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ORIGINAL CONTRIBUTION

Research on electrochemical properties of nonaqueous ionic liquid microemulsions

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Abstract The nonaqueous ionic liquid (IL) microemulsions composed of 1-butyl-3-methylimidazolium tetrafluoroborate, Triton X-100, and toluene were prepared and the electrochemical properties of the nonaqueous IL microemulsions were investigated in this paper. It is shown that characteristics of the nonaqueous IL microemulsions such as electrical conductivity, electrochemical window, and solubility are good, which indicate that the nonaqueous IL microemulsions can be used as electrolyte for electrochemical research. The electrochemical properties of the nonaqueous IL microemulsions were researched by cyclic voltammetry (CV) and electrochemical impedance spectroscopy methods using potassium ferricyanide as electroactive probe. It was found that the reversibility was better and the peak current densities of CV were higher for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrode reaction in the nonaqueous IL microemulsions than those in IL. However, the electrochemical behavior of the probe in the nonaqueous IL microemulsions with different microenvironments (oil-in-IL, IL-in-oil, and bicontinuous) was different. The electrochemical property of the probe in the oil-in-IL microemulsion was the best, which was studied in detail.

Keywords Nonaqueous ionic liquid microemulsions · Potassium ferricyanid · Cyclic voltammetry · Electrochemical properties

Introduction

Ionic liquids (ILs), composed of an organic cation and either an organic or an inorganic anion, have received a great deal of attention recently. Compared to conventional solvents, ILs have a class of interesting and unusual properties, such as nonvolatility, nonflammability, high thermal stability, suitable polarity, and wide electrochemical window [1–3]. Due to these special properties, ILs have been widely used in material preparation, chemical synthesis, and biology technology. ILs have a series of advantages over aqueous solution because of its nonaqueous medium and wide electrochemical window. In electrochemistry field, ILs have been widely investigated in metal eletrodeposion[4, 5], capacitor[6, 7], biosensor[8, 9], electropolymerization[10, 11], and battery [12, 13]. Nevertheless, the electrochemistry systems constructed by ILs have some disadvantages compared with the electrochemistry system constructed by aqueous electrolyte. This is because ionic liquids have higher viscosity, lower conductivity, weaker solubility for some organic and inorganic compounds, and stronger surface activity, which limit the study in IL electrochemistry reactive system. To overcome these disadvantages, using surfactants to form IL microemulsions is an alternative method.

Microemulsions are unique class of thermodynamically stable isotropic dispersions of two or more immiscible liquids which are stabilized by an adsorbed surfactant film at the liquid–liquid interface [14]. Conventional microemulsions, which are composed of water, oil, and surfactant, can be classified as water-in-oil (W/O), oil-in-water (O/W), and bicontinuous phase. Different types of microemulsions have different functions. Microemulsions have been extensively investigated in a variety of fields, such as chemical reaction, separation, drug delivery, material

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synthesis, etc. [15–19]. One of the important applications of microemulsions involves the preparation of nanoparticles, nanowires, and nanorods [20–22]. The electrochemical properties of microemulsions have also been investigated by some workers [14, 23–25]. Recently, we have researched the electrochemical properties of a reverse microemulsion, and the results indicated that the electrode process at the electrode–microemulsion interface was different from that at the electrode–aqueous solution interface [20].

More recently, there are several papers demonstrated that IL could substitute water or oil to form novel microemulsions in the presence of surfactant. Han reported that 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$) can substitute water to form a nonaqueous IL microemulsion with surfactant, and the microemulsion droplets were of the same shape contrast to "classic" droplets of W/O microemulsion [26]. Zheng investigated the microstructures and structural transition of $bmimBF_4$/Triton X-100/toluene three-component nonaqueous microemulsion in which $bmimBF_4$ was used as a substitute for water. Three different microenvironments: IL-in-oil (IL/O), bicontinuous, and oil-in-IL (O/IL) were differentiated by electrical conductivity [27]. Apparently, the changes in the composition and microstructure of nonaqueous IL microemulsions result in the changes of the electric conduction mechanism and electrochemical reactive characteristic of the systems. We can firmly believe that the electrochemical system constructed by electrode and IL microemulsion is totally new; the interfacial structure and electrochemical properties of electrode–ionic liquid microemulsions are quite different from those of electrode–aqueous solution, electrode–ionic liquids, and electrode–traditional microemulsion (W/O or O/W). And, IL microemulsions as electrolytes for electrochemistry study are also special and different from traditional aqueous and conventional microemulsion electrolytes. The research on the electrochemical properties of IL microemulsion is of theoretic and practical significance. In this paper, $bmimBF_4$/Triton X-100/toluene microemulsions were prepared. Electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were applied to study the properties of nonaqueous IL microemulsions using potassium ferricyanide as electroactive probe.

