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Relationships between transport and physical–mechanical properties of ion exchange membranes

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ABSTRACT

This review focuses on the characterization of properties of ion exchange membranes, on the compromises between ion exchange capacity, relative water content and electrochemical properties of ion exchange membranes. Properties of heterogeneous ion exchange membranes prepared from polyethylene as matrix, ion exchange resin powder and polyester fabric were studied. Ion exchange membranes were prepared with using different ion exchange resins. These ion exchange membranes can be used in many electro separation processes like electro dialysis, electrode ionization, membrane electrolysis or electrophoresis. Desalination of brackish and surface water, purification of waste water or mine water, water desalination after tertiary biological treatment, purification of organic substances, stabilization of wine or demineralization of whey are the most frequent applications where these prepared ion exchange membranes can be utilized. All prepared ion exchange membranes were characterized with same methods and monitored the parameters of ion exchange membranes were ion exchange capacity using Mohr method, electric resistance measured in a special experimental cell using a compensation method, permselectivity measured in the same measuring cell as electric resistance and relative water content. The relationships between the transport and physical–mechanical properties were found. An ion exchange membrane with specific required properties can be prepared on the basis of resultant values of monitored properties.

Keywords: Heterogeneous ion exchange membrane; Properties of IEMs; Ion exchange capacity; Electric resistance; Relative water content

1. Introduction

Ion exchange membranes (IEMs) are separation membranes which separate cations and anions form solution if electric field is applied. Thanks to the fact that the IEM contains fixed ionic functional groups free counter-ions can be transported through IEMs but transport of co-ions is limited [1]. Fig. 1 shows the scheme and simple principle of IEMs. An IEM can be anion exchange membrane (AEM) or cation exchange membrane (CEM) depending on the counter-ion which can be transported through IEM.

On the other hand, we can differentiate two types of IEMs. The first type is homogeneous IEM, which is

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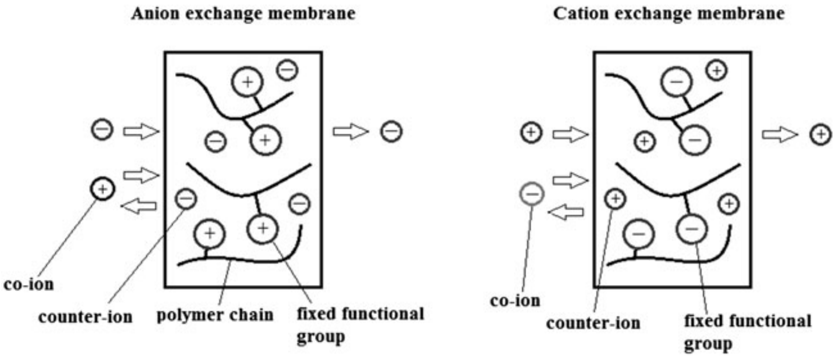

Fig. 1. Scheme of IEMs.

composed of cross-linked polymers with ion exchange groups and the second type is heterogeneous IEM, which consists of polymer matrix (PE, PP, etc.), ion exchange resin and additives. Both types often are reinforced with fitting fabrics (PES, PP, PA). The concentration of ion exchange particles in the matrix varies between 50 and 70 wt.% [2,3].

Homogeneous membranes have excellent electrochemical properties but their mechanical strength is not so good. In contrast, heterogeneous membranes have very good mechanical strength but their electrochemical properties are relatively poor [4].

Early references about heterogeneous IEMs reveal that IEMs can be made by mechanical incorporation of an ion exchange resin powder into sheets of rubber, PVC or some other extrudable or mouldable matrix [5]. Heterogeneous IEMs can be prepared by resin particles dispersed in a solution containing polymer matrix (binder). Subsequently, solvent is evaporated to create the IEM. The second preparation method of IEM is calendaring an ion exchange resin into an inert polymer film. Finally, dry moulding of inert film which consists of polymers and ion exchange resin is used [4,5].

IEMs are used for electro dialysis (ED), electro deionization (EDI), membrane electrolysis, electrophoresis (EF) or in power sources as fuel cells [1,2,6]. Fig. 2 shows the scheme and simple principle of electro dialysis. IEMs are most frequently utilized in desalination of brackish and surface water, purification of waste water, water desalination after tertiary biological treatment, purification of organic substances, stabilization of wine, demineralization of whey, separation of inorganic and organic solutions, purification of organic substances.

