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Research Article

ELECTROCHEMICAL CHARACTERIZATION OF CELLULOSE ACETATE BUTYRATE-PERMUTIT COMPOSITE MEMBRANE IN AQUEOUS UNI-UNI VALENT ELECTROLYTE SOLUTIONS

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Abstract

Co-mixed cellulose acetate butyrate and permutit in a definite composition was prepared and coded as MRS-2. The membrane potential was measured with uni-uni valent electrolyte, NaCl solutions using saturated calomel electrodes (SCEs). The effective fixed charge density of the membrane was determined by TMS method and it showed dependence on the porosity, charge on the membrane matrix, charge and size of permeating ions. Other important electrochemical parameters were calculated. Conductance-time data were generated for the kinetic study of the permeating ions in terms of membrane permeability, flow and flux parameters. Donnan membrane equilibrium condition was examined. Membrane adsorbability showed concave dependence with external electrolyte solution and convex type dependence was showed by swelling and conductance parameters. This membrane had no characteristic of anomalous osmosis, indicates that there is no water flooding will take place during membrane operation.

Keywords: Membrane potential; Effective fixed charge density; Donnan membrane equilibrium; co-mixed membrane; Dissociation equilibrium; Solvent uptake.

Introduction

Membrane processes are currently being studied for numerous applications of practical interest (Singh K and Tiwari A K 1999; Tiwari AK and Ahmad S 2006). Co-mixing is effective methods for modification in membrane activity (Tiwari AK and Ahmad S 2006). To examine it, cellulose acetate butyrate (CAB) and permutit were mixed and their characteristic properties were determined on the basis of membrane potential and conductance-time studies. Membrane potential is determined by the combination of the properties of ions and of the membrane. There is, therefore, a possibility that the properties of ions can be reflected in the membrane potential more effectively by modifying the membrane properties. The transport number, reflecting the membrane selectivity, is determined by the product of the total ionic uptake and the average mobility, which contains the dissociation equilibria (Asaka K 1990; Buchanan, C.M., Edgar, K.J., Wilson, A.K. 1991; Kimura Y Lim H J Iijima T I 1984). It, follows that a membrane may be selectively permeable to ions either by preferential uptake or as a consequence of high mobility. The mobility ratio and the effective fixed charge density can be estimated from the membrane potential. These parameters are associated with the interactions between ions and membrane texture which are the key to understanding the

salt separation mechanism (Bontha J. R. and Pintauro P.N. 1994; Lobo V M M et al 1998; Mills, R. 1965).

Conductance-time study furnishes information regarding the ion dynamics through the membrane along with ionic-adsorption on to the membrane/solution interface (Lobo, V M M et al 1994; Magnar O et al (1992; Mills, R. 1965). These data have been used to estimate permeability, flow and flux parameters for the membrane/solution system. Permeability and flow parameters concavely depend on external electrolyte concentration but flux depends differently.

Experimental

Chemicals and Membrane Materials

Cellulose acetate butyrate, CAB, (John Baker Inc., Colorado, USA) and permutit (CDH, India) were used for membrane formation. Sodium chloride (AR Grade, S.D. Fine Chemicals, India) and acetone (Qualigens Fine Chemicals, India) were used as received.

Membrane preparation

Cellulose acetate butyrate, CAB, and permutit were mixed with 40 mL acetone in proportion given below for the membrane formation. MRS-2 membrane contains 4g CAB and 1g Permutit. To ensure uniformity of composition, the mixture was stirred for over 4h over a magnetic stirrer. The

slurry thus obtained was spread on a clean dried glass plate using a knife to form a desired thick layer. The film was allowed to dry for 15-20 min at laboratory temperature. It was then removed from the glass plate by submerging it in a distilled water bath. Membrane pieces of the required dimensions are cut from the film and fixed in the experimental setup.

