

Supplementary Information

The Role of Carboxylate Side Chains in the Cation Hofmeister Series

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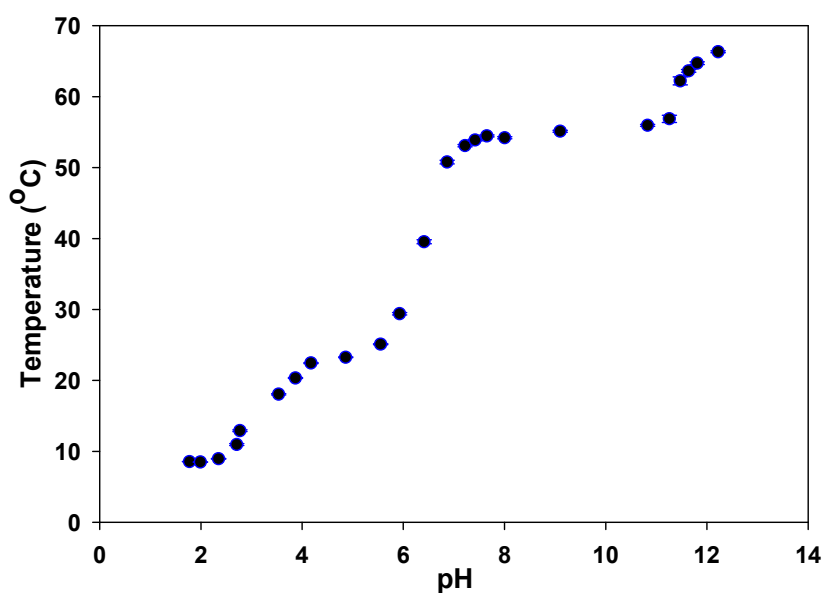
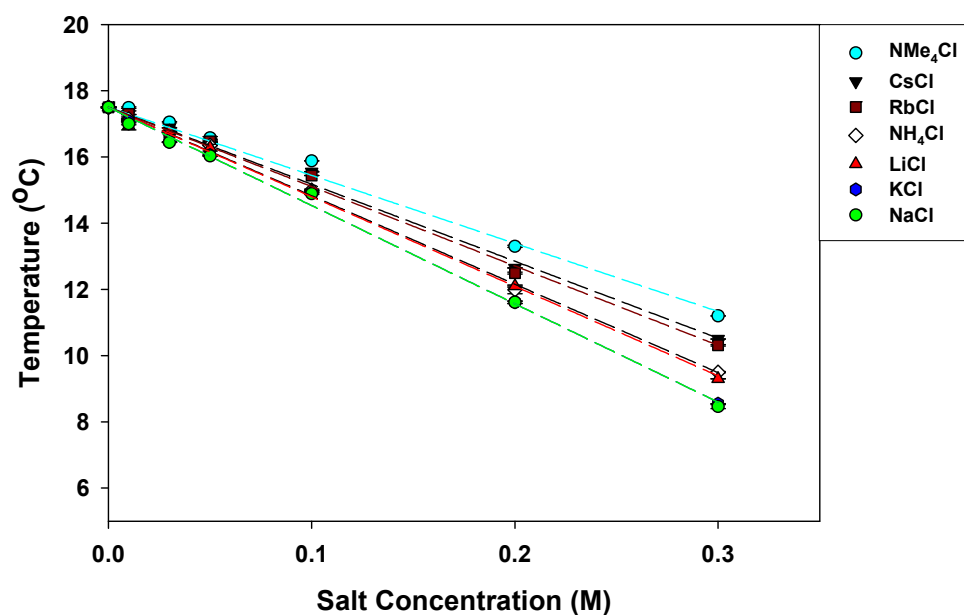
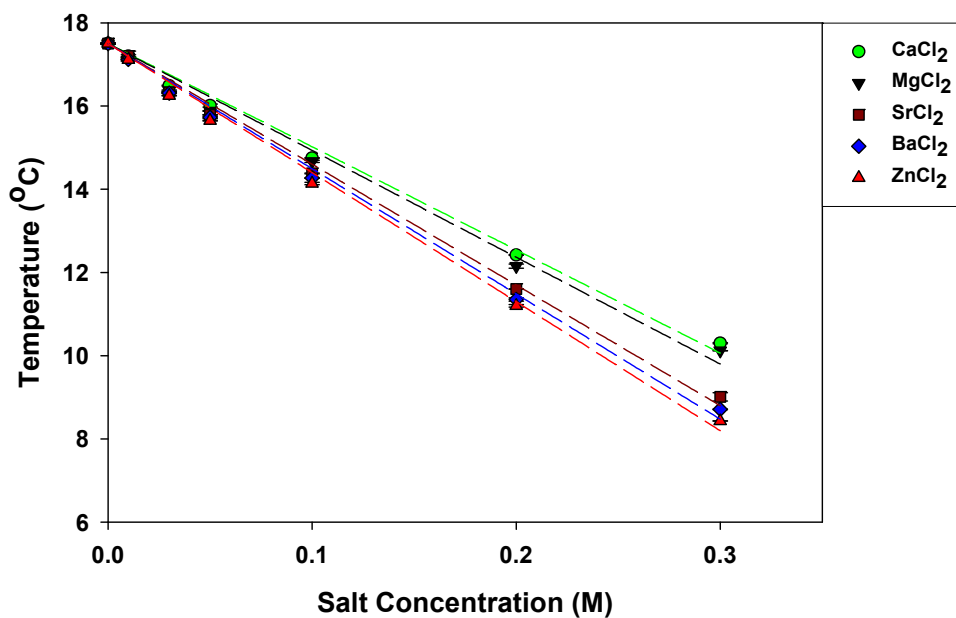


