Solutions of Ions are Complex Fluids

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Ionic solutions are necessarily neutral or they explode. Ions in solution interact so strongly through the electric field that they always come 'in pairs' (within ~1 part in 10^{15}). Most ions also interact through their finite size that creates collisions and changes the electric field, particularly in crowded confines near electrodes, active sites, and ion channels. Thus ionic solutions are not simple fluids, particularly where they are most important. Ionic solutions need to be treated as the complex fluids that they are.

The history of electrochemistry and biophysics is a history of attempts to deal with ionic solutions as simple fluids. The future history will be attempts to deal with ionic solutions as complex fluids.

<u>**Come in pairs calculation:**</u>

Consider a sphere radius a.

Capacitance is $4\pi\varepsilon_0 a = (1.11\times10^{-10})a$

Charge for 1 volt is $4\pi\varepsilon_0 a = (1.11\times10^{-10})a$

Number of unbalanced charges is $\dfrac{4\pi\varepsilon_0 a = (1.11\times10^{-10})a}{1.61\times10^{-19}} = 6.951\times10^{8}\times a\,\text{charges}$

Consider a 1 cm radius sphere of a 1 molar solution.

Number of unbalanced charges is ~7×10^6 charges

Volume of 1 cm radius sphere is $\tfrac{4}{3}\pi a^3 = 4.19\times10^{-6}\ \text{m}^3$

Number of ions is $4.19\times10^{-6}\ \text{m}^3\times6.02\times10^{23}\dfrac{\text{m}}{\text{liter}}\dfrac{10^3\text{liter}}{\text{m}^3} = 2.52\times10^{21}$ ions.

<u>**Unbalanced charges are a small fraction, namely 2.7 × 10-15**</u>

$$\frac{7\times10^{6}}{2.52\times10^{21}} = 2.78\times10^{-15}$$

Scaling:

$$\frac{\text{Number of Unbalanced Charges}}{\text{Number of Ions}} = \frac{\dfrac{4\pi\varepsilon_0 a = 6.951\times10^{8} a}{1.609\times10^{-16}}}{\frac{4}{3}\pi a^3 N_A} = \frac{3\varepsilon_0}{eN_A} a^{-2}$$

$$\frac{\text{Number of Unbalanced Charges}}{\text{Number of Ions}} = \frac{2.66\times10^{-11}\ \text{m}^2}{1.609\times10^{-19}\times6.023\times10^{26}\ \dfrac{\text{particles}}{\text{m}^3} a^2} = 2.74\times10^{-19} a^{-2}$$

$$\frac{\text{Number of Unbalanced Charges}}{\text{Number of Ions}} = \frac{2.74\times10^{-19}}{a^2}$$

Unbalanced charge is more important in small systems.

In a 1 cm radius sphere, fraction is 2.7×10^{-15}

In a 1 µm radius sphere, fraction is 2.7×10^{-7}

In a 1 nm radius active site, the fraction is 0.27