

Supporting Information

Imbalance between Anion and Cation Distribution at Ice Interface with Liquid Phase in Frozen
Electrolyte as Evaluated by Fluorometric Measurements of pH

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pH measurements of frozen solutions

The ratio of the fluorescence intensity measured at $\lambda_{\text{ex}}=455$ nm to that at $\lambda_{\text{ex}}=405$ nm (I_{455}/I_{405}) is a function of pH because the former mainly comes from the dissociated species of pyranine (Py^-) and the latter from the protonated one (HPy). Figure S1 shows a calibration graph for pH in the solution phase at 25 °C. However, this graph is applicable only to the determination of pH at the same temperature and the same ionic strength. The ratio, I_{455}/I_{405} , reflects the dissociation state of pyranine rather than pH in a medium. The calibration graph for pH (the upper graph in Figure S1) was therefore converted to the relation between I_{455}/I_{405} and the dissociation degree of pyranine using the fluorescence intensities measured at pH 4.0 and 10.0 as shown in the lower panel of Figure S1. This relation is applicable to any solution unless the spectral features of pyranine are changed.

Even in a frozen state, fluorescence comes from pyranine dissolved in the WPI. The relation between I_{455}/I_{405} and the dissociation degree of pyranine thus holds true regardless of whether a sample is unfrozen or frozen. With corrected $\text{p}K_{\text{a}}$ of pyranine (given in Table 1), pH of the WPI can be calculated from the dissociation degree of pyranine (α).

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{1 - \alpha}{\alpha}$$

The pH values reported in Figure 3 were thus determined from the experimental fluorescence ratio of a frozen sample.

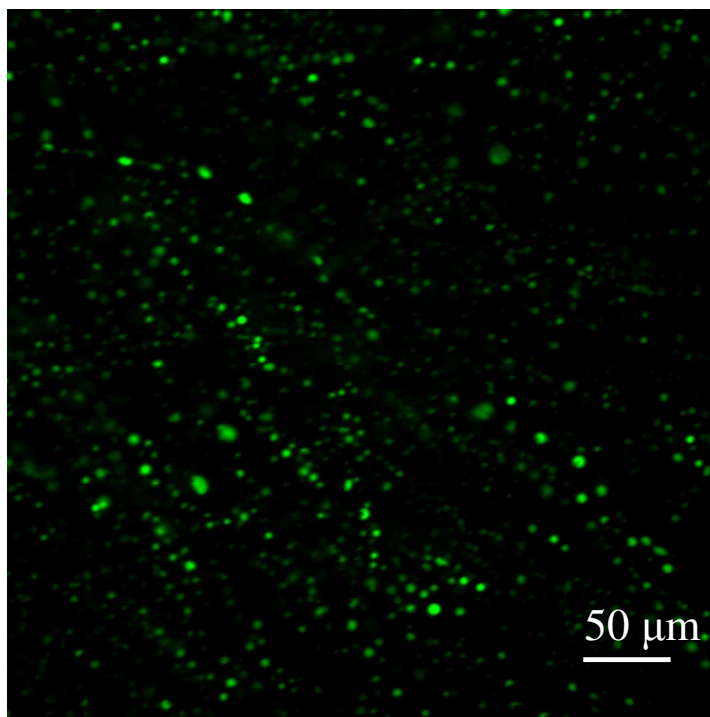


Figure S1 Fluorescence micrograph of a frozen KCl pyranine solution.

The concentrations of KCl and pyranine in the original unfrozen solution were 10 mM and 10 μ M, respectively. Temperature, -5 $^{\circ}$ C. The excitation wavelength (λ_{ex}) and the emission wavelength (λ_{em}) ranges were set to 460-480 nm and 495-540 nm, respectively.

