The vibrational structure of water at the air/solution interface of an ionic solution has been obtained for the first time. Using vibrational sum frequency generation it is determined that ions in solution have a large orientational effect on the structure of the surface water. Electrolytic solutions, ionic in nature, cause water to be oriented into a more regular hydrogen-bonded network through an electric double layer at the interface. In electrolytic solutions where molecular or associated H$_2$SO$_4$ or Cs$_2$SO$_4$ species dominate, the surface water molecules are bound into hydrate complexes. These effects are explained using hard soft acid base (HSAB) theory.