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# A new lateral method for characterizing the electrical conductivity of ion-exchange membranes

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## ABSTRACT

A new method for determining the electrical conductivity of ion-exchange membranes was implemented with four commercial membranes (AMX, CMX, MK-40 and MA-41). It is based on lateral resistance measurements without direct contact between electrodes and membranes. The cell configuration made it possible to determine the membrane conductivity over a wide range of electrolyte concentrations (measurements were carried out in the range $10^{-5}$–$5 \times 10^{-1}$ M). The structural parameters of the different membranes were inferred from AC conductivities and the microheterogeneous model. They were found in good agreement with literature results obtained by normal measurements (i.e. with current lines oriented normally to the membrane surface), thus confirming the reliability of the proposed method. The main advantage of our method is the possibility to characterize ion-exchange membranes even at low salt concentration unlike usual non-contact methods based on normal measurements.

Counterion diffusion coefficients and transport numbers within the membrane gel phase were estimated. The inter-gel phase volume fraction of an anion-exchange membrane (AMX) was also determined for the first time from membrane DC conductivity inferred from streaming potential and streaming current measurements. An excellent agreement was found with structural parameters obtained from AC measurements.

## 1. Introduction

Ion-exchange membranes (IEMs) are used in various industrial processes and electrochemical devices such as electrodialysis or fuel cells, respectively. Electrical conductivity is one of the most important characteristics of IEMs that defines their practical suitability. For example, in electrodialysis the electrical potential gradient (driving force) applied through an IEM, and so the specific energy consumption required to operate a given separation, depend on the membrane electrical conductivity. This latter can be determined from electrical resistance measurements. It has been reported, however, that the experimental value of the electrical conductivity may depend on the measuring method [1–7].

The different methods that can be implemented to measure membrane resistance can be split into different categories according to three main criteria, namely (i) the current lines can be oriented normally or parallel to the membrane surface, (ii) electrodes can be in contact with the membrane or not, (iii) direct current (DC) or alternating current (AC) can be used.

Normal measurements performed in both AC and DC modes were reported in the literature. In AC mode, the most used techniques are (i) the difference method in which the membrane resistance is obtained from the difference between the cell resistance measured with and without the membrane [8–24], and (ii) the contact-mercury method [25–33]. The difference method does not allow characterizing IEMs in too dilute solutions since it becomes highly inaccurate as the solution resistance increases too much with respect to that of the membrane (in most reported works measurements were performed with electrolyte concentrations higher than ~0.01 M). On the other hand the contact-mercury method permits, in principle, characterizing IEMs in solutions of any concentration. However, measurement can be impacted by the partial drying (de-swelling) of membrane samples when transferred from the equilibrating solution to the measuring cell and poorly reproducible results were reported with this technique [2]. The use of a highly toxic metal (mercury) is another drawback of this method. Measurements performed in DC mode were also reported from different cell configurations including Guillou's cell [1], a six-compartment cell with a four-electrode

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arrangement [34–36] or a two-compartment cell with a four-electrode arrangement [37]. A major drawback of methods involving DC measurements is the formation of diffusion boundary layers at membrane/solution interfaces, which impacts resistance measurements, particularly at low electrolyte concentration [1].

Electrical resistance measurements performed with lateral configuration were also reported in AC mode [5,7,38–43]. Most often, the membrane ends are put in contact with metal foils or wire electrodes (direct contact configuration). It has been argued that in such a configuration conduction may be only superficial and then experimental data may not reflect the membrane bulk conductivity [1].

In the present work we propose a new method to determine IEM electric conductivity over a wide range of electrolyte concentrations. Notably, it enables accurate measurements at low electrolyte concentrations unlike standard methods based on normal measurements. The method is based on lateral measurements performed with a measuring cell without electrode/membrane contact. Measurements were carried out with a commercial electrokinetic analyzer (SurPASS instrument, Anton Paar GmbH) allowing direct resistance measurements in AC mode as well as indirect DC resistance determination from both streaming current and streaming potential measurements. Structural parameters of four commercial IEMs (AMX, CMX, MK-40 and MA-41) were obtained from the microheterogeneous model and further combined with the Donnan exclusion model in order to assess ion transport numbers through the membrane gel phase.

## 2. Experimental

### 2.1. Membranes and chemicals

Four commercial IEMs were used in this work, two cation-exchange membranes (CMX Neosepta®, Tokuyama Soda, Japan; MK-40, Shchekinoazot, Russia), and two anion-exchange membranes (AMX Neosepta®, Tokuyama Soda, Japan; MA-41, Shchekinoazot, Russia).

