Estimation of electrical parameters inside nanofiltration membranes in various electrolyte solutions by dielectric spectroscopy analysis†

Kongshuang Zhao,* Qing Lu and Wenjuan Su

1. Introduction

Dielectric spectroscopy is a particularly insightful method because it can monitor relaxation processes of various systems in a non-invasive way, especially heterogeneous systems including membrane–solution. In our previous paper† (to be referred to as Part 1 hereinafter) of this series, the low-frequency dielectric behavior of nanofiltration (NF) membranes have been studied. In Part 1, we proposed an expression for describing low-frequency relaxation by which the structural and electrical parameters such as the pore radius, thickness of the active layer of the NF membrane, surface charged density and zeta potential on the pore wall were obtained. In short, Part 1 demonstrated that dielectric spectroscopy method has obvious advantage in obtaining information inside separation membranes used in liquid systems. However, some key issues, such as the calculations of volumetric charge density and ion solvation energy barrier, are still unresolved. In fact, it is impossible to obtain these parameters only by analyzing low-frequency relaxation. They are particularly important for discussing ion transport process when the membranes are in working conditions (i.e. when membranes were immersed in solution). This is because that they can determine the membrane flux and ion selectivity; the membrane volumetric charge density strongly influence the electrostatic interaction between the membrane and the ions, and the ion solvation energy barrier can represent the degree of dielectric exclusion effect. Analyzing the dielectric relaxation occurring at high frequency can provide information on the electrical properties of the constituent phases of the membrane–electrolyte solution system, especially the membrane and the pore inside the membrane.

Several experimental methods, such as measurement of membrane potential, streaming potential, zeta potential and salt permeability, have been used widely to characterize the NF membrane. Some of these methods can obtain information on the pore radius of the membrane from which the membrane volumetric charge density can be calculated. Furthermore, other researches focus on predicting membrane performance through theoretical model with the help of assumed parameters, such as the pore radius and membrane relative permittivity. Besides, the researches on checking the applicability of the existing model by comparing theoretical with experimental results, and discussing the influence of dielectric exclusion and Donnan exclusion on ion permeability of membrane have been reported. In the former methods, the factors that affect ion transport have not been analyzed, while by the latter methods, it is difficult to give accurate parameters on membrane performance because just assumed parameters were used. Dielectric analysis based on appropriate model can compensate for these defects.

Numerous valuable researches on separation membrane by dielectric spectroscopy or electrical impedance spectroscopy (EIS) have been reported. Among them, the works from Coster and co-workers are representative. They determined the stability of supporting liquid membrane characterized the
electrical properties and porosity of ultrafiltration membranes, discussed fouling of reverse osmosis membranes, and investigated the electrical properties of BSA-fouling of ion exchange membrane by EIS. Besides, Benavente et al. studied the influence of polysulphone membranes that modified with polyethylene glycol and lignosulfate on the electrical properties of membrane. In our previous studies, an effective method to calculate the inner parameters of multi-membrane under solution was proposed, and have been adapted to detect the structural and electrical properties of NF membrane.

In fact, the dielectric analysis method has been widely used to study various heterogeneous systems to obtain inner information of constituent phases of these systems. For the membrane-solution systems, the relative permittivity and conductivity of the membrane phase and solution phase, \( \varepsilon_m \) and \( \varepsilon_w \), can be calculated. Among these phase parameters, the relative permittivity of the membrane \( \varepsilon_m \) is very significant because it is essential to calculate the ion solvation energy barrier that characterize the selectivity of membrane. In addition, by these phase parameters, the porosity of membrane and membrane volumetric charge density can be evaluated. Moreover, taking the advantages of the dielectric analysis method, namely in situ and non-invasive measurement to the system, all the parameters coupled with the transport models can describe the behavior of membrane in real separation process, which is undoubtedly effective for discussing ions permeability.

In the present paper, the dielectric measurements for three types of nanofiltration membrane (NF90, NF-, NF270) immersed in different electrolyte solutions were carried out over a frequency range from 40 Hz to 110 MHz. Choosing these membranes is because that the structural and electrical parameters of these membranes, especially their pore radius and volumetric charge density are different from one another. The objective of this paper is to explain the high-frequency relaxation behavior and obtain the parameters of membrane and electrolyte solution phase, especially the relative permittivity of the NF membrane in varying electrolyte solutions. The relative permittivity is an indispensable value for calculating more electrical parameters by which we estimate the ion permeability and selectivity of the membrane, the porosity of the membrane and membrane volumetric charge density by combining with TMS transport model. We will also derive the expressions describing the relation between the concentration of co- and counter-ions in membrane pores and membrane volumetric charge density. The ion permeability in three types of membranes respectively will also be suggested by using the ion solvation energy barrier.

2. Theory and method

2.1 Dielectric analysis

The dielectric analysis in this work refers to the calculation of electric parameters of membrane phase and electrolyte solution phase by using the dielectric parameters observed in dielectric spectra. From these phase parameters, the porosity of membrane, membrane volumetric charge density, and ion solvation energy barrier can be calculated. Therefore, getting the phase parameters is crucial in this work. For a heterogeneous system comprised of nearly insulated polymer membrane and weak conductivity solutions, an interface exists between membrane and solution. According to Maxwell-Wagner interface polarization theory, when an AC electric field is applied to the solution-membrane-solution system, the charges will accumulate on the interface and an inductive field produce to keep the continuity of the electric current. Under such conditions, the relative permittivity and conductivity of membrane phase and solution phase \( \varepsilon_m \) and \( \varepsilon_w \) will meet following relation: \( \varepsilon_m \kappa_m \neq \varepsilon_w \kappa_w \) (subscript m and w denote the membrane phase and solution phase, respectively), leading to interface polarization, and a relaxation can be observed by measuring frequency dependence of the complex permittivity of the whole system.

In this work, the membrane is sandwiched between two solution phase, so the measuring system can be considered as a solution-membrane-solution construction. From dielectric point of view, when the solutions at both sides of the membrane are the same, the system can be represented to be a series combination of a membrane phase with a complex capacitance \( C_m \) and a solution phase with a complex capacitance \( C_w \). The equivalent circuit of the system is shown in Fig. 1(a), each phase consists of a resistor (of conductance \( G \)) in parallel with a capacitor (of capacitance \( C \)). It should be noted that what observed experimentally is the frequency dependence of apparent capacitance \( C(f) \) and apparent conductance \( G(f) \) of the whole system represented by equivalent circuit Fig. 1(b).

![Fig. 1](image)

Based on the MW theory, the complex capacitance \( C^* \) of the whole measuring system is represented by eqn (1),

\[
\frac{1}{C^*} = \frac{1}{C_m} + \frac{1}{C_w}
\]  

where the complex capacitance can be defined as

\[
C^* = \frac{G^*}{j\omega} = C + \frac{G}{j\omega}
\]

Eqn (2) can also be written by the complex relative permittivity

\[
\varepsilon^* = \varepsilon - j\varepsilon'' = \varepsilon + \frac{\kappa}{j\omega \varepsilon_0}
\]

where \( \varepsilon' \) and \( \varepsilon'' \) are real and imaginary part of the complex permittivity, \( \varepsilon \) and \( \kappa \) are the relative permittivity and the conductivity of the system, respectively, \( \omega (=2\pi f) \) is angular frequency.
frequency, $\varepsilon_0 (=8.8541 \times 10^{-12}$ F m$^{-1}$) is the vacuum permittivity, and $j$ is the imaginary unit.

