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COMMUNICATION

The electrochemical oxidation of toluene catalysed by Co(II) in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide

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The electrochemical oxidation of toluene in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[bmpyr]^+[Ntf_2]^-$) was investigated by cyclic voltammetry and galvanostatic electrolysis in presence of Co(II) at the Pt disc working electrode. Cyclic voltammetry (CV) investigations revealed that Co(II)-Co(III) oxidation is a diffusion controlled electron transfer process. The diffusion co-efficient values of Co(II) were found to increase from 0.38×10^{-7} to 1.9×10^{-7} cm^2/s as the temperature was increased from 25 °C to 80 °C. The CV peak current for toluene electro-oxidation has increased nearly by 7 fold in presence of Co(II) demonstrating a good catalytic effect. Co(II) catalysed galvanostatic electrolysis of toluene at room temperature has shown that benzaldehyde has formed along with a small quantity of 3-methyl-1-hexanol.

Introduction

Room temperature ionic liquids (RTILs) are of much interest electrochemically for various applications such as batteries, fuel cells, capacitors and electrochemical sensors due to their unique physicochemical properties viz., wide electrochemical potential window (compared to aqueous systems), moderate conductivity, high thermal stability and tailored solubility towards hydrophilic and hydrophobic substances.[1-7] RTILs can be used as electrolyte medium for many organic and inorganic substances and hence they look suitable for electro-organic synthesis and chemical modifications and after the reaction the products can be recovered and the ionic liquid electrolyte can be recycled and reused thus offering a green process as against the currently used highly acidic or alkaline electrolytes.[8] The aromatic hydrocarbon solvents such as benzene (B), toluene (T), xylene (X), etc., are extensively used in many industrial applications

and their vapours are toxic to the environment and are difficult to trap in aqueous scrubbers due to their hydrophobic nature and high vapour pressure hence controlling the emission of these volatile organic carbons (VOCs) at the source point is one of the major challenges being faced by industries and research units.[9-10] Many ionic liquids possess the property of absorbing volatile organic carbon compounds thus by proper selection of cations and anions and tailoring the required physicochemical properties of ionic liquids the solubility of VOCs could well be enhanced.[11-12]

Hydrophobic RTILs are capable of solubilizing the solvents such as B, T, X in high concentrations and used for organic pollution control.[13-15] But, for keeping the recovery process in sustainable mode the trapped hydrophobic organic compounds must be transferred from the ionic liquid medium to aqueous medium and this requires the introduction of some hydrophilic functional groups by way of oxidation reactions. Since, some of the RTILs have moderate conductivity, the electro-chemical oxidation of the volatile organic compounds dissolved in RTILs look feasible for incorporating hydrophilic functional groups and studies on direct electrochemical oxidation of organic compounds have been reported in ionic liquid media.[16-17] But, there has been no investigation on the electro-oxidation of hydrophobic organic solvents such as toluene catalysed by a metal ion oxidant such as Co(II) or Ag(I) which have been used previously by many researchers for the electro-oxidation and electrochemical mineralization of target organic compounds in aqueous media for organic synthesis and environmental pollutant degradation applications respectively.[18-21]

In the present work we have investigated the cyclic voltammetric behaviour of Co(II) ion dissolved in the room temperature ionic liquid N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ($[bmpyr]^+[Ntf_2]^-$) at various scan rates and temperatures. The electrocatalytic oxidation of toluene in the presence of Co(II) was studied by cyclic voltammetry (CV) to understand the catalytic effect exhibited by the metal ion mediator. Further the galvanostatic electrolysis experiments were performed in the presence and absence of Co(II) at room temperature, the samples were

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qualitatively analysed by gas chromatography coupled mass spectrometry (GC-MS) and attenuated total reflection - fourier transform infrared (ATR-FTIR) spectroscopy. From the identified electro-oxidation products a probable reaction scheme has been proposed.

