INTERNATIONAL WORKSHOP ON NON-EQUILIBRIUM THERMODYNAMICS IN POROUS MEDIA

ION TRANSPORT NUMBERS IN CHARGED POROUS MEMBRANES

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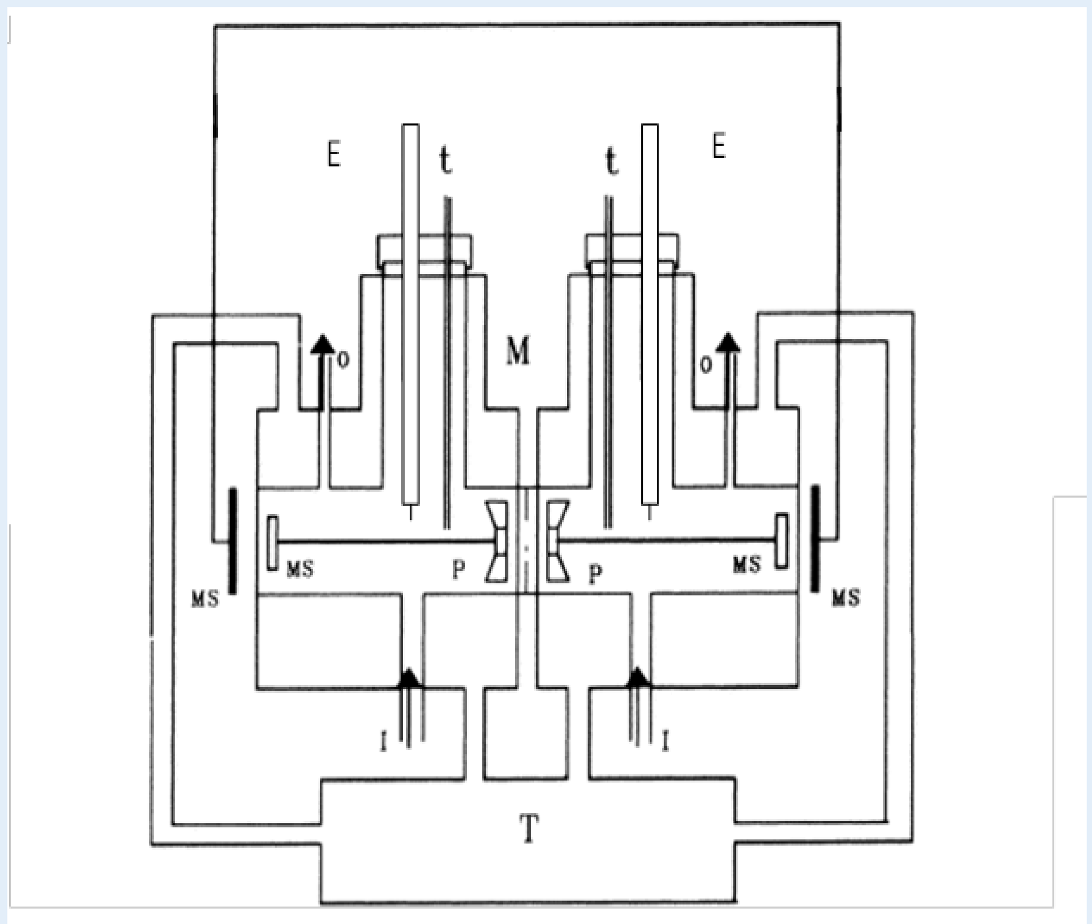
❖ INTRODUCTION

The experimental determination of ion transport numbers is of great interest for the study of charged porous membranes. The influence of temperature is very important, mainly in the case of non isothermal systems. The apparent counter-ion transport number of a cation-exchange membrane is estimated from a method consisting on fitting electromotive force data of a concentration cell as a function of the difference in osmotic pressure among the external solutions. The heterogeneous Ionics CR61 CZL 412 was used as membrane and aqueous potassium chloride solutions were used as electrolyte. The method permits to estimate the value of the cation transport number in the membrane phase as a function of the electrolyte concentration. Measurements have been carried out at different temperatures with the purpose of analysing its effect.

