

Electronic Supplementary Information (ESI)

Microscale pH Inhomogeneity in Frozen NaCl Solutions

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Figure S1 Dependence of the fluorescence intensity from the FCS on the observation
depth

Figure S2 Freezing depression curves for NaCl/water and glycerol/water.

Figures S3-S5 pH distributions in the FCS on the surface of frozen 20 mM NaCl.

Figure S6 Relationship between pH and fluorescence intensity in the FCS.

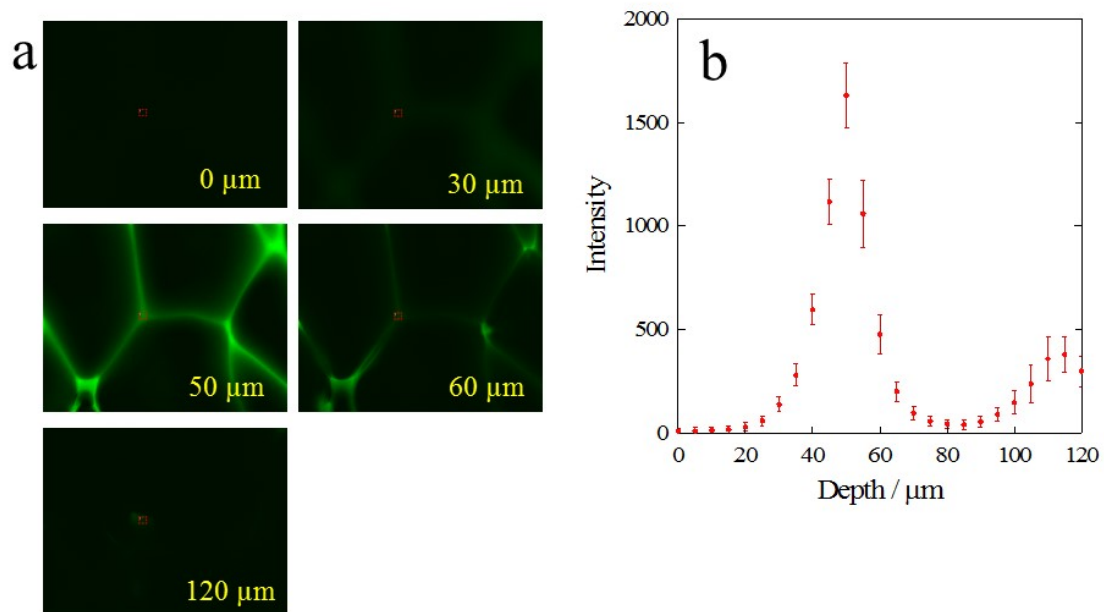


Figure S1 Dependence of the fluorescence intensity from the FCS on the observation depth. Sample, frozen 20 mM NaCl at -7.2 °C. (a) Images measured at various depth. (b) Change in the intensity (measured for 868 pixels) with depth. The zero depth was arbitrarily defined.

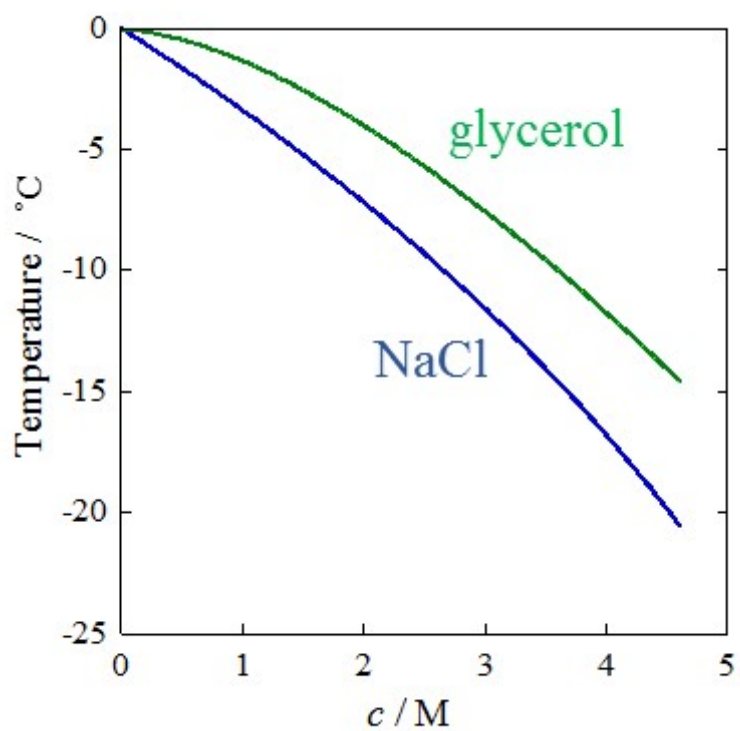


Figure S2 Freezing depression curves for NaCl/water and glycerol/water.

