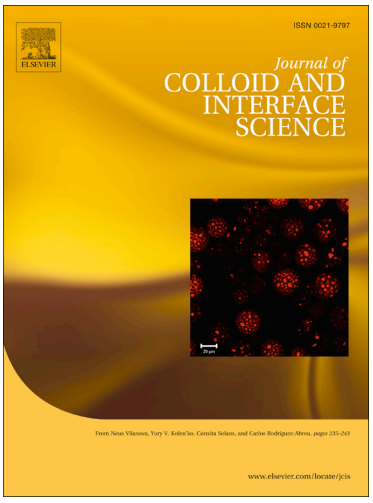

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Counter-ion Transport Number and Membrane Potential in Working Membrane Systems

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Abstract

In this work we use the general space-charge (SC) theory for a combined transport model of fluid and ion through cylindrical nanopores to derive equations for the membrane potential and counter-ion transport numbers. We discuss this approach for ion exchange membranes assuming aqueous domains as interconnected network of cylindrical pores. The transport number calculations from the SC theory are compared with the corresponding ones from the uniform potential (UP) and Teorell-Meyer-Sievers (TMS) models in the case of both zero and non-zero concentration gradient across the membrane and with an applied current density. By using this approach we suggest the optimal conditions for performing membrane potential experiments (i.e. choice of electrolyte and concentration difference) depending on an easily accessible membrane property, namely the volumetric charge density. We also theoretically describe a novel dynamic method to determine in a single experiment the membrane potential and membrane conductivity. To exemplify the use of the dynamic method we report the calculations based on typical operating conditions of the reverse electrodialysis process. The numerical results are presented in terms of the electrical potential difference versus the average pore radius and charge density. The resulting map is a useful tool for a rational design of an effective membrane morphology for a specific electrochemical application.

Keywords: Membrane potential, counter-ion transport number, space-charge model, uniform potential model, phenomenological transport coefficients, reverse electrodialysis

1. Introduction

The membrane potential, i.e. the potential difference arising across a membrane when a concentration difference exists, is an useful parameter to quantify the effectiveness of membranes' co-ion exclusion capabilities [1]. The apparent permselectivity toward co-ions can be defined as the ratio between the membrane potential, $\Delta\phi$, and the Nernst potential, $\Delta\phi_{\mathrm{N}} = -\Delta \ln a \approx -\Delta \ln c$, (reported in its dimensionless formulation) which is the maximum voltage

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