

Scaling Relation between Electrochemical Seebeck Coefficient and Viscosity

The electrochemical Seebeck coefficient α ($= dV/dT$; V is redox potential) is a key parameter for thermal energy harvesting. We systematically investigated α for $\text{Fe}^{2+}/\text{Fe}^{3+}$ in 16 organic solvents. α showed remarkable solvent dependence and was distributed from 0.14 mV/K for glycerin to 3.60 mV/K for acetone. We further found a scaling relation between α and viscosity η of the solvent as $\alpha \sim \eta^{-0.4}$, which is interpreted in terms of the configuration entropy of the solvent molecules. In addition, we found that the O_h -type octahedral coordination of the solvent molecules showed D_{4h} -type deformation with increase in α .

To realize a zero-emission society, it is necessary to develop highly efficient and low-cost thermal energy harvesting devices that produce electric energy from human body heat or waste heat near room temperature. An energy harvesting thermocell consisting of hot/cold electrodes of identical type and solution with redox couple was proposed in the 1950s and 1960s and is still undergoing active research and development. Similarly to a solid thermoelectric device, the thermocell converts temperature difference (ΔT) to voltage difference (ΔV) between the electrodes via the electrochemical Seebeck coefficient α . From a thermodynamical point of view, α is $\Delta S/e$, where e and ΔS are the elementary charge (> 0) and variation in entropy S of the system associated with the reduction process, respectively. In the solution system, ΔS is dominated by variation of the configuration entropy (S_{solvent}) of the solvent molecules around the electroactive solute.

Here, we systematically investigated α for $\text{Fe}^{2+}/\text{Fe}^{3+}$ in 16 organic solvents using a specially-designed thermocell [1]. The electrolyte was an organic solution containing 10 mmol/L $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and

10 mmol/L $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The electrolyte was filled in a $\phi 7.3$ mm polytetrafluoroethylene (PTFE) tube. Both ends were sealed with Pt plates, which worked as collecting electrodes. The temperatures (T_{low} and T_{high}) of the two electrodes were monitored with T-type thermocouples. The difference (ΔV) in the redox potential between the electrodes was measured against $\Delta T (= T_{\text{high}} - T_{\text{low}})$ with T_{low} fixed.

Figure 1 shows the correlation between α and viscosity η for the 16 solvents. We found a scaling relation between α and η even though α was widely distributed from 0.14 mV/K for glycerin to 3.60 mV/K for acetone. The observed empirical relation can be interpreted in terms of the configuration entropy of the solvent molecules. The low- η solvent whose molecular interaction is weak has huge configuration entropy (S_{solvent}), reflecting smaller constraint on the orientation and/or distance between neighboring molecules. Furthermore, the variation ($\Delta S_{\text{solvent}}$) of S_{solvent} associated with the reduction process is also huge in the low- η solvent. In the high- η solvent, strong molecular interaction suppresses S_{solvent} , and hence $\Delta S_{\text{solvent}}$.

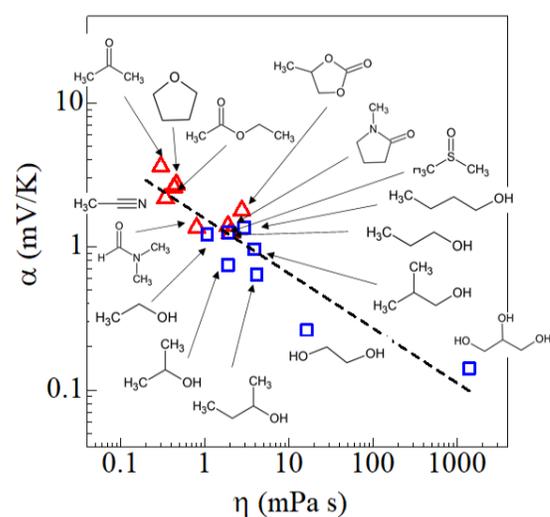


Figure 1: Electrochemical Seebeck coefficient (α) against viscosity (η) of solvent. Squares and triangles represent protic and aprotic solvents, respectively.

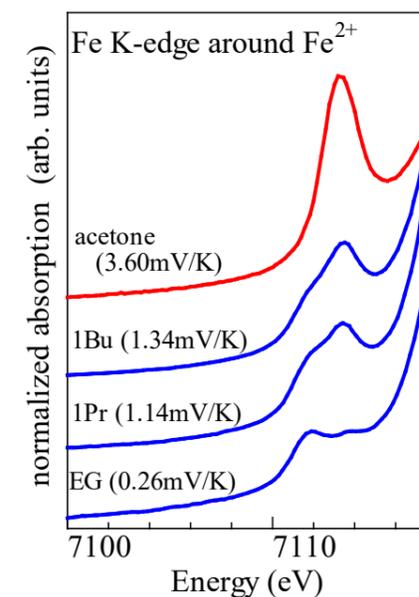


Figure 2: Pre-edge spectra at the Fe K-edge around Fe^{2+} in several solutions. EG, 1Pr, and 1Bu denote ethylene glycol, 1-propanol, and 1-butanol, respectively. Physical quantities in parentheses indicate α of the solvent.

By means of X-ray absorption near-edge structure (XANES) spectroscopy, we further observed C_{4v} -type deformation of the FeL_6 (L is ligand) octahedra as α increased. Fe^{2+} dissolved in H_2O , methanol, or ethanol took the O_h -type octahedral coordination [2]. Figure 2 shows pre-edge spectra at the Fe K-edge around Fe^{2+} in several solutions. Absorbance was normalized by the intensity of the main peak. In the EG ($\alpha = 0.26$ mV/K) spectrum, a clear doublet structure is observed. We note that the pre-edge spectra systematically change as α increases. In the 1Pr (1.14 mV/K) and 1Bu (1.34 mV/K) spectra, the intensity of the higher-lying band becomes stronger even though the doublet structure is still discernible. In the acetone (3.60 mV/K) spectra, the lower-lying band almost disappears. These characteristic spectral changes could be ascribed to C_{4v} -type deformation of the FeL_6 (L is ligand) octahedra, i.e., contraction of one Fe – L distance [3]. Such a C_{4v} -type deformation increases the number of the equivalent ligand configuration, and hence enhances $\Delta S_{\text{solvent}}$.

In conclusion, we found a scaling relation between

α and η of the solvent as $\alpha \sim \eta^{-0.4}$ and interpreted the relation in terms of the enhanced $\Delta S_{\text{solvent}}$ in the low- η solution. Furthermore, α showed strong solvent dependence and was widely distributed from 0.14 mV/K for glycerin to 3.60 mV/K for acetone. Based on the pre-edge spectra at the Fe K-edge around Fe^{2+} , the solvent dependence is ascribed to D_{4v} -type deformation of the FeL_6 octahedra.

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