By substituting the eqn (2) into (1), the capacitance and conductance can be expressed by that of the constituent phases. Hanai et al. derived a series of expressions about the relations between phase parameters i.e. the capacitance and conductance of membrane and solution phase $C_{mC_mG_mG_w}$ (see Fig. 1(a)) and dielectric parameters (i.e. the limiting values of $C$ and $G$ at high (subscript $h$) and low (subscript $l$) frequencies $C_{hC_lG_hG_l}$)$.^{32}$ According to these equations, the values of $C_{mC_mG_mG_w}$ (or $\varepsilon_{m\varepsilon_m\kappa_{m\kappa_w\kappa_w}}$) can be calculated. The corresponding calculation formulas and computational procedures are listed in ESI.$^\dagger$ For additional information about expressions, refer to literature.$^{27}$

### 2.2 Transport models of charged membrane—TMS model

NF membrane is often characterized by three adjustable parameters, pore radius, volumetric charge density, and effective membrane thickness. The three parameters, especially the membrane volumetric charge density play an important role in the understanding of separation mechanism and ion permeability. Theoretically, combining the results of dielectric analysis with transport model, the value of volumetric charge density can be obtained. In this work, we choose the Donnan exclusion—TMS model.

In TMS model, the membrane is described as a gel-phase, ion concentration and electric potential distributed uniformly in the membrane. The basic equations of the model consist of Donnan equation describing the ion dispersions in membrane and in bulk solution and the Nernst-Planck equation that is related to the ion transport in membrane. Besides, the electroneutrality conditions in membrane and solution two phases defined below must be taken into account when the ion partitioning coefficients is calculated. The important parameter of above equations, ion partitioning coefficients, is given by

$$k_i = \frac{c_i^m}{c_i} = \exp\left(-\frac{z_iF\Delta\phi}{RT}\right)$$

(4)

where $c_i^m$ and $c_i$ are the concentration (mol m$^{-3}$) of ion $i$ in membrane and in electrolyte solutions respectively, $z_i$ is the valence of ion $i$; $\Delta\phi$ is Donnan potential difference (V), $F$ is Faraday constant, $T$ is absolute temperature. Combining eqn (4) with the electroneutrality conditions inside membrane and external solutions respectively (see eqn (5) and (6)), the expression of counter- and co-ions concentration in membrane by considering Donnan exclusion can be obtained (see eqn (7)–(11))

$$z_i c_i^m + z_2 c_2^m + c_e = 0$$

(5)

$$z_i c_i^m + z_2 c_2^m = 0$$

(6)

where subscript 1 and 2 denote the counter- and co-ion, respectively, $c_e$ represents the concentration of the fixed charge in membrane.

For 1 : 1 and 2 : 1 type-electrolyte solution, the concentration of co- and counter-ions in membrane can be expressed as:

$$c_i^m = \frac{|c_i| + \sqrt{(|c_i|^2 + 4(c_i^r)^2)}}{2}$$

(7a)

$$c_2^m = -\frac{|c_i| + \sqrt{(|c_i|^2 + 4(c_i^r)^2)}}{2}$$

(7b)

and

$$c_i^m = \left(\frac{|c_i|^3}{27} + (c_i^r)^3\right)^{1/3}$$

$$+ \left(\frac{|c_i|^3}{27} + (c_i^r)^3\right)^{1/3}$$

$$\times /2 - |c_i|/3$$

(8a)

$$c_2^m = \left(\frac{|c_i|^3}{27} + (c_i^r)^3\right)^{1/3}$$

$$+ \left(\frac{|c_i|^3}{27} + (c_i^r)^3\right)^{1/3}$$

$$\times /2 - |c_i|/3$$

(8b)

For 1 : 2 type-electrolyte solution, the concentration of co- and counter-ions in membrane can be expressed as:

When $144(c_i^m)^6 - 4|c_i|^3 (c_i^r)^3 > 0$

$$c_i^m = \left(\left(-|c_i|^3/27 + 4(c_i^r)^3\right)^{1/3} + \sqrt{16(c_i^r)^6 - 4|c_i|^3 (c_i^r)^3}/9\right)$$

$$+ \left(-|c_i|^3/27 + 4(c_i^r)^3\right)^{1/3}$$

$$\times /2 + |c_i|/3$$

(9a)

$$c_2^m = \left(\left(-|c_i|^3/27 + 4(c_i^r)^3\right)^{1/3} + \sqrt{16(c_i^r)^6 - 4|c_i|^3 (c_i^r)^3}/9\right)$$

$$+ \left(-|c_i|^3/27 + 4(c_i^r)^3\right)^{1/3}$$

$$- |c_i|/3$$

(9b)

When $144(c_i^m)^6 - 4|c_i|^3 (c_i^r)^3 < 0$

$$c_i^m = |c_i|/3 \cos(\arccos(108(c_i^r)^3)/|c_i|^3 - 1)/3) + |c_i|/3$$

(10a)

$$c_2^m = 2|c_i|/3 \cos(\arccos(108(c_i^r)^3)/|c_i|^3 - 1)/3) - |c_i|/3$$

(10b)

For 2 : 2 type-electrolyte solution, the corresponding concentrations are expressed as:
4. Result and discussion

4.1 Dielectric analysis of the NF membrane–electrolyte solutions system

4.1.1 Dielectric spectroscopy. Fig. 2 shows three-dimensional representations for the concentration dependence of dielectric spectra of the system of NF90 membrane in K₂SO₄ solution in the concentration range of 0.05–7 mol m⁻³, which is similar to the dielectric spectra of NF90 membrane in MgCl₂ solution shown in Part 1.² Two relaxations can be observed (other systems measured in this work showed similar dielectric spectra). The low-frequency relaxation around at 10⁷ Hz caused by the counterion polarization in the membrane pores had been discussed thoroughly in Part 1.³ This paper focuses solely on the analysis and discussion of high-frequency relaxation. From Fig. 2, it is obvious that it showed a large relaxation intensity and its characteristic frequency shifts to higher frequency as electrolyte concentration increases as illustrated by the arrows.

4.1.2 Estimation of dielectric parameters and determination of relaxation mechanism. In order to obtain the electric properties of the constituent phases of the membrane–solution system (i.e. the phase parameters of the system) and the inner information of the membrane in electrolyte solution, it is necessary to estimate the value of dielectric parameters mentioned in Section 2.1. For clarity, we took the system with NF90 membrane in 0.05 mol m⁻³ K₂SO₄ solution as an example (see Fig. 3, it is the two-dimensional representation of Fig. 2 when the concentration of K₂SO₄ is 0.05 mol m⁻³) to introduce how these parameters were determined from the dielectric spectrum.

Fig. 3(a) and (b) show the frequency dependence of the relative permittivity and the conductivity in different electrolyte concentrations for the NF90 membrane–K₂SO₄ system, respectively. In Fig. 3, ε₁ε₀κ₁κ₂κ₃ termed dielectric parameters in this paper, indicate the limiting value of relative permittivity and conductivity at low and high frequencies, respectively, and f₀ is characteristic relaxation frequency. Generally, in order to estimate dielectric parameters, the “model function method” in which Cole–Cole empirical equation is used to fit dielectric data is often employed.²⁵ However, when the relaxation profile is utterly clear, so called “model free method” are also adopted, i.e. determine the dielectric parameters by plotting. Fig. 4(a) and (b) show the complex plane plots of relative permittivity and conductivity, respectively, and Fig. 4(c) shows the frequency dependence of dielectric loss. The values of ε'' and κ'' were calculated according to following relations respectively, the values of ε₁ε₀κ₁κ₂κ₃, and f₀ were determined from these figures:

\[
\varepsilon'' = \frac{K - K_1}{\omega \varepsilon_0} \tag{12}
\]

\[
\kappa'' = \omega \varepsilon_0 (\varepsilon - \varepsilon_b) \tag{13}
\]

To examine if the dielectric parameters obtained above were accurate, we fitted the dielectric spectrum data using Cole–Cole
equation in trigonometric function (eqn (14)), and only $\varepsilon_0\varepsilon_h$ and $f_0$ were obtained, $k_1$ and $k_h$ were obtained according to the method described in Section 3.2.1 of Part 1.

$$
\varepsilon(f) = \varepsilon_h + \frac{(\varepsilon_0 - \varepsilon_h) \left[ 1 + \left( \frac{f_0}{f} \right)^\beta \cos \left( \frac{\pi}{2} \beta \right) \right]}{1 + 2 \left( \frac{f_0}{f} \right)^\beta \cos \left( \frac{\pi}{2} \beta \right) + \left( \frac{f_0}{f} \right)^{2\beta}}
$$

(14)

where $f$ is the measured frequency, and $\beta$ is the distribution coefficient of relaxation time ($0 < \beta \leq 1$), which reflects the complexity of inner structure of the system. The values of dielectric parameters obtained by fitting dielectric spectra are almost the same as that by model free method. The dielectric parameters for other systems were also obtained in the same way and are summarized in Table 1.