Two specific characteristics of electromembrane processes are important: they are ecologically safe and have low electrical energy consumption. The efficiency of these processes depends on electrochemical and physical characteristics of IEMs when placed in the external electric field. Membrane characterization contains studies on physical–mechanical properties and equilibrium: ion exchange capacity (IEC), water content, thickness of films in dry and wet state, thermal and chemical stability; on transport properties [3,7]: conductivity and specific or areal resistance, transport numbers of ions and permselectivity; and structural characteristics: X-ray spectroscopy, SEM, etc. The problem of characterization of IEMs has been discussed in many reviews [7]. At this point, some characterization method of IEM will be mentioned.

Egal et al. [6] measured the electrochemical impedance using an experimental cell in which a polymer membrane is sandwiched between two electrodes made of platinized platinum. An alternating potential was imposed between these electrodes and it was used with many different frequencies. This measurement provides information about the intrinsic conductivity of the IEM [6]. The transport number can be measured using two different methods; Henderson's method is the static method using Henderson's equation which determines the transport number under diffusion. The experimental cell is separated in two parts by IEM. Every part contains a solution with different concentration. The second, Hittorf's method is the dynamic method which defines the transport number under migration in real conditions. The experimental cell is separated by IEM but the solution is the same in every part. Ions in the solution migrate through IEM. The cationic transport number obtained in the cathodic part and the anionic part is from Hittorf's equation. Hittorf's method is more real than Henderson's method [6].

Cui et al. [8] determined electric resistance of IEMs by impedance spectroscopy using two different cells with gold-plated copper electrodes. The phase angle between voltage and current is equal zero so the results of measurement can be taken as electric

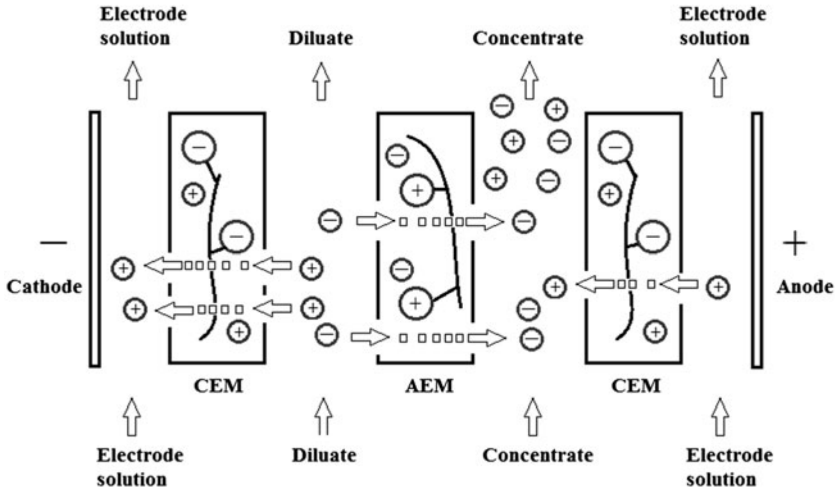

Fig. 2. Scheme of electro dialysis.

resistance of IEMs [8]. Cui et al. also determined many characterization of IEMs as the membrane swelling, permselectivity, thermo gravimetry, DSC or using in ED. Xing et al. [9] analyzed IEMs' properties using NMR, FTIR, DSC (thermal properties), Ubbelohde viscometer, AC impedance spectroscopy (conductivity measurement). Choi et al. [10] characterized IEMs using chronopotentiometry with a two-compartment cell and two Ag/AgCl electrodes like Sistat et al. [11]. Chronopotentiometry is an electrochemical method for studying the time-dependence of an electrode potential produced by a controlled current [11].

The effects of variation of ion exchange resin particle size as well as the resin–binder ratio on different mechanical, electrochemical and morphological properties of the membranes have also been studied [4].