Experimental

Reagents and materials

Triton-100 [$CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_9H$] ($M$=646.86 g mol^{-1}, d_{25}=1.07 g mL^{-1}) was obtained from Alfa Aesar, $bmimBF_4$ (>98%) was purchased from Hangzhou Kemo Co. and dehydrated at 80 °C under vacuum until the weight was consistent. Toluene and $K_3Fe(CN)_6$ were provided by Changsha Chemical Reagent Corporation. Double distilled water was used throughout this study. In all the experiments, the samples were sealed in order to avoid absorption of moisture.

Apparatus and procedures

The nonaqueous IL microemulsions were prepared as reported [27]. The high-speed centrifuge (Eppondorf Centrifuge 5804 R, German) was employed to characterize the IL microemulsions by setting the mixture in the centrifuge with a speed of 10,000 r/min for 5 min. Electrical conductivity measurements were carried out using a conductivity meter (DDS-307, Shanghai Rex Instrument Factory).

Electrochemical experiments were carried out with a CHI model 660B electrochemical workstation (Shanghai Chenhua Instrument Factory, China) with a three-electrode cell, which consisted of a glass carbon working electrode (S=0.0314 cm^2), a platinum wire counter electrode, and a silver wire reference electrode [28]. All potentials were measured versus the reference electrode. Prior to each experiment, the glass carbon electrode was polished to a mirror finish using alumina powder and then was ultrasonicated in ethanol and double distilled water for 5 min, respectively. For CV, the potential was scanned from −0.1 to 0.8 V, and the scan rate range was 20–150 mV s^{-1}. All the experiments were conducted under a nitrogen atmosphere to avoid the effect of water and oxygen at 25±1 °C.

Results and discussion

Characteristics of the nonaqueous IL microemulsions study

Electrical conductivity measurement has been widely employed to study microemulsion systems. Nonaqueous IL microemulsions can be divided into three different microenvironments: IL-in-oil, bicontinuous, and oil-in-IL, and electrical conductivity measurement can identify these microemulsions [27, 29, 30]. Figure 1 illustrates the variation of electrical conductivity of the nonaqueous IL microemulsion as a function of toluene weight at fixed $bmimBF_4$-to-Triton X-100 weight ratio of 0.25 at 25 °C. From Fig. 1, it can be seen that the electrical conductivity increased at first and then decreased with the increasing of toluene. Obviously, the main contribution to the conductivity in the nonaqueous IL microemulsions is IL. The initial increase of electrical conductivity results from the successive increase of conductive O/IL microemulsion droplets. With the adding of toluene, the nonlinear decrease of the electrical conductivity indicated the change of the micro-

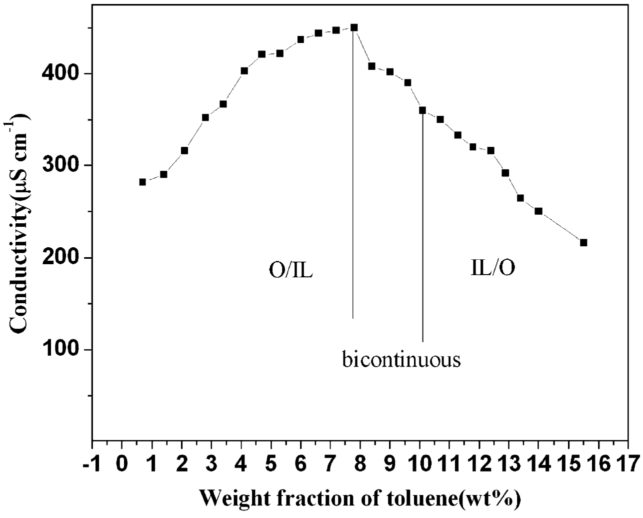

Fig. 1 The electrical conductivity of the nonaqueous IL microemulsion as a function of toluene weight fraction at fixed bmimBF$_4$-to-Triton X-100 weight ratio of 0.25 at 25 °C

structure of the microemulsion and the formation of bicontinous phase. The successive decrease with linearity of the electrical conductivity with increasing toluene content revealed that the microemulsion converted to IL/O microemulsion in which the continuous phase was oil which was nonconductive [27].From Fig. 1, it also can be concluded that the electrical conductivity of the nonaqueous IL microemulsion varied because of its different microstructure; and for the same type of microstructure, the electrical conductivity also varied due to the different compositions of the microemulsion. However, all the three types of the nonaqueous IL microemulsions have good electrical conductivity. Meanwhile, experiments showed that the electrochemical window of the nonaqueous IL microemulsion is the same as that of IL; the nonaqueous IL microemulsions can solubilize larger amount of various solutes than IL. It is possible for nonaqueous IL microemulsions to be used as electrolytes for electrochemical research.