❖ EXPERIMENTAL

EXPERIMENTAL SETUP



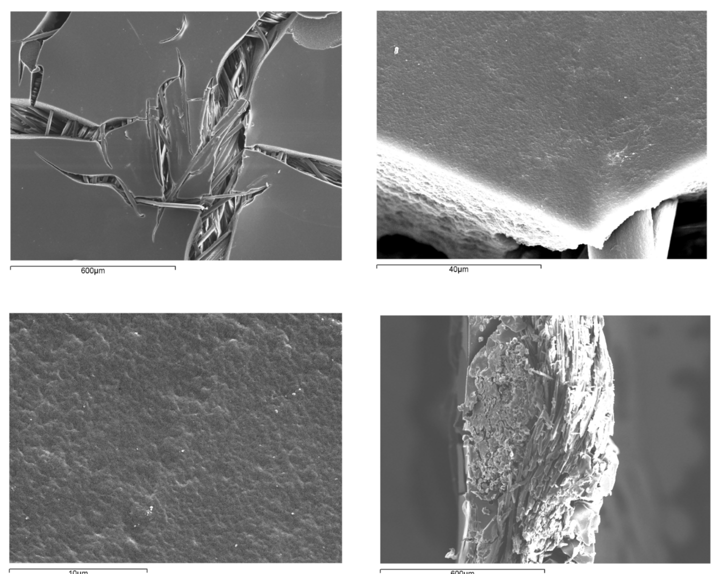
- ✓ M Membrane
- ✓ E Electrodes
- ✓ T Thermostat
- ✓ t Platinum resistance thermometers
- ✓ P Propellers
- ✓ MS Magnetic stirrers
- ✓ I Solution inlet
- ✓ O Solution outlet

Sketch of the experimental setup for measuring electromotive force

Membrane Area
A = 0.79 cm²

Keithley 195 System Scan Voltmeter

CATION-EXCHANGE MEMBRANE



SEM images of the membrane

Ionics CR61 CZL 412

MEMBRANE PROPERTIES	
SELECTIVITY	94 %
ELECTRICAL RESISTANCE*	11 Ω cm²
ION-EXCHANGE CAPACITY	2.7 meq g^{-1}
DRY THICKNESS	520 µm
FRACTIONAL VOID VOLUME	0.032
ELECTROOSMOTIC PERMEABILITY [1,2]	≈ 10^{-9} m^{3}C^{-1}

* Measured in 0.1 mol/L NaCl

❖ THEORY

- **CONCENTRATION CELL**

$$\mathrm{Ag/AgCl}\,|\,\mathrm{KCl}(c_1)\,|\,\mathrm{Membrane}\,|\,\mathrm{KCl}(c_2)\,|\,\mathrm{Ag/AgCl}$$

- **ELECTROMOTIVE FORCE**

$$-\mathrm{d}\varphi^* = \frac{1}{F}\left(t_{+,m}\mathrm{d}\mu + t_{w,m}\mathrm{d}\mu_w\right)$$

- **VOLUME FLOW**

$$J_V = J_{cat}\bar{V}_S + J_{water}\bar{V}_{water}$$

- **OSMOTIC PRESSURE DIFFERENCE**

$$\Delta\Pi = 2RT\left(a_2 - a_1\right)$$

- **ELECTROOSMOTIC PERMEABILITY**

$$W = \left(\frac{J_V}{I}\right)_{\Delta p=0,\Delta\Pi=0}$$

$$\Rightarrow \quad -\mathrm{d}\varphi^* = \frac{1}{F}\left(\frac{t_{+,m}}{c_s}\mathrm{d}\left(\Delta\Pi\right) - FW\mathrm{d}\left(\Delta\Pi\right)\right)$$

- **CATION TRANSPORT NUMBER**

$$t_{+,m} = Fc_S\left(W - \frac{d\varphi^*}{d\Delta\Pi}\right) = Fc_S W + t_{+,m}^{app}$$

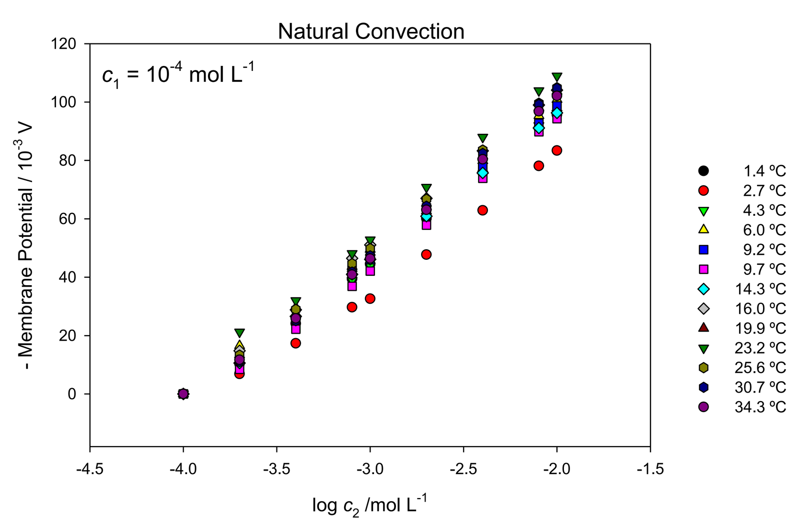
$$\Delta\Pi \approx B\left(a_2 - a_1\right) \quad \Leftrightarrow \quad -\mathrm{d}\varphi^* \approx D\ln\left(\frac{a_2}{a_1}\right)$$

