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Influence of supporting electrolytes with various structures on electrochemical reduction determination of 3,3', 4,4'-tetrachlorobiphenyl at different metal electrodes

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ABSTRACT

1-methyl-3-propylimidazolium iodide (MPII), 3-hexyl-1-methylimidazolium iodide (HMII) and three tetraalkylammonium salts were employed as supporting electrolytes on electrochemical reduction determination of 3,3',4,4'-tetrachlorobiphenyl (PCB-77) at Pt, Ag, Cu electrodes. It was found that HMII and MPII can effectively increase the cathodic peak current of PCB-77 and the electrocatalysis activity of the metal on electrochemical determination of PCB-77 was in the following order: Cu>Ag>Pt.

KEYWORDS

1-Methyl-3-propylimidazolium iodide;
3-Hexyl-1-methylimidazolium iodide;
Supporting electrolytes
Electrochemical reduction determination;
3,3',4,4'-Tetrachlorobipheny,
Electrodes.

INTRODUCTION

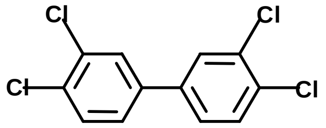
Polychlorinated biphenyls (PCBs) were typical high toxic persistent organic pollutants in various environmental media. Although PCBs have been analytical determined by means of gas chromatography[1-3], electrochemical reduction in some special cases was a good alternative because it could be used in on-scene determination and was cheaper on operational costs. For electrochemical determination of PCBs, it was necessary to use the supporting electrolytes such as sulfuric acid[4, 5], hexadecyltrimethylammonium bromide[6], tetraalkylammonium salts[7-12]. Imidazolium-based ionic liquids display superb electrochemical stability and broad electrochemical window. However, the application of imidazolium-based ionic liquids as supporting electrolytes has not been reported. And the influence of the supporting electrolytes on electrochemical reduction of PCBs has not been compared systematically.

In this paper, 1-methyl-3-propylimidazolium iodide (MPII), 3-hexyl-1-methylimidazolium iodide (HMII) and three tetraalkylammonium salts were employed as supporting electrolytes. The influence of the supporting electrolytes with various structure on 3,3',4,4'-tetrachlorobiphenyl (PCB-77) electrochemical reduction determination at Pt, Ag, Cu electrodes was investigated by cyclic voltammetry(CV).

EXPERIMENTAL

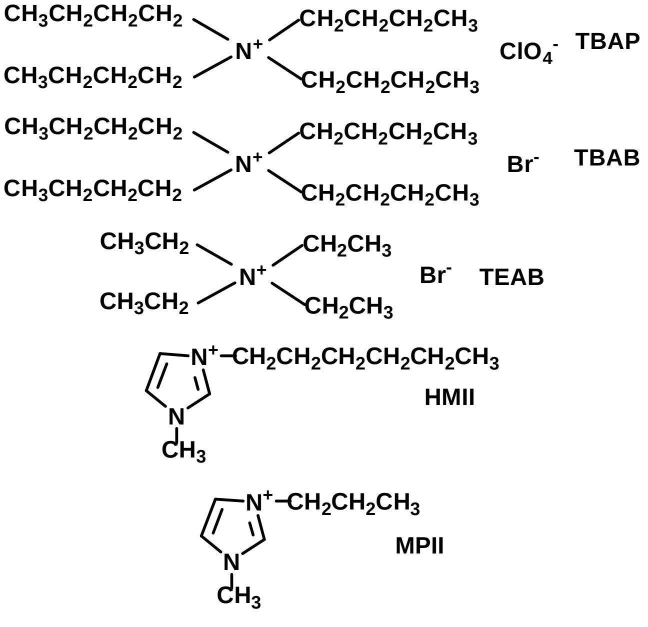
Chemicals

3,3',4,4'-tetrachlorobiphenyl (PCB-77) was obtained from AccuStandard Inc. The structure of PCB-77 was sketched in Scheme 1.



Scheme 1 : Structure of PCB-77

Tetrabutylammonium bromide (TBAB) and Tetraethylammonium bromide (TEAB) were purchased from Guangfu Fine Chemical Research Institute, China. Tetrabutylammonium perchlorate (TBAP) and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. The synthesis of HMII was similar to MPII according to our previous report[13]. The structure of five supporting electrolytes was shown in Scheme 2.