Experimental

N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide was procured from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China, and the purity was confirmed by FTIR spectrum. Toluene (Daejung Chemicals and Metals Co. Ltd, Korea), $CoCl_2$ (Sigma-Aldrich, USA) were used as received. The cyclic voltammetric profiles were recorded using a Princeton Applied Research (VersaSTAT-3) electrochemical workstation interfaced with a personal computer and controlled by Versa studio software. All the electrochemical measurements were performed in a three electrode assembly with Pt disc working electrode (Pine, 5 mm) and Pt rod counter electrode (2 mm) with Ag wire as a quasi-reference electrode. Before each experimental run the working electrode was cleaned by gentle rubbing over alumina slurry (Buehler) on a soft lapping pad and ultrasonicated in ethanol for the removal of any adsorbed impurities. The counter electrode was cleaned in a hot flame and then washed in acetonitrile. For each experimental run a 3 ml volume of ionic liquid was used with either the metal ion or the organic molecule or both in the required concentration. During the experimental run the cell was closed using a parafilm to avoid the entry of moisture yet in contact with oxygen (no purging with inert gas). Generally the passage of inert gases such as Argon or Nitrogen is not suggested owing to the change in mass transport properties.[22-24] The cyclic voltammogram was recorded after clearly establishing the electrochemical window by several trial runs and then recording the current response of the third potential cycle. The galvanostatic experiments were performed using a two electrode system in the same electrochemical workstation in galvanostatic mode at a constant current density by recording changes in potential with respect to time. The current density was properly selected so that the cell potential was kept well within the potential window to avoid the possible breakdown of the ionic liquid under the high potential regions.[25] The diffusion coefficient of Co(II) was calculated using Randles-Sevcik equation for one electron reduction as reported elsewhere.[26] GC-MS and ATR-FTIR instrumental analyses are detailed in E.S.I.

Results and Discussion

Electrochemical oxidation and reduction of CoCl₂ in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide

The metal salt precursor $CoCl_2$ was found to be easily dissolved (0.05 mmol) in 3 mL ionic liquid at the room temperature giving a pale pink coloured solution. The solution was then subjected to cyclic voltammetric (CV) analysis by selecting both the anodic and cathodic potential domains. **Fig. 1A** shows the CV profiles of Co(II) in [bmpyr]$^+$[Ntf$_2$]$^-$ at the scan rate of 50 mV/s at 25 °C. The potential was scanned in the positive going direction. It is clearly observed that the pure [bmpyr]$^+$[Ntf$_2$]$^-$ shows no prominent peak and the background current was very small in magnitude. When $CoCl_2$ containing ionic liquid was taken it showed an increase in anodic peak

current but the changes are not well defined as expected for a redox couple but under magnification the CV profile showed a well-defined behaviour as shown in **Fig. 1B**. The oxidation of Co(II) to Co(III) was found at 1.22 V vs. Ag wire quasi reference electrode and a second oxidation peak appears like a shoulder (~ 2.2 V, Fig. 1A) due to the oxidation of [NTf$_2$]$^-$ anion.
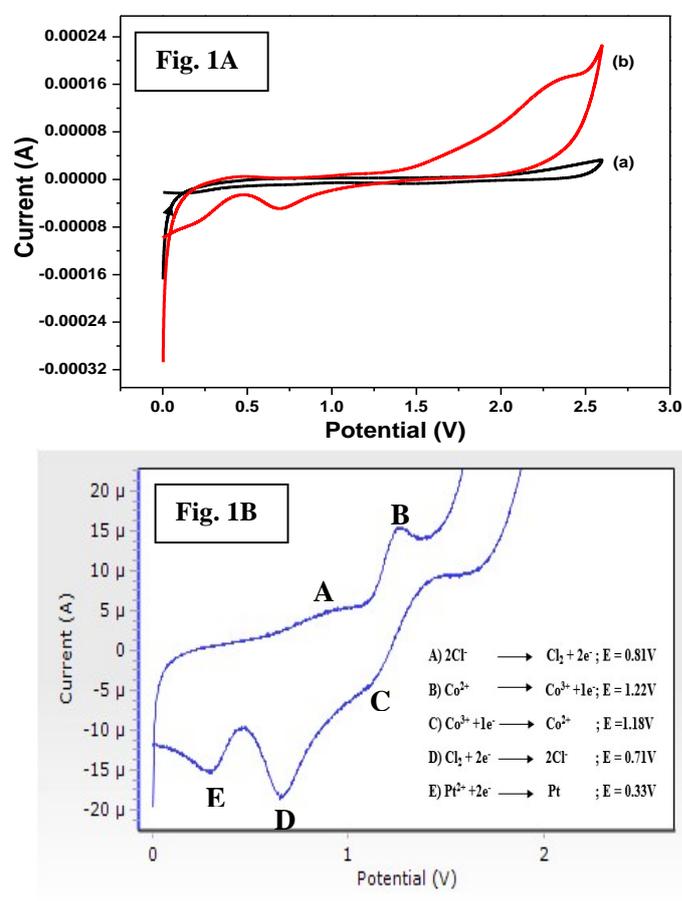

