 mL TX-100 in W/IL; 2 mL K₄Fe(CN)₆ water solution, 0.25 mL IL and 2 mL TX-100 in WIL; 1 mL K₄Fe(CN)₆ water solution, 0.1 mL IL and 3 mL TX-100 in IL/W, respectively. The apparent concentration of K₄Fe(CN)₆ in the three IL microemulsions was 0.01 M. First, the three components were mixed and the resultant mixture was ultrasonically vibrated. Then, the mixture was centrifuged and it was noticed that the solution did not delaminate. The analysis was made in the single-phase

microemulsion region and the weight ratio of [bmim]PF₆ to TX-100 was 0.2 in W/IL, 0.11 in WIL and 0.14 in IL/W [21], respectively, at room temperature.

2.3 Method and apparatus

The electrochemical experiments, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were carried out using a three-electrode electrochemical cell connected with a CHI 660C electrochemical workstation (Shanghai Chenhua Instrument Corporation) at room temperature. In this work, water soluble K₄Fe(CN)₆ was used as the electrochemical probe, a Pt rod (ϕ 1 mm) as the working electrode in addition to an Ag/AgCl reference electrode and a platinum wire counter electrode. Before every experiment the working electrode was polished with metallographic abrasive paper, ultrasonically washed with ethanol for approximately 3 min and rinsed thoroughly with double distilled water. Finally, all electrodes were dried using a blower. The pH of water phase was adjusted using HCl to between 4 and 5. All K₄Fe(CN)₆ concentrations are apparent concentrations.

3 Results and discussion

3.1 Electrochemical potential windows of IL microemulsions

Figure 1 presents the electrochemical potential windows of pure IL and three different IL microemulsions. It was found that, compared with the pure IL system, these three types of IL microemulsions have relatively narrower potential windows, which may be attributed to the water phase in each microemulsion system. This interpretation is supported by

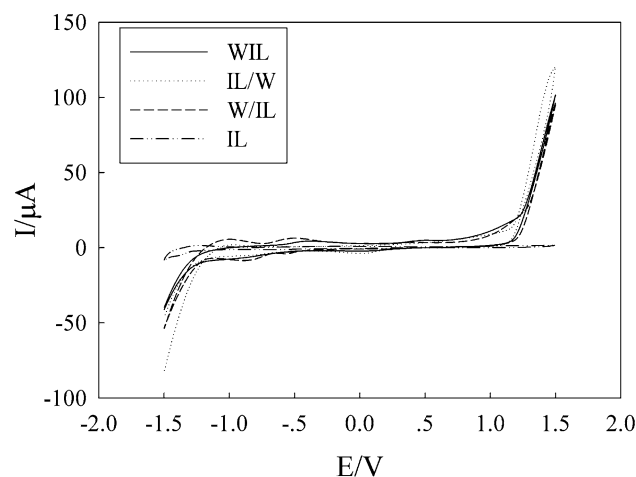


Fig. 1 Electrochemical potential windows of pure IL and the three different IL microemulsions on Pt. Scan rate: 0.025 V s⁻¹

the fact that the IL/W system has the narrowest potential window where water is the continuous phase.

3.2 Cyclic voltammograms of $K_4Fe(CN)_6$ in different systems

Figure 2 shows the cyclic voltammograms of $K_4Fe(CN)_6$ in pure water and pure IL. There is a pair of redox peaks in the pure water system, but no redox peaks in the pure IL system. This is because $K_4Fe(CN)_6$ can dissolve in water but not in [bmim]PF₆. Figure 3 shows that there are obvious redox peaks in the three IL microemulsions. This can be attributed to the fact that $K_4Fe(CN)_6$ can dissolve in these three IL microemulsions. Accordingly, the IL microemulsions can be used as electrolytes for investigating the water soluble electrochemical probes. Compared with the pure water system, the redox potentials of $K_4Fe(CN)_6$ /

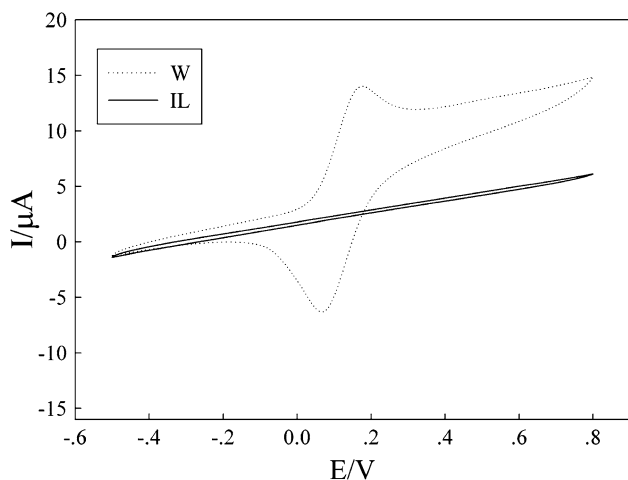


Fig. 2 Cyclic voltammograms of $K_4Fe(CN)_6$ in pure water and IL. $K_4Fe(CN)_6$ concentration: 0.01 M; scan rate: 0.025 V s⁻¹

