Fast and Slow EQCM Response of Zwitterionic Weak Electrolytes to Changes in the Electrode Potential: A p*H*-Mediated Mechanism

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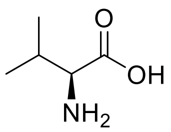
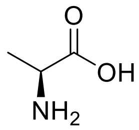
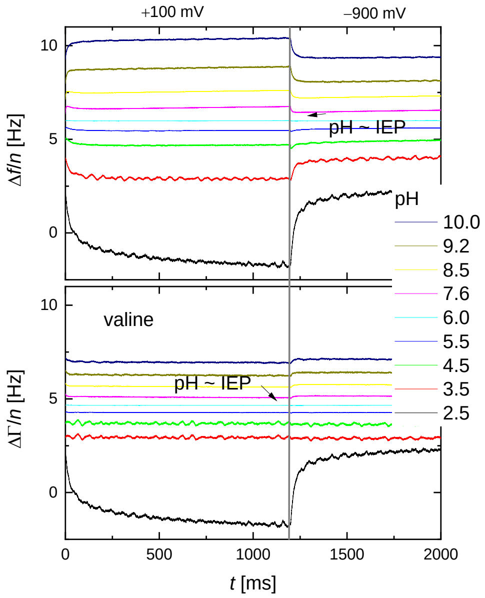
Supporting Information

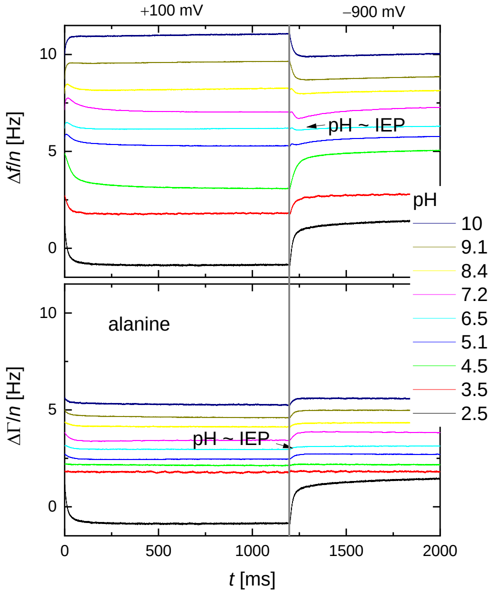


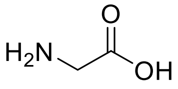
(*S*)-valine
pK_A = 2.27 p*I* = 5.96
pK_B = 9.52



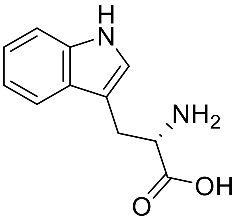
(*S*)-alanine
pK_A = 2.33 p*I* = 6.00
pK_B = 9.87