It is obvious from Table 1 that the dielectric increment $\Delta \varepsilon$ ($=\varepsilon_1 - \varepsilon_h$) is almost invariable as concentration increases, whereas the characteristic frequency $f_0$ and conductivity increment $\Delta k$ ($=k_h - k_1$) depend linearly on the concentration, as shown in Fig. 5. According to our previous researches on membrane–solution system and the literatures, this result indicates a distinctive feature of the interfacial polarization. Therefore, we believe that the high frequency relaxation is caused by the interfacial polarization occurring at the interface between whole membrane and solution, and the analysis method elaborated in Section 2.1 is suitable for analyzing this high-frequency relaxation.

4.1.3 Calculation of phase parameters and comments on the results. In order to explore the structural and electrical properties of the membrane under varying electrolyte solutions, it is indispensable step to calculate the phase parameters. By using the method described in Section 2.1 the phase parameters ($\varepsilon_{wm}, \varepsilon_w, \kappa_w$) for all of NF90 membrane–electrolyte solution systems were calculated from the dielectric parameters in Table 1, and the results are listed in Table 2.

**Relative permittivity and conductivity of the electrolyte solution $\varepsilon_w$ and $\kappa_w$.** It can be seen from Table 2 that the relative permittivity of electrolyte solutions $\varepsilon_w$ is nearly invariable with the electrolyte concentration, and its average value is about 80.37. This is a reasonable value comparing with that of pure water (about 80 at 21–22 °C). Furthermore, the reliability of this result was enhanced by an independent measurement: the dielectric measurements of K$_2$SO$_4$ solutions with various concentrations were carried out under the same conditions with the membrane–solution systems, and the relative permittivity and conductivity $\varepsilon_{w0}, \kappa_{w0}$ without membrane at various concentrations were obtained (also listed in Table 2). The values of $\varepsilon_{w0}$ show surprisingly closely with $\varepsilon_w$ obtained by dielectric analysis. By comparing $\varepsilon_w$ and $\kappa_w$ with $\varepsilon_{w0}$ and $\kappa_{w0}$, we find that the values of $\varepsilon_w/\varepsilon_{w0}$ and $\kappa_w/\kappa_{w0}$ are all close to 1 and independent of the electrolyte concentration (see Table 2). This means that $\varepsilon_w$ and $\kappa_w$ of K$_2$SO$_4$ solution obtained by analyzing dielectric spectrum

Fig. 2 Frequency dependence of the relative permittivity $\varepsilon$ (a) and conductivity $\kappa$ (b) for the system composed of the NF90 membrane and the compartments filled with K$_2$SO$_4$ aqueous solution of various concentrations.

Fig. 3 Frequency dependences of (a) relative permittivity $\varepsilon$ and (b) conductivity $\kappa$ for the cell systems with NF90 membrane in K$_2$SO$_4$ aqueous solutions.
are in good agreement with their actual value, showing that strict dielectric analysis can give accurate inner information of the membrane. The values of $\varepsilon_{0w}/\varepsilon_{0w}'$ and $\kappa_{0w}/\kappa_{0w}'$ for other seven electrolyte solutions (NaCl, KCl, MgCl₂, CuCl₂, Na₂SO₄, MgSO₄, CuSO₄) are similar to that of K₂SO₄. $\varepsilon_{0w}$ will play an important role to evaluate permeability of pore and ion solvation energy barrier.

Relative permittivity and conductivity of the membrane $\varepsilon_{m}$ and $\kappa_{m}$. It is worth mentioning that the relative permittivity of membrane $\varepsilon_{m}$ obtained in this work is vital to calculate accurately the porosity of membrane and ion solvation energy barrier because it is the permittivity of wet membrane rather than that of dry membrane. It is clear from Table 2 that the value of $\varepsilon_{m}$ is almost independent of the electrolyte concentration (actually, $\varepsilon_{m}$ is also independent of the kind of electrolyte solutions, as can be seen in Table 3 below), and the average value of $\varepsilon_{m}$, 2.666, is larger than that of the polymer matrix of the membrane in dry state (relative permittivity of polyamide is about 1.68). For NF- and NF270 membrane, their $\varepsilon_{m}$ are all larger than that in dry state as well as shown in Table 3 (the relative permittivity of mixed aromatic amines and heterocyclic aliphatic amines, which are main components of NF- and NF270, are about 3–4). This is easy to understand because of the permeation of water with high relative permittivity into the porous membrane of low relative permittivity. In this case, $\varepsilon_{m}$ is simply expressed by eqn (15). Here, it should be noted that the value of $\varepsilon_{m}$ is regarded as 80, this is a rough approximation. This is because that the membrane contains two parts: a very thin active layer and a relative porous intermediate layer, the water in the membrane mainly comes from the porous intermediate layer.

$$\varepsilon_{m} = \varepsilon_{0w} + \varepsilon_{m}'(1 - f_{w})$$  \hspace{1cm} (15)

where $f_{w}$ and $1 - f_{w}$ are the volume fraction of water in the whole membrane phase and in membrane matrix of the membrane phase, $\varepsilon_{m}'$ is the relative permittivity of dry polymers. It should be noted here that $\varepsilon_{m}$ in eqn (15) is obtained from dielectric analysis, and it is a mixed value including the contributions of membrane matrix and the water in the pores of membrane.

Taking the relative permittivity of dry NF90 membrane as 1.68 and substituting $\varepsilon_{m}$ and $\varepsilon_{m}'$ listed in Table 2 into eqn (15), the values of $f_{w}$ at various concentrations of K₂SO₄ were calculated. The results showed that $f_{w}$ decreases sharply with the increase of electrolyte concentration within lower concentration and finally tends to remain unchanged as shown in Fig. 6(a),

<table>
<thead>
<tr>
<th>$c$ (mol m⁻³)</th>
<th>$\varepsilon_{1}$</th>
<th>$\varepsilon_{h}$</th>
<th>$\Delta\varepsilon$</th>
<th>$\kappa_{l}$ (µS m⁻¹)</th>
<th>$\kappa_{h}$ (mS m⁻¹)</th>
<th>$\Delta\kappa$ (µS m⁻¹)</th>
<th>$f_{0}$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>2559.11</td>
<td>79.78</td>
<td>2479.33</td>
<td>12.46</td>
<td>2.002</td>
<td>1989.54</td>
<td>11 531</td>
</tr>
<tr>
<td>0.1</td>
<td>2558.34</td>
<td>79.85</td>
<td>2478.49</td>
<td>16.78</td>
<td>2.725</td>
<td>2708.22</td>
<td>18 486</td>
</tr>
<tr>
<td>0.2</td>
<td>2555.32</td>
<td>78.80</td>
<td>2476.52</td>
<td>17.36</td>
<td>5.299</td>
<td>5281.64</td>
<td>34 687</td>
</tr>
<tr>
<td>0.4</td>
<td>2553.95</td>
<td>79.06</td>
<td>2474.89</td>
<td>23.20</td>
<td>9.584</td>
<td>9560.8</td>
<td>65 086</td>
</tr>
<tr>
<td>0.7</td>
<td>2558.02</td>
<td>78.81</td>
<td>2479.21</td>
<td>38.58</td>
<td>16.13</td>
<td>16091.42</td>
<td>122 125</td>
</tr>
<tr>
<td>1.0</td>
<td>2555.46</td>
<td>78.75</td>
<td>2476.71</td>
<td>50.56</td>
<td>22.45</td>
<td>22399.44</td>
<td>167 267</td>
</tr>
<tr>
<td>2.0</td>
<td>2552.33</td>
<td>78.87</td>
<td>2473.46</td>
<td>90.37</td>
<td>41.45</td>
<td>41359.63</td>
<td>268 193</td>
</tr>
<tr>
<td>4.0</td>
<td>2557.42</td>
<td>78.80</td>
<td>2478.62</td>
<td>172.0</td>
<td>76.22</td>
<td>76 048</td>
<td>588 965</td>
</tr>
<tr>
<td>7.0</td>
<td>2550.99</td>
<td>78.74</td>
<td>2472.25</td>
<td>270.9</td>
<td>117.0</td>
<td>116729.1</td>
<td>944 223</td>
</tr>
</tbody>
</table>