The data were taken from ref.37 (NaCl/water) and ref.42 (glycerol/water).

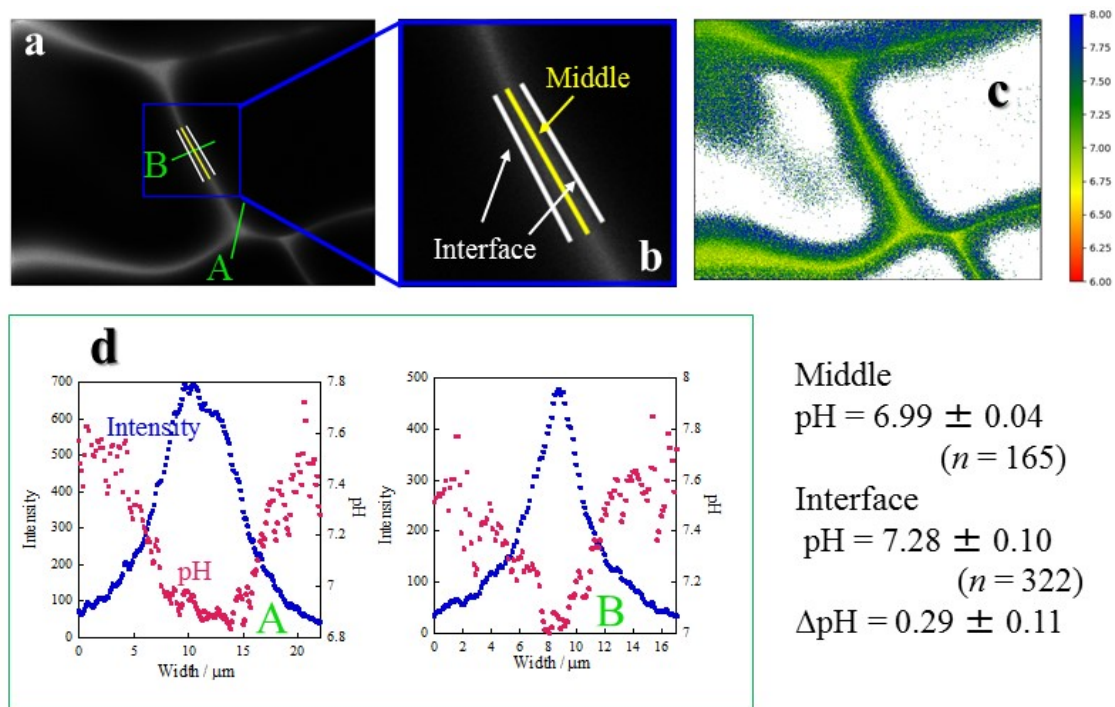


Figure S3 pH distribution in the FCS on the surface of frozen 20 mM NaCl (0.5 μM pyranine) at -7.2 $^{\circ}\text{C}$. (a) Fluorescence surface image measured using the $\lambda_{\text{ex}}=473$ nm laser. (b) Magnified fluorescence image of the area specified with a blue rectangle in part a. White and yellow lines represent interfacial and middle lines, respectively, along which pH values were collected. (c) pH distribution map. (d) Cross-sectional fluorescence intensities and pH distributions across a triple junction (line A shown in part a) and a vein (line B). The pH values in the middle and at the interface are also summarized.