Cyclic voltammetric characteristics of the nonaqueous IL microemulsions

CV measurements were carried out to characterize the nonaqueous IL microemulsions using potassium ferricyanide as electroactive probe. Figure 2 shows the CV curves of the glass carbon electrode in IL and nonaqueous IL microemulsions with different microenvironments. Comparing curve (a) with curves (b)–(d) in Fig. 2, it is clear to note that the electrochemical behavior of the probe in IL and nonaqueous IL microemulsions was totally different. For the CV of IL system (as shown in curve a), the anodic and cathodic peak current densities were almost equal of about 0.007 mA cm^{-2}, the anodic and cathodic peak potentials were 0.550 and 0.344 V, and the separation between the anodic and cathodic peak potentials (ΔE_p) was about 206 mV, suggesting an irreversible electron-transfer process. For the CV of O/IL microemulsion (as shown in curve d), the anodic and cathodic peak potentials were 0.206 and 0.142 V, the ΔE_p was about 64 mV, and the anodic and cathodic peak current densities were almost equal of about 0.022 mA cm^{-2}, indicating a fast electron transfer reaction and a reversible redox couple. For the CV of bicontinuous microemulsion (as shown in curve c), the anodic and cathodic peak potentials were 0.206 and 0.136 V, the ΔE_p was about 70 mV, and the peak current densities of the anode and cathode were almost equal of about 0.019 mA cm^{-2}, which were a little smaller than those in the O/IL microemulsion system. The redox couple in it could also be regarded as reversible. For the IL/O microemulsion system (as shown in curve b), the anodic and cathodic peak current densities were about 0.016 mA cm^{-2}, the anodic and cathodic peak potentials were about 0.290 and 0.010 V, and the ΔE_p was about 190 mV, which suggested that the redox couple was irreversible.

Comparing curve (a) with curves (b)–(d), it is obvious that the electrochemistry property of the probe in nonaqueous IL microemulsion was better than that in IL, which indicated that the addition of surfactant and oil changed the composition and structure of the electrolyte and then made the conduction mechanism and the interfacial structure changed. From curves (b)–(d), it can be known that the microenvironment of the nonaqueous IL microemulsions influenced the probe's electrochemical property. The electrochemical reactive characteristic of the probe in the

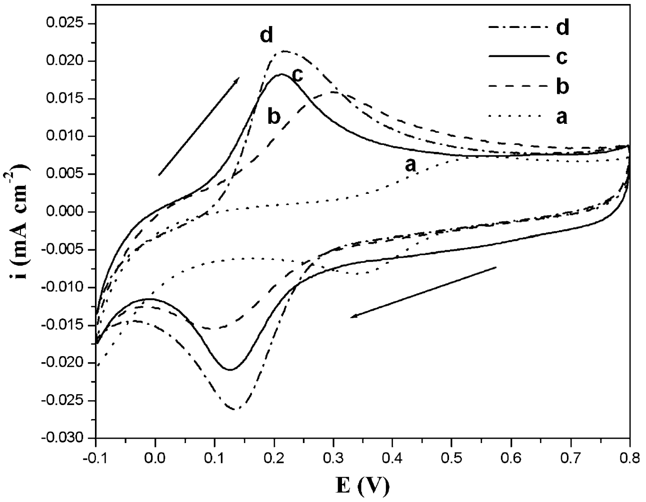

Fig. 2 CV curves of glass carbon electrode in *a* IL(bmimBF$_4$), *b* IL/O microemulsion (7.1% IL + 54.9% Triton X-100 + 38% toluene), *c* bicontinuous microemulsion (13.4% IL + 62.5% Triton X-100 + 24.1% toluene), *d* O/IL microemulsion (19.2% IL + 78.1% Triton X-100 + 2.7% toluene), in which the same apparent concentration (3.27 mmol L^{-1}) of probe was added. Scan rate: 50 mV s^{-1}