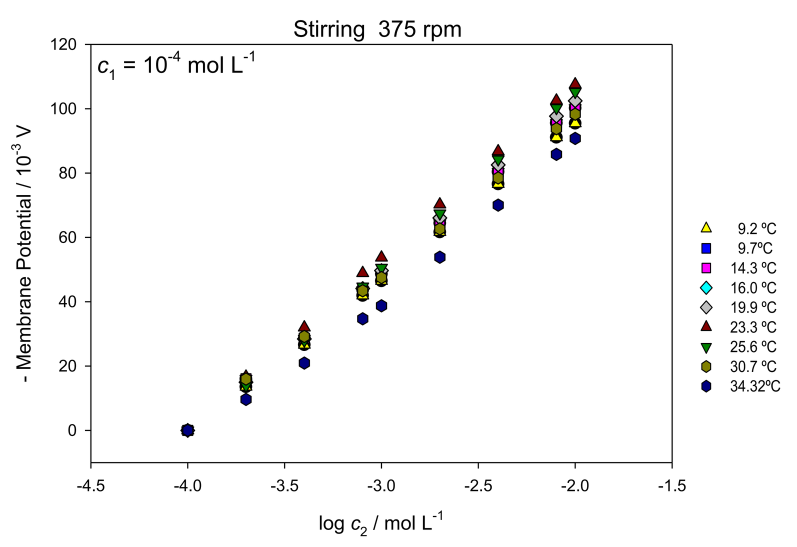
$$-\mathrm{d}\varphi^* = D\ln\left(1 + A\Delta\Pi\right) \rightarrow m = -\frac{\mathrm{d}\varphi^*}{\mathrm{d}\left(\Delta\Pi\right)} = \frac{DA}{1 + A\Delta\Pi}$$

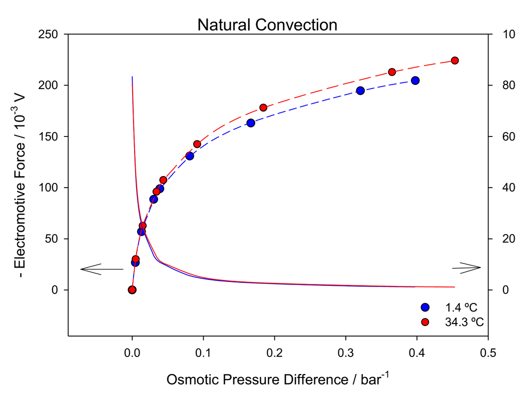
$$t_{+,m} = Fc_s\left(m + W\right) \xrightarrow{W \ll m} t_{+,m} \simeq Fc_s m$$

