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# Determination of the ion-exchange capacity of anion-selective membranes

F. Karas<sup>a</sup>, J. Hnát<sup>a</sup>, M. Paidar<sup>a</sup>, J. Schauer<sup>b</sup>, K. Bouzek<sup>a,\*</sup>

<sup>a</sup> Department of Inorganic Technology, Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

<sup>b</sup> Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague, Czech Republic

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## ABSTRACT

The ion-exchange capacity (IEC) is one of the fundamental characteristics of ion-selective membranes. So far, the most widely used technique for IEC determination is titration. However, this method is very sensitive to experimental conditions, especially when anion-selective membranes are treated. This study compares three different methods of IEC determination of anion-selective membranes, namely titration of  $\text{Cl}^-$  ions, spectrophotometric determination of  $\text{NO}_3^-$  ions and determination of  $\text{OH}^-$  ions exchanged by the membrane for different counter-ions by ion-selective electrode. Differences of up to 24% were observed, a discrepancy mainly caused by the presence of weakly basic functional groups in the membrane. With respect to the utilization of this type of material as an alkaline solid polymer electrolyte, it is important to distinguish between the types of functional groups.

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## 1. Introduction

Currently interest in technologies utilizing anion-selective membranes is rapidly increasing, with large-scale exploitation mainly in the areas of water treatment and the food industry [1]. Electrodialysis and electrodeionisation represent another fast-growing field of application [2]. However, anion-selective polymer electrolytes are also the subject of intensive research pertaining mainly to energy storage and recovery. This especially concerns alkaline fuel cells and water electrolysis [3]. The state of the art alkaline water electrolyzers utilize a diaphragm as an electrode separator and concentrated KOH (i.e. 30 wt.%) as an electrolyte [4].

Although currently used alkaline water electrolysis is a highly robust technology, its efficiency is low and thus energy consumption is unacceptably high with respect to its utilization in the field of energy storage. A promising approach to improve this situation is to replace the currently used diaphragm separating the electrode compartments by an anion-selective membrane. This would permit not only a reduction of the KOH concentration in the system, but also changes in the cell construction. This mainly concerns utilization of the 'zero gap' configuration resulting in process intensification and an increase in its flexibility. Research into the development and optimization of new alkaline polymer electrolytes is accompanied by the need for sound and well-understood characterization methods. Surprisingly enough, the situation

\* Corresponding author. Tel.: +420 2 2044 4019.

E-mail addresses: [Karel.Bouzek@vscht.cz](mailto:Karel.Bouzek@vscht.cz), [bouzekk@vscht.cz](mailto:bouzekk@vscht.cz) (K. Bouzek).

is not very clear in the field of ion-exchange capacity (IEC) determination of alkaline polymer electrolytes. This is due to the varying strength of the anion-selective functional groups potentially present in the material. Since this characteristic determines the concentration of free charge carriers in the polymer electrolyte, it represents one of the basic characteristics to be evaluated. Therefore, this work focuses on potential methods of IEC determination and an evaluation of their suitability for polymer electrolyte characterization.

In general, ion-selective membranes can be divided into two main groups: cation-selective membranes (CMs) containing negatively charged functional groups, typically  $-\text{SO}_3^-$ ,  $-\text{COO}^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{PO}_3\text{H}^-$  and  $\text{C}_6\text{H}_4\text{O}^-$ ; and anion-selective membranes (AMs) carrying positively charged groups, typically  $-\text{NH}_3^+$ ,  $-\text{NRH}_2^+$ ,  $-\text{NR}_2\text{H}^+$  or  $-\text{NR}_3^+$ . Alternatives such as  $-\text{PR}_3^+$  and  $-\text{SR}_2^+$  are also possible [5]. The functional groups of both anion and cation-selective membranes can again be subdivided into strong and weak ion-exchangers according to the dissociation constants of the individual functional groups. The dissociation constants of commonly used functional groups of both AMs and CMs are summarized in Table 1. One evident disadvantage of AMs over the more widespread CMs is their instability if they are treated or operated under harsh conditions, e.g. high temperature, high pH, etc. Under such circumstances AMs can decompose by different mechanisms, depending on the conditions. Important examples are E1 and E2 (Hofmann degradation) elimination or nucleophilic substitution [6].