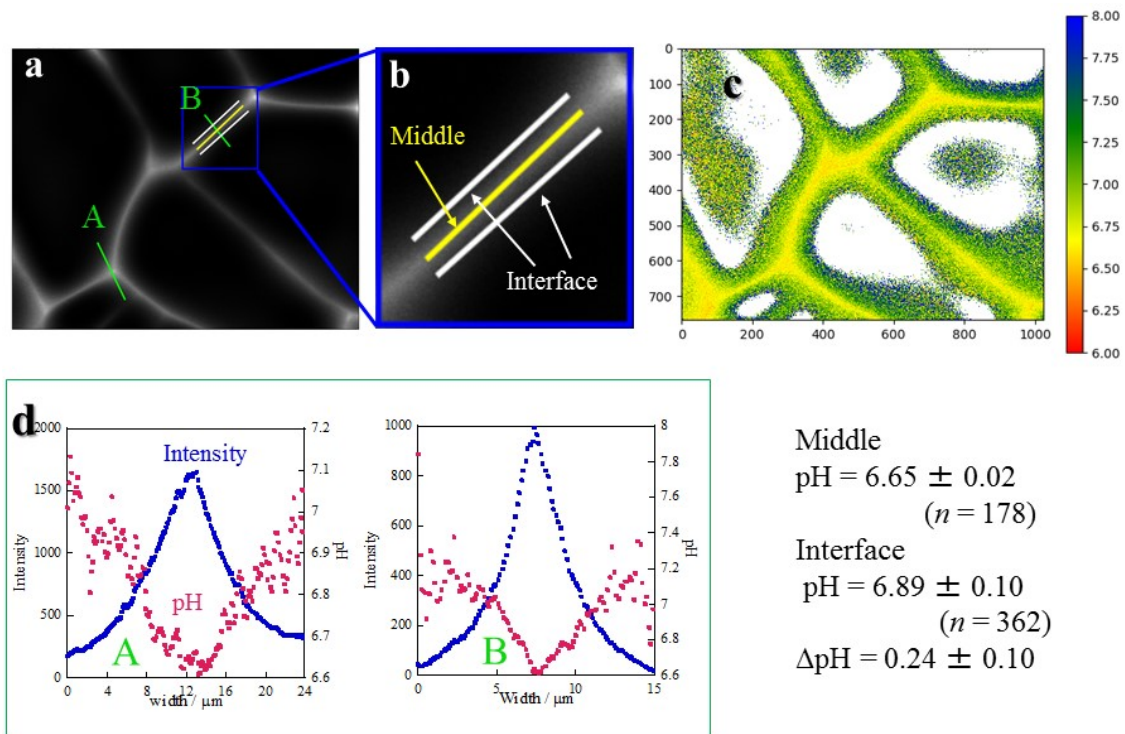


Figure S4 pH distribution in the FCS on the surface of frozen 20 mM NaCl (0.5 μ M pyranine) at -7.2 $^{\circ}$ C. (a) Fluorescence surface image measured using the $\lambda_{\text{ex}}=473$ nm laser. (b) Magnified fluorescence image of the area specified with a blue rectangle in part a. White and yellow lines represent interfacial and middle lines, respectively, along which pH values were collected. (c) pH distribution map. (d) Cross-sectional fluorescence intensities and pH distributions across a triple junction (line A shown in part a) and a vein (line B). The pH values in the middle and at the interface are also summarized.