2. Experimental

2.1. Preparation of IEM

Ion exchange membranes were prepared in several processing steps. Initially, ion exchange resin particles were dried in an industrial dryer and powdered in a vibratory mill at ambient temperature. Powdered ion exchange resin was mixed with polyethylene matrix in Buss co-kneader. Prepared granulates was extruded into membrane foil, which are in same production step, laminated on both sides by polyester fabric. IEMs were prepared with using different ion exchange resins supplied by Purolite and DOW Chemical. Different types of IEMs were named as anion exchange membrane with ion exchange resin Amberjet^{TM} (ABJ A), anion exchange membrane with Amberjet^{TM} and Purolite$^{®}$ (ABJ A + PUR), cation exchange membrane with ion exchange resin Dowex^{TM} (DOW C) and cation exchange membrane with DOWEX^{TM} and Purolite$^{®}$ (DOW C + PUR).

2.2. Ion exchange capacity

IEMs' granulate was swelled in demineralized water at room temperature. The next operation is membranes' conditioning (membranes' pre-treatment) in 1 M NaOH solution and the change from NaOH solution to 1 M HCl solution to convert granulate into the particular form. IEMs' granulate was washed with demineralized water between particular operations. Subsequently, granulate was dried in an oven at 105°C for 4 h and weighed in the dry form. AEMs' granulate was immersed in 4% $NaNO_3$ and the solution (without AEMs) was titrated using Mohr method. On the other side, CEMs' granulate was immersed in 0.1 M NaOH and the IEC of CEMs was determined from increasing of acidity by titration [5,6].

2.3. Relative water content

The relative water content was determined in the following way. IEMs were dried in an oven at 75°C to constant weight and weighed in the dry form (m_{dry}). Subsequently, IEMs were swelled in demineralized water at room temperature for 24 h and dabbed with a filter paper to remove excess water. The weight of IEMs in the wet form was measured (m_{wet}). Then, the relative water content was determined using this formula [8]:

$$\text{Relative water content} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\%$$

2.4. Specific resistance

IEMs for measurement of resistance had to be swollen in demineralized water at room temperature. The next operation was the same as in the IEC measurement (membranes' conditioning). IEMs were equilibrated in 0.5 M NaCl for 24 h. Electric resistance was measured in 0.5 M NaCl solution at room temperature in a special experimental cell using a compensation method. The experimental cell consisted of two parts separated from each other. The appropriate solution was mixed in experimental cell. Electric resistance was measured between reference electrodes and then the direct current was applied between platinum electrodes. Electric resistance was determined by two measurements of potential difference. The first measurement was performed without the IEM (only solution) and the second with the IEM between the two parts [5,6]. The active area of IEM was 0.785 cm^2.

2.5. Permselectivity

Permselectivity of IEMs was determined by Henderson's method in the same measuring cell as electric resistance but with the following KCl solution pair 0.1–0.5 M in separated part and without applied direct current. IEMs were equilibrated in 0.5 M KCl for 24 h before the measurement [8].

3. Results

It is difficult to find the IEM with ideal parameters because monitored parameters of IEMs determining different properties often have opposing effects.

The most desired properties required for successful IEMs are:

- High permselectivity—an IEM should be highly permeable to counter-ion and impermeable to co-ions.
- Low electrical resistance—an IEM should have low electrical resistance for process of energy-saving electro dialysis.
- Good mechanical stability—an IEM should be mechanically resistant and have a low degree of swelling for arrangement in electro dialysis.
- High chemical stability—an IEM should be stable over the whole pH-range [12] from 0 to 14.

3.1. Effect of ion exchange capacity on relative water content

Ion exchange capacity of IEMs is an important property because ionic transport properties (electric resistance) of IEMs depend on the type and amount of ion exchange groups. IEC is expressed as milli equivalent of bound dissociated groups in an IEM per gram of dry IEM [13].

The relative water content does not only determine the membrane dimensional stability but also has an effect on membrane selectivity, electrical resistance and hydraulic permeability, etc. [12].