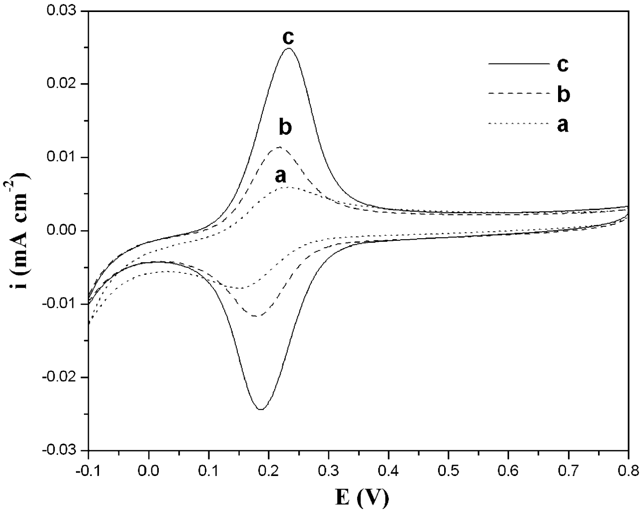

Fig. 3 CV curves of glass carbon electrode in the nonaqueous IL microemulsion with different probe apparent concentrations *a* 0.97 mmol L^{-1} *b* 2.03 mmol L^{-1} *c* 4.45 mmol L^{-1}. Scan rate: 50 mV s^{-1}

microemulsuion whose continuous phase was IL was much better than that in the microemulsion whose continuous phase was oil. This may be because the continuous phase was toluene and the probe was not solubilized in it, so it is hard for the electrochemical reaction to occur at the interface between the microemuluion and electrode; thus, the anodic peak potential shifted positively and the current became smaller. It is noticeable that although the continuous phase of microemulsion was oil, the electrochemical behavior of the probe was also better than that in IL. In the IL/O microemulsion, the electrochemical probe could be solubilized in the IL dispersed-phase and the surfactant interface membrane. Due to the structure characteristic of microemulsion, the dispersion of the probe in the microemulsion was asymmetric, which was different from that in the pure IL. And, although the apparent concentration of the probe was the same, the real concentration in the local microemulsion was higher than that in the pure IL because the probe cannot be solubilized in toluene. And, the electrode reaction can take place only when the droplets containing probe collide with the electrode by Brownian motion, so the electrochemical behavior of the probe in the microemulsion is also different from that in the pure IL. These may be the reasons why the electrochemical properties were improved. The influence of microenvironments on electrochemistry properties of nonaqueous IL microemulsions will be studied in detail in our future work. The results above indicated that the nonaqueous IL microemulsions had promising electrochemical properties and some metal salts or biochemicals can be solubilized in them [31], which makes the nonaqueous IL microemulsions as nanoreactors possible for chemical and electrochemical applications. Because O/IL microemulsion had the best electrochemical properties in our experiments, we choose it for further investigation as shown in the following sections.

Effect of scan rate, probe apparent concentration, and temperature on i_p of CV in O/IL microemulsion

In CV, the peak current density i_p for a reversible system was described by the Randles–Sevcik equation [14]:

$$i_p = 0.447 F^{\frac{3}{2}} A n^{\frac{3}{2}} D^{\frac{1}{2}} C v^{\frac{1}{2}} R^{-\frac{1}{2}} T^{-\frac{1}{2}}$$

where n is the number of electrons involved in oxidation or reduction, A is the area of the working electrode, D is the diffusion coefficient of the electroactive probe, C is the concentration of electroactive probe, v is the scan rate, F is the Faraday constant, R is the gas constant, and T is the absolute temperature.

The effect of scan rate on the peak current density was investigated. As expected from the Randles–Sevcik equation, the peak current densities increased linearly with the square root of scan rate. The results indicated that the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrode reaction in the O/IL microemulsion was diffusion controlled.

Figure 3 shows the effect of probe apparent concentration on CV in O/IL microemulsion. It can be seen from Fig. 3 that the peak potential was almost invariable and the redox peak current densities increased with the increasing of the probe apparent concentration. From the Randles–Sevcik equation, the diffusion coefficient values (D) of the probe with different concentrations could be calculated, and we found that the D values were nearly consistent. The reason may be that the shape and size of the droplets were