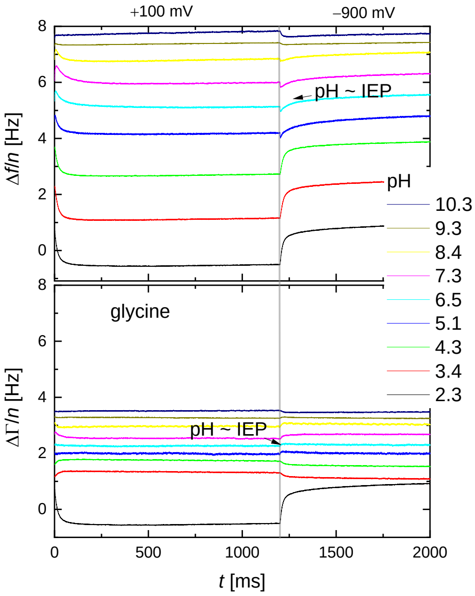


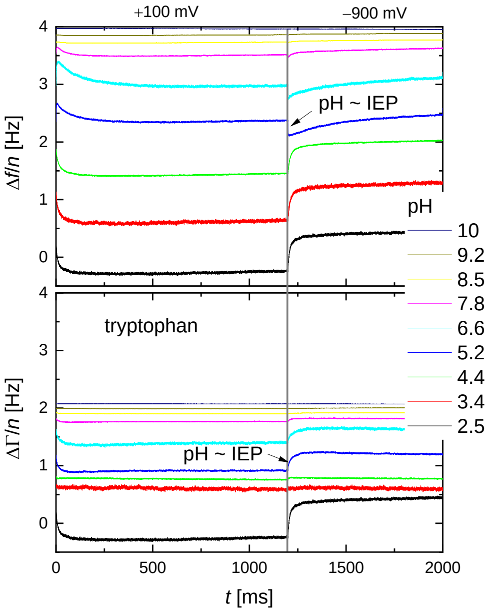


glycine
pK_A = 2.34 p*I* = 5.97
pK_B = 9.58



(*S*)-tryptophan
pK_A = 2.38 p*I* = 5.89
pK_B = 9.34
pK_B = 17.6





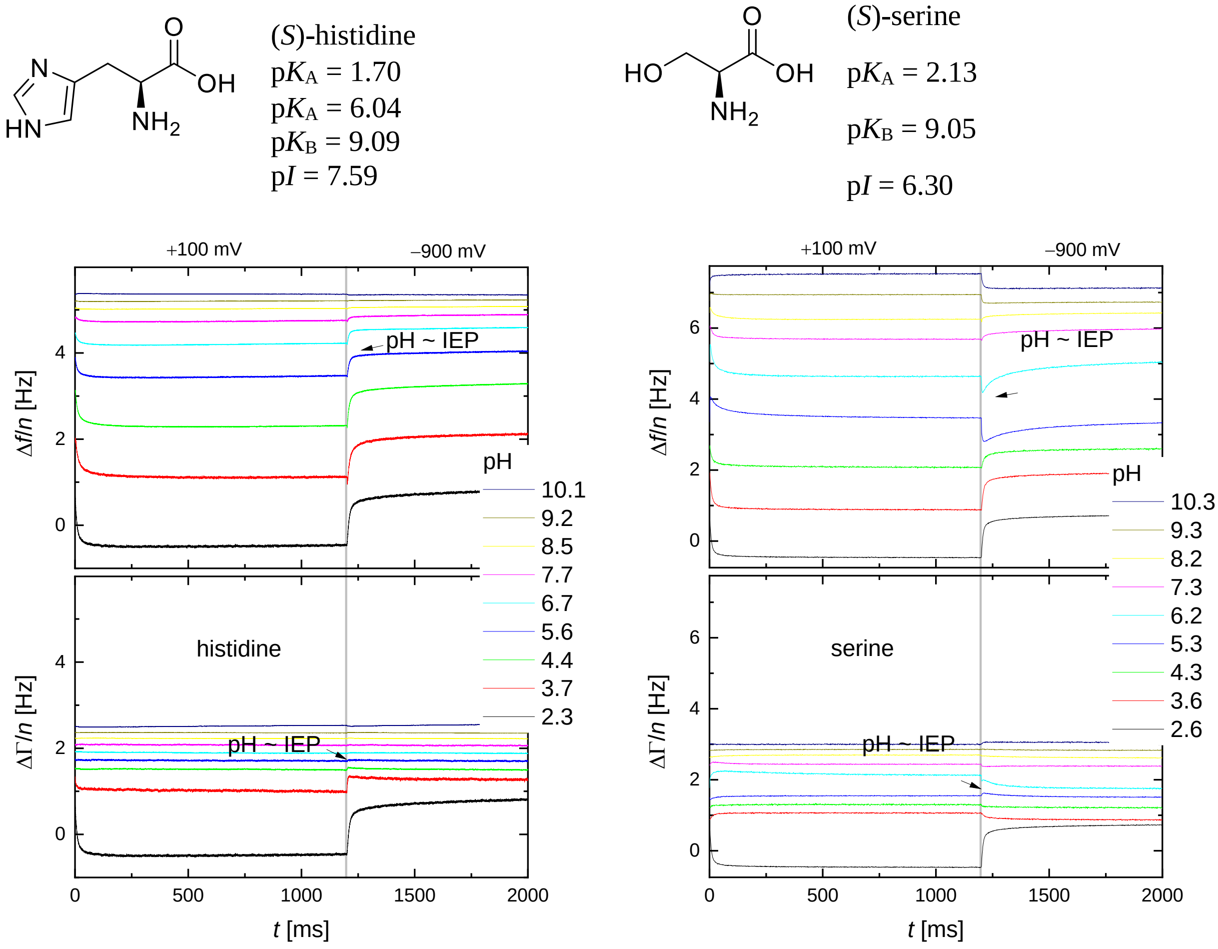


Fig. S 1

Time traces of Δf/n and ΔΓ/n at 15 MHz for valine, alanine, glycine, tryptophan, histidine, and serine. This sign of the response to potential switching depends on pH. The pK_A, the pK_B, and the pI as shown above each graph were obtained from Ref. [1].