Table 1 Dielectric parameters obtained by fitting with eqn (16) for NF90 membrane in K₂SO₄ aqueous solution.
electrostatic repulsion between polymeric backbones will be charged, when the counter-ions enter the membrane pores, be interpreted as follow: because the membrane is electrical compact structure and ions are hard to pass through the low. Therefore, we can speculate that the membrane has a 0.004, indicating that the water content in membrane is very sharply near the concentration of 0.7 mol m⁻³. Therefore, in following calculations, we took the mean value of \( \varepsilon_m \) (2.065 for NF90 membrane in K₂SO₄) in varying electrolyte concentrations as the relative permittivity of membrane. The mean values for three kinds of membranes NF90, NF- and NF270 in eight electrolyte solutions are listed in Table 3.

From the Table 3 it is obvious that for NF90 membrane \( \varepsilon_m \) is almost independent of the kind of the electrolyte and has an average of 2.4, while the values for both NF and NF270 membranes are indeterminate for different electrolyte type. \( \varepsilon_m \) fluctuates between 3.3 and 6.3 and average is about 4.5 for NF-membrane, and it changes ranging from 3.7 to 8.9 and average is about 6.0 for NF270 membrane. These fluctuations of data can be believed to be caused by the error during calculation process because the results in Table 3 are obtained through two times calculation processes starting from raw data. In addition, the values of \( \varepsilon_m \) for both NF and NF270 membranes are greater than that of NF90. This may be related to the porosity of these membranes.

In our previous paper, we have calculated thickness and pore diameter of the three membranes. The average values of the thickness in different concentrations are 0.2335 μm, 0.2337 μm and 0.2334 μm, and the average values of pore diameter are 0.2838, 0.3250, 0.3582 nm for NF90, NF- and NF270 membrane, respectively. Obviously, the pore diameter for NF- and NF270 membrane are approximately equal but greater than that of NF90. Therefore, the reason of the difference in relative permittivity between three membranes can be explained as follows: the membrane with high water content has higher relative permittivity, therefore the values of \( \varepsilon_m \) for both NF- and NF270 membrane are greater than that of NF90. This can also be supported by the data of porosity of the three membranes (see a later Table 5).

To investigate the selectivity and permeability of ions in the NF membranes, the dependency of membrane conductivity \( \kappa_m \) on electrolyte concentration for the three membranes in eight

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>NF90</th>
<th>NF-</th>
<th>NF270</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>2.729</td>
<td>3.408</td>
<td>3.741</td>
</tr>
<tr>
<td>KCl</td>
<td>2.912</td>
<td>3.966</td>
<td>4.228</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>2.187</td>
<td>3.552</td>
<td>7.532</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>2.145</td>
<td>3.981</td>
<td>6.774</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>2.201</td>
<td>6.021</td>
<td>8.924</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>2.065</td>
<td>3.292</td>
<td>3.839</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>2.312</td>
<td>6.315</td>
<td>5.419</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>2.207</td>
<td>5.542</td>
<td>7.919</td>
</tr>
<tr>
<td>Average</td>
<td>2.395</td>
<td>4.510</td>
<td>6.047</td>
</tr>
</tbody>
</table>

when concentration of K₂SO₄ is above 0.7 mol m⁻³ \( f_w \) is about 0.004, indicating that the water content in membrane is very low. Therefore, we can speculate that the membrane has a compact structure and ions are hard to pass through the membrane, leading that ions can be effectively retained in the membrane.

The concentration dependency of \( \varepsilon_m \) has similar changing trend with that of \( f_w \) (Fig. 6(b)), i.e. both of \( \varepsilon_m \) and \( f_w \) decrease sharply near the concentration of 0.7 mol m⁻³. The reason may be interpreted as follow: because the membrane is electrical charged, when the counter-ions enter the membrane pores, electrostatic repulsion between polymeric backbones will be shielded gradually, giving rise to aggregate and reunite between polymer chains in a relatively compact state. Accompanied with this change, \( f_w \) decreased, so did the relative permittivity of the membrane \( \varepsilon_m \). While when fixed charges were shielded completely because of the ions permeating into the membrane, increasing the concentration of electrolyte solution will no longer impact on the aggregation state of polymer backbones. As a result, \( f_w \) and \( \varepsilon_m \) have no change over the concentration range of 1–7 mol m⁻³. Therefore, in following calculations, we took the mean value of \( \varepsilon_m \) (2.065 for NF90 membrane in K₂SO₄) in varying electrolyte concentrations as the relative permittivity of membrane. The mean values for three kinds of membranes NF90, NF- and NF270 in eight electrolyte solutions are listed in Table 3.

![Fig. 6](image-url) Concentration dependence of \( f_w \) (a) and \( \varepsilon_m \) (b) for system of NF90 membrane in K₂SO₄ electrolyte solutions.
electrolyte solutions was plotted in Fig. 7. It is obvious that \( \kappa_m \) increases linearly with increasing electrolyte concentration for each system, however, the increase rates are different each other. For different types of electrolyte solutions, the increase rate of \( \kappa_m \) for NF membranes in four types of electrolyte solutions follow the trend: \( 1 : 2 > 1 : 1 > 2 : 2 > 2 : 1 \). This is because that under AC field, ions transporting into membrane was influenced by dielectric exclusion, Donnan exclusion and steric hindrance, because the interaction between the ions with different valences and three kinds of membranes respectively are not the same, such, the degree of difficulty that the ions of different types of electrolyte transfer into membrane are also different. As a result, there are differences in \( \kappa_m \) for different types of electrolyte.

For NF-membrane, univalent counter-ions are easier to transport into the membrane than bivalent counter-ions. The lower the valence of co-ions, the easier the electrolyte transporting into the membrane. It can be seen from Fig. 7 that, for different types of electrolytes, the increase rate of \( \kappa_m \) for NF90 membrane in four electrolyte solutions follow the trend: \( 1 : 2 > 1 : 1 > 2 : 2 > 2 : 1 \), while for NF270, it seems irregularly. In short, increasing rate of \( \kappa_m \) for the three types of NF membranes in different types of electrolytes are various, showing that the interaction between ions and membrane matrix are different, this is because these membranes have different structural and electrical properties, i.e. pore radius, membrane volumetric charge density and relative permittivity of membrane. Therefore, the difficulty for electrolytes transporting into the three types of NF membranes are different. We will further discuss the influence factors of ions transport by combining the TMS model and the ion solvation energy barrier.

