**Supplementary Information for**

Electro-osmotic coefficients of water-methanol mixtures through Nafion membranes revisited: Composition and temperature dependence

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**S1. Volume correction**

According to Eqns. (5) and (6) of the main text, the cathodic and anodic correction to the measured volumes can be estimated by resorting to volumetric properties of the solid Ag and AgCl and the HCl solution. The data for the partial molar volume of HCl is available for aqueous solutions but not for the methanol-water and pure methanol solutions.

Table S1 summarizes the data for the molar volume of the solids and the partial molar volume of HCl in pure water as a function of temperature, along with the volume correction calculated for a total charge of ~ 10 coulombs, which is the upper limit for the charges used in our measurements. that have opposite signs for the cathodic (positive) and anodic (negative) sides.

**Table S1:** Molar volumes of Ag(s),1 AgCl(s),2 apparent partial molar volume of HCl (aq),3 and volume correction for a charge of 10 coulombs, as a function of temperature

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **25 oC** | **40 oC** | **50 oC** | **60 oC** |
| Ag (s) (cm3.mol-1) | 10.27 | 10.28 | 10.29 | 10.29 |
| AgCl (s) (cm3.mol-1) | 25.77 | 25.77 | 25.77 | 25.77 |
| *V*HCl (aq) (cm3.mol-1) | 18.27 | 18.68 | 18.74 | 18.64 |
| Δ*V* (cm3) | 0.00028 | 0.00032 | 0.00033 | 0.00032 |

The volume changes measured on the cathodic and anodic sides of the cell were in the range 0.006-0.012 cm3 for charges that reached a maximum of 0.5.10-4 F (≈ 5 coulombs). Thus, the correction never exceeds 2-3% of the measured volume change, within the experimental error. We have adopted the values for pure water to correct the measured volumes in methanol-water mixtures with the criteria that these corrections are close to the experimental error of the measurements.

The following figure shows a typical example of an electro-osmotic experiment for a solution at 40 oC with *x*m = 0.44 and HCl concentration 0.50 mol.kg-1. The current during the measurements was *I*= 0.6 mA



**Figure S1:** Electroosmotic experiment corresponding to a solution *x*m = 0.44 at 40 oC. The results correspond to a duplicate run (circles and triangles) and the changes of position of the solution in the capillary tube as a function of time for the cathodic and anodic sides of the cell.

**S2. Electro-osmotic drag coefficient of water in Nafion membranes**

Table S2 summarizes the measured electro-osmotic drag coefficients of water through Nafion membranes of different types, indicating the range of temperature and water content explored and the media in contact with the membrane.

**Table S2.** Electro-osmotic drag coefficient (**ξ)** of water in Nafion membranes

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Membrane** | **Methoda** | **Media** | **T (K)** | **λ** | **ξH2O** | **Ref.** |
| 117 | WAGC | vapor | 298 | 1-14 | 0.2-1.4 | 4 |
| 117 | WAGC | vapor | 303 | 1.4-14 | 1.0 | 5 |
| 112 | WAGC | vapor | 248-263 | 7-11 | 1.0 | 6 |
| 117 | WAGC | vapor | 296.5 | 29 | 0.99 | 7 |
| 112 | WAGC | vapor + H2 | 333-353 | 0.15-0.75b | 0.7-1.1 | 8 |
| 117 | H2MEAH2 | vapor | 398 | 0.05-0.38b | 0.2-0.7 | 9 |
| 117 | H2MEAH2 | Vapor  liquid | 303-353  288-358 | 2-12  16.8 | 0.34-1.1  1.8-2.7 | 10 |
| 112, NRE212 | HP | liquid | 298-353 | 1.5-8 | 0.1- 1.1 | 11 |
| 117 | HP | liquid | 293-363  298 | 22.5  12-18 | 2.0-3.4  1.2-2.0 | 12 |
| 117 | DMFC | liquid + O2 | 288-403 | 22 | 2.0-5.1 | 13 |
| 117 | DMFC | liquid + O2 | 288-383 |  | 2.3-5.2 | 14 |
| 117 | RTC | liquid | 295 |  | 3.2-8.0 | 15 |
| 117 | SPC | 0.003 – 1 M HCl | RT |  | 2.4-2.8 | 16 |
| 117 | eNMR | pure water | 296-353 | 11-20 | 1.7-2.8 | 17 |
| 115 | PEME | water + H2 and HCl (g) | 333-353 |  | 3.5-3.8 | 18 |
| 117 | TCCC | pure water | 303 | 22 | 2.5-2.9 | 19,20 |
| unknown | TCCC | 0.1 M HCl | 298 | 12-39 | 1.7-6.0 | 21 |
| 117 (K+-form) | TCCC | 0.01 M KCl | 298 |  | 9.2 | 22 |
| 117 | TCCC | * 1. -1 M HCl   0.01-1 M H2SO4  0.01-1 M H3PO4 | unknown |  | 2.8-7.1  3.0-6.1  2.2-3.8 | 23 |
| NRE-212 | TCCC | HNO3 (pH= 2.1 -5.1)  KOH (pH=11.9) | unknown |  | 5.5-6  27 | 24 |

aWAGC: Water activity gradient cell; H2MEAH2: Single Nafion MEA with H2 on both sides; HP: hydrogen pump; RTC: radiotracer transport cell; SPC: streaming potential cell; eNMR: electrophoretic NMR; PEME: PEM electrolyzer; TCCC: two compartments capillary cell.

bwater activity. RT: room temperature.

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