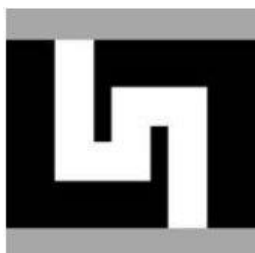


1. Tortuous pores:

Imagine for the following pore (white) through a separator (black) between two electrodes (gray). The pore only contains a solvent, with no ions. There is a uniform electric field between these two electrodes - i.e. the gradient of the potential field is constant, and the iso-lines are parallel to the two electrodes.



Starting with just a single pair of ions in the middle of the pore (i.e. a near perfectly dilute solution), if these two ions dissociate, then they will follow the electric field in opposite directions. However, starting in the middle means that they won't make it to the electrode surface as they'll get stuck in the bend of the pore! If the migration is entirely driven by the field (i.e. photons) from electrodes, then this only generates a force normal to the electrodes, which means that horizontal motion (and especially backflow) must be diffusion controlled.

I totally agree with you: diffusion matters, especially perpendicularly to the electric field. As far as I know, continuum models cannot take this phenomenon into account in a complex porous medium.

1. Dilute solution:

Imagine a two plate capacitor across which we suddenly apply a potential difference (one electrode defined at 1 V, compared to the 0 V of the other). Initially, we know that electric field between the two flat plates is uniform, as the electric field strength is simply the spatial gradient of the potential, which is linear from one electrode to the other. However, if the gap between the electrodes contains an electrolyte, consisting of dissociated ions in a solvent, then these ions will start to migrate under the force of the electric field (units: $[N/C]=[V/m]$).



The ions will build up at their respective electrodes and the double layer will form. Then, eventually, the ions must stop exhibiting net migration due to one of two reasons:

1) The solution is sufficiently concentrated that the double layer will fully form and (through the superposition principal) the double layer will shield (cancel out) the effect of the electrodes on the electrolyte, such that the electric field only exists within the double layer itself and is zero in the rest of the electrolyte. The potential through most of the bulk thickness of the electrolyte would be 0.5 V; although the fact that this is not the more intuitive "0 V" is an artefact of our initial electrode definition of 0 V and 1 V, instead of -0.5 V and +0.5 V.

I agree about this picture: the electric field should be completely shielded by DLs. This is something I found also in the Bazant's note and Bard's book.

2) The solution is very dilute, such that the double layer does not fully form and the electric field is not fully shielded, so the gradient of potential extends out of the double layer. However, no migration occur as there simply aren't any ions there to feel it.

This picture makes sense too. However, I can hardly think about ions being fully displaced at the opposite DLs, with no species in the middle, because a chemical potential gradient will introduce counter-diffusion to balance

the electric field. Nevertheless, no matter if the bulk of the solution has zero ion concentration or not, the point remains the same: chemical diffusion matters!

1. Starting from a charge state:

Now let's consider a sinusoidal stimulation, with two electrodes going from -0.5 V to +0.5 V, but they are 180deg out of phase, which is analogous to a signal of amplitude 1 V. If the ion concentration is very low, then there will be no double layer, but rather all cations start at one electrode and all anions at the other. At the electrode surface there is a dynamic process of the ions jostling about and occasionally moving away from the surface, but being pulled back. The stronger the potential difference, the more tightly they are held. As the signal is a sinusoid, next it will start relaxing towards zero potential difference, and the ions will relax and start to diffuse further on average from the surface before being pulled back. At 0 V, the ions will be free to diffuse from the surface; however, their not-uniform distribution will create its own electric field, which will speed up the rehomogenisation – the relative influence of migration to diffusion on this process presumably depends on some non-dimensional like $\omega/(D/L^2)$, where ω is the frequency, D is the diffusivity and L is the separation of the electrodes.

This reminded me that the DL capacitance (as well as the permittivity of a material) depends on the frequency. In fact, such a frequency-dependence takes into account the reorganisation of the DL. I suspect it may take place at large frequency values since the Debye length is really small, but I have no experience.

Coming to the larger length-scale of the separator, there is surely a dimensionless value taking into account the ratio between migration to diffusion flux. We should write down the equations in dimensionless form. It looks like we need to consider the full Poisson-Nernst-Planck equations.

Imagining this same scenario, but now we keep increasing the concentration until eventually, the double layer is able to fully form. Now, there is no electric field in the middle of the electrolyte, as once again it is fully shielded. As the potential difference drops to zero, the ions relax, but now there are anions and cations at both sides (although not the same number). As the potential goes beyond zero, becoming negative, only a subsection of the ions will need to change sides (half the number as the total stored charge).

If we continue to increase the concentration, still, the same number of ions need to change sides when the potential switches as in the previous case, but now they can do this in a chain. No single ion need to travel the full thickness, but instead many can take one small step in the right direction. As the double layer can largely form from the ions already in its neighbourhood (?), the electric field is quickly (?) shielded, but the ions that do travel across will feel what's left of the electric field. Diffusion will also be acting, but the concentration difference is very small (in fact the more concentrated the solution, the smaller the relative concentration difference will be).

Amazing!

So, in the case of Tu's experiment with highly dilute solution (c. 10 mM), I would expect diffusion to make a significant contribution.

Commenté [L1]: Because only one part of Ions moves to their respective surface to compensate the electric field as double layer. The rest wouldn't move so we have anions and cations at both sides