Scheme 2 : Structure of the supporting electrolytes

Apparatus and procedures

CV was performed through an electrochemical workstation (CHI660B, China) at a scan rate of 100 mV·s^{-1} and the potential range were between -1.4 and -2.2 V in all CV measurements. The three electrode-system was employed and the working electrodes were Pt wire (CHI115, d=0.27 mm), Ag wire (laboratory-made, d=0.12 mm) and Cu wire (laboratory-made, d=0.20 mm), respectively. The reference electrode was a 3 M aqueous Ag/AgCl/KCl electrode and Pt wire was used as counter electrode. The concentration of the electrolytes was 0.1 mol/L in all experiments.

RESULTS AND DISCUSSION

Influence of supporting electrolytes on PCB-77 electrochemical reduction at Pt electrode

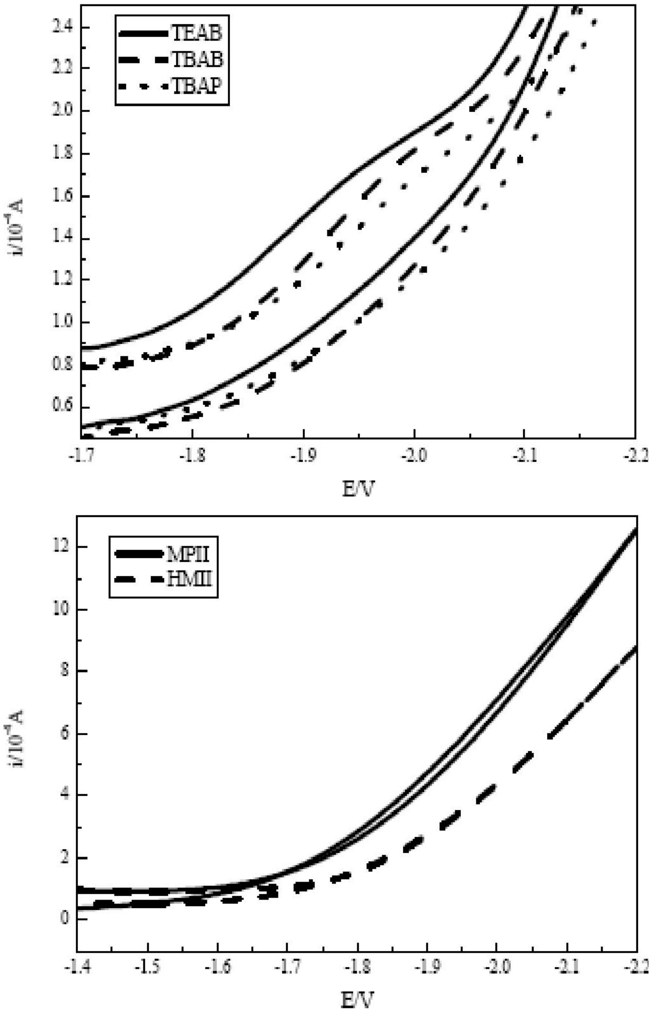


Figure 1 : CV curves of 1.65×10^{-3} mol/L PCB-77 in DMF with different supporting electrolytes at Pt electrode.

The CV curves of PCB-77 in DMF with different supporting electrolytes at Pt electrode are shown in Figure 1. Weak cathodic peaks at approximately -1.95 V when TEAB, TBAB and TBAP were used as supporting electrolytes, indicating when tetraalkylammonium was the cation of the supporting electrolytes, there was no difference between anions of bromide and perchlorate[14]. It was no obvious reduction peak observed on MPII and HMII curves, which showed that PCB-77 can not be reduced when organics with aromatic ring was used as supporting electrolytes at Pt electrode. Moreover, the results showed that Pt was not an appropriate electrode due to the low electrocatalysis activity on the reduction of PCB-77.

Influence of supporting electrolytes on PCB-77 electrochemical reduction at Ag electrode

TABLE 1 : Cathodic peak current of PCB-77 with different supporting electrolytes at Ag electrode

Supporting electrolytes	Cathodic peak current/ µA
TEAB	2.1
TBAB	2.2
TBAP	2.1
MPII	5.6
HMII	5.1

Figure 2 showed the CV curves of PCB-77 in DMF with different supporting electrolytes at Ag electrode. The primary reduction peak was detected at roughly -1.85 V in all five supporting electrolytes curves due to the dechlorination of the first chlorine atom on PCB-77. It was interesting to investigate that the small reduction peak at approximately -2.10 V, seen only with TBAB, TBAP and TEAP containing aliphatic chain as supporting electrolyte, was determined, yet only one cathode peak was observed using MPII and HMII with aromatic ring as supporting electrolytes, which indicated the existence of different dechlorination mechanisms. From TABLE 1, it was noticeable to find that the anodic peak current values with TBAB, TBAP and TEAP were equal to about 2.1 µA. These values were sharply increased to above 5.0 µA when MPII and HMII were used as supporting electrolytes. It was obvious that imidazolium-based ionic liquids were appropriate supporting electrolytes due to the high anodic peak current values of PCB-77 compared with aliphatic organics at Ag electrode. What is more, Ag displayed a good electrocatalysis activity on reduction determination of PCB-77 for Ag can form a chemical bond with chloride atom of PCB-77, which reduced the carbon-halogen bond[15].