Membrane Potential Measurement

The membrane potential was measured as a function of the salt concentration for the system mentioned elsewhere (Singh K Tiwari A K 1999; Magnar O et al 1992). The potential / conductance-time measuring cell is illustrated in Figure 1 and was made of glass. Each compartment of the system was filled with aqueous electrolyte solution of different concentrations. The membrane area was cm². Characteristic properties of the membrane are summarised in Table 1

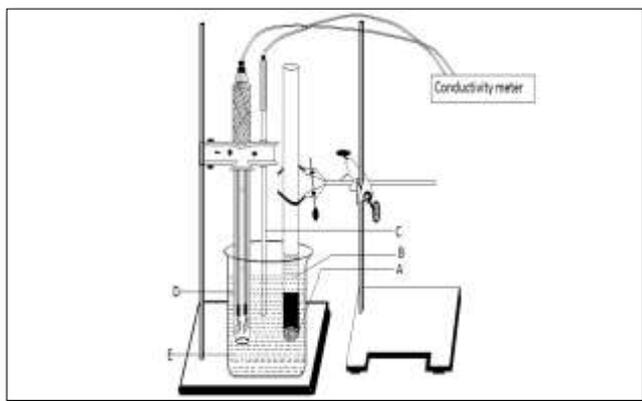


Fig 1: Schematic presentation of membrane system from which conductance-time and membrane potential data was acquired

[A= Cellulose acetate Butyrate membrane fixed with glass joint; B= Electrolyte Solution (Source); C= Automatic Temperature Compensation; D= Conductivity cell; E= Distilled Water (Sink)]

Table 1: Characteristic properties of the membrane used during study

Characteristic properties of the membrane used		
R (%)	Qw (wt%)	L (cm)
56.25	45.40	0.00212

Abbreviations used: R=Rejection of a salt; Qw = Water content; l = Thickness of swollen membrane

Water Content

The membrane was conditioned by immersing it for 24h in water at 25°C, after which it was removed from the water, blotted with a filter paper to remove any excess water, weighed; its weight was recorded as ‘wet weight’. The membrane was then dried for 24h in desiccators and weighed; its weight was recorded as ‘dry weight’. The water content was calculated as

$$Q_w = (\text{wet weight} - \text{dry weight}) / \text{dry weight}$$

Results and Discussion

Fig.2 shows the concentration dependence of the membrane potential across the CAB-Permutit (zeolite) membrane. Membrane potential decreases with the increase in external sodium chloride mean concentration.

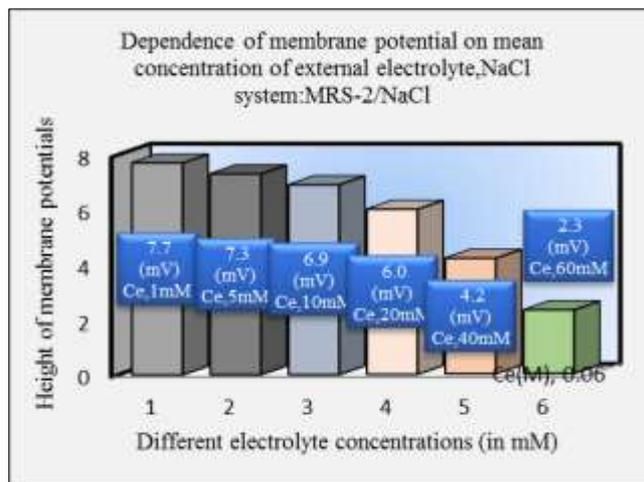


Fig 2: Dependence of membrane potential on the mean concentration of external electrolyte.

The concentration dependence of the membrane potentials shows the characteristics of positively charged membrane. According to the TMS theory (Okita, M (1995); Piedade, A.P. et al. 1995), the membrane potential, E_m consists of the difference of the two Donnan potentials at the interfaces between membrane and solutions, E_{Don} and diffusion potential inside the membrane, E_d being obtained by the following equation

$$E_m = E_{Don} + E_d \tag{1}$$

Membrane potential in a more general and convenient form can be expressed as

$$E_m = \frac{R.T}{F} \left(\frac{t_-^m}{z_-} - \frac{t_+^m}{z_+} \right) \ln \left(\frac{C_1}{C_2} \right) \tag{2}$$

Where $\frac{t_-^m}{z_-}$ and $\frac{t_+^m}{z_+}$ denote ratio of membrane phase anion transport number to anion valency and membrane phase cation transport number to cation valency respectively. C1 and C2 denote concentration of external electrolyte bathing the membrane on either sides.