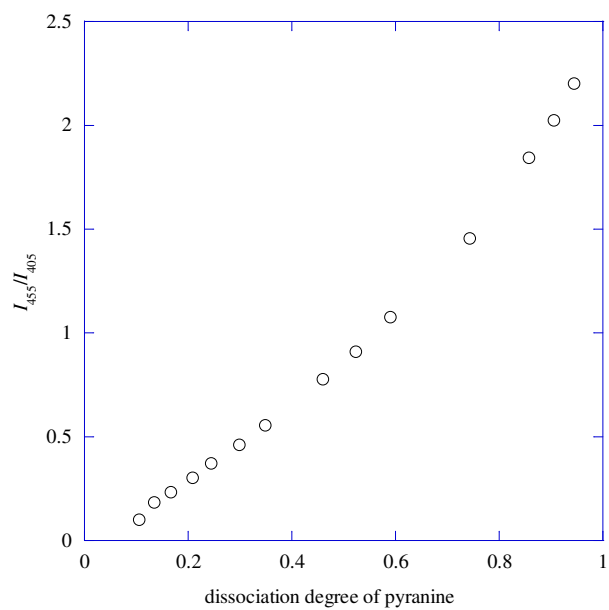
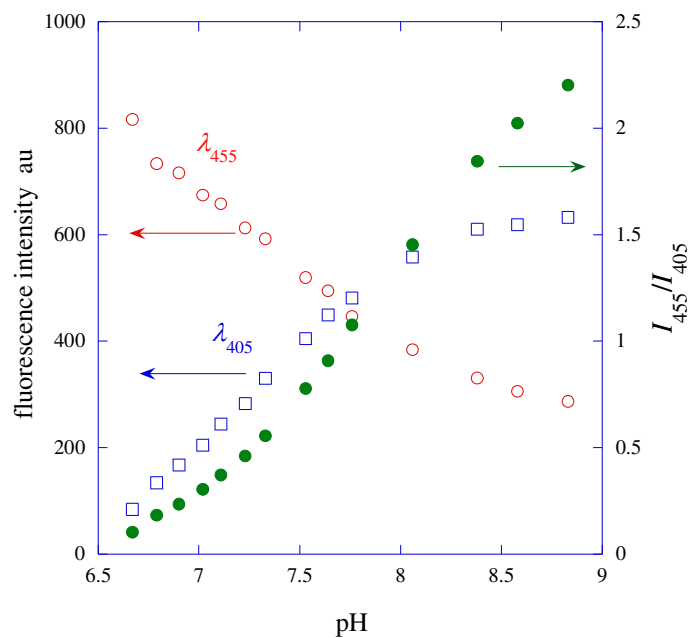


Figure S2 Typical calibration graphs for pH determination from the fluorescence intensity ratio (upper) and the relation between the dissociation degree of pyranine and the fluorescence intensity ratio in solution.

Phosphate buffer of 2 mM containing 2 μ M pyranine. Fluorescence measurement at 510 nm.

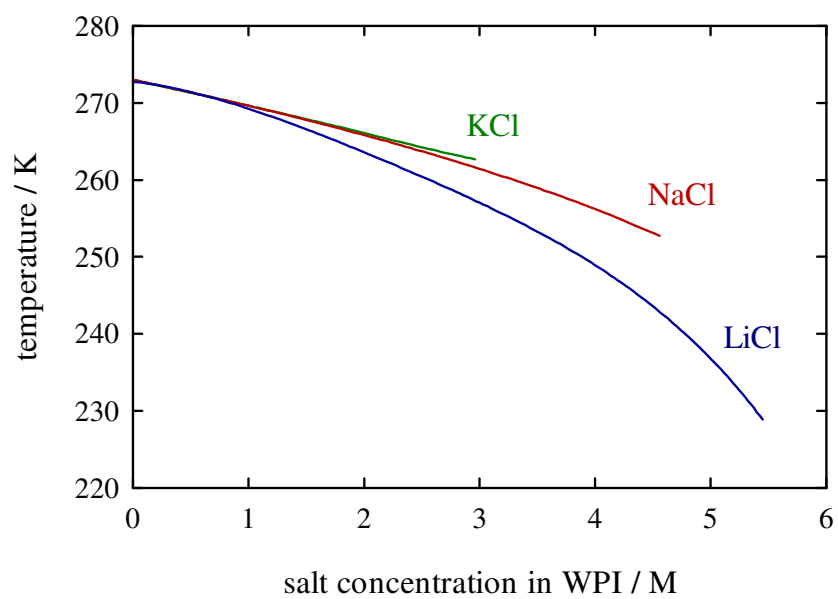


Figure S3 Freezing point depression curves for LiCl, NaCl, and KCl/water systems.