4.2 Calculation of some important parameters of membrane

4.2.1 Porosity of membrane. According to the discussions in Section 4.1.3, the relative permittivity \( \epsilon_m \) or capacitance \( C_m \) of the membrane is from the contributions of two parts: polymer matrix and solution in membrane pores, as expressed by following equation:

\[
C_m = C_p + C_m = [\epsilon_p\epsilon_0Sp]a + [\epsilon_m\epsilon_0(1 - p)S]/a
\]  

(16)

where \( C_m \) is capacitance of the polymer matrix, \( C_p \) and \( \epsilon_p \) are the capacitance and relative permittivity of the pore filled with electrolyte solution; \( p \) and \( a \) are porosity and thickness of the membrane, respectively. The meaning of other symbols in eqn (16) are the same to that defined in earlier sections.

From eqn (16), \( p \) can be represented as

\[
p = [(aC_m\epsilon_0\epsilon_m) - \epsilon_m]/[\epsilon_p - \epsilon_m]
\]

(17)

In this formula, the relative permittivity of dry polymers \( \epsilon_0 \) is known (see Section 4.1.3), so \( C_m \) can be calculated according to \( \epsilon_m = C_m(aS\epsilon_0) \), where the membrane thickness \( a \) for three membrane have been obtained in Part 1. While \( \epsilon_p \) was calculated by following equation:  

\[
\epsilon_p = \epsilon_w - 2(\epsilon_w - \epsilon_d)(d/h) + (\epsilon_w - \epsilon_d)(d/h)^2
\]

(18)

Eqn (18) shows that the pore is consisted of one layer of oriented water molecules at the pore-wall (the relative permittivity and the thickness of the water layer are \( \epsilon_d \) and \( d \) respectively) and solution inside the pore which is different from bulk solution because under AC field the rotation of the water molecules in the pore is restrained. So, relative permittivity \( \epsilon_p \) inside the pore is different from that \( \epsilon_w \) of bulk water. According to literature, the values of \( \epsilon_d \) and \( d \) are 6 and 0.28 nm respectively. The pore radius have also been obtained in Part 1. The calculated \( \epsilon_p \) are listed in Table 4.

By substituting \( \epsilon_p \) in Table 4 into eqn (17), the porosity of three NF membranes \( p \) in different electrolyte solutions were calculated and are listed in Table 5. It is clear that for any type of membrane, the porosity in different electrolytes has no significant differences, and the porosity has a sequence of NF270 > NF- > NF90. For the convenience of comparison, the dependency of membrane conductivity \( \kappa_m \) of three membranes on \( K_2SO_4 \) concentration \( c \) were plotted in Fig. 8, it is obvious that the increase rate of \( \kappa_m \) of three membranes as \( K_2SO_4 \) concentration \( c \) are different: NF270 > NF- > NF90, this sequence is in

![Fig. 7 Dependence of conductivity of membrane \( \kappa_m \) on solution concentration \( c \) for systems composed of NF membranes and eight kinds of electrolytes: (a) NF90; (b) NF-; (c) NF270.](image-url)
line with the porosity of the three membranes. Because the magnitude of $\kappa_m$ is proportional to the amount of electrolyte in membrane as discussed above, the difference in $\kappa_m$ between the three membranes suggested the possibility that the magnitude of the porosity influences ions transporting into membrane.

4.2.2 Calculation of concentrations of co- and counter-ions in membrane pore. Returning to Table 2, the conductivity of membrane and solution phase, $\kappa_m$ and $\kappa_w$, increase with the increment of electrolyte concentration $c_i$ and the value of $\kappa_m$ is much smaller than that of $\kappa_w$ because $\kappa_m$ is a mixed value including the contribution of the polymer. It is should be mentioned that maybe the value of $\kappa_m$ is greater than that of $\kappa_w$ for the case of inorganic membrane in electrolyte solution, such as porous alumina membrane. $\kappa_m/\kappa_w$ was plotted as a function of $c_i$ in Fig. 9. It is obvious that $\kappa_m/\kappa_w$ is far less than 1, and decreases sharply at low concentrations and then reaches a stable value when the concentration is above 0.5 mol m$^{-1}$, showing a typical phenomenon of ions through charged membrane as described by Donnan exclusion.[31,40] Therefore, the membrane volumetric charge density can be estimated according to the variation of the conductivity in membrane and solution phase.

In our previous work, a certain relation among $\kappa_m/\kappa_w$, the ion concentrations in membrane and in solution, and transport numbers of ion in bulk solution had been derived as the following.

$$\frac{\kappa_m}{\kappa_w} = \frac{U_1^{m} \frac{c_1^{m} c_1^{w}}{c_1^{m} + c_1^{w}} + U_2^{m} \frac{c_2^{m} c_2^{w}}{c_2^{m} + c_2^{w}}}{U_1^{w} \frac{c_1^{m} c_1^{w}}{c_1^{m} + c_1^{w}} + U_2^{w} \frac{c_2^{m} c_2^{w}}{c_2^{m} + c_2^{w}}}$$

(19)

where subscript 1 and 2 represent counter-ion and co-ion, $U_1^m$ and $U_1^w$ are the mobility of ions in membrane and solution respectively, $c_1^m$ and $c_1^w$ are the concentration of ions in membrane and solution respectively, $c_1^m$ and $c_1^w$ are the transport numbers of counter-ion and co-ion in solution, respectively.

Because the experiment results show that the distribution of ions in solution and in membrane obeys Donnan equilibrium principle, we adopted the TMS model in this study. Combining TMS model with eqn (21), the membrane volumetric charge density $c_e$ for all systems were calculated using the phase parameters obtained from dielectric analysis.

Further, by substituting the expressions eqn (7)–(11) into (19), the expression of $\kappa_m/\kappa_w$ for 1 : 1, 1 : 2, 2 : 1, and 2 : 2 type-electrolyte solution with two variables were derived. The two variables, $U_1^m$ and $U_1^w$, are defined as $P_1 = U_1^{m}/U_1^{w} = U_2^{m}/U_2^{w}$, i.e., the ratio of ion mobility in membrane and solution, and $P_2 = c_e$ (i.e., the membrane volumetric charge density). Then, by fitting the $\kappa_m/\kappa_w$ obtained experimentally for all membrane systems to the expression of $\kappa_m/\kappa_w$ for by varying values of $P_1$ and $P_2$, the values of $c_e$ for NF90, NF-, NF270 membranes in eight kinds of electrolyte solutions were obtained and the results are listed in Table 6. It is obvious from Table 7 that for any NF membrane, $c_e$ is almost independent of the kinds of electrolyte solutions, and $c_e$ of NF90 is larger than that of NF- and NF270.

By substituting $c_e$ in Table 6 back into eqn (7)–(11), the concentrations of co- and counter-ions were calculated. Table 7 shows the results for the systems of the three membranes and K$_2$SO$_4$ solution. For clarity, the dependences of co- and counter-ions concentration in membranes on the electrolyte concentration $c_i$ are plotted in Fig. 10. The concentrations of both co-ions $c_1^m$ and counter-ions $c_2^m$ in membrane pore increase linearly as $c_i$ increased. The only difference between them is their growth rate with $c_i$. Specifically, for 1 : 1 and 2 : 2 type-electrolyte solutions in Fig. 10(a), (b), (g) and (h), $c_2^m$ is larger than $c_2^w$ over the whole concentration range, and the growth rate of $c_1^m$ and $c_2^m$ are the same. For 1 : 2 type-electrolyte in Fig. 10(c) and (d), $c_1^m$ is larger than $c_1^w$ while $c_2$ is relatively low. However, as the growth rate of $c_1^m$ is over that of $c_1^w$, $c_2^m$ becomes larger than $c_2^w$ gradually, which can be explained as follows: when $c_i$ exceeds $c_e$, the fixed charge in membrane was neutralized gradually, Donnan exclusion was weakened. On the other hand, the concentration of co-ions $c_2$ is

![Fig. 8](image82x79_to_253x196) Concentration dependence of $\kappa_m$ of NF90, NF- and NF270 in K$_2$SO$_4$ electrolyte solutions.

