Analysis of water in room temperature ionic liquids by linear sweep, differential pulse and square wave cathodic stripping voltammetries

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1. Introduction

Room temperature ionic liquids (RTILs) are very useful solvents for many different chemical systems and applications, notably including both fundamental and applied electrochemical research [1] since they possess an inherently high ionic conductivity as well as other interesting physical and chemical properties, such as negligible vapor pressure, high thermal stability, a wide electrochemical window, and the ability to dissolve a larger number of both organic and inorganic solutes [2]. The properties of the RTILs strongly vary from one compound to the other [3], being also clearly dependent on the amount and nature of the different impurities commonly found in these family of compounds [4]. Particularly, the content of water can substantially modify many physicochemical and electrochemical properties of the RTILs, such as density, viscosity [5], conductivity [6], or even their chemical stability. Many second generation RTILs, based on anions such as tetrafluoroborate or hexafluorophosphate, may undergo hydrolysis when in contact with water, resulting in the formation of protic and toxic impurities such as hydrogen fluoride [7].

The high sensitivity of electrochemical experiments demands a rather strict control of the impurities present in these solvents, including other ions, gases and water. Studies conducted in twelve RTILs demonstrated that the amplitude of the electroactive window depends on the amount of water remaining in the solvent after undergoing a given drying process [8]. The electrochemical window shortens, being larger for vacuum-dried RTILs than for water-containing RTILs. Clearly, purity is a determinant factor in the physicochemical properties of RTILs. It has been reported that the presence of chloride in an ionic liquid substantially increases its viscosity, whereas the presence of water reduces it [5]. Water can also alter the mass transport properties [6,9,10] and the reactivity of some electroactive substrates in RTILs [11–13]. Therefore, water is in practice not only an impurity in RTILs, but a rather important modifier of their chemical reactivity.

In RTILs, when the size of the diffusing species is similar to the size of the RTIL ions, the Stokes–Einstein equation seems to work properly [14], thus one of the major factors influencing the diffusion coefficient, D, of electroactive species is the viscosity of the medium, η [15]. Therefore, the water content of the RTILs should be reported in order to prevent systematic errors and incorrect comparisons when calculating data such as the Walden product, Dη.

Water electrolysis in RTILs has been previously reported as a measure to control its presence in these solvents. However, this process does not allow one to determine the amount of water that the RTIL will capture due to handling or storage. Furthermore, various solutes of interest with redox properties might be electrolyzed before water [16]. Water sorption in RTILs has been measured by gravimetric methods, but the exact content of water in the RTILs cannot be determined and the measurement chamber described is not suitable for electrochemical purposes [17]. Although different electroanalytical methods exist for the determination of water content in non-aqueous solvents, most of them are destructive, require large quantities of sample or need extra