

Supplementary Information

for

Ion-specific Protein/Water Interface Determines the Hofmeister Effect on the Kinetic Stability of Glucose Oxidase

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Fig. S1

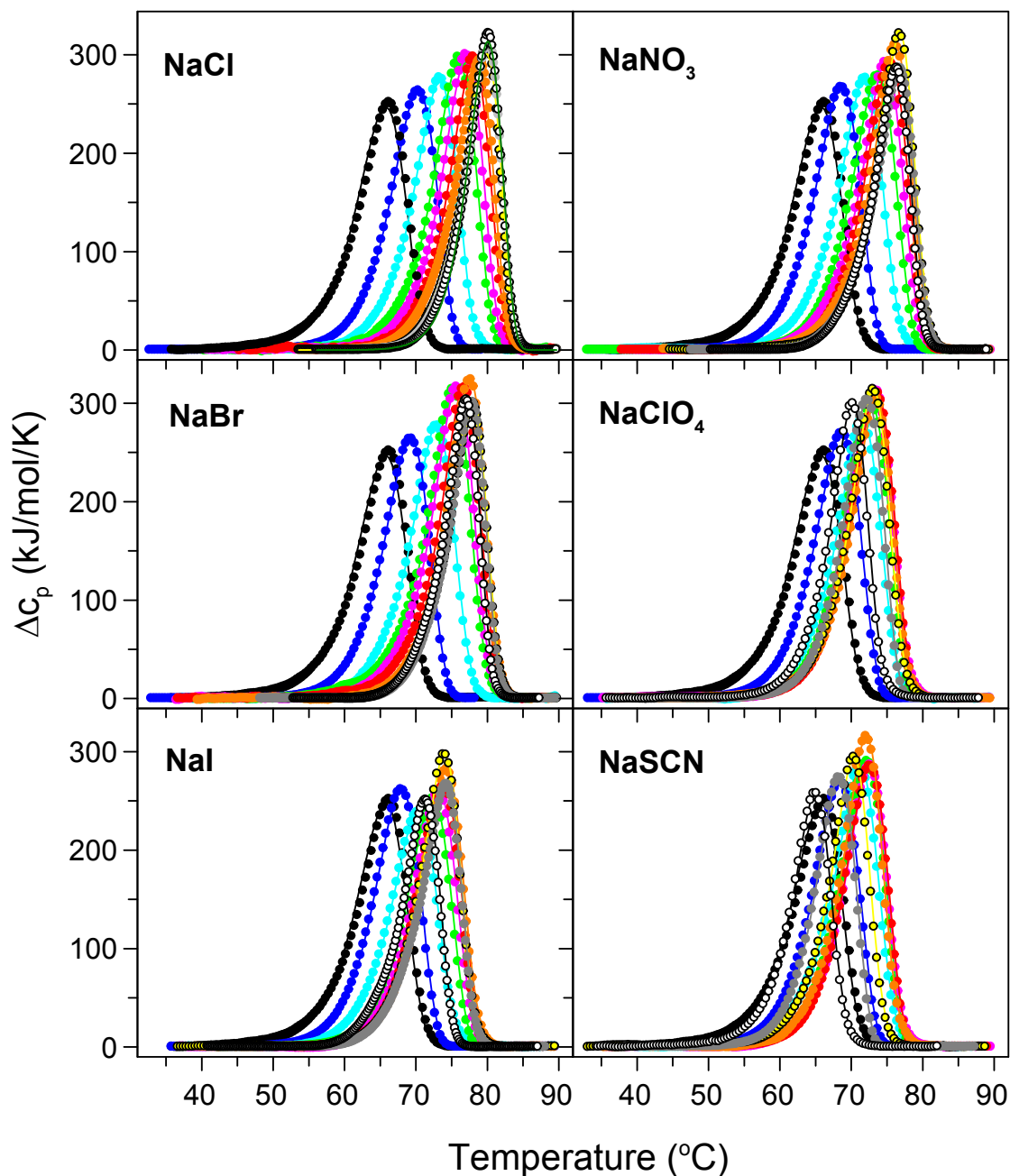


Fig. S1. DSC scans of GOX in the presence of sodium chloride, bromide, iodide, nitrate, perchlorate, and thiocyanate at concentrations 0.15M (blue), 0.3M (cyan), 0.5M (green), 0.6M (magenta), 0.7M (red), 0.9M (orange), 1.3M (yellow), 1.5M (dark grey), and 2.0M (white). DSC scan of GOX in the absence of salt is shown in black. Experimental points are shown as dots and the corresponding fits are shown as solid line. Scan rate was 1.5 °C/min in all cases.