![Fig. 9](image185x227) Concentration dependence of $\kappa_m/\kappa_w$ of NF90, NF- and NF270 in K$_2$SO$_4$ electrolyte solutions.

**Table 5** Porosity of NF membranes for all the measured systems

<table>
<thead>
<tr>
<th>Electrolyte solutions</th>
<th>$P_{(NF90)}$ (%)</th>
<th>$P_{(NF-)}$ (%)</th>
<th>$P_{(NF270)}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>3.24</td>
<td>5.33</td>
<td>6.15</td>
</tr>
<tr>
<td>KCl</td>
<td>3.85</td>
<td>7.12</td>
<td>7.69</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>1.73</td>
<td>6.20</td>
<td>18.7</td>
</tr>
<tr>
<td>CuCl$_2$</td>
<td>1.59</td>
<td>7.60</td>
<td>16.0</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>1.78</td>
<td>14.3</td>
<td>22.7</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>2.00</td>
<td>5.34</td>
<td>6.73</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>2.84</td>
<td>15.4</td>
<td>11.7</td>
</tr>
<tr>
<td>CuSO$_4$</td>
<td>1.80</td>
<td>12.7</td>
<td>19.4</td>
</tr>
<tr>
<td>Average</td>
<td>2.35</td>
<td>9.25</td>
<td>13.6</td>
</tr>
</tbody>
</table>
twice that of counter-ions in bulk solution $c_1$, therefore, $c_2^{m}$ becomes larger than $c_1^{m}$ gradually as $c$ increase. The membrane volumetric charge density $c_e$ was determined from the intersection of the lines of co-ions and counter-ions. For 2 : 1 type-electrolyte in Fig. 10(e) and (f), because $c_t$ is twice that of co-ions $c_2$ in bulk solutions, the growth rate of $c_2^{m}$ is larger than $c_1^{m}$.

The parameters above obtained, $c_0$, $c_2^{m}$ and $c_0^{m}$ in four types electrolyte solutions, will be used to discuss the influence of Donnan exclusion on the transport of different electrolyte in three membranes in following 4.3 Section.

### 4.2.3 Ion solvation energy barrier

As we know, the dielectric exclusion is caused by the interactions of ions with the bound charges that induced by the ions at interface between substances of different relative permittivity. Therefore, due to the difference of relative permittivity between membrane pores and solution, when ions transfer from solution with high relative permittivity (about 80) to membrane pores with low relative permittivity (about 31–34, see Table 4), dielectric exclusion occurs, thereupon ion solvation energy barrier arises (which will clearly increase salt rejection). Born solvation energy barrier represents the effect of dielectric exclusion and its magnitude influences the ions entering into the pores. Therefore, by this value, the permeability of ions for different kinds of electrolytes in membrane can be evaluated.

Considering the change of electrostatic free energy (or relative permittivity) of an ion from bulk to membrane pore, based on Born equation\(^\text{22}\) in which only the relative permittivity of whole membrane was considered, an expression of ion solvation energy barrier $\Delta W_i$ for ion $i$ was proposed:\(^\text{39}\)

$$\Delta W_i = \frac{z_i^2 e^2}{8\pi \varepsilon_0 \varepsilon_r} \left( \frac{1}{\varepsilon_p} + \frac{0.393}{b/r_i c_m} \left( 1 - \frac{\varepsilon_m}{\varepsilon_p} \right)^2 - \frac{1}{\varepsilon_p} \right)$$  \hspace{1cm} (20)

where $r_i$ is Stokes radius of ion, the meaning of other symbols is the same as defined above. The value of $r_i$ for the 6 kinds of ions studied in this work (see Table 8) are from the literature.\(^\text{40}\)

Using the Stokes radius of ions, the relative permittivity of membrane pores in Table 4, the relative permittivities of membrane and solution in Tables 2 and 3, the energy barrier that hydrated ions transfer into pores, $\Delta W_i$, for three NF membranes were calculated by eqn (20), and are summarized in Table 9.

For the sake of greater clarity, the values of $\Delta W_i$ in Table 9 were plotted against the types of electrolyte in Fig. 11. It can be seen that for any kind of NF membrane, $\Delta W_i$ varies with the kinds of electrolyte. For 1 : 1 and 2 : 2 type-electrolyte solutions, $\Delta W_i$ of co- and counter-ions are close to each other, while for 1 : 2 and 2 : 1 type-electrolyte, the values of $\Delta W_i$ between the co- and counter-ions have obvious difference. This shows that the valence of ion is a crucial factor influencing ion solvation energy barrier. For the three NF membranes, the sequence of $\Delta W_i$ for electrolyte solutions is as below: 2 : 2 > 2 : 1, 2 : 1 > 1 : 1, which implies that for two kinds of electrolyte solutions, when the valence of co-ion is the same, $\Delta W_i$ with higher valence of counter-ion is larger than that of lower valence. Furthermore, $\Delta W_i$ of 2 : 2 type-electrolyte is much larger than that of 1 : 1, 1 : 2 and 2 : 1, which shows the higher ion valence results in a larger ion solvation energy barrier, thereby ions to permeate the membrane became more difficulty. Therefore, from the perspective of ion solvation energy barrier, it can be concluded that for 2 : 2 type-electrolyte with the highest ion valence in these eight kinds of electrolyte, the permeation of ion is the most difficult.

From above discussion it is clearly that the influence of ion solvation energy barrier $\Delta W_i$ on the ion permeation into different kinds of NF membranes are different. This is because there are the difference for the three membranes in structural and electrical properties which are strongly associated with interactions between membrane and electrolytes. The interaction have been extensively investigated based on the Donnan exclusion and dielectric exclusion.\(^\text{41,42}\)

### 4.3 Influence of dielectric exclusion and Donnan exclusion on membrane permeation of ion

In Sections 4.2.2 and 4.2.3, concentrations of co- and counter-ions in membrane pores and the ion solvation energy barrier for three membranes in eight kinds of electrolyte solutions were calculated. On the other hand, in our previous work,\(^\text{1}\) a model of cylindrical pores for interpreting low-frequency relaxation has been developed, according to the model surface charged density

---

**Table 6** Membrane volumetric charge density $c_e$ of NF membranes for all the measured systems calculated from eqn (7)–(11) and (15)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Electrolyte</th>
<th>NaCl</th>
<th>KCl</th>
<th>MgCl$_2$</th>
<th>CuCl$_2$</th>
<th>Na$_2$SO$_4$</th>
<th>K$_2$SO$_4$</th>
<th>MgSO$_4$</th>
<th>CuSO$_4$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF90</td>
<td>($c_e$ [mol m$^{-3}$])</td>
<td>0.88</td>
<td>0.85</td>
<td>1.13</td>
<td>1.09</td>
<td>0.90</td>
<td>0.81</td>
<td>1.05</td>
<td>1.03</td>
<td>0.97</td>
</tr>
<tr>
<td>NF-</td>
<td>($c_e$ [mol m$^{-3}$])</td>
<td>0.62</td>
<td>0.36</td>
<td>0.76</td>
<td>0.41</td>
<td>0.55</td>
<td>0.33</td>
<td>0.70</td>
<td>0.34</td>
<td>0.51</td>
</tr>
<tr>
<td>NF270</td>
<td>($c_e$ [mol m$^{-3}$])</td>
<td>0.69</td>
<td>0.41</td>
<td>0.57</td>
<td>0.55</td>
<td>0.56</td>
<td>0.42</td>
<td>0.59</td>
<td>0.58</td>
<td>0.55</td>
</tr>
</tbody>
</table>

