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室温离子液体[BMIM]BF₄中马来酸和马来酸酐的电
化学还原及原位红外光谱研究

**Electrochemical Reduction of Maleic Acid and Maleic
Anhydride in [BMIM]BF₄ Room Temperature Ionic Liquid and
In situ FTIR Spectroscopic Studies**

楼 乔 奇

指导教师姓名: 陈 声 培 副 教 授

孙 世 刚 教 授

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**Electrochemical Reduction of Maleic Acid and Maleic
Anhydride in [BMIM]BF₄ Room Temperature Ionic Liquid and
In situ FTIR Spectroscopic Studies**



A Dissertation Submitted to the Graduate School of Xiamen University

for the Degree of

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By

Qiao-Qi Lou

This work was carried out under the supervision of

Associate Prof. Sheng-Pei Chen

Prof. Shi-Gang Sun

At

Department of Chemistry, Xiamen University

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摘 要

室温离子液体是指在室温或接近室温温度下由阴阳离子组成的液态物质, 具有不挥发、不易燃、电化学窗口宽、电导率高、可循环使用等优点。近几年来, 室温离子液体因其独特的物理化学性质, 作为绿色溶剂或电解液在基础研究和工业应用等方面都引起了极大的关注。迄今为止将离子液体应用于有机电合成方面的研究尚处于起步阶段。本论文自行合成1-丁基-3-甲基咪唑四氟硼酸盐 ([BMIM]BF₄) 室温离子液体, 以此为电解液, 研究了马来酸及马来酸酐的电还原过程。主要内容和结果如下:

1. 采用两步合成法成功制备了离子液体[BMIM]BF₄, 并用微波辐射的新方法制备了[BMIM]Cl, 同时运用 FTIR、NMR 和循环伏安法对[BMIM]BF₄ 的结构和性能进行表征。发现[BMIM]BF₄ 具有宽阔、稳定的电化学窗口(-2.0~2.0V), 在电化学研究中具有一定的优势。

2. 运用电化学循环伏安法研究了离子液体中马来酸在不同电极上的电化学反应还原过程, 测定了马来酸的扩散系数 D , 进而求得标准反应速率常数 K_s 。研究结果指出马来酸在 GC 电极上还原是受扩散控制的不可逆过程, 测得扩散系数 $D=8.96 \times 10^{-8} \text{cm}^2/\text{s}$, 标准反应速率常数 $K_s=2.10 \times 10^{-4} \text{cm/s}$; 在 Pt 电极上的还原则为受扩散控制的准可逆过程, 测得 $D=1.00 \times 10^{-7} \text{cm}^2/\text{s}$, $K_s=1.75 \times 10^{-4} \text{cm/s}$ 。

3. 运用电化学原位红外光谱从分子水平研究了离子液体中马来酸电化学反应还原的机理。结果指出, 离子液体中马来酸的一个羧基首先发生还原, 获得一个电子生成阴离子自由基, 随后可能发生两个反应: (1) 阴离子自由基再获得一个电子, 生成二价阴离子; (2) 阴离子自由基再获得一个电子, 在 2 个 H⁺作用下生成醛类物质和水。

4. 运用电化学循环伏安法和电化学原位红外光谱技术研究了离子液体中马来酸酐的电化学反应还原过程。研究结果指出, 在离子液体中马来酸酐电化学反应还原为受扩散控制的不可逆反应, 生成CO₂和丙烯酸。

本文的研究结果充分显示室温离子液体在有机分子电还原过程中的独特作用, 对于电化学基础研究和拓展离子液体在有机电合成中的应用具有重要意义。

关键词: 室温离子液体 有机电合成 电化学原位红外光谱

Abstract

Room-Temperature Ionic Liquids (RTILs) are those materials that are composed anions and cations and are liquids at or near room temperature. The RTILs exhibit wide electrochemical windows, negligible vapor pressures and high ionic conductivities, and have attracted extensive attentions in fundamental research and industrial applications. As a green solvent or electrolyte the RTILs present interests in organic electrosynthesis. In this thesis, 1-butyl-3-methylimidazolium tetrafluoroborates ([BMIM]BF₄) ionic liquid has been synthesized and used as solvent and electrolyte, with which the electrochemical reduction of maleic acid and maleic anhydride were studied using cyclic voltammetry (CV) and *in situ* FTIR spectroscopy. The main results are as follows.

1. The ionic liquid [BMIM]BF₄ was synthesized by two steps and characterized by FTIR, NMR and CV. The [BMIM]BF₄ exhibits a wide and stable electrochemical windows (-2.0V~2.0V), and presents certain advantages in electrochemical research.

2. The electrochemical reduction of maleic acid in ionic liquid at various electrodes have been studies by cyclic voltammetry. The diffusion coefficient D of maleic acid and the reaction rate constant K_s were determined quantitatively. The results illustrated that the reaction of maleic acid on GC electrode is taken place as an irreversible process controlled by diffusion. The diffusion coefficient D of maleic acid has been determined to be $8.96 \times 10^{-8} \text{ cm}^2/\text{s}$, the K_s $2.10 \times 10^{-4} \text{ cm/s}$. While the reaction at Pt electrode is a quasi-reversible process controlled also by diffusion, The D is $1.00 \times 10^{-7} \text{ cm}^2/\text{s}$, and the K_s $1.75 \times 10^{-4} \text{ cm/s}$.

3. The electrochemical reduction mechanism of maleic acid in [BMIM]BF₄ ionic liquid was investigated by *in situ* FTIR spectroscopy. The results demonstrated that the reduction of maleic acid in ionic liquid is occurred on one carboxyl. The first step of maleic acid reduction is to form radical anion, which reduces successfully either to generate dianion species or produce aldehyde species and water as a result of interaction of two protons.

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