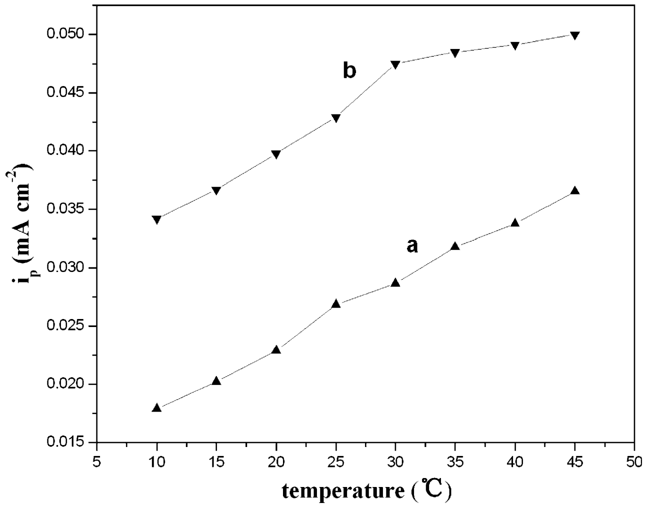

Fig. 4 The peak current density on CVs as a function of temperature: 10, 15, 20, 25, 30, 35, 40, 45 °C in the nonaqueous IL microemulsion: 18.4% IL + 73.8% Triton X-100 + 7.8% toluene with 3.2 mmol L^{-1} probe apparent concentration. Scan rate for curve a=10 mV s^{-1}, curve b=50 mV s^{-1}

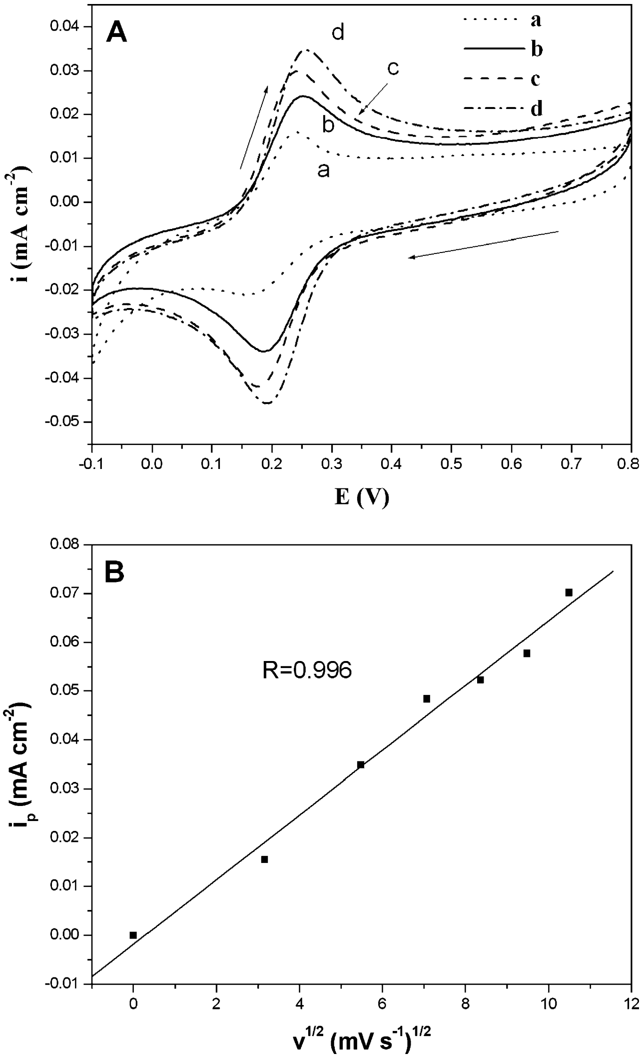

Fig. 5 **a** CV curves of glass carbon electrode in the nonaqueous IL microemulsion (18.7% IL + 76.0% Triton X-100 + 5.3% toluene) using 2.5 mmol L^{-1} $K_3Fe(CN)_6$ as probe with different weight fraction of water: *a* 0%, *b* 1.5%, *c* 1.8%, and *d* 2.1%. Scan rate: 50 mV s^{-1}. **b** The peak current density as a function of the square root of scan rate in the nonaqueous IL microemulsion with 1% weight fraction of water. Scan rate: 10~110 mV s^{-1}

not disturbed by the presence of the electroactive probe [27]. According to the results above, it could be deduced that the apparent concentration of the electroactive probe had little effect on the diffusion coefficient value at a certain range of the probe apparent concentration.

The effect of temperature on i_p of CV in O/IL microemulsion has also been studied. From Fig. 4, it can be observed that the peak current densities increased slowly with the increasing of temperature at different scan rates. This may be because that the viscosity of the microemulsion decreased and the size and distribution of the droplets were changed when the temperature increased, and thus resulted in the augment of the diffusion coefficient values, so the peak current densities increased. The results above showed that temperature had an influence on the electrochemical property of O/IL microemulsion.