**Table 7** Concentration of co- and counter-ions in pores of NF membranes for all the measured systems

<table>
<thead>
<tr>
<th>Concentration of $c_i$ (mol m$^{-3}$)</th>
<th>NF90/K$_2$SO$_4$</th>
<th>NF-/K$_2$SO$_4$</th>
<th>NF270/K$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_i^{m}$</td>
<td>$c_i^{m}$</td>
<td>$c_i^{m}$</td>
<td>$c_i^{m}$</td>
</tr>
<tr>
<td>0.05</td>
<td>0.8080</td>
<td>0.0008</td>
<td>0.3364</td>
</tr>
<tr>
<td>0.1</td>
<td>0.8184</td>
<td>0.0060</td>
<td>0.3823</td>
</tr>
<tr>
<td>0.2</td>
<td>0.8877</td>
<td>0.0406</td>
<td>0.5439</td>
</tr>
<tr>
<td>0.4</td>
<td>1.1764</td>
<td>0.1850</td>
<td>0.9254</td>
</tr>
<tr>
<td>0.7</td>
<td>1.7268</td>
<td>0.4601</td>
<td>1.5182</td>
</tr>
<tr>
<td>1.0</td>
<td>2.3081</td>
<td>0.7508</td>
<td>2.1154</td>
</tr>
<tr>
<td>2.0</td>
<td>4.2877</td>
<td>1.7406</td>
<td>4.1122</td>
</tr>
<tr>
<td>4.0</td>
<td>8.2781</td>
<td>3.7338</td>
<td>8.1107</td>
</tr>
<tr>
<td>7.0</td>
<td>14.274</td>
<td>6.7338</td>
<td>14.110</td>
</tr>
</tbody>
</table>
The relation between the concentrations of co-ions $c_m^2$ and counter-ions $c_m^1$ and charge density in pore $c_{pe}$ can be expressed as the following expression.

$$c_{pe} = \left( \frac{z_1^* c_m^1}{C_0} \right) - \left( \frac{z_2^* c_m^2}{C_0} \right)$$

Table 8 Stokes radius of the related ions

<table>
<thead>
<tr>
<th>Ions</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stokes radius $r_s$ (nm)</td>
<td>0.184</td>
<td>0.125</td>
<td>0.347</td>
<td>0.325</td>
<td>0.121</td>
<td>0.230</td>
</tr>
</tbody>
</table>

$\sigma_0$ on pore-wall has been calculated. The relation between the concentrations of co-ions $c_m^2$ and counter-ions $c_m^1$ and charge density in pore $c_{pe}$ can be expressed as the following expression.

$$c_{pe} = \left( \frac{z_1^* c_m^1}{C_0} \right) - \left( \frac{z_2^* c_m^2}{C_0} \right)$$
From this expression, it is clearly that from the view of Donnan exclusion, the larger the surface charged density $s_0$ on pore-wall, the higher the charge density $c_{pe}$ in pore should be. Therefore, by comparing $c_{pe}$ with $s_0$, the influence of Donnan exclusion on ion permeation can be clarified. That is, if the experimental results (here refers to $s_0$) are in accordance with the calculated results under the consideration of Donnan exclusion (refers to $c_{pe}$), Donnan exclusion is dominant influence factor in ion permeation process (see 4.3.1 for a specific example). On the other hand, because $\Delta W_i$ represents the dielectric exclusion effect, in any kind of electrolyte solution, the closer the value of $\Delta W_i$ between co- and counter-ions, the lower the surface charge density $s_0$ on pore-wall. Therefore, by comparing the level of similarity of $\Delta W_i$ between co- and counter-ions with $s_0$, we can estimate the influence of dielectric exclusion on ion permeation of membrane. That is, if $s_0$ obtained experimentally can correspond to $\Delta W_i$, solvation energy barrier will reflect the ion permeation. In a word, on the base of $s_0$, $c_{pe}$ and $\Delta W_i$, the dominating factor that affects ion separation process of the three kinds of NF membranes can be clarified.

### 4.3.1 NF90 membrane

The charge density $c_{pe}$ in the pores of NF90 membrane in eight kinds of electrolytes solutions respectively with different concentrations was calculated by eqn (21) (see Fig. 12(b), Fig. 12(a) is the surface charge density $s_0$ on pore-wall, which have been obtained in Part 1 (ref. 1)). It can be seen in Fig. 12(a) that $s_0$ increases sharply at lower concentrations, and then gradually approaches to stable value as concentration increases. In addition, at lower concentrations, $s_0$ follow the trend: 2 : 1 > 1 : 2 > 1 : 1 , while when concentration rises, $s_0$ follow the trend: 2 : 1 > 1 : 2 > 1 : 1 – 2 : 2. In contrast, the charge density $c_{pe}$ remain virtually unchanged in experimental concentration range. This is because electroneutrality condition were taken into account in the derivation of the ions concentration in membrane (see Section 2.2), in other words, the absolute value of $c_{pe}$ is equal to that of membrane volumetric charge density $c_e$. Moreover, from Fig. 12(b), we can find that $c_{pe}$ in different electrolyte solutions

![Fig. 11](image1.png)

**Fig. 11** Dependence of born solvation energy barrier of the counter- and co-ions between electrolyte solutions and NF membranes on kinds of electrolytes.

![Fig. 12](image2.png)

**Fig. 12** The dependence of the surface charge density on the pore-wall (a) and the charge concentration in the pore (b) of NF90 membrane of eight electrolytes on the concentration of the electrolyte solutions.

### Table 9

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Electrolyte</th>
<th>Na$^+$ Cl$^-$</th>
<th>K$^+$ Cl$^-$</th>
<th>Mg$^{2+}$ Cl$^-$</th>
<th>Cu$^{2+}$ Cl$^-$</th>
<th>Na$^+$ SO$_4^{2-}$</th>
<th>K$^+$ SO$_4^{2-}$</th>
<th>Mg$^{2+}$ SO$_4^{2-}$</th>
<th>Cu$^{2+}$ SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF90</td>
<td>(Δ$W_i$ × 10$^{-20}$ J)</td>
<td>6.06</td>
<td>6.71</td>
<td>5.81</td>
<td>6.45</td>
<td>27.7</td>
<td>8.15</td>
<td>28.8</td>
<td>8.38</td>
</tr>
<tr>
<td>NF-</td>
<td></td>
<td>9.06</td>
<td>13.1</td>
<td>8.65</td>
<td>12.8</td>
<td>22.8</td>
<td>13.4</td>
<td>21.3</td>
<td>12.6</td>
</tr>
<tr>
<td>NF270</td>
<td></td>
<td>7.35</td>
<td>10.5</td>
<td>7.12</td>
<td>10.3</td>
<td>13.5</td>
<td>9.58</td>
<td>13.6</td>
<td>8.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Electrolyte</th>
<th>Na$^+$ Cl$^-$</th>
<th>K$^+$ Cl$^-$</th>
<th>Mg$^{2+}$ Cl$^-$</th>
<th>Cu$^{2+}$ Cl$^-$</th>
<th>Na$^+$ SO$_4^{2-}$</th>
<th>K$^+$ SO$_4^{2-}$</th>
<th>Mg$^{2+}$ SO$_4^{2-}$</th>
<th>Cu$^{2+}$ SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF90</td>
<td>(Δ$W_i$ × 10$^{-20}$ J)</td>
<td>6.06</td>
<td>6.71</td>
<td>5.81</td>
<td>6.45</td>
<td>27.7</td>
<td>8.15</td>
<td>28.8</td>
<td>8.38</td>
</tr>
<tr>
<td>NF-</td>
<td></td>
<td>9.06</td>
<td>13.1</td>
<td>8.65</td>
<td>12.8</td>
<td>22.8</td>
<td>13.4</td>
<td>21.3</td>
<td>12.6</td>
</tr>
<tr>
<td>NF270</td>
<td></td>
<td>7.35</td>
<td>10.5</td>
<td>7.12</td>
<td>10.3</td>
<td>13.5</td>
<td>9.58</td>
<td>13.6</td>
<td>8.79</td>
</tr>
</tbody>
</table>
follow the trend: 2 : 1 > 2 : 2 > 1 : 2 > 1 : 1, being similar to that of $\sigma_0$ at low concentrations. This means that Donnan exclusion is dominating factor of ion permeation. Further, it can be seen from Table 9 and Fig. 11 that for NF90 membrane, the values of $\Delta W_i$ between co- and counter-ions for 1 : 1 and 2 : 2 type-electrolytes are close to each other. This suggest that $\sigma_0$ for 1 : 1 and 2 : 2 type-electrolytes are relatively small, being consistent with the order of $\sigma_0$ at high concentrations, which shows that dielectric exclusion becomes more important to membrane permeation of ion at higher concentrations.

