STUDY OF THE IMIDAZOLIUM-BASED IONIC LIQUID – Ag ELECTRIFIED INTERFACE ON THE CO$_2$ ELECTROREDUCTION BY SUM FREQUENCY SPECTROSCOPY.

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Imidazolium based ionic liquids (ILs) have been used as a promising system to improve the CO$_2$ electroreduction at lower overpotential than other organic or aqueous electrolytes$^1$. Although the detailed mechanism of the CO$_2$ electroreduction on Ag has not been elucidated yet, we have developed a methodology to study the electrified interface during the CO$_2$ electroreduction using sum frequency generation (SFG) spectroscopy in combination with cyclic voltammetry$^2$. In this work, we tuned the composition of imidazolium-based ILs by exchanging the anion or the functional groups of the imidazolium. We use the nonresonant SFG (NR-SFG) to study the IL-Ag interface and resonant SFG (RES-SFG) to identify the CO adsorbed on the electrode and monitor the Stark shift as a function of cell potential. In previous studies on CO$_2$ electroreduction in the IL: 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF$_4$) on Ag, we showed three events occurred at the same potential (-1.33 V vs. Ag/AgCl): the current associated with CO$_2$ electroreduction increased, the Stark shift of the adsorbed atop CO doubled in magnitude and the EMIM-BF$_4$ underwent a structural transition$^3$. In addition, we also observed how the structural transition of the EMIM-BF$_4$ electrolyte shift to lower potentials when the IL is mixed with water. It is known that water enhances the CO$_2$ electroreduction producing more CO$^4$. Moreover, the CO is adsorbed in multi-bonded and in atop sites when more water is present in the electrolyte.