

As I move forward with my efforts to model various electrochemical scenarios, I have come to realize that there has been a fair amount of confusion (especially on my part!) regarding the diffusion coefficient and/or mobility parameters for protons in various electrolyte-solvents of interest. In order to get, once and for all, to the bottom of it, I have read several books, a few technical papers and have visited quite a number of websites. To date, the most complete and understandable discussions I found are presented in the book “Modern Electrochemistry” by Bockris and Reddy and “Diffusion” second edition by Cussler (see attached PDF files of most useful pages). Here is what I have learned:

1. The net current density (flux of charged particles) that flows in an electrolytic solution is the net sum of the fluxes of all the charged particles moving in and with the fluid.
2. The flux of the charged particles is driven by three principal “forces” (there are others – magnetic, for example):
  - a. Bulk fluid motion (convection)
  - b. Concentration gradients (diffusion)
  - c. Charge Migration (electrophoresis)
3. Each of the forces “drives” a particle flux that is, to a first approximation, is linearly proportional to the driving force. These proportionality constants are:
  - a. For convection: “Viscosity”
  - b. For Diffusion: “Diffusion Coefficient”
  - c. For Migration: “Conductivity”
4. At low concentrations, conductivity is proportional to the ion mobility times ion concentration times the charge the ion carries (valence) summed over all the ionic species that are present.
5. Viscosity, diffusion coefficients and mobility data are tabulated in many references but, because the rule of electro-neutrality couples the movement of the ions in a strong manner, and because the mechanism of proton movement is different in different solvents, the given values need to be applied with extreme care to the particular case of interest.

#### The Diffusion Coefficient:

In circumstances where electric fields are of zero or near zero strength (little or no space charge or conduction current flow), the diffusion coefficient of the proton is equal to the harmonic average:  $(|z_1|^{-2} + |z_2|^{-2}) / (|z_2|/D_1 + |z_1|/D_2)$  of the proton,  $D_1$ , and its charge balancing counter ions,  $D_2$  weighted by their valences (see Cussler 2<sup>nd</sup> edition page 146 equation 6.1-12). For  $H^+$  and  $SO_4^{-2}$  (present in equal concentration) the value for  $D_{average} = 2.59 \times 10^{-5} \text{ cm}^2/\text{sec}$ . This is well below the typical published diffusion coefficient for  $H^+$  in water.

Interestingly and importantly: When the concentration of  $H^+$  is much less than the concentration of the other ions, the formula reduces to the value of the low concentration electrolyte! This is the case when a supporting electrolyte is present in huge concentration. It seems that the isolated proton only needs to drag a tiny fraction of the nearby ions along with it in order that charge neutrality be preserved. Therefore, it zooms right along at almost top speed.

Apparently, the  $9.31 \times 10^{-5} \text{ cm}^2/\text{sec}$  diffusion coefficient typically given for  $H^+$  in water (which is about nine times higher than that stated for  $SO_4^{-2}$  ions) will be true when supporting electrolytes are used and protons are abundant.

## The Mobility Coefficient:

In circumstances where an electric field is present (such as in the Helmholtz double layer at electrode surfaces, regions exhibiting high differential diffusion coefficients between charged species, certain charge conducting and separating membranes ... and ... when a conduction current is flowing), the mobility coefficient of the proton (in water) is (from Bockris and Reddy page 472) about 7 times that of other “normal” ions ( $36 \text{ E}^{-4} \text{ cm}^2 / \text{sec}^* \text{ volt}$  as opposed to  $5 \text{ E}^{-4} \text{ cm}^2 / \text{sec}^* \text{ volt}$  for the  $\text{K}^+$  ion in water ).

This excess mobility, which causes an excess equivalent conductivity, is greatly reduced (down to zero excess conductivity) in certain circumstances (non-aqueous solvents). For example (see figure 5.9 - Bockris and Reddy - page 473), when methanol is mixed with water, the resultant equivalent conductivity excess is apparently reduced to zero at about 85 mole percent methanol, as compared to the  $\text{K}^+$  ion. At 20 mole percent methanol, the solution excess conductivity is about 2 and a half times. The figure 5.9 conductivity graph “tops out” with a equivalent conductivity excess of about times 4 for the case of pure water (compared to the  $\text{K}^+$  ion).

## Regarding the Viscosity Coefficient:

I will get into this at a later date.

## Conclusions:

It seems that as long as the concentration of protons in an aqueous solution is low compared to all the other constituents, its diffusion coefficient will be around  $9 \text{ E}^{-5} \text{ cm}^2/\text{sec}$ . Also, it seems that the addition of methanol to water substantially reduces the proton excess mobility in response to an electric field. In the case of non-aqueous solvents, protons apparently have little or no excess mobility.

## Therefore:

1. When no conduction current and/or electric field is present, I will use an average ionic diffusion coefficient (Cussler page 149) for the protons in the electrolyte of  $9 \text{ E}^{-5} \text{ cm}^2/\text{sec}$ . This is slightly lower than the diffusion rate usually given for protons in water, but is probably close to the truth. This diffusion coefficient relates to concentration gradient driven particle fluxes only!
2. In pure water, when an electric field is present, I will use a proton mobility of  $36 \text{ E}^{-4} \text{ cm}^2 / \text{sec}^* \text{ volt}$  (from Bockris and Reddy page 472 ) and calculate conductivities, velocities and transference numbers accordingly. This coefficient relates to electric field gradient driven particle fluxes in pure water only!
3. In circumstances where electric fields are present (electric field driven conduction current is flowing) and the solvent is moderately dilute methanol in water, I will use a proton mobility of  $15 \text{ E}^{-4} \text{ cm}^2 / \text{sec}^* \text{ volt}$  ( $2.5 \times$  the  $\text{K}^+$  ion value). This number is loosely based on figure 5.9 - Bockris and Reddy - page 473 . and relates to electric field gradient driven particle fluxes in common electrolytes.
4. Lastly, in circumstances where electric fields are present and the solvent is not aqueous, I will use a proton mobility coefficient of  $5 \text{ E}^{-4} \text{ cm}^2 / \text{sec}^* \text{ volt}$ , which is the value for the  $\text{K}^+$  ion in water.