

Influence of addition of ionic liquids precursors with bisulphate and sulphate anions on hydrogen and oxygen evolution potential

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Please cite as: CHEMIK 2016, 70, 9, 509–514

Introduction

Ionic liquids are often mentioned as chemical compounds fulfilling the principles of green chemistry. An indisputable advantage of this type of compounds is the possibility of changing their physical or chemical properties by modifying a cation or an anion [1–5].

Thanks to a number of unique properties, including high conductivity, thermal and chemical stability, low volatility or low toxicity, they are used in various fields of chemical industry, including electrochemistry. They are used among others in galvanotechnical processes, electrochemical synthesis of conductive polymers, supercapacitors, lithium-ion batteries and other electrochemical cells. [6–9].

The effect of ionic liquids on the overpotential of hydrogen and oxygen generation during the hydrolysis of aqueous systems is one of the extremely important properties of ionic liquids. The increase in the electrochemical stability of water outside the range limited by H₂O thermodynamic stability shows, for instance, a positive effect on the operation of lead-acid cells [10]. It can also prove useful in electrodeposition processes [9]. The decrease in the hydrogen evolution potential on cathodes results in the inhibition of the generation of gas bubbles on the electrode surface and prevents roughness of the deposited layer.

The paper presents the studies on the effect of quaternary ammonium ionic liquids on the oxygen and hydrogen evolution potential on glassy carbon and platinum electrodes. Ionic liquids consisting of the cation of the alkyl substituent of different lengths and bisulfate anion were compared. Moreover, their properties were compared with analogues containing a sulfate anion. Differences between electrochemical properties were found depending on the anion used and the length of the alkyl substituent.

Experimental part

Compounds

The tested ionic liquid precursors are listed in Table I. They were synthesised in a thermostated reactor equipped with a magnetic stirrer. 0.01 mole of appropriate alkyltrimethylamine and 20 ml of methanol were added and stirred until complete dissolution. Then, a stoichiometric amount of concentrated sulfuric acid was added portionwise to the reaction mixture. The entire mixture was stirred for 30 minutes (in case of sulfate liquids until pH = 7 is obtained), after which the mixture was evaporated. The product obtained was dried in a vacuum drier at 40°C for 36 h.

Table I

Examined ionic liquids precursors

Formula	Name	Designation
$\text{H}_{25}\text{C}_{12}-\text{N}^+-\text{HSO}_4^-$	Dodecyltrimethylammonium bisulfate	C12HSO4
$\text{H}_{33}\text{C}_{16}-\text{N}^+-\text{HSO}_4^-$	Hexadecyltrimethylammonium bisulfate	C16HSO4
$\text{H}_{37}\text{C}_{18}-\text{N}^+-\text{HSO}_4^-$	Octadecyltrimethylammonium bisulfate	C18HSO4
$\text{H}_{45}\text{C}_{22}-\text{N}^+-\text{HSO}_4^-$	Docosyltrimethylammonium bisulfate	C22HSO4
$\text{H}_{25}\text{C}_{12}-\text{N}^+-\text{SO}_4^{2-}$	Di(dodecyltrimethylammonium) sulfate	C12SO4
$\text{H}_{33}\text{C}_{16}-\text{N}^+-\text{SO}_4^{2-}$	Di(hexadecyltrimethylammonium) sulfate	C16SO4
$\text{H}_{37}\text{C}_{18}-\text{N}^+-\text{SO}_4^{2-}$	Di(octadecyltrimethylammonium) sulfate	C18SO4
$\text{H}_{45}\text{C}_{22}-\text{N}^+-\text{SO}_4^{2-}$	Di(docosyltrimethylammonium) sulfate	C22SO4

Electrochemical tests

Solutions of ionic liquid precursors were analysed. In 1 cm³ of 37% sulfuric acid aqueous solution (Merck), 1L content was 5 mg. Sulfuric acid was used to increase the conductivity of the tested solutions.

The working electrode was a glassy carbon electrode of 3 mm in diameter and a platinum electrode of 1.6 mm in diameter. In order to avoid measurement errors, an auxiliary electrode was used with approx. 10-fold larger surface area than the working electrode. Mercurous sulfate electrode served as a reference electrode and the results were presented in relation to a standard hydrogen electrode (SHE).

The tests were performed by means of linear voltammetry with a potential scan rate of 10 mV s⁻¹, initially towards anodic potentials in relation to open circuit potential and then towards cathodic potentials.

Results and discussion

The effect of ionic liquid precursors on the potential of hydrogen and oxygen evolution on the glassy carbon electrode is presented in Figure 1. The evolution potentials determined for pure 37% sulfuric acid were marked with horizontal lines.

