Application of ionic liquid to the construction of Cu(II) ion-selective electrode with solid contact

Joanna Lenik¹, CecyIia Wardak¹*, Małgorzata Grabarczyk¹

¹Department of Analytical Chemistry and Instrumental Analysis, Chemical Faculty, M. Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3, Lublin 20-031, Poland

Abstract

Potentiometric properties of copper ion-selective electrodes (ISEs) with solid contact based on polymeric membrane were investigated. For the electrode construction ionic liquids (ILs), alkylmethylimidazolium chlorides are used as transducer media. The addition of ionic liquid to the membrane phase was found to improve the analytical parameters of the studied electrodes. The best results were obtained for electrode having membrane doped with 1-ethyl-3-methyl imidazolium chloride. The electrode shows a Nernstian response for copper ions over a wide concentration range (1x10⁻⁷-1x10⁻¹ mol L⁻¹) and the slope of 28.9 mV/decade. The limit of detection is 3.2x10⁻⁸ mol L⁻¹. It has a fast response time of 5-10 s and can be used for more than 4 months without any divergence in potential. The proposed sensor is not pH sensitive in the range 2.5-6.0 and shows a very good discriminating ability towards Cu²⁺ ion in comparison with some alkali, alkaline earth, transition and heavy metal ions.

Keywords: ionic liquid; copper-selective electrode; solid contact;

1. Introduction

The new generation of ion-selective electrodes with internal solid contact has attracted much attention for the past few years. These electrodes will have certain advantages over conventional ones, such as the small size, lower cost of production, and ability to operate in high pressure environments where conventional ISEs might be damaged. Furthermore, this type of electrode allows for low detection limit, which was attributed to the absence of transmembrane ion fluxes [1]. The aim of this work was developed
of solid contact Cu\(^{2+}\) - ISE using chloride ionic liquid as transducer media. ILs act as very promising solid contact of ISE with polymeric membrane because they connect two functions in one membrane component. On the one hand ILs keep constant concentration of chloride ions in the membrane phase what guarantee the stability of potential of internal Ag/AgCl reference electrode. On the other hand they lower the membrane resistance and reduce anion interference, altogether improving the analytical parameters of the electrode such as detection limit, measuring range, working pH range and selectivity [2,3].

In this work the membranes containing three ionic liquid: 1-ethyl-3-methyl imidazolium chloride (EMImCl), 1-butyl-3-methyl imidazolium chloride (BMImCl), 1-hexyl-3-methyl imidazolium chloride (HMImCl), as well as the commonly used potassium tetrakis(p-chlorophenyl) borate KTpClB were investigated. The 2- nitrophenyl octyl ether (NPOE) was used as membrane plasticizer and N,N,N′,N′-tetracyclohexyl-2,2′-thiodiacetamide was used as ionophore.

2. Experimental

2.1. Preparation of the electrode

The Ag/AgCl electrode was used as an internal reference electrode. It was prepared as follows: a clean silver wire was anodized electrochemically for 5 min in 4 mol L\(^{-1}\) HCl with constant current 5 V voltage forming an Ag/AgCl electrode. Then the electrode was rinsed with water, dried with tissue-paper and covered by the inner membrane phase.

The electrode membrane phase consists of two layers placed in a Teflon holder. The inner layer contains plasticizer, PVC and lipophilic additive (ionic liquid or KTpClB) in which the Ag/AgCl electrode is placed. The outer layer contains the same components and an ionophore. The outer layer is placed on the inner layer and it is contacted with the tested solution. In order to prepare the inner layer the membrane components were weighed, mixed thoroughly and the mixture was deaerated by means of a vacuum oil pump. The Teflon holder was filled with the mixture so that the silver-silver chloride electrode was immersed in it. Then the mixture was gelated at 80 °C for 30 min. In order to prepare the outer layer the ionophore was dissolved in a plasticizer and then mixed with other components. The mixture was deaerated, placed on the inner layer and gelated at 80 °C for 10 min. After cooling to room temperature the sensor was mounted in the electrode body and conditioned for at least 24 hours in 1×10\(^{-3}\) mol L\(^{-1}\) Cu(NO\(_3\))\(_2\) to saturate PVC membrane in the primary ions and then for at least 24 hours in the appropriate conditioning solution before potentiometric measurements. Concentrations of conditioning solutions were as follows: a) 1×10\(^{-3}\) mol L\(^{-1}\), b) 1×10\(^{-5}\) mol L\(^{-1}\), c) b1×10\(^{-7}\) mol L\(^{-1}\) and d) 1×10\(^{-9}\) mol L\(^{-1}\).