AMX and CMX membranes are homogeneous membranes made of functionalized polystyrene cross-linked with divinylbenzene and mixed with finely powdered poly(vinylchloride) (PVC), which are coated on a PVC cloth used as a reinforcing material. The membrane fixed-charge comes from the presence of sulfonate groups ($-SO_3^-$) in CMX membrane and from the presence of quaternary ammonium groups ($-N^+(CH_3)_3$) in AMX membrane. Both charged groups are grafted directly to the basic polymer structure so that ionic charges are distributed over the whole membrane material.

On the other hand, MA-41 and MK-40 heterogeneous membranes are composite materials made of ion-exchange resins embedded in polyethylene. Ion-exchange resins consist in functionalized polystyrene (with $-N^+(CH_3)_3$ groups for MA-41 membrane and $-SO_3^-$ groups for MK-40 membrane) cross-linked with divinylbenzene.

The main properties of these IEMs are collected in Table 1.

Electrolyte solutions were prepared from KCl and NaCl (Fisher Scientific, analytical grade) and deionized water (resistivity: 18 MΩ cm). They were further used without pH adjustment (pH was found to be 5.7 ± 0.1 for all solutions).

### 2.2. Membrane thickness measurement

Membrane thickness was measured with a Dial Indicator (model 2046S, Mitutoyo, Japan) equipped with a 10 mm diameter flat contact point. Membrane samples were first soaked in a highly concentrated NaCl or KCl solution in order to exchange original membrane counterions with $Na^+$ or $K^+$ (CMX and MK-40 membranes) or $Cl^-$ (AMX and MA-41 membranes). Samples were further equilibrated with the measuring electrolyte solution at room temperature (24 ± 1 °C) for 24 h. Samples were then extracted from the solution and thickness was measured. For each sample, seven measurements were performed at different locations and the average value was considered as the membrane thickness ($e_m$).

### 2.3. Electrical resistance measurement

Membrane electrical resistance were measured with a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) after thickness measurements.

The cell we used required two samples of the same membrane materials. Each membrane sample was cut and adjusted to the sample holder dimensions (length ($L$): 2 cm and width ($W$): 1 cm) and fixed using double-sided adhesive tape. To prevent any leakage between the membranes and the sample holders, the membranes were firmly pressed against sample holders for 30–60 s.

Measurements were conducted with an adjustable-gap cell inside which both membrane samples face each other (see schematic of the measuring cell shown in Fig. 1). Thanks to micrometric screws the distance between the samples ($h_{ch}$) could be set and varied without dismounting the cell [48]. The cell was surrounded by two cylindrical Ag/AgCl electrodes through which the measuring solution could flow (Fig. 1). Since membrane swelling was likely to be modified when fixing the membranes onto the sample holders, circulating the measuring solution through the flow-cell enabled recovering equilibrium conditions prior to electrical resistance measurement. The solution flow was created by a pair of syringe pumps and the resistance was measured in AC mode ($r_{cell\_AC}$) by means of the conductivity meter incorporated in the SurPASS instrument and a pair of reversible Ag/AgCl electrodes with surface area of 10 cm$^2$ each.

The SurPASS electrokinetic analyzer also allows determining

**Table 1**
Main properties of AMX, CMX, MA-41 and MK-40 membranes.

| | AMX | CMX | MA-41 | MK-40 |
|---|---|---|---|---|
| **Manufacturer** | Tokuyama Soda (Japan) | | Shchekinoazot (Russia) | |
| **Type** | Homogeneous | | Heterogeneous | |
| **Thickness (mm)**[a] | 0.14 | 0.17 | 0.3–0.5 | 0.3–0.5 |
| **Specific resistance ($\Omega$ cm$^2$) in 0.5 M NaCl solution**[a] | 2.4 | 3.0 | ≤ 10.0 | ≤ 10.0 |
| **Ion exchange capacity (mmol equiv/g)** | 1.30 ± 0.05[b] | 1.65[c] | 1.25[d] | 2.53[c] |
| **Water content (g $H_2O$/g dry membrane)** | 0.10–0.14[b] | 0.275[c] | 0.29[d] | 0.503[c] |
| **Membrane density (g/cm$^3$)** | 1.10[b] | 1.19[c] | – | 1.13[c] |

[a] Manufacturer data; Refs. [44,45].
[b] Ref. [33].
[c] Ref. [46].
[d] Ref. [47].