Influence of supporting electrolytes on PCB-77 electrochemical reduction at Cu electrode

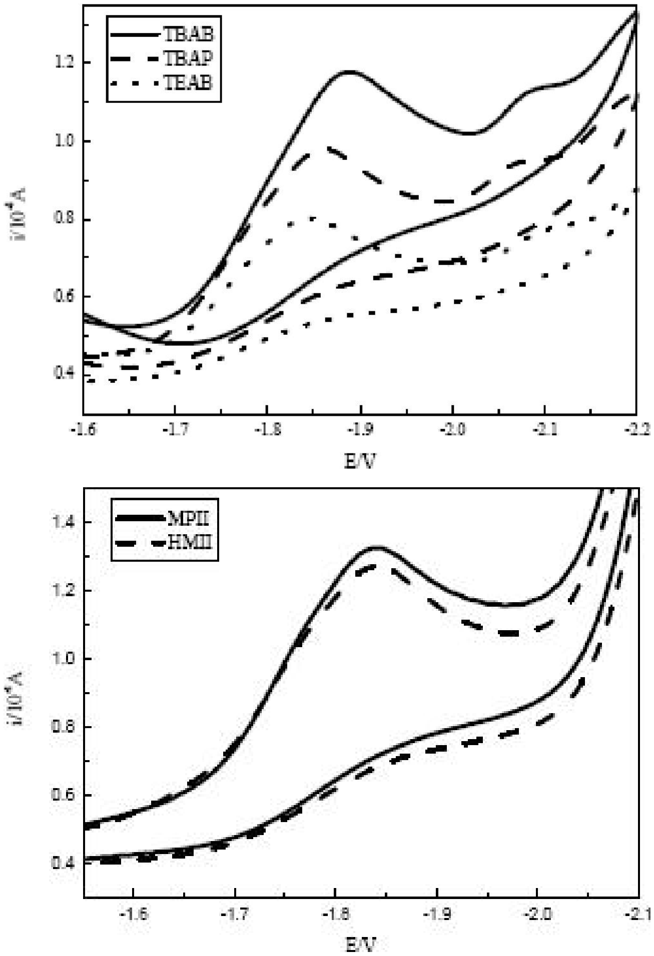


Figure 2 : CV curves in 1.65×10^{-3} mol/L PCB-77 in DMF with different supporting electrolytes at Ag electrode.

Figure 3 was CV curves of PCB-77 in DMF with different supporting electrolytes at Cu electrode. The main reduction peak at about -1.90 V was found when TBAP and TBAB were employed as supporting electrolytes. And the reduction potential at roughly -1.87 V was detected in TEAB curve. It was interesting that there were two reduction peak observed in TBAB, HMII and MPII curves. The obvious reduction peak of HMII and MPII curves was detected at -1.85 V, while the weak peak was observed at about -2.1 V. From TABLE 2, the anodic peak current values of PCB-77 with TBAB, TEAB, TBAP, MPII, HMII were 2.1, 2.1, 2.4, 3.8, 4.5 µA, respectively. It was in fair agreement with the result at Ag electrode that aromatic ring can effectively increase the cathodic peak current compared with aliphatic chain at both Ag and Cu electrodes.