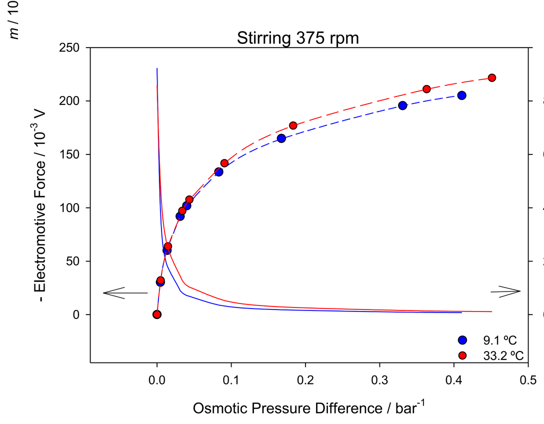
❖ RESULTS AND DISCUSSION

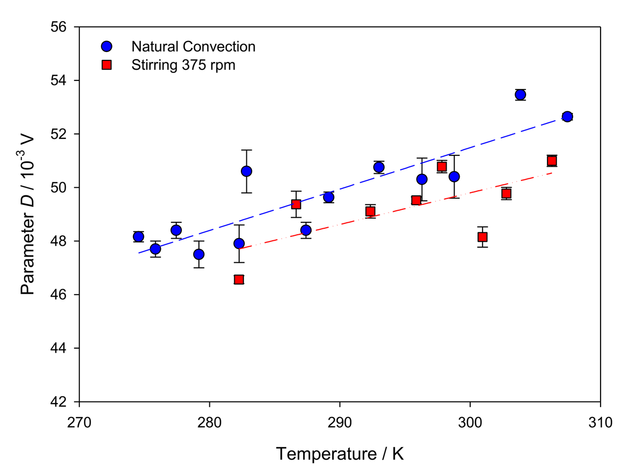
MEMBRANE POTENTIAL

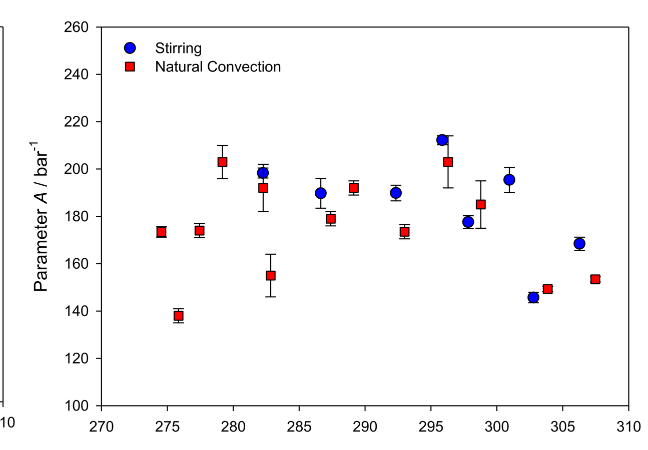




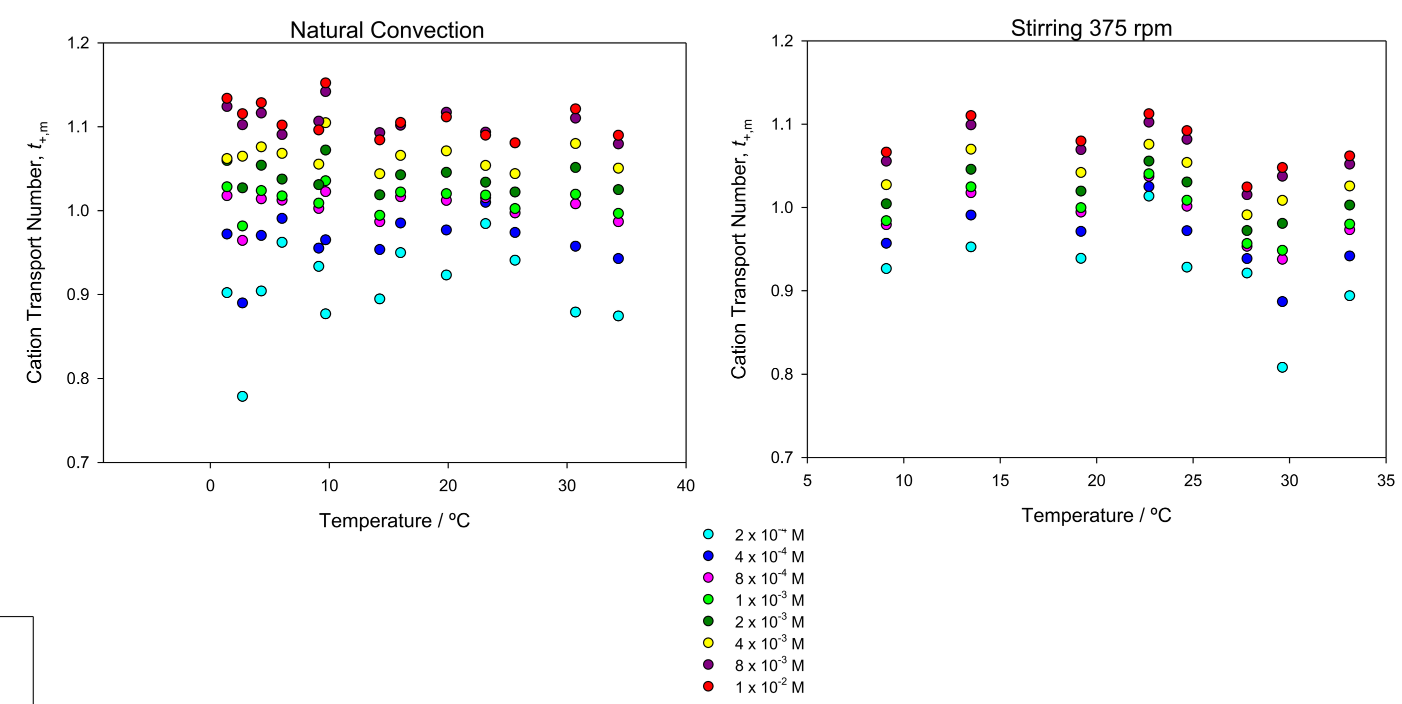


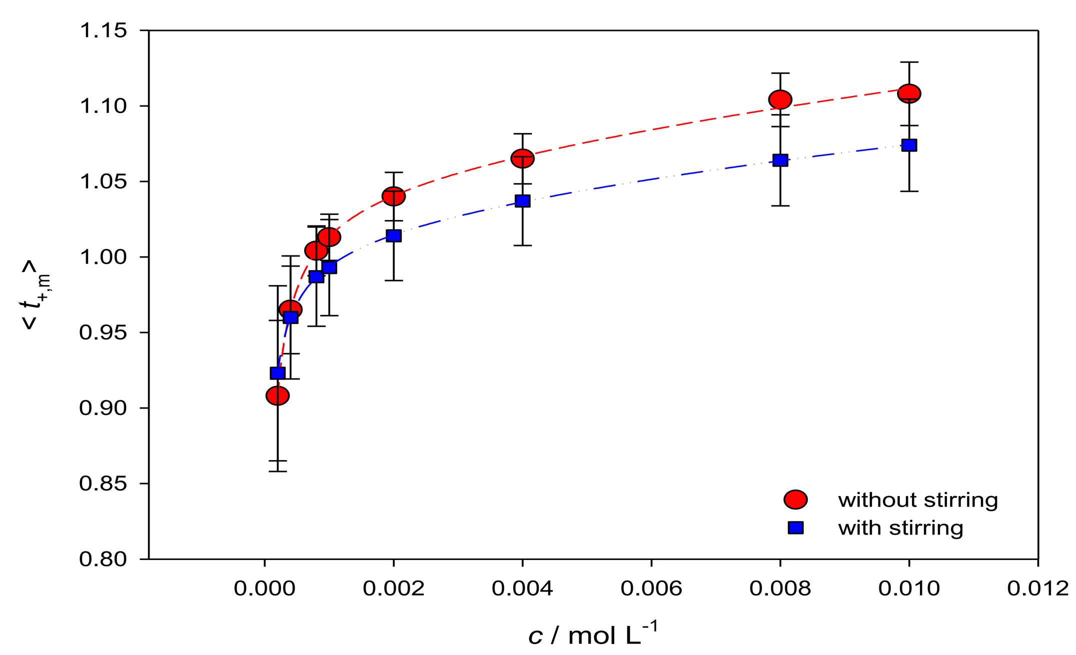






CATION TRANSPORT NUMBER





❖ CONCLUSIONS

- ✓ Cation transport numbers of a heterogeneous porous cation-exchange membrane have been determined at different temperatures by applying a method based on the dependence of the electromotive force of a concentration cell with the osmotic pressure difference.
- ✓ The values obtained are close to the unity, indicating the high selectivity of the membrane.
- ✓ No significant influence of the temperature on the estimated cation transport numbers has been observed in the studied interval, except at the lowest KCl concentration 2x10^{-4} mol L^{-1}.
- ✓ At low electrolyte concentrations, the cation transport number is under-evaluated probably due to not considering the effect of the electroosmotic contribution, which increases when the electrolyte concentration decreases.
- ✓ Lower values of cation transport numbers were obtained when the solutions were stirred.

❖ REFERENCES

[1] V. M. Barragán, C. Ruiz-Bauzá, J. I. Mengual, On current dependence of the electro-osmotic permeability in ion-exchange membranes, J. Membr. Sci. 95 (1994) 1-10.

[2] V. M. Barragán, C. Ruiz- Bauzá, J. I. Mengual, Effect of unstirred solution layers on electro-osmotic permeability of cation-exchange membranes, J. Colloid Int. Sci. 168 (1994) 1-10.

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