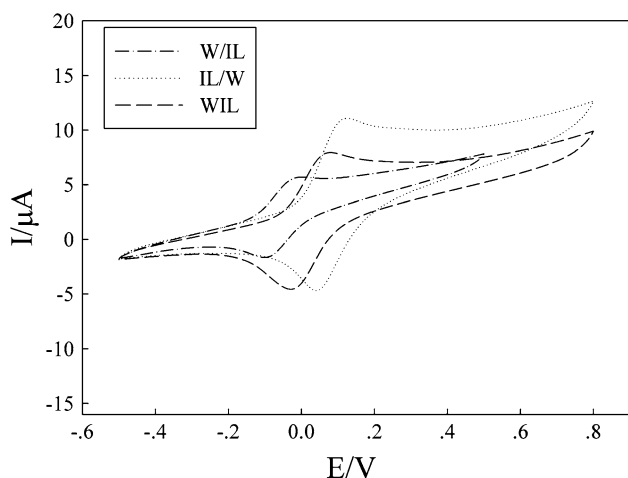


Fig. 3 Cyclic voltammograms of $K_4Fe(CN)_6$ in the three different IL microemulsions. $K_4Fe(CN)_6$ concentration: 0.01 M; scan rate: 0.025 V s⁻¹

Table 1 Redox peak currents (I_p) and peak potentials (E_p) measured from CV experiments

Systems	$E_p/V(\text{vs Ag/AgCl})$			$I_p/\mu A$		
	E_{pR}	E_{pO}	ΔE	I_{pR}	I_{pO}	I_{pR}/I_{pO}
W	0.066	0.177	111	9.272	10.01	0.926
IL/W	0.041	0.126	93	5.293	7.033	0.753
WIL	-0.028	0.080	108	4.735	4.978	0.951
W/IL	-0.103	0.002	105	2.475	2.842	0.871

$K_3Fe(CN)_6$ in IL microemulsions shift negatively, and the redox peak currents decrease in terms of IL/W, WIL, W/IL. The negative shift of the redox potentials implies that IL microemulsions may favor the redox of $K_4Fe(CN)_6$ / $K_3Fe(CN)_6$. The decrease in peak currents indicates that the mass transfer resistance in IL microemulsions, caused by their high viscosity, special microstructure, composition and way of mass transfer, is higher than that in pure water. The values of the redox peak potentials and peak currents are listed in Table 1.

As a bulk electrolyte, microemulsion is an isotropic multiphase system and has a special microstructure, so the interface of electrode/IL microemulsion is different from that of electrode/pure water. The mass transfer behavior of $K_4Fe(CN)_6$ in these two systems is also different. Figure 4 presents a module for the interfacial structure between an electrode and a W/IL microemulsion. Due to the surface activity of TX-100 and [bmim]PF₆, the electrode surface might adsorb a layer of organic film (TX-100, organic cations), which could significantly affect the electron exchange process of $K_4Fe(CN)_6$ / $K_3Fe(CN)_6$ and the reaction resistance. In W/IL, [bmim]PF₆ is the continuous phase and water is the dispersed phase. As aforementioned, there is no solubility for $K_4Fe(CN)_6$ in [bmim]PF₆, and so the $K_4Fe(CN)_6$ has to be in the water phase. Because of thermal movement, the nano-sized water dispersed phase with the dissolved $K_4Fe(CN)_6$ can pass through the organic film adsorbed at the interface of electrode/microemulsion, and

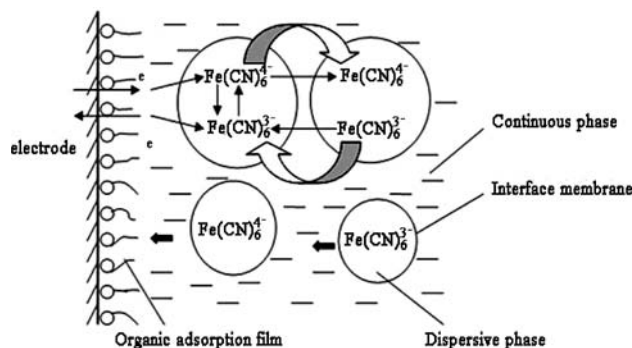


Fig. 4 Sketch map of the interfacial structure between an electrode and a W/IL microemulsion

then contact the electrode. Subsequently, the electrochemical reaction for $K_4Fe(CN)_6$ takes place. In contrast, the mass transfer of $K_4Fe(CN)_6$ in IL/W and WIL microemulsions with water as the continuous phase is similar to that in the pure water system except for a small fraction. Mass transfer of electroactive particles can affect the electrochemical behavior of $K_4Fe(CN)_6$ in the three IL microemulsions and this may be the reason for the change in redox currents.