2.2. The measurement of the electromotive force

The measurement of the electromotive force (EMF) of the system: copper electrode - reference electrode Orion 90-02 was carried out at room temperature in a solution stirred with a mechanical stirrer by means of potentiometric system consisting of a 16-channel data acquisition system (Lawson Labs. Inc., USA) and IBM PC computer. A multifunction computer meter CX-741 (Zabrze Mikulczyce Poland) and an Orion 81-72 glass electrode were used for pH measurement. Sequential dilutions of stock solutions were performed using the 700 Dosino and 711 Liquino pump systems (Metrohm, Switzerland).

2.3. The measurement of membrane resistance
The resistance of the cell containing the studied electrodes was determined by measuring the time loading of condenser from 100 up to 500 mV voltage by constant current flowing through the studied electrode. The electrode resistance is directly proportional to the time of the condenser loading. The measurement system was previously calibrated by using the following precision resistors: 150 kΩ, 500 kΩ, 1 MΩ, 11.7 MΩ, 23Ω, 47.9Ω.

3. Results and discussion

In order to evaluate the effect of ionic additive to the membrane, basic analytical parameters of studied copper electrodes were determined and collected in Table 1.

Table 1. Composition of electrode membrane and sensors performance

<table>
<thead>
<tr>
<th>No electrode</th>
<th>Membrane composition, %wt.</th>
<th>Limit detection, mol L⁻¹</th>
<th>Slope, mV/decade</th>
<th>Measuring range, mol L⁻¹</th>
<th>Response time, s</th>
<th>Resistance, Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ionophore, %wt.</td>
<td>PVC, %wt.</td>
<td>NPOE, %wt.</td>
<td>Ionic additive, %wt.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>0.5</td>
<td>33</td>
<td>63.5</td>
<td>3, EMImCl</td>
<td>3.5x10⁻⁷</td>
<td>28.6</td>
</tr>
<tr>
<td>1b</td>
<td>0.5</td>
<td>33</td>
<td>63.5</td>
<td>3, EMImCl</td>
<td>1.4x10⁻⁷</td>
<td>30.4</td>
</tr>
<tr>
<td>1c</td>
<td>0.5</td>
<td>33</td>
<td>63.5</td>
<td>3, EMImCl</td>
<td>3.2x10⁻⁸</td>
<td>28.9</td>
</tr>
<tr>
<td>1d</td>
<td>0.5</td>
<td>33</td>
<td>63.5</td>
<td>3, EMImCl</td>
<td>8.9x10⁻⁸</td>
<td>30.9</td>
</tr>
<tr>
<td>2a</td>
<td>0.5</td>
<td>33</td>
<td>63.5</td>
<td>3, BLMImCl</td>
<td>5.0x10⁻⁶</td>
<td>36.6</td>
</tr>
<tr>
<td>3a</td>
<td>0.5</td>
<td>33</td>
<td>63.5</td>
<td>3, HLMImCl</td>
<td>4.0x10⁻⁶</td>
<td>36.1</td>
</tr>
<tr>
<td>4a</td>
<td>0.5</td>
<td>33.5</td>
<td>65.5</td>
<td>0.5, KTPclPB</td>
<td>5.2x10⁻⁶</td>
<td>33.6</td>
</tr>
</tbody>
</table>

Abbreviations a,b,c,d are concerned with conditioning solutions

All studied electrodes exhibit cationic response to Cu²⁺ ions with the Nernstian or super –Nernstian slope, both those with IIs as well as this with conventional ionic additive. The effect of ionic additive on potentiometric response of studied electrodes is shown in Figure 1a where can be seen, that the best response exhibits electrode containing EMImCl in the membrane.

It was demonstrated previously that potentiometric properties of solid contact electrodes depends on their conditioning procedure[4]. Therefore the effect of conditioning solution concentration on electrodes response was studied. The obtained results for the electrode based on EMImCl are presented in Figure 1b.

Selectivity is one of the most important parameter of any ion-selective electrode. The selectivity coefficients were determined by the separate solutions method (SSM) by extrapolating the response functions to a_i=a_j=1mol L⁻¹. The results obtained indicate that the electrodes with IL are characterized by preferable selectivity coefficients in comparison with the electrode based on KTPCLPB. The values of selectivity coefficients log K^[pot]Cu/M for the electrode 1c are as follows: Cd²⁺ -3.84; Ca²⁺ -4.93; Mg²⁺ -6.22; Zn²⁺ -3.39; Co²⁺ -3.16; Ni²⁺ -3.02; Na⁺ -4.95; K⁺ -5.21; Li⁺ -5.11.
4. Conclusions

The research has found that the ionic liquid can be used as lipophilic ionic component of polymeric ion-selective membranes. The application of an ionic liquid as transducer media results in a decrease of membrane resistance and short response time. Furthermore the ionic liquid maintains constant concentration of chloride ions in the membrane phase, which guarantees the potential stability of internal Ag/AgCl electrode, which in turn results in a small potential drift of 0.3 mV per day. Due to the absence of internal solution the presented electrode construction is simple to construct and easy to transport. It is convenient to use because can work in any position and can operate in high pressure environments.

References


