Iron is the most abundant metal on Earth and is involved in many critically important processes. Iron is commonly found in nature in its mineral forms, and in aqueous solutions as a complex with other soluble salts where hydration also plays a key role in its subsequent speciation. Aqueous interfaces are the gateway to many natural and biological reactions, including those that involve soluble Fe(III). Yet, interfacial iron complexation and surface prevalence are not well understood, especially under the inherently acidic conditions of FeCl₃ solutions. In this study, we investigate interfacial Fe(III) species using second harmonic generation (SHG) combined with surface tension and UV/visible absorption. Surface selective techniques such as SHG have been widely applied to unveil the unique properties of substances within the air-aqueous interface. Here, we observe two different interfacial regions with increasing concentration marked by two distinctly different SHG electric-field (E-field) trends. Below 2.0 mol/kg water aqueous FeCl₃, nonresonant SHG behavior is observed, similar to the E-field generated from the aqueous sodium iodide surface, but much larger in magnitude than aqueous NaCl and NaBr solution surfaces. Above 2.0 mol/kg water, a significant increase in the SHG slope is observed, much larger than that of the aqueous sodium halide electrolyte surfaces. Through further evaluation of symmetry and resonant behavior, we determine the existence of the neutral [FeCl₃](H₂O)₃ complex.