

Validation of a quantitative analysis for intramolecular vibrations of electrolytes in the heterophase system by the near-infrared (NIR) spectroscopy

(¹Graduate School of Engineering, Kobe University, ²Faculty of Chemistry, Jagiellonian University) ○Jingchao Xu,¹ Hideshi Maki,¹ Minoru Mizuhata^{1,2}

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Ionic-solvent interactions reflecting the solvation structure of electrolyte solutions are often discussed by infrared and Raman spectroscopy, but the extremely strong infrared absorption and poor quantitative Raman spectroscopy are not suitable for their quantitative analysis very much. In particular, for electrolytes coexisting with solids, where the influence of the interface is reflected, an analytical method with quantitative capability that takes into account the volume fraction of the liquid is necessary. Near-infrared (NIR) spectroscopy can be measured with an ordinary optical cell and has excellent quantitative properties.¹ In this study, the quantitative properties of various aqueous electrolyte solutions and its coexisting system with fumed silica were discussed.

NIR spectra of aqueous chloride solutions containing Li⁺, Na⁺, K⁺, and Ca²⁺ were measured in the wavelength range of 1200-1800 nm using a JASCO V7200 with a 1-mm optical path length cell. Each water occupied volume is calculated from the value of each weight ratio and density. The NIR spectra of liquids coexisting with solids were measured by mixing them with fumed silica to obtain an arbitrary solid phase fraction at the same method. Each intensity of absorption bands assigned to the dissolving species is calculated was calculated from the area intensity based on the spectral shape with the wavenumber as the horizontal axis as shown Fig.1.

Variations of detected absorption intensity of $\nu_1+\nu_3$ at ca 6300cm⁻¹ with water occupied volume in each solution are shown in Fig.2. In all electrolyte systems, the absorbance was lower than the theoretical value expected based on the number of solvent molecules present in the system, whereas the absorbance decreases in proportion to the volume ratio of the water coexisting with fumed silica. This is thought to be due to a decrease in the dielectric constant of the dissolved molecules and a decrease in the absorption coefficient. The difference between the measured and theoretical values in aqueous cationic solutions with different charge densities shows different trends with concentration, which, in combination with the variation of the absorption peaks of water at each concentration, offers the possibility of quantitatively studying the changes in the network structure of water. The relationship between NIR intensity and occupied volume will be discussed in the presentation.

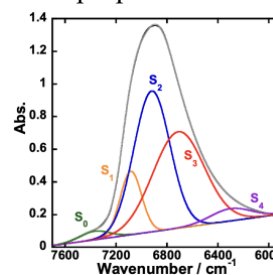


Fig. 1. OH combination band $\nu_1+\nu_3$ of H₂O at ca. 6800 cm⁻¹.

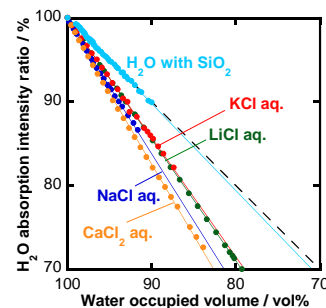


Fig. 2. Absorption intensity ratio of $\nu_1+\nu_3$ of H₂O to occupied volume of water for various circumstance.

Ref. 1) D. H. Dagade et al., *ChemPhysChem*. **2016**, *17*, 902.