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Cyclic voltammetry investigation of diffusion of ferrocene within propylene carbonate organogel formed by gelator

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ABSTRACT

Propylene carbonate organogel containing $LiClO_4$ was formed in the presence of gelator bis-(4-stearoylaminophenyl) methane (BSAPM). The electrochemical behavior and diffusion of ferrocene (Fc) and ferricenium (Fc^+) entrapped within the organogel was investigated by cyclic voltammetry. The Fc molecules still show redox activity within the organogels in comparison with corresponding solutions of propylene carbonate containing $LiClO_4$. The shape of the cyclic voltammograms of the Fc electrooxidation in organogel was similar to that in corresponding solutions. The results indicated that redox reactions of Fc/Fc^+ were a quasi-reversible process of diffusion-controlled single electron transfer in organogels. The diffusion coefficients of Fc and Fc^+ in organogels decreased with an increase of the concentration of gelator BSAPM, but increased with an increase of temperature. The temperature dependence of the diffusion coefficient in organogels followed classical Arrhenius equation. The activation energy in organogels was found of no difference from that in corresponding solutions.

1. Introduction

Organogels formed by self-assembly of low molecular-weight gelators (LMWGs) in organic solvents through the intra- or intermolecular non-covalent interactions such as hydrogen bonding, π–π stacking, Van der Waals, etc. are a class of supramolecular materials [1,2]. As stable matrix materials, some small molecules such as organic dyes and drugs can be entrapped in organogels by simply adding them to the sol prior to its gelation. Therefore, a better understanding of the mass transfer behavior of small molecules in organogel is required not only for the development of fundamental research on host/guest interaction, but also for potential applications such as drug delivery and gel electrolytes.

Cyclic voltammetry, an efficient and convenient approach for the *in situ* characterization of mass transfer of probe molecules, has been used to evaluate the diffusion of redox-active reagents in many systems [3–6]. In addition, because the redox reaction of ferrocene/ferricenium (Fc/Fc^+) is reversible or Nernstian in most organic solvents and the redox potential of Fc/Fc^+ couple is little influenced by such solvents, Fc is usually chosen as redox probe for non-aqueous system [7]. Opallo and Kukulka [8] and Walkiewicz [9] reported the electrochemical behavior of Fc encapsulated in silica with embedded organic electrolyte by cyclic voltammetry, chronoamperometry, differential pulse voltammetry and impedance spectroscopy on ultramicroelectrodes. The results showed that the shape of the cyclic voltammograms corresponding to the electrooxidation of Fc was similar to that in liquid electrolyte. They also pointed out that the precursor, salt and solvent affected the motion rate of the redox probe. Reiter et al. [10] reported investigation of electrochemical properties of Fc in polymer (polymethylmethacrylate, PMMA) gel electrolytes by cyclic voltammetry and impedance spectroscopy using new solid-state PMMA–Cd–Cd^{2+} reference electrode. They found that the apparent diffusion coefficients of Fc and Fc^+ decreased by three orders during the polymerization from the liquid monomer to the gel polymer. The diffusion of small molecules in other polymer gels has also been extensively investigated [11].

However, to our knowledge, few studies concentrating on the diffusion in the supramolecular organogel have been reported. Galindo et al. [12] investigated the fluorescence quenching in organogel and found that a standard photochemical electron-transfer reaction could take place in organogel at a reaction rate analogous to that in pure liquid. Their result indicated that the gel status seemed to present no limitation to the diffusion of probe molecules. As we and other researchers reported previously, the conductivity of organogel formed by self-assembly of gelators was practically identical in comparison with corresponding solution at the same temperature [13,14]. But the conductivity of polymer gel electrolytes remains several orders of magnitude lower than that of liquid electrolytes [15]. To date, no study on diffusion of

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redox molecules in organogels by cyclic voltammetry has been reported.

In present work, we report electrochemical behavior of a redox probe entrapped in propylene carbonate (PC) organogels formed by self-assembly of gelator bis(4-strearoylaminodiphenyl) methane (BSAPM) [16]. Fc was used as a model compound. Electrochemical behavior and mobility of Fc and Fc^+ couple in PC organogels and corresponding PC solutions was investigated by cyclic voltammetry using conventional glassy carbon (GC) electrode.

2. Experimental

2.1. Materials

The gelator, bis(4-stearoylaminodiphenyl) methane was synthesized according to a method described previously and identified by IR, ^1H NMR and elemental analysis [16]. Ferrocene (Fc, 99%, Aldrich) was recrystallized from 95% ethanol. $LiClO_4$ (analytical grade, Sinopharm Chemical Reagent Co.) was dried at 120 °C in vacuum and used as the supporting electrolyte. Propylene carbonate (PC, 99.7%, Aldrich) was distilled before use. Water was purified with a Millipore water purification system. The PC solution containing lithium salt (0.1 mol/L) and Fc (1 mmol/L) was prepared by dissolving $LiClO_4$ and Fc in PC (the solution was designated as Fc/Li/PC solution) [10]. In a typical organogel preparation, BSAPM (1.2, 2, 2.5, 3 and 4 wt%) was added into Fc/Li/PC solutions and subsequently heated until the solid completely dissolved. The solutions were then allowed to cool to room temperature. The resulted organogels (designated as Fc/Li/PC organogel) exhibited no gravitation flow. Similarly, the organogels (designated as Li/PC organogel) were prepared by adding BSAPM in Li/PC solutions (without Fc). All the other reagents used in the experiments were of analytical grades and used as received. All preparations were carried out in an Ar-filled glove box.

