Supplementary Information For:

Coordinative Properties of Highly Fluorinated Solvents with Amino and Ether Groups

Paul G. Boswell,[†] *Elizabeth C. Lugert,*[†] *József Rábai,*[‡] *Elizabeth A. Amin,*[†] *and Philippe Bühlmann**[†]

[†]University of Minnesota, Department of Chemistry 207 Pleasant Street SE, Minneapolis, Minnesota 55455

[‡]Eötvös Loránd University, Department of Organic Chemistry, P.O. Box 32, H-1518, Budapest 112, Hungary

E-mail: buhlmann@chem.umn.edu

Proof of $\Phi_{\mathrm{j,ref}} - \Phi_{\mathrm{i,ref}} = (\mathrm{R}T/z\mathrm{F})\ln K_{\mathrm{i,j}}^{\mathrm{pot,ref}}$

Equation 10 applied to an electrode based on the reference membrane responding to a solution A containing ion i gives

$$\Delta E_{\mathrm{i,ref}} = E_{\mathrm{i,ref}}^{o} + \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\frac{a_{\mathrm{i,aq}}}{c_{\mathrm{i,ref}}} \tag{S1}$$

The response of the same electrode to a solution B containing ion j (with the same charge as ion i) at the same activity is given by

$$\Delta E_{\mathrm{j,ref}} = E_{\mathrm{j,ref}}^{o} + \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\left(\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{j,ref}}}\right) \tag{S2}$$

Using a selectivity coefficient, the response of the same electrode can also be formulated as follows (note the change in the index i of the $E_{\mathrm{i,ref}}^{o}$ and $c_{\mathrm{i,ref}}$ terms):

$$\Delta E_{\mathrm{j,ref}} = E_{\mathrm{i,ref}}^{o} + \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\left(K_{\mathrm{i,j}}^{\mathrm{pot,ref}}\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,ref}}}\right) \tag{S3}$$

The difference between the electrode's response to solution B and to solution A equals $\Phi_{\mathrm{j,ref}} - \Phi_{\mathrm{i,ref}}$ and can be obtained from equations S2 and S3:

$$\Phi_{\mathrm{j,ref}} - \Phi_{\mathrm{i,ref}} = \Delta E_{\mathrm{j,ref}} - \Delta E_{\mathrm{i,ref}} = E_{\mathrm{i,ref}}^{\mathrm{o}} + \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\left(K_{\mathrm{i,j}}^{\mathrm{pot,ref}}\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,ref}}}\right) - E_{\mathrm{i,ref}}^{\mathrm{o}} - \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\frac{a_{\mathrm{i,aq}}}{c_{\mathrm{i,ref}}} \tag{S4}$$

Since the activities of the ions in the two aqueous solutions are identical, this can be simplified to

$$\Phi_{\mathrm{j,ref}} - \Phi_{\mathrm{i,ref}} = \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\left(K_{\mathrm{i,j}}^{\mathrm{pot,ref}}\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,ref}}}\right) - \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\frac{a_{\mathrm{i,aq}}}{c_{\mathrm{i,ref}}} = \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln K_{\mathrm{i,j}}^{\mathrm{pot,ref}} \tag{S5}$$

Proof of $c_{\mathrm{i,ref}}/c_{\mathrm{i,co}} = K_{\mathrm{i,j}}^{\mathrm{pot,co}}/K_{\mathrm{i,j}}^{\mathrm{pot,ref}}$ (Equation 11)

Equation 10 applied to an electrode with a membrane based on a fluorous solvent with the ability to interact with cations and responding to solution A containing ion i gives

$$\Delta E_{\mathrm{i,co}} = E_{\mathrm{i,co}}^{\mathrm{o}} + \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\frac{a_{\mathrm{i,aq}}}{c_{\mathrm{i,co}}} \tag{S6}$$

The response of the same electrode to solution B with ion j is given by

$$\Delta E_{\mathrm{j,co}} = E_{\mathrm{j,co}}^{\mathrm{o}} + \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\left(\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{j,co}}}\right) \tag{S7}$$

Using a selectivity coefficient, the response of the same electrode could also be formulated as follows:

$$\Delta E_{\mathrm{j,co}} = E_{\mathrm{i,co}}^{\mathrm{o}} + \frac{\mathrm{R}\,T}{z\mathrm{F}}\ln\left(K_{\mathrm{i,j}}^{\mathrm{pot,co}}\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,co}}}\right) \tag{S8}$$

The difference between the potentiometric responses of the two electrodes to solution B can be obtained from equations S2 and S7 to be

$$\Delta E_{\mathrm{j,co}} - \Delta E_{\mathrm{j,ref}} = E^{\mathrm{o}}_{\mathrm{j,co}} + \frac{\mathrm{R}\,T}{z\mathrm{F}} \ln\left(\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{j,co}}}\right) - E^{\mathrm{o}}_{\mathrm{j,ref}} - \frac{\mathrm{R}\,T}{z\mathrm{F}} \ln\left(\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{j,ref}}}\right) \tag{S9}$$

The same difference between the potentiometric responses of the two electrodes to solution B can also be obtained from equations S3 and S8:

$$\Delta E_{\mathrm{j,co}} - \Delta E_{\mathrm{j,ref}} = E^{\mathrm{o}}_{\mathrm{i,co}} + \frac{\mathrm{R}\,T}{z\mathrm{F}} \ln\left(K^{\mathrm{pot,co}}_{\mathrm{i,j}} \frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,co}}}\right) - E^{\mathrm{o}}_{\mathrm{i,ref}} - \frac{\mathrm{R}\,T}{z\mathrm{F}} \ln\left(K^{\mathrm{pot,ref}}_{\mathrm{i,j}} \frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,ref}}}\right) \tag{S10}$$

Since the right hand side of equation S9 must be equal to the right hand side of equation S10, it follows that

$$\ln\left(\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{j,co}}}\right) - \ln\left(\frac{a_{\mathrm{j,aq}}}{c_{\mathrm{j,ref}}}\right) = \ln\left(K^{\mathrm{pot,co}}_{\mathrm{i,j}} \frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,co}}}\right) - \ln\left(K^{\mathrm{pot,ref}}_{\mathrm{i,j}} \frac{a_{\mathrm{j,aq}}}{c_{\mathrm{i,ref}}}\right) \tag{S11}$$

Since for the non-coordinating ion i it is true that $c_{\mathrm{i,co}} = c_{\mathrm{i,ref}}$, equation S11 can be further simplified to give the desired equation:

$$\frac{c_{\mathrm{j,ref}}}{c_{\mathrm{j,co}}} = \frac{K^{\mathrm{pot,co}}_{\mathrm{i,j}}}{K^{\mathrm{pot,ref}}_{\mathrm{i,j}}} \tag{11}$$