Transport number in the membrane phase is defined in different way in comparison to the transport number in the solution phase. Both can be expressed as

$$t_i^m = \frac{c_i^m u_i^m}{\sum c_j^m u_j^m} \quad \text{and} \quad t_i = \frac{u_i}{\sum u_j} \tag{3}$$

Both phases obey electroneutrality condition. Membrane phase consists of counter-ion, co-ion and effective fixed charge density but in the solution phase there is no existence of effective fixed charge density and only cation and anion play their respective role. Membrane phase nomenclature is not applicable to the solution phase.

In present system $t_+^m > t_-^m$ and t_+^m value decreases with the increase in mean concentration of NaCl. t_+^m follows the opposite trend of variation. When both transporting ions possess approximately equal transport number value leads to zero membrane potential value. But membrane selectivity retains its character at this value also (Tiwari AK Ahmad S 2006; Theresa M. et al 2013). Variation of membrane potential with mean concentration even when concentration ratio was kept constant indicated a change in the membrane characteristics as a result of which counter-ion was affected. Membrane potential E_m can be expressed in terms of mean concentration C_e as $E_m=A+B.C_e(M)$ where A and B are adjusting parameters, and $A>0$ and $B<0$. This variation may be attributed to (i) increased adsorbability of ion (ii) reduction in swelling of the membrane matrix with increase in concentration, or (iii) increase in membrane conductance at higher mean concentration. In present case ionic adsorbability onto the membrane-solution interface increases with the electrolyte concentration. Membrane system adsorbability is found of convex nature. Reduction in swelling of the membrane matrix in the electrolyte solution is found of concave nature. With the increase of electrolyte concentration, membrane conductance increases and giving rise convex type curve. Increased membrane conductance will also contribute towards lowering of membrane potential. It appears that factors (i) and (ii) together predominates, since a substantial decrease in membrane potential with increase in mean concentration has been observed.

The conductance of the membrane denotes the ability of a membrane to conduct charges through the selectivity is the ability of a membrane to separations. There is no strict relationship between the synthesis parameters and properties. Some of them are even counteracting. Generally speaking, a high value of conductivity does not favour a high selectivity (Tiwari AK 2013; Xuan T L 2008). In our case membrane selectivity concavely depends on the membrane conductance as shown in Fig. 3.

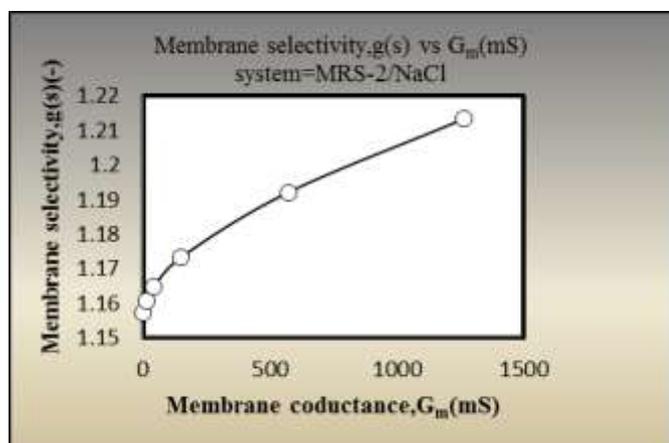


Fig 3: Dependence of membrane selectivity, g(s) on membrane conductance, Gm.

The explanation of the variation in membrane conductance has been explained elsewhere (Tiwari AK Ahmad S 2006) in terms of two equilibrium constants, (i) $K_d^S = f(C_+^m, C_-^m, \text{ and } C_s^m)$ (ii) $K_d^f = f(C_+^m, \phi X_T \text{ and } X_T)$ terms used herein have usual significance. The dependence of the ratio K_d^S/K_d^f on NaCl concentration is shown in Fig. 4:

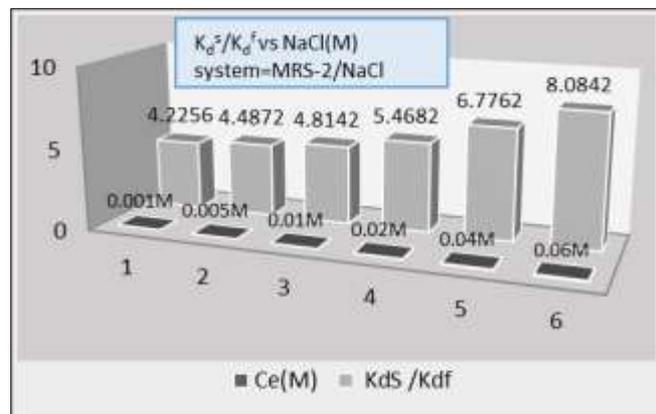


Fig 4: Dependence of the ratio, $[K_d^S / K_d^f]$ on the mean concentration of external electrolyte.