Fig. 1A Cyclic voltammograms of (a) N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide and (b) [bmpyr]$^+$[Ntf$_2$]$^-$ containing 0.05 mmol of $CoCl_2$ at the same scan rate of 50 mV/s at 25 °C (Pt disc (5 mm) working electrode, Ag wire as quasi reference electrode and Pt rod (2 mm) counter electrode). **Fig. 1B** CV profile shown in Fig. 1A with zoom-in view showing the well-defined anodic and cathodic waves.

During the cathodic scan the Co(III) reduction peak appeared at 1.18 V like a shoulder also the Cl$^-$ anion part of $CoCl_2$ showed a smaller anodic peak at 0.81 V and a well-developed reduction peak at 0.71 V due to Cl_2 formed anodically from Cl$^-$ anion. **Fig. S1** shows the CV profiles of [bmpyr]$^+$[Ntf$_2$]$^-$ containing Co(II) at various scan rates measured at 25 °C. The smaller magnitude of capacitance current observed for blank run shows that macro sized 5mm Pt working electrode could well be used for viscous ionic liquid solutions. The diffusion coefficient values calculated for the one electron oxidation of Co(II) to Co(III) was found to range from 0.38 x 10^{-7} to 1.9 x 10^{-7} cm^2/s in the temperature range of 25 - 80 °C. The diffusional activation energy was calculated and found to be 26.48 kJ/mol. This value is in agreement with the literature

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reported value for Cc$^+$/Cc couple (0.5 – 2.5 x10^{-7}).[26] In order to find the cathodic limit and nature of Co(II) species in the negative potential region, the working electrode was scanned separately from 0.0 to –1.8 V. The CV profiles showed a very clear Co(II)-Co(I) reduction peak at –0.92 V and after crossing the switching potential in the positive going direction a peak at – 1.68 V appeared which might be due to the oxidation of adsorbed [bmpyr]$^+$ (**Fig. S2**). The re-oxidation of Co(I) to Co(II) appears as a broad peak at –0.6 V. As the scan rate is increased from 10 to 100 mV/s the anodic peak current at –1.68 V increases but when the temperature was raised from 25 – 80 °C this peak current decreased indicating the desorption of [bmpyr]$^+$ from the electrode surface. Thus, the oxidation and reduction behaviours of Co(II) on both the anodic and cathodic potential scans resulted in the reversible generation of Co(II)/Co(III) and Co(I)/Co(II) species which could be used for catalysing the organic electro-oxidation and reduction reactions for chemical synthesis and organic pollutant degradation applications. In order to confirm the Cl$^-$ oxidation and Cl$_2$ reduction, 0.03 mmol of NaCl was added along with CoCl$_2$ and the CV profile was verified (**Fig. S3**) and also to detect the presence of moisture a known quantity of water (0.08 mmol (500 ppm) & 0.16 mmol (1000 ppm)) was added, ultrasonicated and then CV scans were recorded. It was seen that (**Fig. S4**) the ionic liquid is completely hydrophobic and even the presence of water neither affected the potential window nor resulted in new peaks anywhere in the region.