Figure S1. LCST values of ELP DV₂F-64 as a function of solution pH. All measurements were done with 10 mg/ml ELP dissolved in 300 mM NaCl solutions in 10 mM sodium phosphate buffer at each respective pH value. Each data point represents an average of six measurements. As can be seen, the LCST increases steadily from pH 3.0 until approximately 7.5, where a plateau is reached. This should correspond to the deprotonation of carboxylate groups on the ELP in agreement with the VSFS results in Figure 3. As such, LCST results taken at 9.76 (Figure 1 & 2) are nearly insensitive to small deviations in pH. The further rise in the LCST just above pH 11 should be caused by the deprotonation of a lysine residue near the *N*-terminus of the polypeptide sequence.



(A)



(B)

Figure S2. LCST response of ELP DV₂F-64 at pH 2.5 in the presence of (A) monovalent chloride and (B) divalent chloride salts. All experiments were performed with 10 mg/ml ELP in 10 mM Tris HCl. Each data point represents an average of six measurements and the dashed lines are the best fits to the data points.

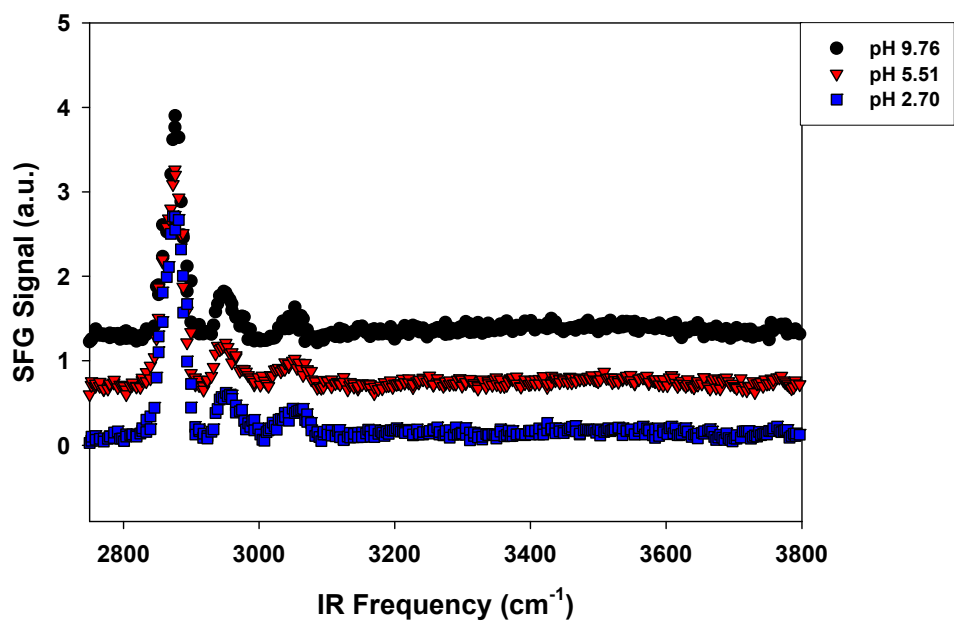


Figure S3. VSFS spectra of ELP DV₂F-64 as a function of pH at the air/water interface using D₂O. All experiments were performed with 1 mM Tris buffer made with 99.9% D₂O at pH 9.76. The pH was adjusted to lower values by the addition of a small amount of concentrated HCl. The spectra are offset by 0.6 units each for the sake of clarity.