The effect of small amount of water on O/IL microemulsion

The IL microemulsion system is nonaqueous, so the effect of addition of small amount of water in O/IL microemulsion has been studied. From Fig. 5a, it is clear to note that all the curves (with and without water) displayed similar characteristics, there was a pair of redox peaks between 0.2 and 0.3 V, which implied that the electrochemical behavior of the probe in the microemulsion had not been changed by the addition of small amount of water. It can also be observed that the peak current densities increased with the increasing of the weight fraction of water. This may be due to the increase of the electrical conductivity and the decrease of the interaction between droplets in the microemulsion system [32]. The results indicated that the addition of small amount of water had improved the electrochemical property of the microemulsion system.

The relationship between i_p and $v^{1/2}$ for the O/IL microemulsion with 1% weight fraction of water has also been investigated. From Fig. 5b, it can be observed that a plot of i_p versus $v^{1/2}$ was linear, which implied that the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrode reaction in this microemulsion system was also diffusion controlled. The result indicated that the addition of small amount of water had not changed the controllable step for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrode reaction.

In order to obtain more electrochemical information about the nonaqueous IL microemulsion, EIS measurement has been carried out. Figure 6 depicted the Nyquist plots of the glass carbon electrode in the nonaqueous IL micro-

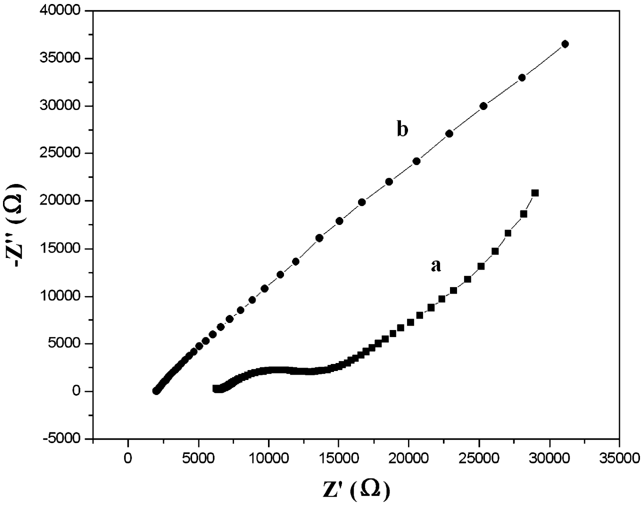

Fig. 6 The Nyquist plots of the electrochemical impedance spectroscopy of the glass carbon electrode in the nonaqueous IL microemulsion (*curve a*) and in the same microemulsion system with addition of 1% weight fraction of water (*curve b*)

emulsion (curve a) and the same microemulsion system with addition of 1% weight fraction of water (curve b). Fig. 6a presented a depressed semicircle at the high frequency region and an about 45° straight line at the low frequency region. The depressed semicircle at high frequency region represented the charge-transfer process, which was usually described by the charge transfer resistance R_{ct}. The line at low frequency region could be explained as the diffusion-controlled which was attributed to Warburg impedance. These features indicated that the electrode process was limited by both charge-transfer kinetics and diffusion step [33, 34]. However, the curve (b) was just an about 45° straight line at all frequencies, which was attributed to Warburg impedance. The result indicated that the electrode process was only limited by diffusion step, which was consistent with the result of CV experiment.

Conclusions

The nonaqueous IL microemulsions have a good electrical conductivity, wide electrochemical window, and better solubility, which can be used as electrolytes for electrochemistry research and application. The CV results indicated that the nonaqueous IL microemulsions compared to IL had special electrochemical properties for the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ electrode reaction. The microenvironments of the nonaqueous IL microemulsions not only influenced their electrical conductivity, but also influenced the reversibility of the electrochemical reaction. The results revealed that the reversibility of the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ electrode reaction in O/IL and bicontinuous microemulsion systems was better than that in IL/O microemulsion and IL. The $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ electrode reaction in the O/IL microemulsion was diffusion controlled and the probe apparent concentration had little effect on the diffusion coefficient *D* values. The effect of small amount of water on the O/IL microemulsion has also been studied, and it was shown that the addition of small amount of water to the O/IL microemulsion contributed to the better electrochemical behavior for the probe. So, this work is helpful for the attempt of using nonaqueous IL microemulsion as electrolyte for electrochemical applications such as nanomaterial synthesis and electroplating.

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