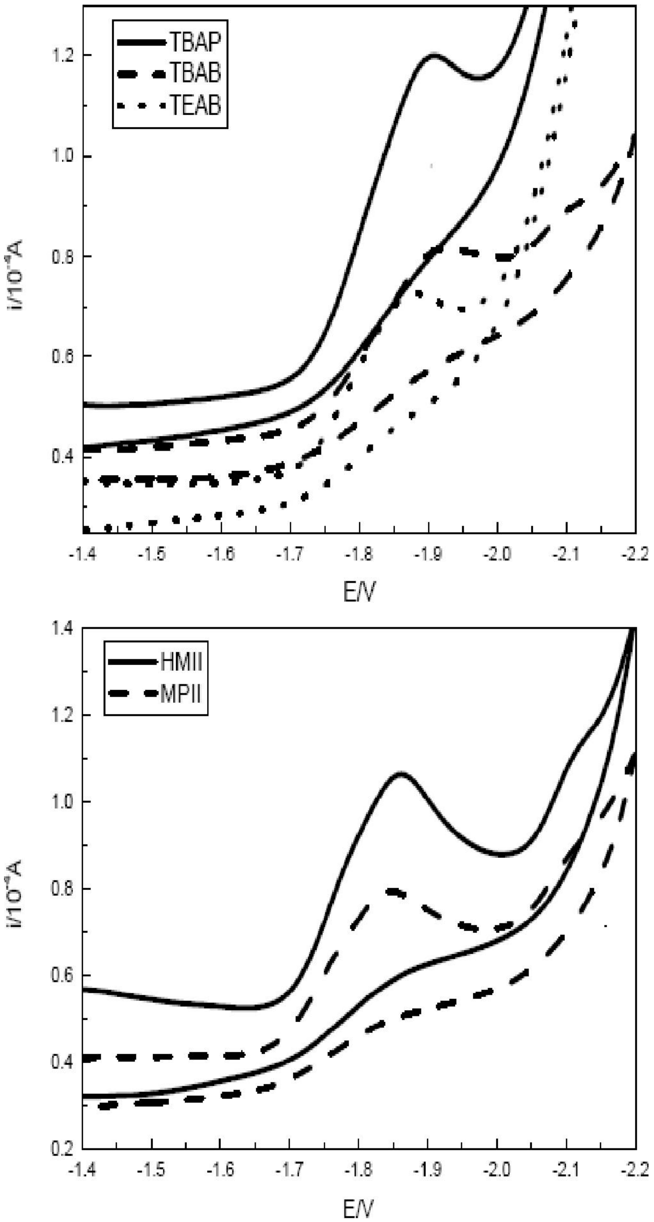


Figure 3 : CV curves in 1.65×10^{-3} M PCB-77 in DMF with different supporting electrolytes at Cu electrode.

TABLE 2 : Cathodic peak current of PCB-77 with different supporting electrolytes at Cu electrode

Supporting electrolytes	Cathodic peak current/ μA
TEAB	2.1
TBAB	2.1
TBAP	2.4
MPII	3.8
HMII	4.5

Determination limit of PCB-77

Figure 4 was CV curves in 1.65×10^{-4} mol/L PCB-77 in DMF with HMII at Cu electrode. Considering the cathodic peak current value, HMII was used as supporting electrolyte at Cu electrode. An obvious reduction peak at the potential of -1.85 V was observed, indicating the determination limit was found to be 1.65×10^{-4} mol/L. Therefore the electrocatalysis activity of the metal on the electrochemical determination of PCB-77 was in the following order: Cu>Ag>Pt.

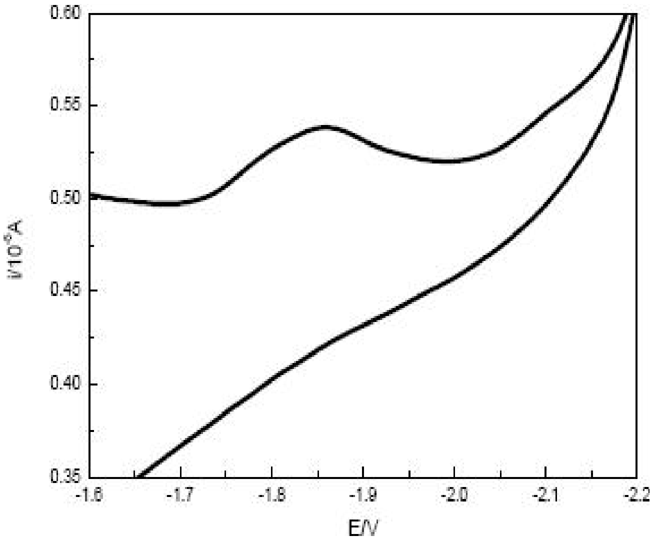


Figure 4 : CV curves in 1.65×10^{-4} mol/L PCB-77 in DMF with HMII at Cu electrode.

CONCLUSIONS

In this paper, 1-methyl-3-propylimidazoliumiodide (MPII), 3-hexyl-1-methylimidazoliumiodide (HMII) and three tetraalkylammonium salts were employed as supporting electrolytes. The influence of the supporting electrolytes with various structure on 3,3’,4,4’-PCB electrochemical reduction determination at Pt, Ag, Cu electrodes was investigated by cyclic voltammetry. It was found that MPII and HMII can be promising alternatives as supporting electrolytes due to the high cathodic peak values of 3,3’,4,4’-PCB. The determination limit was found to be 1.65×10^{-4} mol/L at Cu electrode, therefore the electrocatalysis activity of the metal on the electrochemical determination of PCB-77 was in the following order: Cu>Ag>Pt.

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