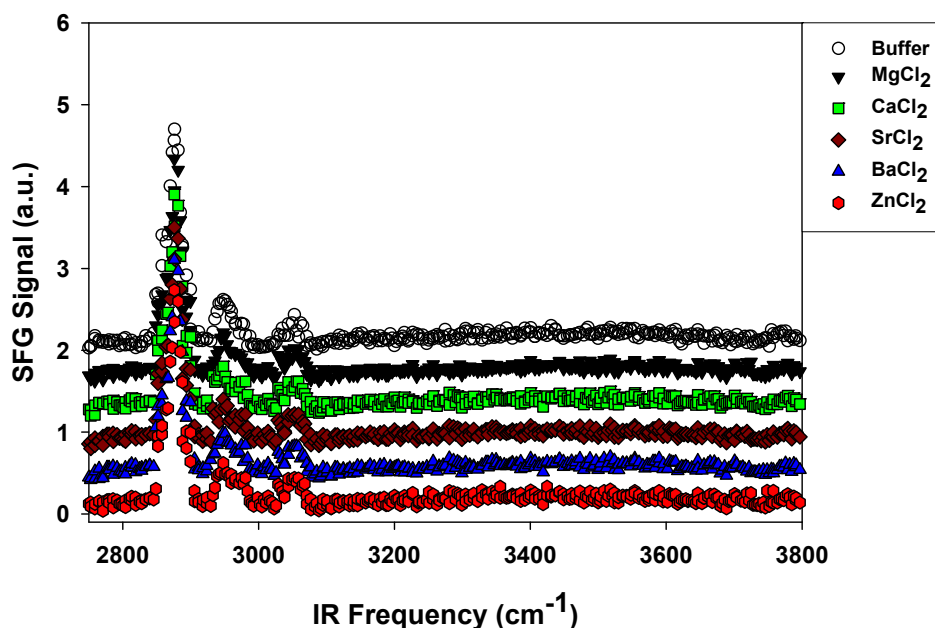


Figure S4. VSFS spectra of ELP DV₂F-64 in the presence of deuterated solutions of 16.66 mM divalent chloride salts. All experiments were performed with 1 mM Tris buffer made with 99.9 % D₂O at pH 9.76. The spectra are offset by 0.4 units each for the sake of clarity.

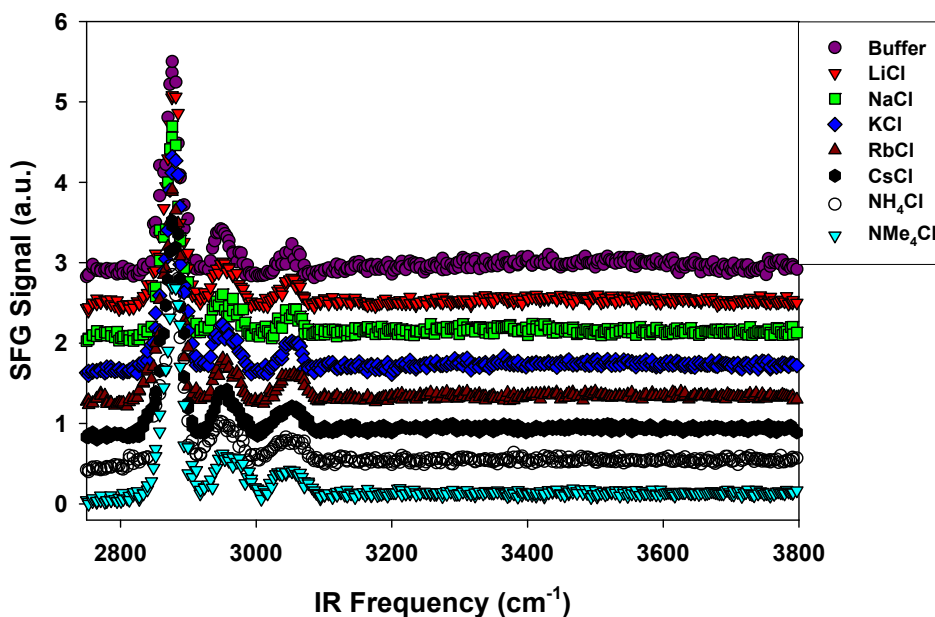


Figure S5. VSFS spectra of ELP DV₂F-64 in D₂O with 50 mM monovalent chloride salts. All experiments were performed with 1 mM Tris buffer made with 99.9% D₂O at pH 9.76. The spectra are offset by 0.4 units each for the sake of clarity.