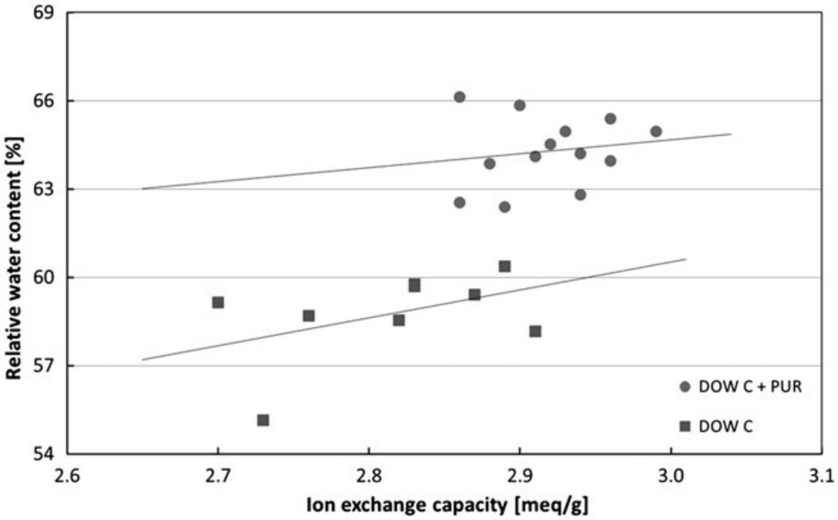

Fig. 3. Dependence of relative water content on ion exchange capacity of CEMs.

In Fig. 3, the dependence of relative water content on ion exchange capacity is depicted for CEMs with using different ion exchange resins. The same dependence is described in Fig. 4 but for AEMs with using two different ion exchange resins.

It can be seen from Figs. 3 and 4 that relative water content increases with higher values of ion exchange capacity. The same dependence was found for both IEMs (CEMs and AEMs) in which hydrophilic groups on the membrane matrix are responsible for water absorption [8]. Another role in process of swelling has type of membrane polymer matrix and also cross linking of ion exchange resin. This is a main reason for different dependence of IEMs prepared from various ion exchange resins. Lower ion exchange resin cross linking results higher water content.

3.2. *Effect of ion exchange capacity on specific resistance of IEMs*

Electric resistance of IEMs is an important property for process of energy-saving electro dialysis [13]. In Figs. 5 and 6, specific resistance of IEMs in dependence on their IEC is presented.

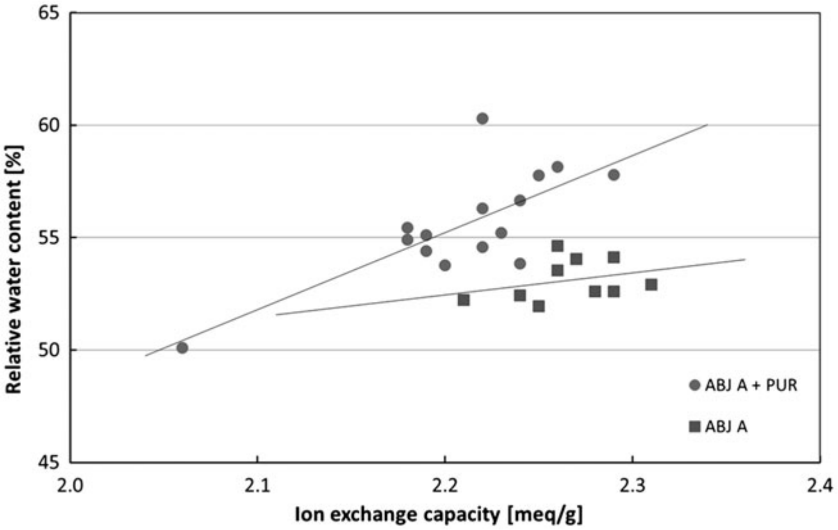

Fig. 4. Dependence of relative water content on ion exchange capacity of AEMs.