The fixed groups, counter-ions and co-ions, are related by the following Donnan membrane equilibrium, which holds between solutions inside and out-side of the membrane (Tiwari AK and Ahmad S 2006; Tiwari AK 2013)

$$(y_{\pm} \cdot C)^2 = y_{\pm}^m \cdot C_{\pm}^m (y_{\pm}^m \cdot C_{\pm}^m + y_p^m \cdot X_T) \tag{4}$$

where y_{\pm} is the mean activity coefficient of the electrolyte in solution. y_{\pm}^m is that in the membrane and y_p^m is the activity coefficient of counter-ions in the membrane phase. Here $\phi = \frac{y_p^m}{y_{\pm}^m}$. ϕ increases with the increase of the external electrolyte concentration. After introducing ϕ , in the above equation, it becomes

$$(y_{\pm} \cdot C)^2 = (y_{\pm}^m)^2 \cdot C_{\pm}^m (C_{\pm}^m + \phi X_T) \tag{5}$$

Dividing both sides of the above of the above equation by $(C_{\pm}^m + X_T)$, one can obtain

$$\left(\frac{C_{\pm}^m + \phi X_T}{C_{\pm}^m + X_T} \right) = \left[\frac{(y_{\pm} \cdot C)^2 / (C_{\pm}^m + X_T)}{(y_{\pm}^m)^2 \cdot C_{\pm}^m} \right] \tag{6}$$

The above expression is dependent of an external electrolyte, NaCl. There is possibility that $(C_{\pm}^m + \phi X_T) \approx (C_{\pm}^m + X_T)$ when NaCl concentration becomes equal to 5.124mM. Under such condition following equality can be obtained

$$\left(\frac{y_{\pm}^m}{y_{\pm}} \right) = \left\{ \frac{C^2}{C_{\pm}^m (C_{\pm}^m + X_T)} \right\} \tag{7}$$

In the above relation, y_{\pm} and y_{\pm}^m , both are the function of external electrolyte and their values decreases with the increase of external electrolyte. It indicates solute uptake by the membrane increases with the increase external salt concentration. Donnan membrane equilibrium (i) affects

salt concentration and (ii) vary the ratio of co-ion and counter-ions within the membrane. It has been estimated that $C_T < X_T$ and $K_d^s > K_d^f$ where C_T and X_T denote the total concentrations of salt and fixed groups in the membrane phase. It is obvious that the variation in the ϕ_{XT} value must affect the counter-ion and co-ion concentrations in the membrane phase, along with K_d^s and K_d^f . The necessary condition to observe Donnan exclusion is also examined for the system which is shown in Fig. 5 below wherein r_1 denotes ratio of co-ion to counter-ion concentrations and r_2 denotes ratio of $[K_d^s \cdot C_T] / [K_d^f \cdot X_T]$:

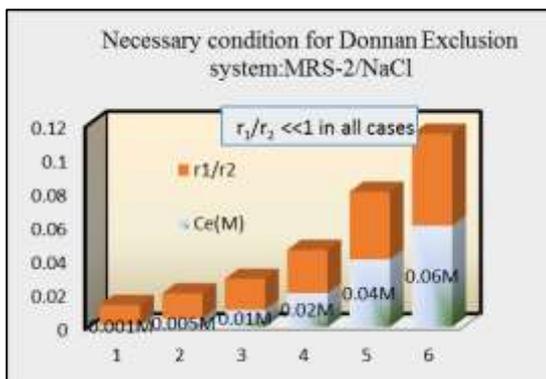


Fig 5: Dependence of the ratio, r_1/r_2 , on the mean concentration of external electrolyte.