Numerous values describing membrane properties (water uptake, permeability, ionic conductivity, ion-exchange capacity, mechanical properties, etc.) are usually determined to characterize newly developed membrane materials or for quality control purposes in industry. Nevertheless, IEC is usually the first quantity of interest [6,7]. The IEC provides a first clue about the performance and suitability of a membrane for a desired process and its use as a material for subsequent testing.

The most generally accepted definition of IEC is that it corresponds to the number of counter-ion equivalents in a specified quantity of a material [8]. For a precise interpretation of the data obtained, however, it is always necessary to pay due attention to the IEC units and the method by which the value was obtained.

In the case of CMs the situation is relatively simple and the methods of IEC determination are well established. The most commonly used functional group is the sulfonic group characterized by high stability to most counter-ions, including  $\text{H}^+$ , and by the negligible impact of standard air atmosphere on its form. Thus, IEC can be determined by various techniques which, within the framework of their sensitivity, provide identical results. Acid–base titration [9,10] and the glass pH electrode [11] are most commonly applied to determine the amount of  $\text{H}^+$  ions exchanged by the membrane for different cations present in excess in the solution surrounding the sample. Another method of determining the IEC of CMs is based on ion chromatography [12,13], which can also be used for that of AMs. However, it is seldom utilized due to the expensive equipment required. Finally, the IEC of CMs can also be determined on the basis of spectroscopic techniques providing information on the content of functional groups capable of dissociation in the polymer membrane structure. FTIR spectroscopy [14] or NMR [15] are notable examples. However, IEC values determined by these methods are theoretical and provide no information on real ion-exchange capacity, i.e. the amount of functional groups in the polymer structure accessible to ion exchange, which, in general, is different from the total content.

The most frequently used functional group in AMs is quaternary ammonium, in particular the benzyl trimethyl ammonium group (BTMA) [16]. So far, the most common technique for determining the IEC of AMs is acid–base titration. This simple method is based on the transition of the AM to the  $\text{OH}^-$  form by immersing it in a solution of, for example, NaOH followed by its transition into the  $\text{Cl}^-$  form by immersing it in a solution of HCl or NaCl [17]. In the case of AMs this approach has one serious drawback: the functional groups converted to the  $\text{OH}^-$  form are susceptible to being switched into the  $\text{HCO}_3^-$  form, known as  $\text{CO}_2$  poisoning, when exposed to an environment containing  $\text{CO}_2$  (air atmosphere, water saturated by air, etc.). This phenomenon can significantly affect IEC determination [18].

Two different methods can be used to evaluate the amount of exchanged  $\text{Cl}^-$  ions: (i) chloride ions in the membrane are exchanged by other counter-ions, e.g.  $\text{OH}^-$  or  $\text{SO}_4^{2-}$ , and the released  $\text{Cl}^-$  ions are then titrated using an  $\text{AgNO}_3$  aqueous solution ( $0.1 \text{ mol dm}^{-3}$ ) (Mohr method [19–21]).  $\text{K}_2\text{CrO}_4$  is typically used as an indicator; (ii) the second option is acid–base titration [22,23] where the membrane is converted to the  $\text{Cl}^-$  form by a known volume of HCl standard solution. The excess of HCl is then titrated with NaOH solution using phenolphthalein as indicator. Back titration can also be used. Both of the above-mentioned methods suffer from inaccurate determination of the equivalence point, which could introduce a significant error into the resulting IEC values.

As stated by Sata [7], by means of titration it is also possible to determine the number of weakly basic amino groups present in the membrane. This method requires two titrations under different conditions. Firstly, the membrane is equilibrated with e.g.  $1 \text{ mol dm}^{-3}$  HCl solution in order to activate weakly basic anion-exchange groups by their protonation and to transfer them together with strongly basic anion-exchange groups to the  $\text{Cl}^-$  form. The excess of  $\text{Cl}^-$  ions in the membrane, not corresponding to IEC, is removed by washing with

**Table 1 – Selected functional groups of AMs and CMs and their respective pK values [5,7].**

Functional group	pK
<i>Anion-selective membranes</i>	
$\equiv\text{N}^+$	1–2
$=\text{N}$	4–6
$=\text{NH}$	6–8
$-\text{NH}_2$	8–10
$-\text{N}(\text{CH}_3)_3\text{OH}$	>13
<i>Cation-selective membranes</i>	
$-\text{SO}_3\text{H}$	1–2
$-\text{PO}_3\text{H}_2$	2–5
$-\text{COOH}$	4–6
$-\text{OH}$	9–10

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