Fig. S2

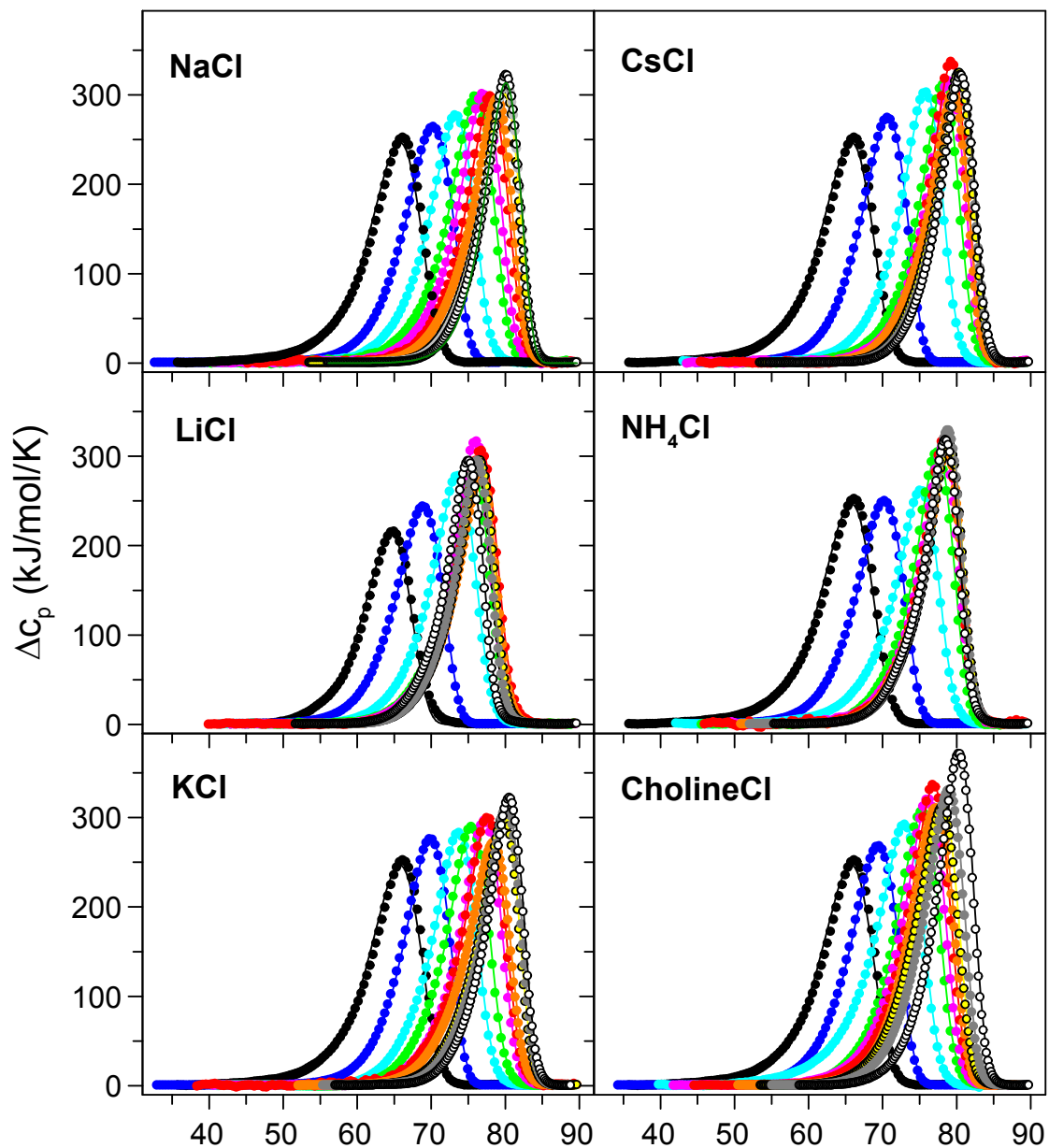


Fig. S2. DSC scans of GOX in the presence of chloride sodium, lithium, potassium, cesium, ammonium, and choline at concentrations 0.15M (blue), 0.3M (cyan), 0.5M (green), 0.6M (magenta), 0.7M (red), 0.9M (orange), 1.3M (yellow), 1.5M (dark grey), and 2.0M (white). DSC scan of GOX in the absence of salt is shown in black. Experimental points are shown as dots and the corresponding fits are shown as solid line. Scan rate was 1.5 °C/min in all cases.