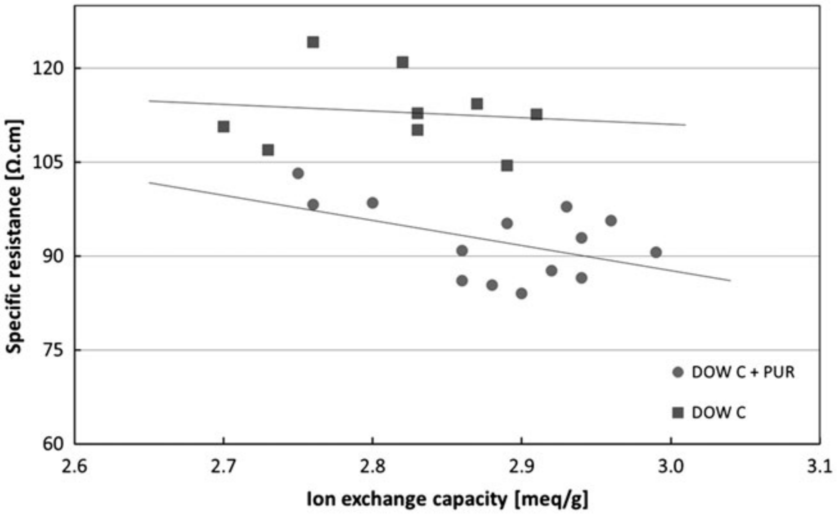

Fig. 5. Dependence of specific resistance on ion exchange capacity of CEMs.

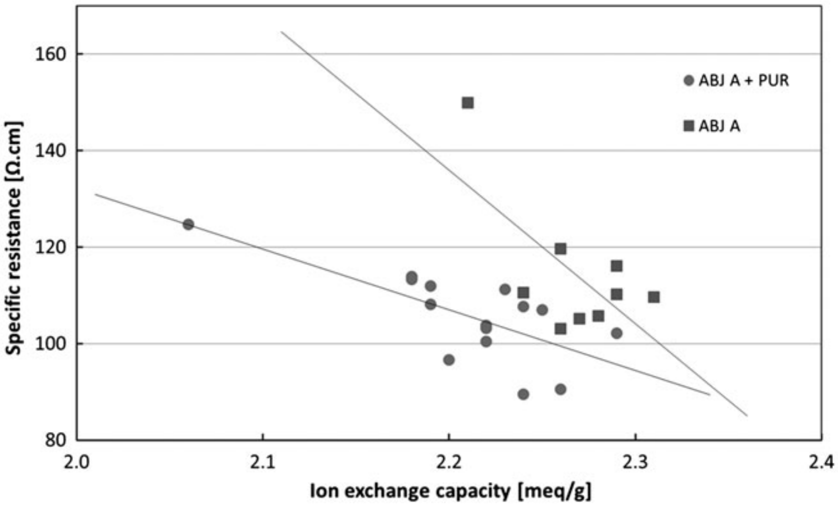

Fig. 6. Dependence of specific resistance on ion exchange capacity of AEMs.

It can be seen from Figs. 5 and 6 that specific resistance of IEMs decreases with increasing value of IEC. A high IEC of IEMs means more sites for counter-ion hopping (higher number of channels available for counter-ion crossing through IEMs) and decrease in electric resistance of IEMs. But it also causes stronger swelling of IEMs due to enhancement of hydrophilicity which is caused by ion exchange groups [5,13]. Lower ion exchange resin cross linking increases kinetics of ion exchange and therefore decreases the specific resistance of IEMs. Also, higher water content (means the higher free volume) could contribute to additional decrease in specific resistance.

3.3. *Effect of ratio of ion exchange capacity/relative water content on permselectivity of IEMs*

Permselectivity is an important property of IEMs because it expresses difference in the membrane permeability for counter-ions and co-ions. IEMs with permselectivity of 100 % can allow the permeation of only the counter-ions in ED process [5,13]. Permselectivity is proportional to the concentration of ionic functional groups [5]. The strong influence of relative water content on permselectivity can be seen at the dependence of ratio of IEC/relative water content [8]. In Figs. 7 and 8, the dependence of permselectivity on ratio of IEC/relative water content of IEMs is presented.