3.3 Influence of scan rate on the electrochemical reaction of $K_4Fe(CN)_6$ in IL microemulsions

The diffusion coefficient of the probe in IL microemulsions can be determined by CV, and the structural transition of the microemulsions can be identified on the basis of the change in diffusion coefficient. The peak current (I_p) (from the relevant cyclic voltammogram) for the concentration polarisation system, can be described by Eq. 1 or 2 [27].

$$I_p = 2.69 \times 10^{-5} n^{3/2} C^0 D^{1/2} \nu^{1/2} \quad (1)$$

$$I_p = 0.496 n F \left(\frac{2.303}{b} \right)^{1/2} D^{1/2} C^0 \nu^{1/2} \quad (2)$$

where n is the number of electrons exchanged, F is the Faraday constant, C^0 is the concentration of the electroactive ions, D is the diffusion coefficient of the electroactive ions, ν is the scan rate, b is the Tafel slope, D is the apparent diffusion coefficient because $K_4Fe(CN)_6$ is soluble in water, but insoluble in [bmim]PF₆. For diffusion controlled or mixing controlled electrode reaction system, as ν increases, the amount of time needed to reach the same potential gets shorter. The diffusion layer is weaker and diffusion becomes easier; thus the current increases. Equations (1) and (2) show that I_p is related to n , D and ν in all cases and increases linearly with $\nu^{1/2}$ when other parameters are fixed.

Figure 5 shows the linear relationships between I_p and $\nu^{1/2}$ for the three different IL microemulsions. The electrochemical reactions for $K_4Fe(CN)_6$ in these three IL microemulsions are controlled by diffusion. According to Eqs. 1 and 2, D can be obtained from the slope of the plot. $D_{IL/W}$ is the largest, D_{WIL} is in the middle, and $D_{W/IL}$ is the smallest.

3.4 Influence of $K_4Fe(CN)_6$ concentration on the electrochemical reaction

In IL/W and WIL systems, the $K_4Fe(CN)_6$ apparent concentration can be changed over a relatively wide range of 0–0.08 M as water is the continuous phase. In comparison, when IL is the continuous phase, the poor solubility of $K_4Fe(CN)_6$ limits its concentration in W/IL and the result

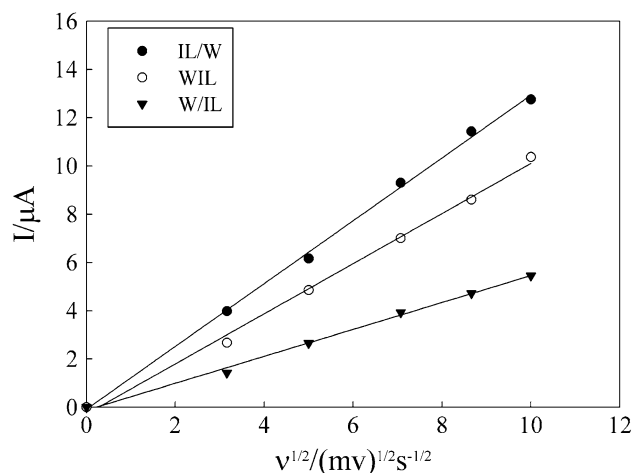


Fig. 5 Peak current I_{pO} profile as a function of $\nu^{1/2}$. $K_4Fe(CN)_6$ concentration: 0.01 M

shows that the apparent concentration of $K_4Fe(CN)_6$ can only be changed in the range 0–0.035 M.

According to Eqs. 1 and 2, I_p is linear with $K_4Fe(CN)_6$ concentration when other parameters are fixed. Figure 6 presents the influence of $K_4Fe(CN)_6$ concentration on I_p in the three IL microemulsions. In the IL/W system the plot of peak current I_p against $K_4Fe(CN)_6$ concentration is almost linear. In the WIL system, when the $K_4Fe(CN)_6$ concentration is increased to 0.04 M, the plot deviates from linearity. In contrast, in the W/IL system, not only is the $K_4Fe(CN)_6$ apparent concentration limited, but also I_p is not linear with $K_4Fe(CN)_6$ concentration. In the IL/W system where water is the continuous phase, the mass transfer behavior of $K_4Fe(CN)_6$ is similar to that in the pure water system. In the WIL system, although water is still the continuous phase, the change in the microemulsion microstructure influences the mass transfer behavior of $K_4Fe(CN)_6$. In the W/IL system,