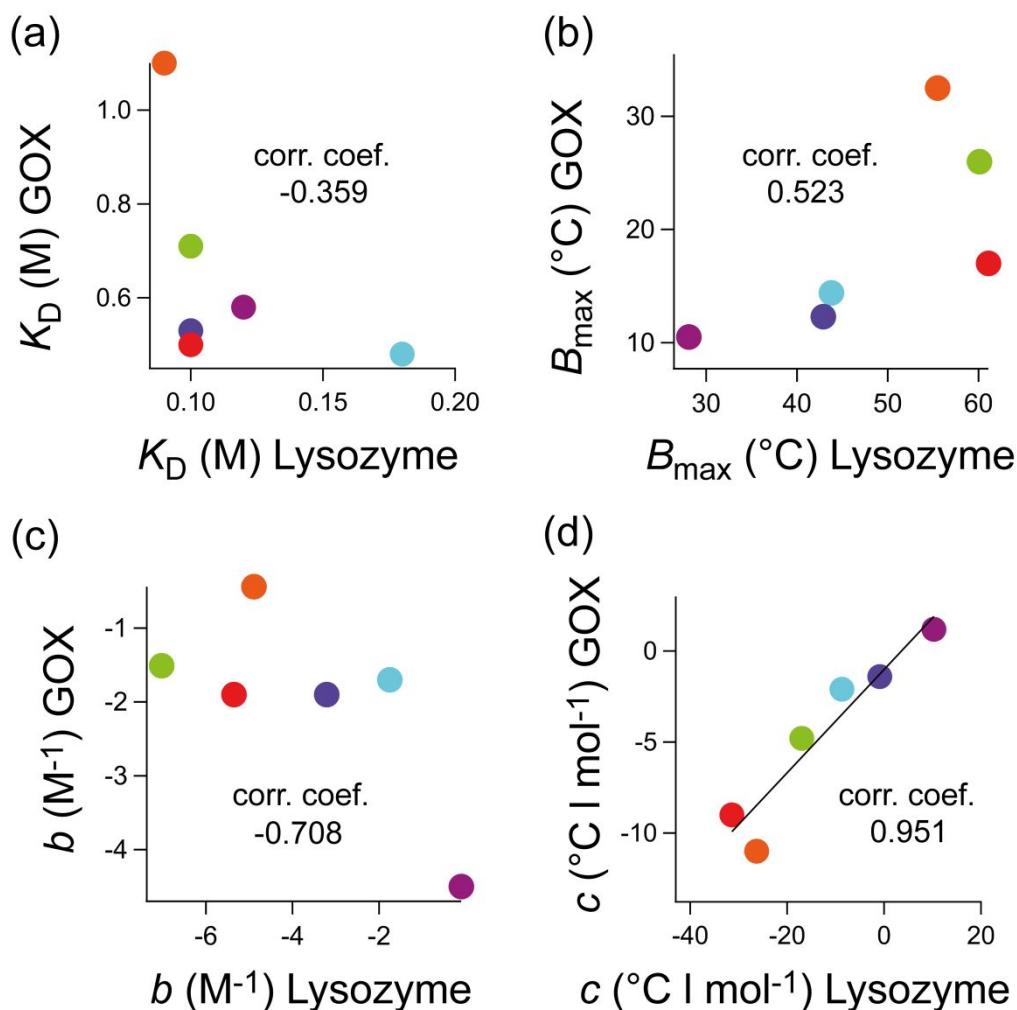


Fig. S3. Correlation between values obtained from the extended Langmuir adsorption model for GOX and lysozyme obtained for different anions. Plots (a)-(c) show very weak/no correlations, which indicate that these parameters are highly protein-specific and hence different between GOX and lysozyme. On the other hand, plot (d) shows high positive correlation between the c -values for GOX and lysozyme. Color codes for anions: thiocyanate (red), iodide (orange), perchlorate (green), bromide (light blue), nitrate (dark violet) and chloride (magenta).

