X-ray absorption spectroscopy study of queous electrolyte solution critical properties

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The goal of this study is quantify the properties of electrolytes at near-critical conditions using X-ray Absorption Spectroscopy (XAS) techniques on BM30b FAME beamline at ESRF (Grenoble, France) using hydrothermal spectroscopy cell and high-pressure autoclave [1]. Two types of measurements were performed: transmission XAS density measurements and High Energy Resolution Fluorescence Detection (HERFD) XAS measurements via crystal analyzers [2].

With heating from 25 to 500°C at constant pressure (280, 300, 345 and 400bar), the absorption coefficients of chloride and bromide solutions decreases slowly until ~373°C (similarly with pure water), but then increases up to ~380°C, and finally decreases to gas-like values at higher temperatures. These absorption measurements reflect the anomalous density behavior at near-critical T-P-x region. At the same electrolyte concentration 0.3 mol/kg of H_2O, the relative density increase in this critical zone is more pronounced in order Li < Na < K < Rb < Cs for both bromides and chlorides. Complementary HERFD XAS measurements at Br K-edge in bromide solutions at similar T-P-x indicate that this density phenomenon is probably accompanied by structural changes (ion-pairing). Our new data complement previous synchrotron small angle X-ray scattering measurements [3] and open new perspectives for studies on electrolyte aqueous fluid properties in near-critical state.

References

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