Electro-oxidation of toluene catalysed by Co(II)

RTILs have been used as the solvent medium for the direct oxidation of organic compounds and investigated by CV studies.[27-28] Therefore, to understand the direct oxidation of toluene during anodic scan, CV experiments were performed with 0.015 mmol toluene under various scan rates and temperatures. It has been reported that for enhancing the electro-oxidation of phenol in [bmpyr]$^+$[NTf$_2$]$^-$ during the anodic sweep in presence of oxygen, the cathodic potential of – 2.15 V has to be reached to generate the superoxide ion (O$_2$$^{.-}$). But, this superoxide species reacts with phenoxide ion to give phenoxy radical which combines with triflate anion ([NTf$_2$]$^-$) to give phenoxy triflate molecule instead of phenol oxidation product.[29] Therefore, in order to find the catalytic effect of Co(II) ion on the oxidation of toluene, the potential region was chosen only in the positive direction from 0.0 – 2.6 V at various temperatures under different scan rates. **Fig. S5** shows the CV profiles for direct electro-oxidation of toluene at various temperatures from 25 – 80 °C in which toluene oxidation currents were observed at around 2.0 V. When Co(II) containing [bmpyr]$^+$[Ntf$_2$]$^-$ was used for toluene oxidation the oxidation peak potentials negatively shifted reducing the overpotential for organic oxidation. **Fig. 2** shows the comparison of CV profiles for direct and Co(II) mediated electro-oxidation of toluene at 50 mV/s recorded at 25 °C. The oxidation peak current has increased nearly 5 fold in the presence of Co(II) species indicating clearly the catalysing effect of Co(II). **Fig. 3** shows the Co(II) catalysed oxidation of toluene at various temperatures from 25 - 80 °C. As the temperature increases the peak current also increases up to 65 °C and after that nearly remains the same indicating the attainment of limiting value and also it can be observed that the

peak currents rise sharply from the baseline at higher temperatures and both these effects are understandably due to the decrease in the viscosity of the ionic liquid solutions.
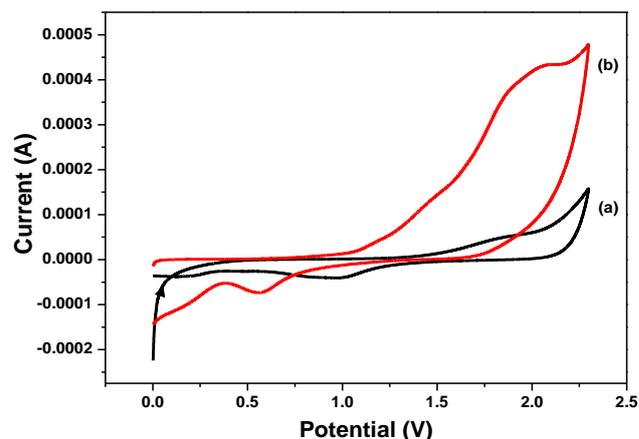

Fig. 2 Cyclic voltammograms N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide containing 0.015 mmol of toluene (a); 0.015 mmol toluene + 0.05 mmol CoCl$_2$ (b) measured at the scan rate of 50 mV/s and at 25 °C (*working electrode: Pt disc and Ag wire as quasi reference electrode*).
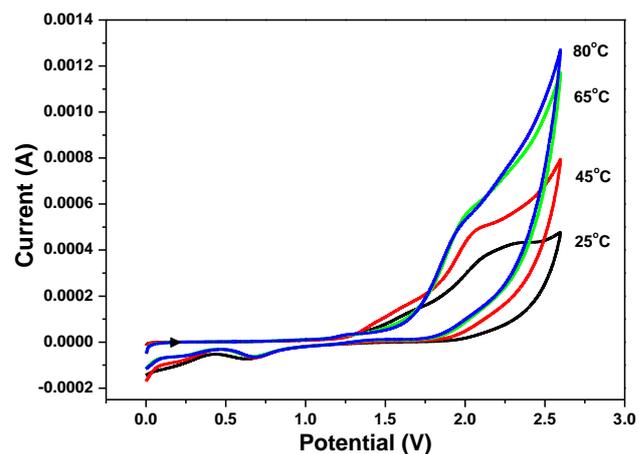

Fig. 3 Cyclic voltammograms of N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide containing 0.05 mmol CoCl$_2$ and 0.015 mmol toluene at the scan rate of 50 mV/s at various temperatures (Working electrode: Pt disc and Ag wire as quasi reference electrode).