The system under consideration follows the criteria of efficient salt rejection (Valente A J M. et al 2000; Tiwari AK 2013; Tiwari AK and Ahmad S 2006)

$$C_w^m / C_w \gg C_s^m / C_s \text{ or } \left\{ \frac{C_w^m}{C_w} - \frac{C_s^m}{C_s} \right\} = H \quad [8]$$

where H is extent of hydrophilicity of the membrane which depends on solute-solvent coupling, sieve action with hindrance factor of the membrane. The collective effect of these parameters is shown in Fig. 6. Membrane hydrophobicity shows concave dependence on the external electrolyte concentration. It means that membrane hydrophobicity increases with the increase of external electrolyte concentration.

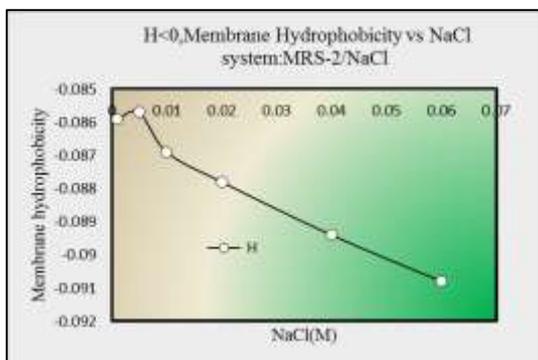


Fig 6: Dependence of membrane hydrophobicity, H, on the mean concentration of external electrolyte.

For the conductance-time study (Okita, M 1995), membrane is arranged in such a way that it separates source and receiving compartments. Source compartment contains

known electrolyte concentration and receiving compartment has distilled water of known volume is connected with conductivity bridge. As time passes, conductance of the receiving phase increases which imparts information regarding the membrane permeability, $P(\text{cm/s})$; flow, $F(\text{cm}^3/\text{s})$ and flux, $J_s(\text{mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-1})$. The representative plot of conductance vs time is mentioned in Fig. 7 and dependence of P, F and J_s on the concentration of external electrolyte is shown in Fig. 7, 8 & 9. The conductance-time data imparts the information regarding the variation of concentration difference between the source and receiving compartments with time. Percentage of reduction in concentration difference between the two compartments estimated is 34.41%.

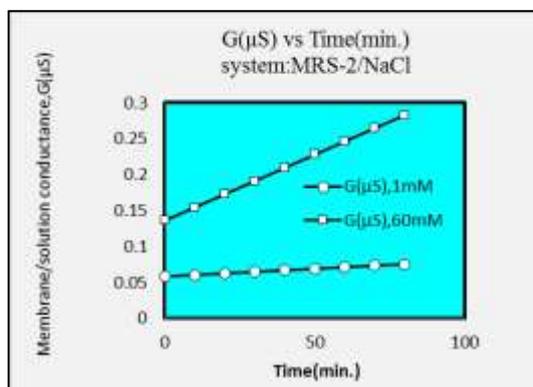


Fig 7: A representative plot of membrane-solution conductance (receiving compartment) versus time.

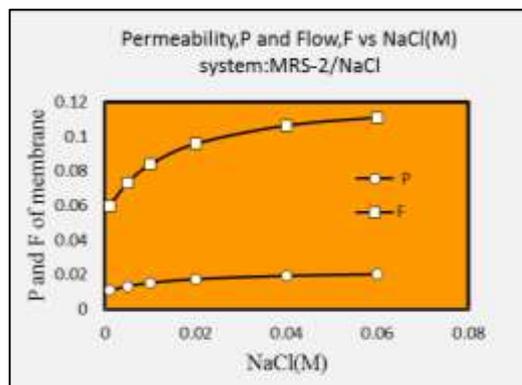


Fig 8: Dependence of membrane permeability, P and flow, F on the mean concentration of external electrolyte.

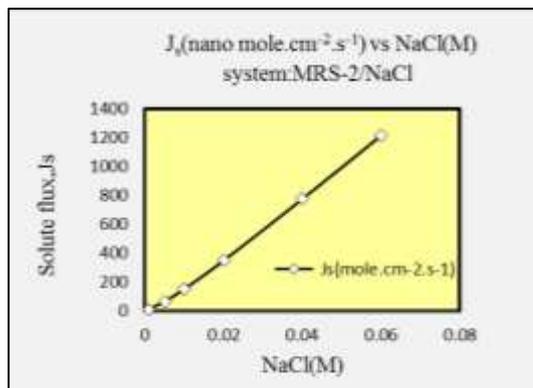


Fig 9: Dependence of membrane flux, J_s , on the mean concentration of external electrolyte.