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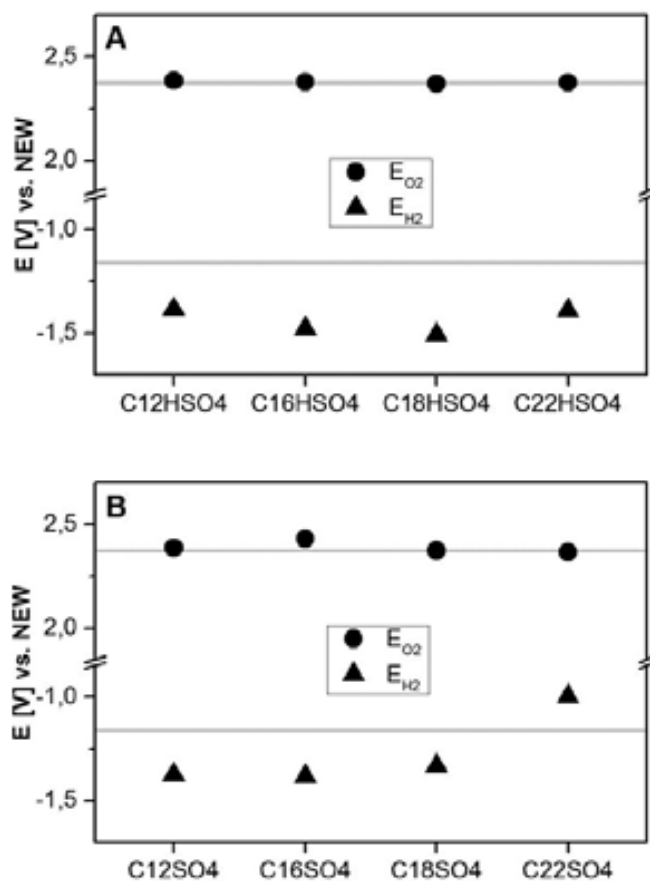


Fig. 1. Influence of ionic liquid precursors on overpotential of oxygen and hydrogen evolution on glassy carbon electrode: A- influence of ionic liquid precursors with bisulphate anion, B- influence of ionic liquid precursors with sulphate anion

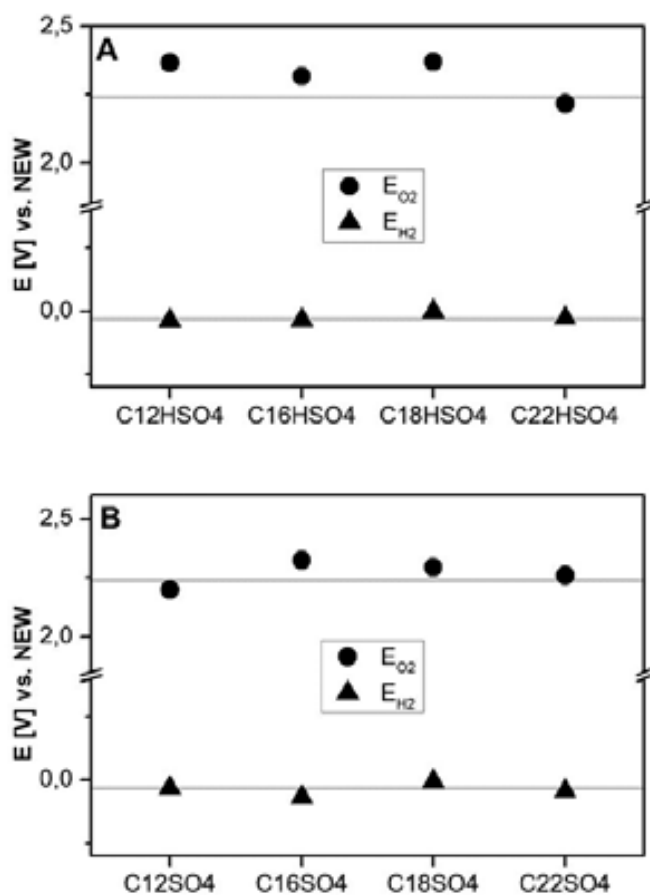


Fig. 2. Influence of ionic liquid precursors on overpotential of oxygen and hydrogen evolution on platinum electrode: A- influence of ionic liquid precursors with bisulphate anion, B- influence of ionic liquid precursors with sulphate anion

In case of a carbon electrode, an insignificant effect of ionic liquid precursors on the oxygen evolution potential was observed; however, a significant effect on the hydrogen evolution potential was observed. Moreover, a relation between the hydrogen evolution overpotential and the alkyl substituent length was observed. A decrease in the hydrogen evolution potential was observed for series C12HSO4 – C18HSO4. The further increase in the length of alkyl substituent resulted in the increase in the hydrogen evolution potential.

Changing anion to sulfate caused a large decrease in the hydrogen evolution overpotential, which in the extreme case of the ionic liquid precursor C22SO4 resulted in the increase in the hydrogen evolution potential above the value obtained for the solution containing no ionic liquid precursors.

In case of the use of the working electrode made of platinum, a different behaviour of solutions was observed (Fig. 2). Due to the properties of platinum electrode (particularly due to almost zero overpotential of hydrogen evolution), the difference in hydrogen evolution potential is unnoticeable. However, the difference in the oxygen evolution overpotential is emphasised. The best properties were observed for ionic liquid precursor C18HSO4 just like in the case of the glassy carbon electrode. It was also found that there is a significant increase in the gas evolution rate after replacing bisulfate anion with sulfate anion just like in the case of the glassy carbon electrode.

Conclusions

The studies conducted on changes in the oxygen and hydrogen evolution potential as a result of the addition of the ionic liquid precursor to the electrolyte showed a significant effect of the type of the organic cation and anion used.

Ionic liquid precursors containing bisulfate anion in their structure showed much better properties reducing the gas evolution on the test electrodes than their analogues containing sulfate anion.

The bisulfate liquid with octadecyltrimethylammonium cation proved to be the best inhibitor of gas evolution among the tested ionic liquid precursors.

Acknowledgments

The authors would like to gratefully acknowledge the financial support from the National Centre for Research and Development (NCBiR), grant no. PBS3/A5/43/2015.

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