Galvanostatic electrolysis and product analyses

The galvanostatic electrolysis experiments were performed to qualitatively determine the products of electrolysis. A 0.05 mmol of Co(II) in ionic liquid solution was mixed with 0.05 mmol of toluene and the solution was electrolyzed at a constant current density of 2.75 mA/cm^2 for 5 h at room temperature. **Fig. S6** shows the optical images of the ionic liquid samples during long term electrolysis in which the colour change from pale pink to light green due to the oxidation of Co(II) to Co(III) is clearly seen. The ionic liquid sample after electrolysis was mixed with an equal volume of diethyl ether solvent and the products of electrolysis were extracted. The ether extract was subjected to GC-MS (**Figs. S7A & S7B**) and FTIR (**Fig. S8**) analyses. The mass spectral analysis clearly confirmed the formation of benzaldehyde together with a small quantity of 3-methyl-1-hexanol. The obtained FTIR spectra

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was matched with NIST catalogue for the identified compounds and confirmed the introduction of new functional groups after electro-oxidation. Based on the convincing qualitative observation of the reaction products the probable reaction scheme for toluene oxidation is provided below. Since the oxidation of toluene to benzaldehyde results in the formation of two protons and one oxygen atom, the additional formation of 3-methyl-1-hexanol by way of ring opening could be envisaged. Since the employed ionic liquid is quite expensive the recovery and reuse of the electrolyte after the electrolysis was attempted. After the galvanostatic oxidation of toluene the products formed were extracted with double distilled water by three successive steps and finally the recovered ionic liquid was analysed by cyclic voltammetry. **Fig. S9** compares the CV profiles recorded for Co(II), Co(II) with toluene before galvanostatic oxidation and after extraction and recovery. It is to be noted that the CV profile observed after the recovery process is quite similar to the initial pattern demonstrating the effective use of $[bmpyr]^+[NTf_2]^-$ for organic synthesis and organic pollutant removal in particular for hydrophobic organic solvents.

$$C_6H_5\text{-}CH_3 + Co(III) + O_2 \rightarrow C_6H_5CHO + O^{2-} + 2H^+ + 2e^-$$
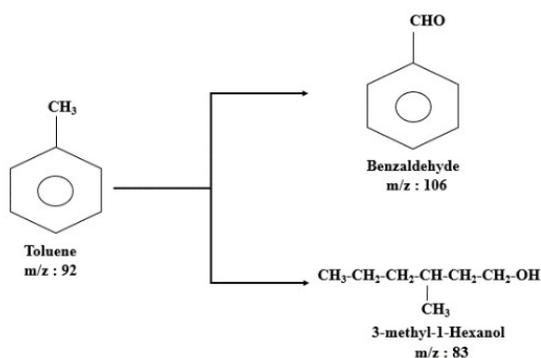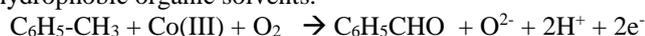
Conclusions

In summary, we have for the first time shown that Co(II) from an ionic liquid medium could be used as an electrocatalyst for the oxidation of toluene at room temperature. CV studies revealed that Co(II) species undergoes anodic oxidation reversibly to form Co(III) and cathodic reduction to form Co(I) quasi-reversibly in the hydrophobic RTIL $[bmpyr]^+[Ntf_2]^-$. The diffusion coefficient of Co(II) was found to be in the range 0.38×10^{-7} to 1.9×10^{-7} cm^2/s with diffusional activation energy value of 26.48 kJ/mol. From CV profiles it was inferred that the toluene oxidation current found to be enhanced nearly by 7 fold in presence of Co(II). GC-MS and FTIR analyses of the ether extract confirmed the formation of benzaldehyde and 3-methyl-1-hexanol. Also we have demonstrated the recovery and reuse of the ionic liquid after electrolysis in an attempt to understand the ability of the ionic liquid after recovery for cost effective applications.

Acknowledgements

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