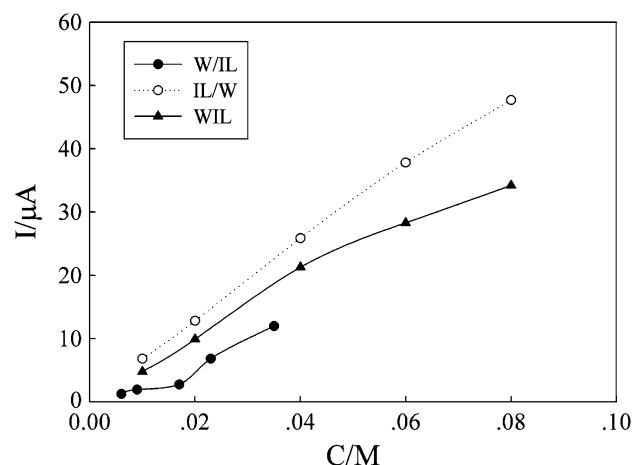


Fig. 6 Relationship between peak current I_{pO} and $K_4Fe(CN)_6$ concentration. Scan rate: $0.025 V s^{-1}$

where water is the dispersed phase, the mass transfer behavior of $K_4Fe(CN)_6$ is completely different from that in the pure water system. So, in the three different IL microemulsions, the response characteristics of I_p to $K_4Fe(CN)_6$ concentration are different.

3.5 EIS study

EIS spectra were recorded under an open circuit potential and a frequency range from 0.01 Hz to 100 kHz. A conventional three-electrode cell was used in the EIS study (a Pt disk as the working electrode, a spiral Pt wire as counter electrode and an Ag/AgCl electrode as reference). Figure 7 shows the Nyquist plots of the Pt electrode in the three IL microemulsions. The solution impedances are 750, 950, and 1,350 Ω in IL/W, WIL, and W/IL, respectively. The difference in the impedances of these three IL microemulsions may be caused by the components, microstructures and viscosities of the systems.

Both the Nyquist plots recorded in the IL/W and WIL systems have a capacitive resistance arc in the high frequency region and a straight line in the low frequency region, which is related to charge transfer and diffusion, respectively. In the WIL and IL/W systems, the solution impedances are significantly lower than the charge transfer impedances (about 3 and 8 k Ω , respectively). However, the Nyquist plot of the W/IL system is only a 45° straight line and no capacitive resistance arc is observed in the whole frequency region, indicating diffusion as the controlling step. Therefore, for the three different IL microemulsions systems, the reaction dynamic characteristics are different because of the difference in the mass transfer behavior of $K_4Fe(CN)_6$.

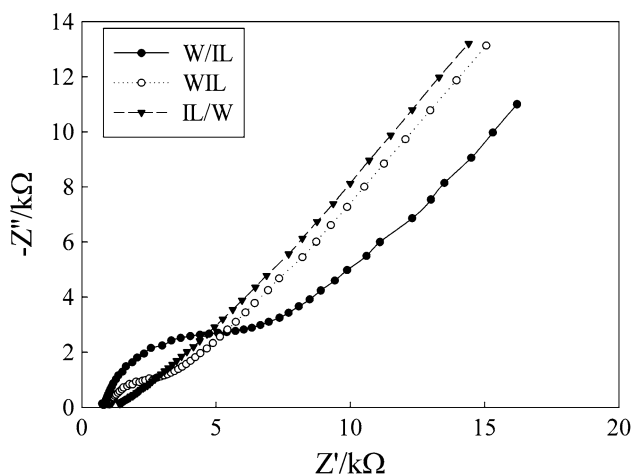


Fig. 7 Nyquist plots in the three IL microemulsions. $K_4Fe(CN)_6$ concentration: 0.01 M; frequency range: 0.01 Hz to 100 kHz; working potential: open circuit potential

4 Conclusions

The electrochemical behavior of $K_4Fe(CN)_6$ in [bmim]PF₆/TX-100/water microemulsions and pure water was investigated. CV results show that the redox potentials of $K_4Fe(CN)_6/K_3Fe(CN)_6$ shift negatively and the redox peak currents decrease in the order pure water, IL/W, WIL, W/IL. The redox peak currents of the three IL microemulsions increase linearly with the square root of scan rate and the diffusion coefficient increases as W/IL, WIL, IL/W. EIS measurements indicate that for the IL/W and WIL systems, the electrochemical reactions are controlled by charge transfer and diffusion steps at high and low frequencies, respectively. For the W/IL system, diffusion is the controlling step at all frequencies. The environmental-friendly IL microemulsions overcome many disadvantages of traditional organic microemulsions and pure ionic liquids, and are expected to have potential applications in many fields, such as nanomaterials preparation and electrochemical and chemical reactions.

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