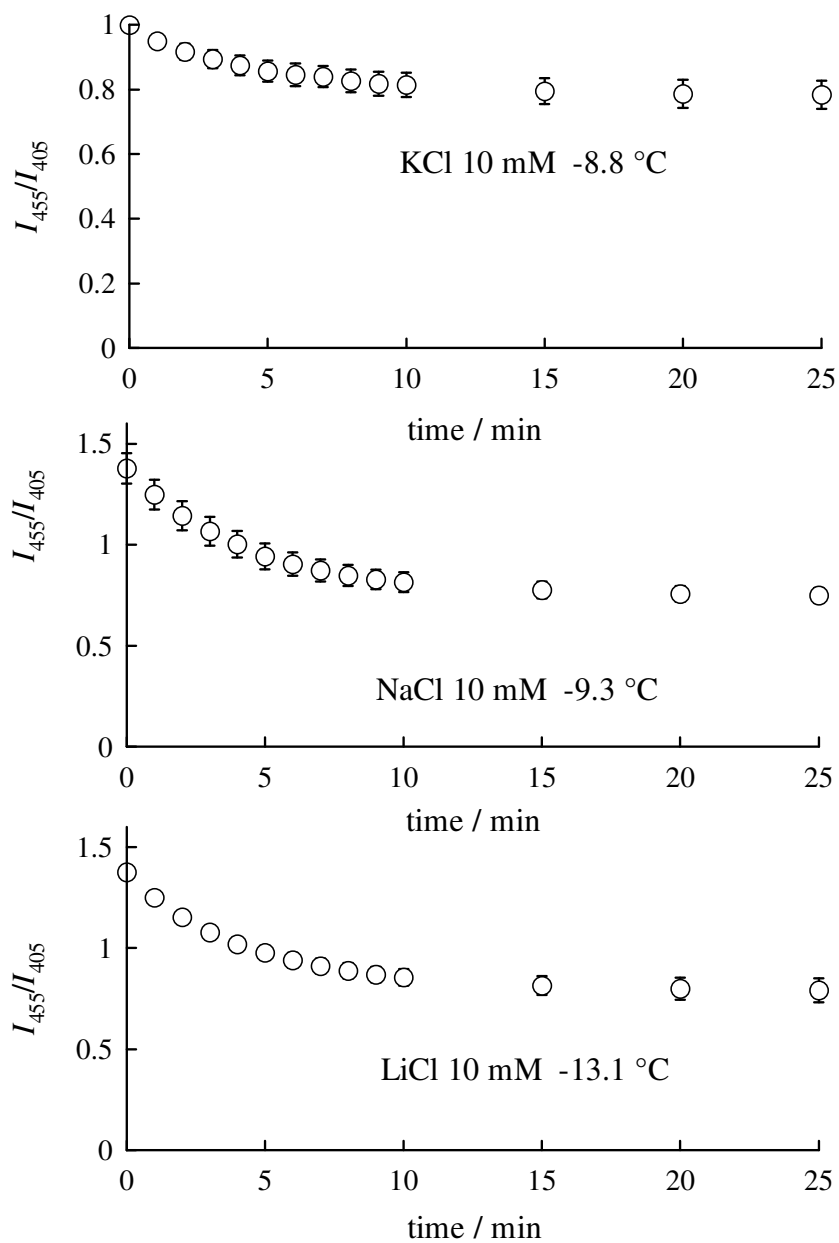


Figure S4 Time changes of fluorescence intensity ratio (I_{455}/I_{405}) with time after the sample was

transferred on the Peltier array set at the individual temperature

Standard errors are shown by error bars ($n=4$)

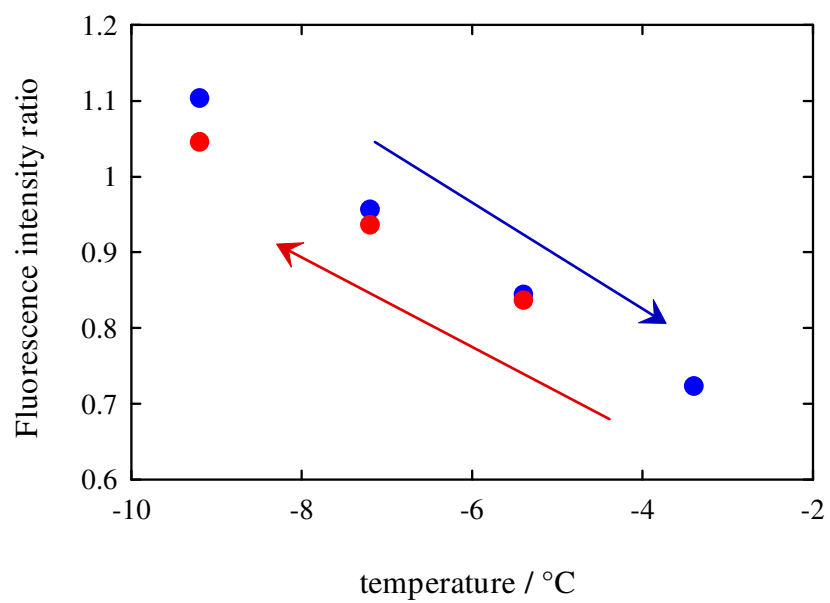


Figure S5 Hysteresis of fluorescence intensity ratio for frozen NaCl/water system