Conclusions

In a separation process, it is a basic requirement for the membrane to have uniform distribution of water through it. When such membrane comes in to contact with electrolyte solution, sorption takes place in the membrane texture. This sorption depends on fixed charge groups. These charge groups are responsible for the performance of the membrane.

1. Undissociated salt concentration in the membrane phase increases with external electrolyte.
2. Effective fixed charge density, ϕX , of the membrane increases with external electrolyte concentration.
3. K_d^s and K_d^f both increase with increased NaCl concentration.
4. Membrane hydrophobicity increases with increase of electrolyte concentration.
5. Since moderate hydrophobicity is the dominating characteristic of the current membrane, and expected that there will be no water flooding during the membrane operation.

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References

- Asaka K (1990) Dielectric properties of cellulose acetate membranes in aqueous salt solutions. *J. Membr. Sci.* **50**:71-84.
- Bontha JR and Pintauro PN (1994) Water orientation and ion salvation effects during multicomponent salt partitioning in Nafion cation exchange membrane. *Chem. Eng. Sci.* **49**: 3835-3851.
- Buchanan CM, Edgar KJ, Wilson AK (1991) Preparation and characterization of cellulose monoacetates: The relationship between structure and water solubility. *Macromolecules*, **24** (11): 3060-3064.
- Kimura Y Lim HJ Iijima TI (1984) Membrane potentials of charged cellulosic membranes. *J. Membr. Sci.* **18**:285-289.
- Lobo VMM, Ribeiro ACF, Verissimo LMP (1998) Diffusion coefficients in aqueous solutions of potassium chloride at high and low concentrations. *J. Mol. Liq.* **78**: 139-149.
- Lobo, V.M.M., Valente, A J M(1994) Diffusion coefficients of electrolyte solutions in polymers. *Int. J. Polymer Mater.* **25**:139-142.
- Magnar O, Tormod F, Slgne K, RatkJe Steffen MH (1992) Membrane transference numbers from a new emf method. *J. Membr. Sci.* **74**: 1-8.
- Mills R (1965) Diffusion in electrolytes *J. Electroanal. Chem.* **9** (1): 57-69.
- Okita, M (1995) Time-lag method and transport properties of gel. *Jpn. J. of Appl. Phys. Part 1*,**34**: 2418-2422.
- Piedade AP, Guthrie JT, Kazlauciusas A, Gil MH (1995) Characterization of cellulose derivatives - Relevance to sensor development. *Cellulose* **2**(4): 243-263.
- Singh K and Tiwari AK (1999) Studies on the electrochemical characterization of cellulose acetate and Dowex-50 membranes for uni-univalent electrolytes in aqueous solutions. *J. Colloid Interface. Sci.* **210**: 241-250.
- Theresa M., Pendergast M., Ghosh AK, Hoek EMV (2013) Separation performance and interfacial properties of nano composite reverse osmosis membranes. *Desalination* **308**: (180–185).
- Tiwari AK (2013) Electrochemical characterization and assessment of performance of zirconium phosphate and zinc zirconium phosphate membranes in aqueous sodium chloride solutions. *J.Ind.Eng.Chem.*<http://dxdoi.org/10.1016/j.jiec.2013.04.011>.
- Tiwari AK Ahmad S (2006) Studies on electrochemical characterization and performance prediction of cellulose acetate and zeocarb-225 composite membranes in aqueous NaCl solutions. *J. Colloid Interface. Sci.* **298**: 274-281.
- Tiwari AK Sonkar R Tanveer S Tiwari PK (2013) Effect of hydrotrope on the electrochemical behaviour of Dowex-50 membrane in aqueous solution of uni-univalent electrolyte. *Desalination* **313**:125-133.
- Valente AJM, Polishchuk A, Ya Lobo VMM and Burrows HD (2000) Transport properties of concentrated aqueous sodium dodecyl sulfate solutions in polymer membranes derived from cellulose esters *Langmuir* **16**: 6475-6479.
- Xuan TL (2008) Permselectivity and microstructure of anion exchange membranes. *J. Colloid Interface Sci.* **325**: 215–222.