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Silver(I) chlorides speciation and its relationship to the design, construction and evaluation of true $Ag_{(s)}/[AgCl_n]^{1-n}$ reference electrodes for their use in bis(trifluoromethylsulfonyl)imide room temperature ionic liquids

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ABSTRACT

This study describes a methodology for the design of true reference electrodes of the second kind based on the chemical speciation of the system $AgCl_{(s)}/[AgCl_n]^{1-n}$ in both homogeneous and heterogeneous systems in bis(trifluoromethylsulfonyl)imide room temperature ionic liquids (RTIL), based on measurements of the open circuit potential (OCP) of $Ag_{(s)}$ or $Ag_{(s)}|AgCl_{(s)}$ indicator electrodes immersed in solutions of Ag $[NTf_2]$ and $[C_2mim]Cl$ in RTIL, as well as on representative potentiometric titrations of Ag(I) or of chloride ions in the same media. The found values of the apparent equilibrium constants of the chemical equilibrium processes associated to the electrode potential at the metal|RTIL interface, lay the foundation for the design of true reference electrode systems. To test the usefulness of the information collected during the chemical speciation of these systems, four true reference electrodes were built for their use in four imidazolium-based bis(trifluoromethylsulfonyl) RTIL, and their electrode potentials were determined over time using the $[Co(Cp)_2]^{+/0}$ or $[Fe(Cp)_2]^{+/0}$ redox couples as internal redox references. The aim of this work is to provide a simple method for the development and characterization of true reference electrodes for their use in RTIL, thus averting the use of QRE and enabling the construction of comparable potential scales in RTIL.

1. Introduction

Room temperature ionic liquids (RTIL) are a large family of chemical compounds generally consisting of a bulky and asymmetric organic cation and an organic or inorganic anion. The purity, the size ratio of anions to cations and their structural motifs define the physical and chemical properties of ionic liquids [1,2]. As a general rule, RTIL have melting points lower than 100 °C and relatively high ionic conductivities [3,4], making them relevant in electrochemical applications, i.e. electrosynthesis or electroanalysis, where they can act as electrolytes or solvents [5,6]. Despite the importance of RTIL as relatively new materials in electrochemical cells or electrodes [5–7], revealed by the nearly 15-fold increase in the number of papers published that describe their use in electrochemical systems in the last 15 years (according to a bibliographic search in Web of Science), the control of the working electrode potential in these media is not trivial due to the lack of sufficiently stable reference electrodes (RE). There are not commercial RE for each RTIL used [1], and in many cases, it is difficult to build and evaluate the behavior of true RE in RTIL. This situation results in experimental complications for the use of RTIL as solvents.

Some authors have used quasi-reference electrodes (QRE) for various purposes when working with RTIL as solvents or electrolytes. Reports using silver [3,9–14] or platinum [15–18] QRE in ionic liquids are abundant, and in these works it is usually assumed that their electrode potentials, unknown beforehand, tend to vary from one assay to the other. For some RTIL, it has been reported that the cations composing the IL may act as a ligand, favoring metal solubilization of the QRE into the RTIL. This process occurs by the oxidative addition of the cation forming a metal-carbene complex [2]. For such phenomena in QRE, there is no certainty of the nature

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