The above result is easy to understand: according to Donnan equilibrium principle, there is particular distribution of ions in electrolyte solution and membrane with fixed charges. When the electrolyte concentration of solution is relative lower, the counter ions in solution will be attracted strongly into the pores by the fixed charges owing to Donnan potential, resulting in the electrochemical potential of ions in the solution and membrane is equal. However, when the concentration becomes higher, the fixed charges in membrane are shielded by a large number of counter ions, Donnan exclusion loses effectiveness partially, and dielectric exclusion plays a major role in ion permeation.  

4.3.2 NF- membrane. Similarly, the charge density $c_{pe}$ in the pores of NF- membrane in eight kinds of electrolyte solutions with different concentrations are shown in Fig. 13(b) (similarly $\sigma_0$ of NF-membrane in Fig. 13(a) was obtained in Part 1 (ref. 1)). The concentration dependency of $\sigma_0$ and $c_{pe}$ is similar to that of NF90 membrane. However, in experimental concentration, the magnitude of $\sigma_0$ follows: 1 : 1 > 2 : 1 > 1 : 2 > 2 : 2; while $c_{pe}$ of NF- membrane in different electrolytes follows: MgCl$_2$ > MgSO$_4$ > NaCl > Na$_2$SO$_4$ > CuCl$_2$ > KCl > CuSO$_4$ > K$_2$SO$_4$, which is irregular comparing with the trend of $\sigma_0$. On the other hand, in Fig. 11(b) for NF- membrane, the similarity of solvation energy of counter-ion in different electrolytes follows: 1 : 1 > 2 : 2 > 2 : 1 > 1 : 2, which is similar to the trend of $\sigma_0$. This may suggest that dielectric exclusion plays an important role in the ion permeation process of NF- membrane at low concentration, because in the case of low the membrane volumetric charge density $c_e$ (see Table 6), Donnan exclusion is not so obvious comparing with that of NF90 membrane.

4.3.3 NF270 membrane. Fig. 14(a) and (b) are the concentration dependence of $c_{pe}$ and $\sigma_0$ of NF270 membrane. $\sigma_0$ of NF270 follows the trend: 1 : 1 > 2 : 1 > 1 : 2 > 2 : 2, over the experimental concentration range. While $c_{pe}$ of NF270 membrane in different electrolytes follows the irregular trend: NaCl > MgCl$_2$, CuCl$_2$, Na$_2$SO$_4$ > K$_2$SO$_4$, KCl > CuSO$_4$, MgSO$_4$, which is different with the trend of $\sigma_0$. On the other hand, for NF270 membrane from Fig. 11(c), the level of similarity of $\Delta W_i$ of counter-ion follows the trend: 2 : 2 > 2 : 1 > 1 : 2, which is different from the trend of $\sigma_0$. This result can not give a clear explanation whether Donnan exclusion or dielectric exclusion is a dominating factor of ion permeating into NF270-membrane. Strictly speaking, the changes of salt concentrations may more or less alter the pH of the solution, and then changes the surface charge density $\sigma_0$. For this, the pH of stock solutions of
all salts at all concentrations were measured (see the Fig. S1 of the ESI†). It is obvious that different salts and different concentrations of identical salts show big differences in pH values. The differences may also affect the protonation of the carboxylate groups located the pore walls, giving rise to different surface charge density. But for all this, the changing trends of $\sigma_0$ with concentrations shown in Fig. 12(a), 13(a) and 14(a) can still assess the dominating factor of Donnan exclusion in the membrane permeation of ion.

5. Concluding remarks

The conclusions of this paper include three aspects. First, on the basis of the interfacial polarization theory, the high-frequency dielectric relaxation was analyzed and relative permittivity and conductivity of membrane and solutions, $\varepsilon_{\text{m}}$, $\kappa_{\text{m}}$, $\varepsilon_{\text{w}}$, $\kappa_{\text{w}}$ were calculated. These parameters are inaccessible by any other individual experimental method. Furthermore, by discussing the variations of these parameters with concentration and species of the electrolyte, we found that ion permeation would lead to alteration of electrostatic interaction between polymer backbones of the membrane.

Secondly, the porosity of the NF membranes in wet state were calculated using $\varepsilon_{\text{m}}$, radius and thickness of the membrane. By combining $\kappa_{\text{w}}/\kappa_{\text{w}}$ with TMS model, the membrane volumetric charge densities of the three types of membranes, which is an vital membrane parameter in research of membrane separation performance, were calculated. The expressions of concentrations of co-ions $c_{i}^{\text{m}}$ and counter-ions $c_{i}^{\text{m}}$ in membranes were deduced under the consideration of Donnan exclusion. Ion solvation energy barrier was calculated by using $\varepsilon_{\text{m}}$ of wet membrane. The energy barriers to the solvation of ion into pores of three types of NF membranes in eight electrolytes solutions were discussed in detail, it was found that for 2 : 2 type electrolytes with the highest ion valence in these electrolyte solutions, ions permeation is the most difficult in terms of energy barrier. The all electrical parameters obtained in this work should be closer to the practical membrane process, because the relative permittivity of wet membrane was used in the calculations.

Finally, by combining the surface charge density $\sigma_0$ with concentrations of co- and counter-ions and energy barrier, the factor influencing ion separation process were suggested. From the view of Donnan exclusion, the larger the surface charge density $\sigma_0$ on pore-wall, the larger the charge density $c_{\text{pe}}$ in pore; on the other hand, from the view of dielectric exclusion, in one kind of electrolyte solution, the closer the value of solvation energy barrier of co- and counter-ions, the lower the values $\sigma_0$. From this, main factor are clarified for each type of NF membrane. For NF90 membrane, Donnan exclusion is the dominating factor of ion permeation at low concentration, while when the concentration increases, dielectric exclusion becomes the dominating factor. For NF- and NF270 membrane, dielectric exclusion plays an important role in ion permeation of membrane over all of the experimental concentration range.

In summary, NF membranes immersed in electrolyte solutions were systematically investigated and some information on ion permeability and selectivity through membrane by analyzing dielectric spectra coupled with the transport models. Additionally, this paper may provide some enlightenments for solving the problems that are always encountered in complex membrane–solution systems. However, it should be noted that although the dielectric analyzing method proposed by us has provided a lot of information about the membrane and ion transfer process from the membrane, including some unique parameters just by analyzing the relaxation processes, the analysis procedure is still rather tedious and complex. Therefore, it is inevitable that during the analyzing processes the errors in electrical and structural parameters are brought by the computation and fitting experiment data, which may affect accurate judge to some conclusions. In addition, it is also hard to obtain these parameters simultaneously when two or more variables are requested to change, for example, like the pH and concentration in this work. Due to the above disadvantages and relative merits of the method, it will be necessary to model the studied system appropriately and lessen the variables in analyzing equations for improvement fitting precision.

Acknowledgements

Financial support of this work by the National Natural Science Foundation of China (no. 21173025, 21473012) and the Major Research Plan of NSFC (21233003) are gratefully acknowledged.

References