Transport Phenomena of High Concentrated Nonaqueous Electrolyte Solutions: A Comparison between Li- and Na-System

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In order to understand deeply the transport phenomena of the ions in electrolyte solutions at high concentrations, the solution density, viscosity and ionic conductivity of Liand Na-TFSI dissolved in GBL and PC were measured at $0.1 \le C/\text{mol}\cdot\text{dm}^{-3} \le 2.0$ and $278 \le T/K \le 328$ (TFSI = bis(trifluoromethanesulfonyl)imide, GBL = γ -butyrolactone and PC = propylene carbonate). The partial molar volume of the solute, derived from the density, confirmed that the Na-systems occupy more volume in the electrolyte solutions than the Li-systems. On the other hand, the viscosity and ionic conductivity suggested that the Na-systems are more fluid and conductive than the Li-systems. The relative viscosity vs. the molarity follows a modified empirical Jones-Dole equation. The molar conductivity linearly decreased with respect to the cube-root of the molarity, which was analyzed by the pseudolattice model. The Raman spectroscopy revealed that, while the solvation number is comparable at 1-2 for either the Li- or Na-systems, Li⁺ is more tightly bound to the solvent molecules than Na⁺. The higher fluidity and conductivity of the Na-systems than those of the Li-systems result from the less occurrence of the solvent-shared ion pairs in the former than in the latter.