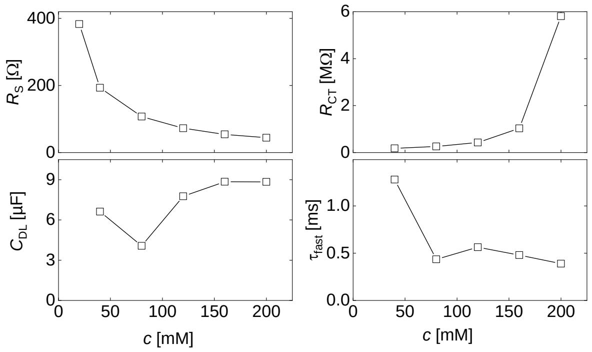


Fig. S 2
Concentration dependence of fit parameters obtained by EIS for a glycine solution at pH = 6.0.

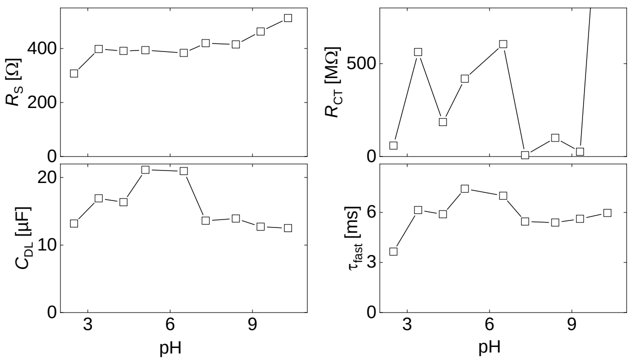


Fig. S 3
pH dependence of fit parameters obtained by EIS for a 20 mM glycine solution.

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[1] "Properties of Amino Acids", in CRC Handbook of Chemistry and Physics, Internet Version 2006, David R. Lide, ed., Taylor and Francis, Boca Raton, FL, **2006**.

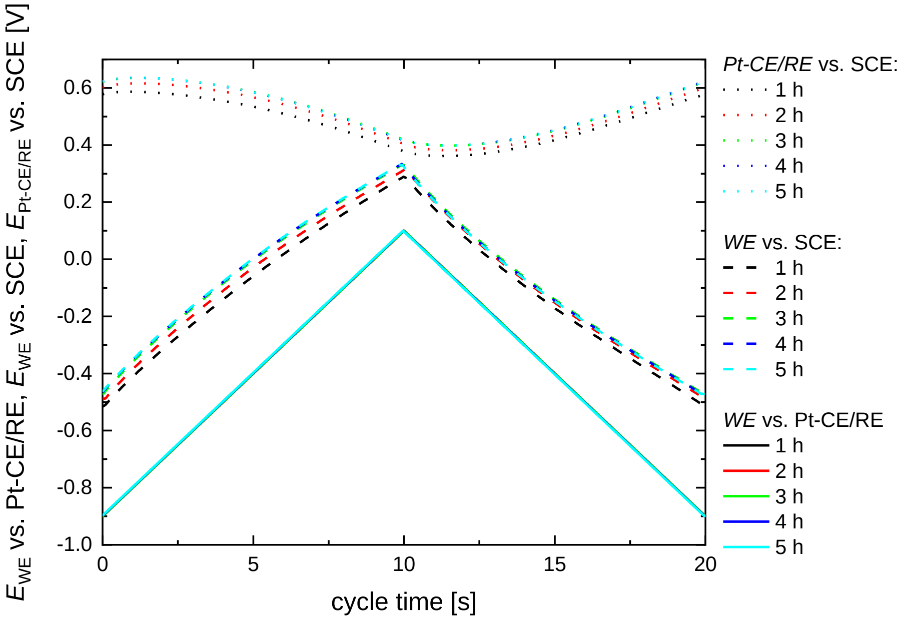

Fig. S 4

Because the experiment employed a two-electrode setup with a polarizable pseudo-reference electrode (Pt-CE/RE), the nominal voltage slightly differed from the potential drop at the surface of the working electrode. To check for artifacts related to this problem, a similar cell was constructed, which did contain a standard calomel electrode (SCE) as a reference electrode. A first potentiostat was made to control the voltage between the WE and the pseudo-reference electrode (as in the experiments reported in the main text). To this first potentiostat, the counter electrode at the same time was the reference electrode. These voltages are shown as straight lines. A second potentiostat measured the potentials of both electrodes against the SCE. The dashed lines show the potential of the working electrode (WE) against SCE. Firstly, these potentials are not strictly the same as the nominal potentials. Also, they drift by 40 mV over a time of 5 hours.