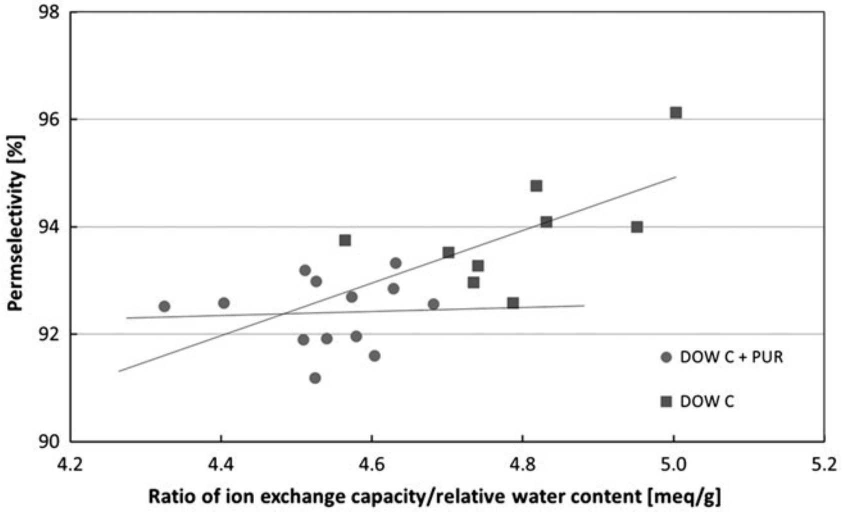

Fig. 7. Dependence of permselectivity on ratio of IEC/relative water content of CEMs.

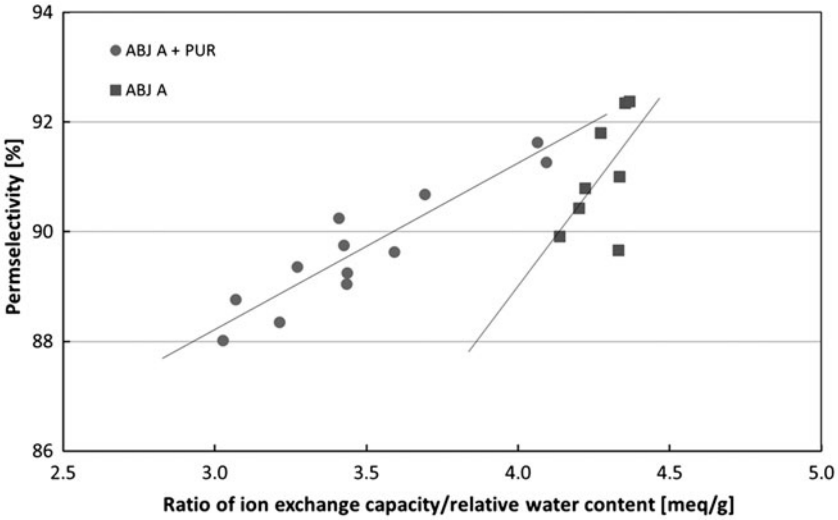

Fig. 8. Dependence of permselectivity on ratio of IEC/relative water content of AEMs.

In a CEM, the fixed anions are in electrical equilibrium with mobile cations in the interstices of the matrix. The mobile anions (co-ions) are more or less excluded from the polymer matrix. Their electrical charge is identical to the fixed ions. This type of exclusion is called Donnan exclusion. Due to the exclusion of co-ions, a CEM can transfer only cations. In an AEM, it is the same process but with the ions it has opposite electric charge [12].

From Figs. 7 and 8, we can see that permselectivity of IEMs increases with increasing ratio of IEC/relative water content. This influence can be explained in the following way: the higher relative water content indicated by a lower ratio of IEC/relative water content, the worse Donnan exclusion of IEMs for co-ions which finally causes lower permselectivity [8].

4. Conclusion

Good correlations were found between transport and physical–mechanical properties of IEMs. For both types of IEMs (CEMs and AEMs) relative water content increased with higher values of ion exchange capacity which is caused by hydrophilic groups bonded in the polymer matrix responsible for water absorption. The second dependence is correlation between IEC and specific resistance. Specific resistance of IEMs was lower with higher value of IEC. A high IEC of IEMs means more sites for counter-ion hopping results in a decrease in IEMs' electric resistance. The influence between ratio of IEC/relative water content and permselectivity can be explained in the following way: the higher water content indicated by lower ratio of IEC/relative water content, the worse Donnan exclusion of IEMs for co-ions which causes lower permselectivity. An ion exchange membrane with specific required properties can be prepared on the basis of resultant values of monitored properties.

Acknowledgements

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