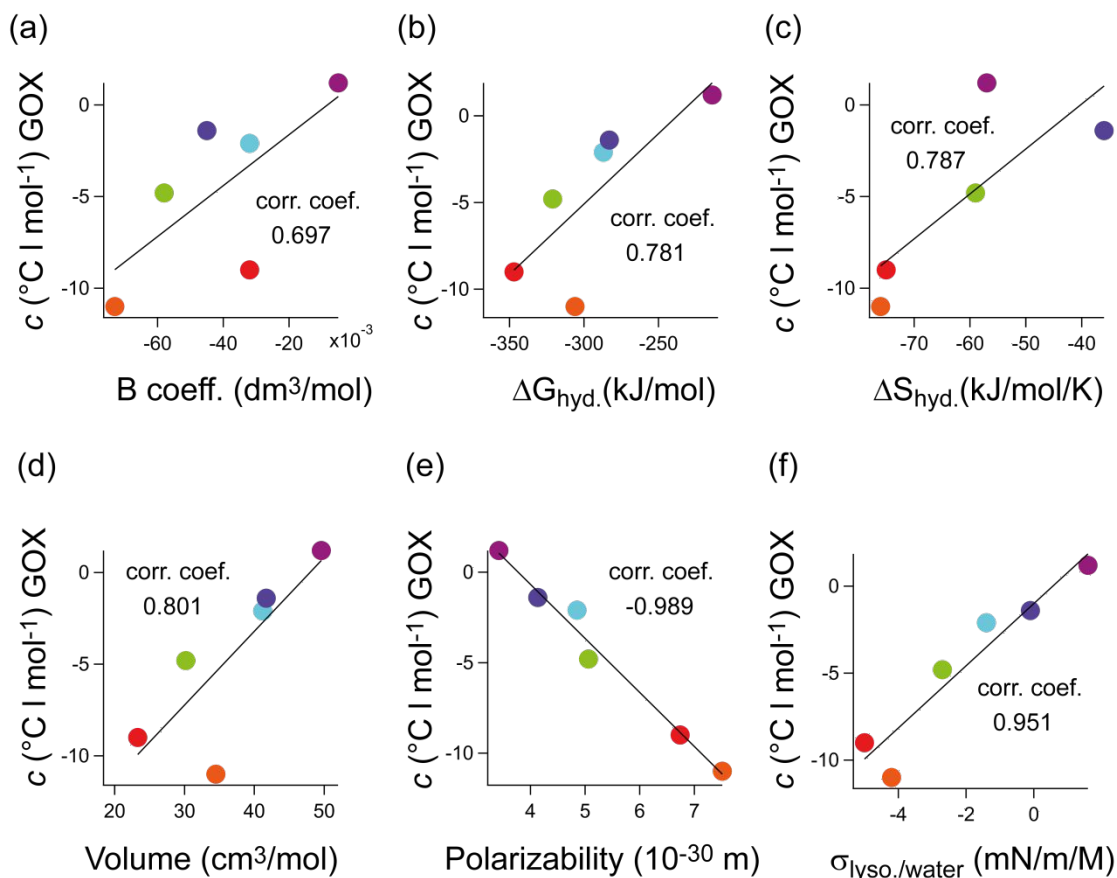


Fig. S4. Correlation between the c-parameter from the extended Langmuir model and other physical properties such as: (a) Jones-Dole coefficient for a given ion, (b) free energy of ion hydration, (c) entropy of ion hydration, (d) ion volume, (e) ion polarizability, and (f) protein/water surface tension of a given ion taken from¹. Color codes for anions: thiocyanate (red), iodide (orange), perchlorate (green), bromide (light blue), nitrate (dark violet) and chloride (magenta).

Table S1. Parameters, E_a - activation energy, T_k - temperature at which rate constant of the irreversible transition is 1 min^{-1} , T_m – transition temperature corresponding to the maximum of DSC curves, ΔH_{cal} – calorimetric enthalpy corresponding to the area under the DSC curve, of irreversible thermal transitions of GOX in the presence of sodium anions measured by DSC.

Salt	(mM)	E_a^* (kJ/mol)	T_k (°C)	T_m (°C)	ΔH_{cal} (kJ/mol)	Salt	(mM)	E_a (kJ/mol)	T_k (°C)	T_m (°C)	ΔH_{cal} (kJ/mol)
none	0**	283	68.9	66.2	2229						
NaCl	150	310	72.0	69.9	2231	NaNO ₃	150	310	71.0	68.5	2240
	300	333	75.4	73.3	2185		300	319	74.1	72.0	2257
	500	344	78.0	75.9	2302		500	329	75.9	73.8	2270
	600	361	78.8	76.9	2235		600	338	76.8	74.7	2290
	700	371	79.7	78.0	2175		700	344	77.4	75.2	2296
	900	383	80.4	78.9	2070		900	357	77.9	76.1	2305
	1300	420	81.1	79.9	1991		1300	390	78.1	76.7	2200
	1500	428	81.2	80.2	1994		1500	375	78.2	76.8	2026
2000	443	81.1	80.1	1971	2000	401	77.5	76.4	1895		
NaBr	150	313	71.6	69.4	2200	NaClO ₄	150	311	71.0	68.8	2258
	300	326	75.1	73.1	2238		300	321	73.8	71.7	2300
	500	334	77.3	75.1	2486		500	332	74.9	72.6	2400
	600	343	77.7	75.7	2454		600	338	75.4	73.3	2445
	700	358	78.5	76.9	2358		700	340	75.5	73.4	2453
	900	372	79.1	77.7	2290		900	349	75.3	73.6	2248
	1300	392	79.2	78.0	2047		1300	357	74.8	73.0	2307
	1500	408	79.0	77.8	1971		1500	366	73.8	72.1	2207
2000	424	78.1	77.1	1905	2000	373	71.6	70.2	2073		
NaI	150	311	70.4	67.9	2175	NaSCN	150	311	70.8	68.5	2252
	300	321	72.8	70.1	2032		300	322	73.5	71.2	2309
	500	330	74.5	72.3	2031		500	333	74.3	72.2	2315
	600	338	75.3	73.1	2031		600	339	74.5	72.6	2218
	700	342	75.8	73.8	2081		700	341	74.6	72.5	2232
	900	349	76.1	74.3	2145		900	350	73.9	72.0	2350
	1300	364	75.6	73.8	2107		1300	357	72.0	70.4	2127
	1500	363	75.8	74.3	1928		1500	356	70.0	68.2	2003
2000	382	72.7	71.4	1695	2000	351	66.5	65.1	1840		