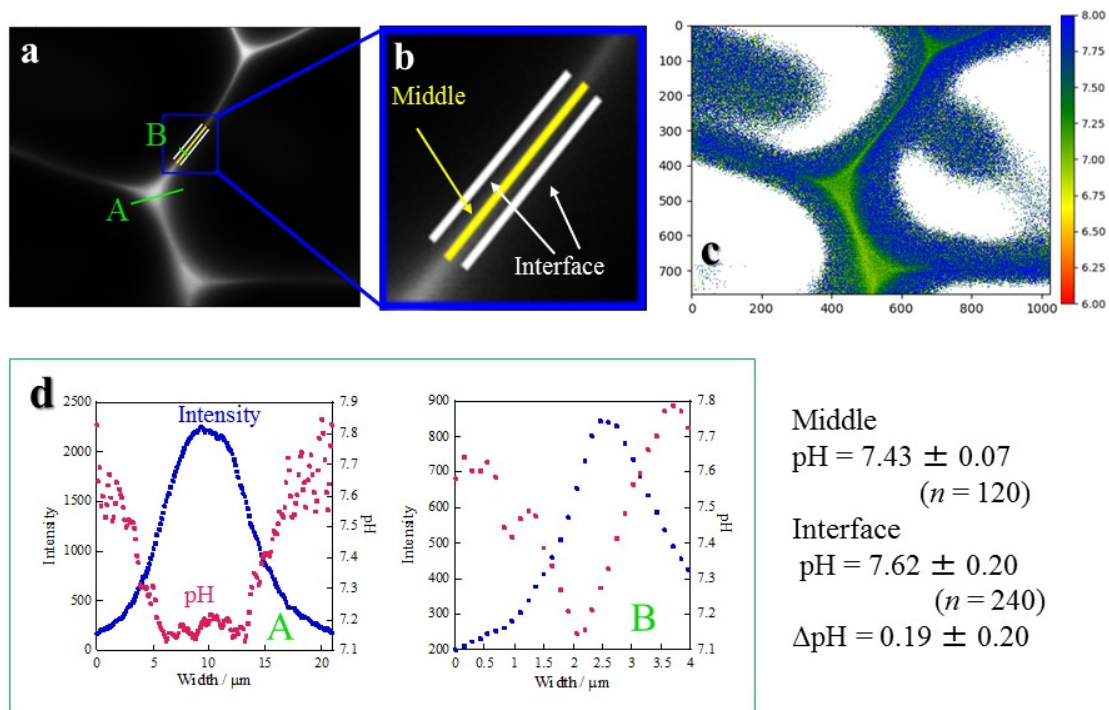


Figure S5 pH distribution in the FCS on the surface of frozen 20 mM NaCl (20 μM pyranine) at -7.2 °C. (a) Fluorescence surface image measured using the $\lambda_{\text{ex}}=473$ nm laser. (b) Magnified fluorescence image of the area specified with a blue rectangle in part a. White and yellow lines represent interfacial and middle lines, respectively, along which pH values were collected. (c) pH distribution map. (d) Cross-sectional fluorescence intensities and pH distributions across a triple junction (line A shown in part a) and a vein (line B). The pH values in the middle and at the interface are also summarized.

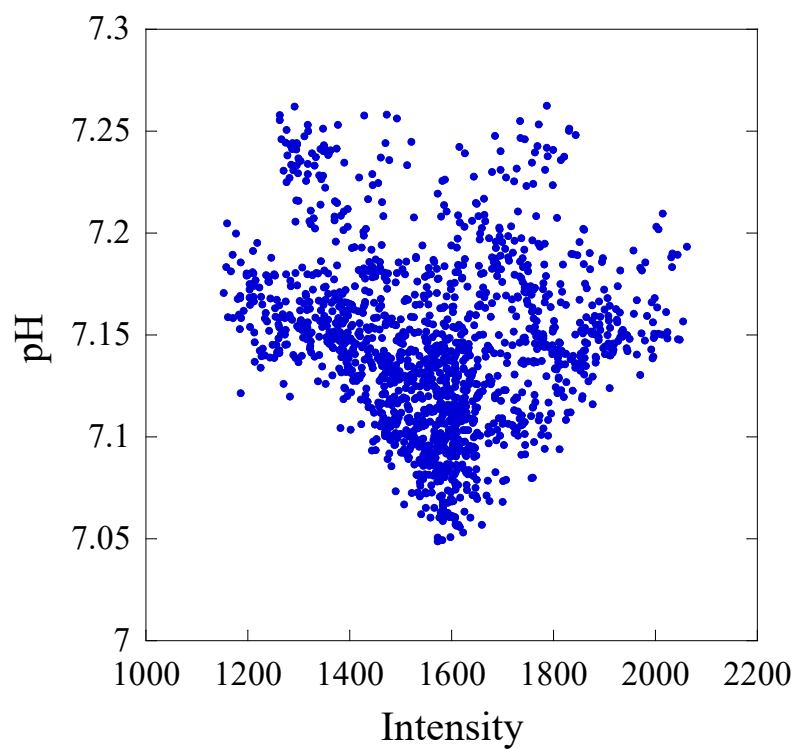


Figure S6 Relationship between pH and fluorescence intensity in the FCS measured at $\lambda_{\text{ex}}=473$ nm. Data points were taken from Figure 2e.