2.2. Characterization of the organogels

Transmission electron microscopy (TEM) was performed on a JEOL 1200EX electron microscopy at 80 kV, and the samples were prepared by placing some organogel onto a formar/carbon-coated copper grid (300 meshes) and then removing the excess organogel after 1 min and allowing the samples to dry overnight at room temperature before imaging. All gel–sol phase transition temperatures (T_{GS}) were determined using “dropping ball” method [17], which consists of carefully placing a stainless steel ball (55 mg, 1.5 mm in diameter) on top of already prepared gels in 4 mL glass vials and subsequently placing these vials in an oil bath. The temperature of the oil bath was increased by 2 °C/min and the T_{GS} was defined as the temperature at which the steel ball reaches the bottom of the vial.

The Li/PC solution or the Li/PC organogel was placed in a glass cell with a platinum electrode (Pt 260, Shanghai Leici). Ionic conductivities of the solution and the organogel were measured by the impedance technique (IM6e electrochemical working station, Zhanner, Zview software) in a frequency range from 50 mHz to 1 MHz.

2.3. Cyclic voltammetry

Cyclic voltammetry was performed using a Princeton Applied Research VersaStat II potentiostat (AMETEK, NT, USA). A cylindrical glass cell (30 mm × 50 mm) equipped with three electrodes was used for all experiments. The desired temperature was maintained by a constant temperature box with a precision of ±0.5 °C. A glassy carbon disc electrode cemented in PTFE rod (GC; 2.7 mm disk diameter, Tianjin Aida Hengsheng Technology Ltd. Co., China) was used as a working electrode, and Platinum wire (1 mm in diameter) was served as a counter electrode. The Ag/AgCl reference electrodes were prepared by electrochemically depositing AgCl on a clean silver wire followed by aging for at least one day. The surface of GC electrode was freshly polished by alumina powder, and then cleaned by sonication in diluted nitric acid followed by sonicate in acetone and water before use.

Five milliliters of Fc/Li/PC hot solution containing BSAPM was placed in the cylindrical glass cell in the constant position and allowed to form organogel after cooling at room temperature. Similarly, 5 mL of Fc/Li/PC solution without BSAPM was placed in the cylindrical glass cell. The samples of organogel were allowed to stand for 0.5 h at room temperature and equilibrated at desired temperature (298, 313, 323 and 333 K) for 12 h. Cyclic voltammograms were recorded at least in triplicate from 0.0 to 0.7 V at scan rates of 0.02–0.2 V/s and peak currents were measured after background subtraction. All preparation and measurements were performed in an Ar-filled glove box.

3. Results and discussion

3.1. Gel–sol phase transition temperatures (T_{GS}) and microstructure of Fc/Li/PC/organogel

BSAPM exhibits excellent gelation ability for many organic solvents [16], not only for common solvents, such as benzene, chloroform, *n*-butanol, etc. but also for some solutions containing salts, such as $LiClO_4$/PC solution. It is well known that $LiClO_4$/PC solution is extensively used as electrolyte in lithium battery. In present work, white, homogeneous opaque organogels were prepared by adding gelator BSAPM (1.2 wt%) into PC containing 0.1 mol/L of $LiClO_4$. This organogel shows good stability for months. Generally, the stability of organogels can be characterized by T_{GS} which responsible to the concentration of gelator. Fig. 1 shows effect of BSAPM concentration on the T_{GS} of Li/PC organogels with or without Fc. As expected, gel–sol transition temperatures increase with an increase of BSAPM concentration. The presence of Fc (1 mmol/L) in organogels seems to be no influence on the stability of organogels.

Fig. 2 shows TEM images of Li/PC organogel formed by BSAPM. The BSAPM molecules spontaneously self-assembled into entangling ribbon-like aggregates with average width of 300–700 nm and

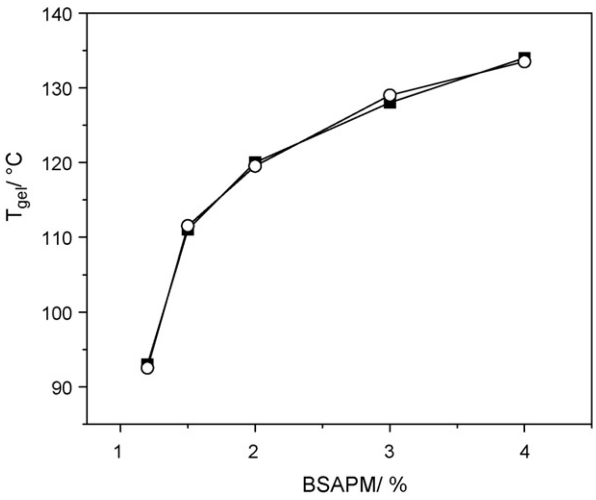

Fig. 1. The dependence of BSAPM concentration on T_{GS} of Li/PC organogel (■) and Fc/Li/PC organogel (○).