Ionic Drift and Diffusion Potential

In order to understand the link between ionic drift and diffusion potential, consider a solution of monovalent electrolyte with concentration $c$. Now assume that this solution is brought in contact with pure water and the boundary of contact is assumed to be $x = 0$. Owing to the concentration gradient, both cation as well anions will start moving into pure water immediately.

Figure 9. The general depiction electrolytic solution and concentration in contact with water in start.
Now owing to different absolute ionic mobilities of cations and anions (say $\bar{u}_+ > \bar{u}_-$), the Einstein relation can be written for cations and anions as given below.

$$D_+ = \bar{u}_+ kT$$

(162)

and

$$D_- = \bar{u}_- kT$$

(163)

Where $D_+$ and $D_-$ are the diffusion coefficients for cations and anions, respectively. The symbol $k$ is simply the Boltzmann constant and $T$ is the temperature. The symbol $\bar{u}_+$ and $\bar{u}_-$ represent the absolute ionic mobilities for cation and anion, respectively. Since we have assumed that $\bar{u}_+ > \bar{u}_-$, the following must be true

$$D_+ > D_-$$

(164)

This implies that the cations will move faster in comparison to anions, will lead the anions in their diffusion race. Now consider two unit-volume elements at distance $-x_1$ and $-x_2$ in the water phase with $-x_2$ on more left than $-x_1$. Since the cations are moving faster than anions, the concentration ratio of the two ($c_+/c_-$) will be higher in volume element at $-x_2$ than in the volume element at $-x_1$ distance. In other words, the ratio $c_+/c_-$ will increase as we move from the boundary to the waterside of the system.

Figure 10. The development of diffusion potential due to different ionic mobilities.

Consequently, a situation will arise in which the positive and negative charges are separated with a negative layer on the left and positive layer on the right. All this will lead to the development of a potential difference that will oppose the faster movement of cations and will reinforce the slower movement of anions. This potential is generally called as the “diffusion potential” and tries to level the ionic mobilities of cations and anions; and hence, tries to maintain the electroneutrality in different parts of the solution. It should also be noted that diffusion potential is also called as the “liquid junction potential” in the case of concentration cells and “membrane potential” if the two solutions are separated by an uncharged membrane.
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