* Estimated errors of E_a , T_k , T_m , and ΔH_{cal} are $\pm 5\%$, ± 0.1 °C, ± 0.1 °C, and $\pm 5\%$, respectively.

**Buffer 50 mM sodium phosphate buffer, pH 7.2, was used.

Table S2. Parameters, E_a - activation energy, T_k - temperature at which rate constant of the irreversible transition is 1 min^{-1} , T_m – transition temperature corresponding to the maximum of DSC curves, ΔH_{cal} – calorimetric enthalpy corresponding to the area under the DSC curve, of irreversible thermal transitions of GOX in the presence of chloride cations measured by DSC.

Salt	(mM)	E_a^* (kJ/mol)	T_k (°C)	T_m (°C)	ΔH_{cal} (kJ/mol)	Salt	(mM)	E_a (kJ/mol)	T_k (°C)	T_m (°C)	ΔH_{cal} (kJ/mol)
none	0**	304	67.3	65.0	1777						
LiCl	150	320	71.2	68.9	1980	NH ₄ Cl	150	319	72.5	70.3	2051
	300	340	75.5	73.8	2151		300	341	77.2	75.1	2025
	500	359	77.4	75.6	2055		500	386	78.9	77.5	2127
	600	372	77.6	76.2	2213		600	398	79.6	78.0	2089
	700	378	78.3	76.9	2164		700	408	79.7	78.4	2107
	900	386	78.1	76.7	1929		900	403	80.0	78.7	2030
	1300	409	77.7	76.5	1913		1300	420	80.0	78.8	2001
	1500	416	77.4	76.1	1875		1500	425	79.9	78.8	2062
	2000	419	76.2	75.0	1848		2000	429	79.6	78.6	1973
	KCl	150	329	72.0	69.8		2195	CholineCl	150	313	71.8
300		341	75.7	73.8	2189	300	308		75.3	72.7	2452
500		354	77.3	75.5	2178	500	352		77.1	75.2	2316
600		358	78.9	77.2	2152	600	359		77.9	76.0	2383
700		362	79.4	77.6	2231	700	369		78.5	76.8	2440
900		366	80.1	78.4	1997	900	368		79.0	77.3	2303
1300		397	81.2	79.7	2046	1300	367		79.7	77.9	2287
1500		411	81.4	80.2	2051	1500	388		80.3	78.8	2305
2000		434	81.6	80.4	2020	2000	434		81.4	80.3	2337
CsCl		150	328	72.9	70.7	2199					
	300	358	77.6	76.0	2251						
	500	385	79.6	78.2	2175						
	600	398	80.4	78.9	2153						
	700	412	80.6	78.9	2238						
	900	395	80.9	79.5	2050						
	1300	426	81.4	80.2	2064						
	1500	435	81.6	80.5	2006						
2000	441	81.6	80.6	1992							

* Estimated errors of E_a , T_k , T_m , and ΔH_{cal} are $\pm 5\%$, $\pm 0.1^\circ\text{C}$, $\pm 0.1^\circ\text{C}$, and $\pm 5\%$, respectively.

**Buffer 50 mM HEPES, pH 7.2, was used in the case of lithium chloride due to the low solubility of lithium cation in the presence of phosphate. All other salts were measured in the presence of 50 mM sodium phosphate buffer, pH 7.2.

References

- (1) Zhang, Y.; Cremer, P. S. *Proc Natl Acad Sci U S A* **2009**, *106*, 15249.