Supplementary material

Detection of ITP zones with fluorescent counterion

We used a fluorescent counterion Rhodamine 6G as the electric field tracer to image the shape of conductivity (and electric field) gradients between the LE and TE zones. Rhodamine 6G is here an ionic fluorophore which is not focused by our ITP process. It therefore electromigrates through ITP zones, and its concentration adjusts itself to conserve the electromigration flux along the channel. The fluorophore is present in trace concentration compared to the background electrolytes (LE and TE) and therefore, does not contribute significantly to the conductivity (and electric field) of the ITP zones; hence ITP dynamics are not disturbed by this tracer molecule.[1]

Consider two adjacent ITP zones (in plateau mode), such as zones 1 and 2 in figure A1. The electric field in the two zones is related to the effective mobility of the analytes in each zone as

$$\nu_{eff,1}E_1 = \nu_{eff,2}E_2 = V_{ITP} \qquad 1$$

A fluorescent counterion in trace concentration will have equal electromigration fluxes in zones 1 and 2, as dictated by mass conservation. We write the electromigration flux balance for the fluorophore across zones 1 and 2 as

$$\left(\nu_{fl,1}E_1 + V_{ITP}\right)C_{fl,1} = \left(\nu_{fl,2}E_2 + V_{ITP}\right)C_{fl,2} \qquad 2$$

where $\nu_{fl,i}$ is the mobility and $C_{fl,i}$ is the concentration. of the fluorescent counterion in zone i.

On simplifying eqs 1 and 2, we arrive at a relation between the concentration of the fluorescent marker in the two zones, as

$$\frac{C_{fl,1}}{C_{fl,2}} = \frac{\left(\nu_{fl,2} + \nu_{eff,2}\right)}{\left(\nu_{fl,1} + \nu_{eff,1}\right)} \frac{E_2}{E_1} \qquad 3$$

We know the intensity of the fluorescent tracer counterion is directly proportional to its concentration (Chambers and Santiago[1] have verified this for Rhodamine 6G in independent dilution experiments). Therefore, fluorophore signal intensity is a measure of the local electric field in each ITP plateau region (i.e., wherever diffusion fluxes are negligible compared to the electromigration fluxes, as in the TE or LE). The carbamate and carbonate zones visualized here have non-negligible gradients (presumably due to finite kinetic rates and accumulation processes), and so diffusion fluxes may be important. As such, the fluorescent tracer is only an approximate, qualitative description of electric field regions within the carbamate and carbonate zones.

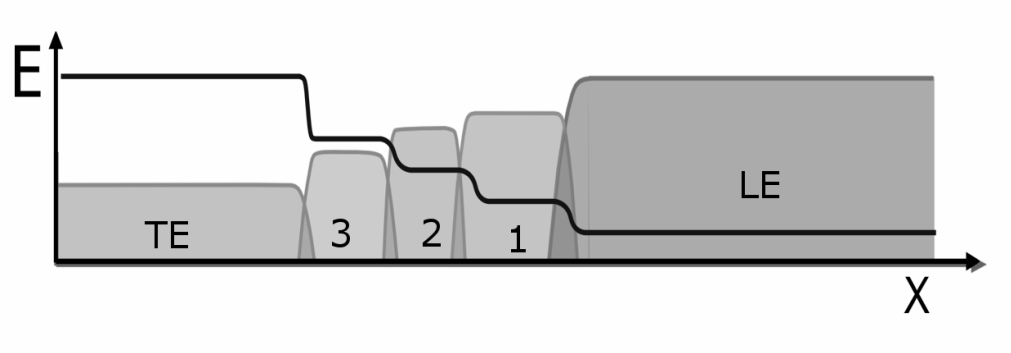

Figure A1. Schematic of the plateau shaped zones between LE and TE zones in ITP under steady state conditions. The electric field profile is overlaid on the concentration profile in each ITP zone.

1. R. Chambers and J. G. Santiago, in preparation.