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Characteristics and inner information of membrane/ solution system as viewed from dielectric spectroscopy: With an emphasis on dielectric analysis based on electrical model

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Abstract

This chapter presented an extended explanation on the validity of the application of dielectric spectroscopy (DS) method on membrane/solution systems, namely, on why the information of dielectric

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constant plays an important role in the permeation process of membrane systems and why DS method is able to effectively inspect the information on the structural and electrical properties of a membrane/solution system under working conditions. Based on the Maxwell-Wagner interfacial polarization theory, several dielectric models, including elementary dielectric models of membrane/solution systems on the basis of electric equivalent circuit model and dielectric models aiming at membranes with planar multilayer structure and a distribution of electric properties, as well as the results of simulation by means of these models, were simply introduced. Furthermore, by taking ion-exchange membrane that contains a concentration polarization layer, dipolar membrane, reverse osmosis membrane, and nanofiltration membrane as actual examples, the effectiveness of dielectric analysis, which is based on appropriate dielectric models, on in-situ obtaining inner information of membranes was illustrated. Then the prospect of the application of DS method in the field of membrane was commented as the conclusion. We apologize to those authors whose works have escaped our notice.

1. Introduction

Although not until the latest three decades has dielectric spectroscopy (DS) method become one of the most effective tools in the characterization of a variety of materials, the successful application of this method in membrane systems has undergone a very long history. Biological membrane [1] is the earliest one investigated by DS method, which can be traced to the second decade of last century, and then the artificial membranes such as lipid bilayer membranes [2-4]. In the latest 20 years, DS method has been extensively applied to composite membranes used in industrial material separation. One of the main reasons accounting for this extensive application is DS method's capability to characterize the electric properties of membrane under working condition, and to provide valuable information on membrane, solution, and interfaces, through dielectric measurement and dielectric analysis. On this, a lot of research papers and enlightening reviews have been reported [5-17]. On the other hand, since membrane/solution systems in practical use are typical heterogeneous systems with layered structure, dielectric models based on interfacial polarization theory are comparatively easier to be applied to the dielectric analysis on these systems, so that much more in-situ information can be obtained. This chapter will present a review on the application of DS method in membrane/solution systems from the viewpoint of model establishing and dielectric analysis, and the adopted examples are mainly restricted to the research works carried out by Hanai's group and Zhao's group.

1.1. Ion permeation of membrane

Nowadays, it is an important branch of membrane science to use functional polymer membrane for material separation in aqueous solutions, and attention has been increasingly paid to the inner configuration and separation mechanism of this kind of membrane. Carrying out DS study on systems of functional polymer membranes under working condition, which can be treated as planar multilayer, sandwich-like solution/membrane/solution systems according to its actual performing circumstance, as well as estimating the permeation behavior of ions in membrane and inner configuration of the membrane through viewing the change in permittivity (dielectric constant hereinafter) of the system in a non-invasive way is the original intention of the present review.

To begin with, let us consider how dielectric constant influences membrane permeation from a relatively abstract point of view. Briefly speaking, polymer membrane is an "oil" phase when compared with water. Therefore, when ions transfer from water into polymer membrane, namely, transfer from a phase with a large dielectric constant (≈ 80) into a phase with a small one (≤ 10), they have to overcome a large energy barrier that corresponds to the difference of the "self energy" [18] of ions between in water and in polymer membrane (e.g. a monovalent ion with a radius of 2Å have to overcome an energy barrier of 68 kT when it transfers from water into an oil phase with a dielectric constant about 2), and this is nearly impossible. Whereas, if a channel filled with water exists in the polymer membrane, the difference of polarizability or dielectric constant between aqueous solution and polymer membrane will be decreased, and the energy barrier will be markedly decreased as a result. In other words, as can be easily concluded, for membrane its dielectric constant and the radius of the pore are the measure of membrane permeation, while for solvated ions are their size and charge magnitude [18]. Except for the above-mentioned long-range interaction between solvated ions and membrane that is due to their difference of polarizability or dielectric constant, short-range interaction between ions and the fixed charge in membrane, which basically arises from Donnan potential, can also remarkably influence the energy barrier [19]. Accordingly, a combination of dielectric exclusion and Donnan exclusion constructs the theoretical groundwork of membrane permeation phenomenon, and simultaneously considering both above interactions is the basis of investigations on this phenomenon. From another point of view, since ions that permeate into a membrane will confront all kinds of resistances including dielectric exclusion, steric hindrance, and Donnan exclusion, while all these effects are closely related to the difference of dielectric constant between membrane's and solution's, one can conclude that this dielectric constant difference is the essential reason for retarding ions from permeating a membrane [20,21].

On the other hand, membrane permeation can also be characterized by the conductivity of the membrane that is immerged in solution. The DS method, which measures complex dielectric constant ε^* of a system, can give us frequency dependence of these two physical quantities, namely conductivity (κ) and dielectric constant (ε), and they are interrelated by the following relation:

$$\varepsilon^* = \varepsilon - j\varepsilon'' = \varepsilon - j\frac{\kappa}{2\pi f \varepsilon_0} \tag{1}$$

where ε^* is complex dielectric constant, ε'' is the imaginary part of complex dielectric constant (dielectric loss), f is frequency, ε_0 is dielectric constant of vacuum, and $j = \sqrt{-1}$. Conductivity and dielectric constant thus can be easily determined through dielectric measurement and dielectric analysis. Accordingly, it is rather necessary to carry out dielectric analysis, in combination with basic membrane permeation theory, so as to understand the membrane permeation processes. On the basis of the understanding of the conceptions mentioned above, let us validate the effectiveness of DS method in the study on membrane/solution systems and in obtaining basal information such as membrane's inner structure and the distribution of ions in membrane.

1.2. Background of the application of DS to membrane systems

Dielectric spectroscopy, sometimes also called AC impedance spectroscopy (IS), is able to investigate various polarization processes in a very wide frequency range ($10^{-6} \sim 10^{12}$ Hz), it is also non-invasive and very sensitive to the change of the systems under study, hence this method now has become one of the most effective tools in the characterization of the structure and dynamics of all kinds of materials [17,22], and has been extensively used in many scientific fields such as physics, biology, chemistry and materials. The earliest application of DS method in membrane systems can be traced to 1920s when cell membrane was first studied by the IS method [1], while not until the 1980s has this method been applied to artificial membrane. Now DS has been successfully applied to a variety of membrane systems, and a great number of representative works, in theory, experiment, and methodology, have been reported by many research groups, each with their own characteristics, especially Coster's group in Australia. Known as the UNESCO center for membrane science and technology, this group has long been engaged in dielectric study on membrane systems. The theoretical analysis approach of this group is mainly to obtain phase parameters through simulating each phase of the system by means of equivalent circuit model, and the membrane systems

under investigation involves lipid bilayer membrane [23,24], ultrafiltration membrane [5], supported liquid membranes [6], bipolar membranes [25], conducting membranes [26,27], and so on. Their early works were mainly based on low frequency (0.1-100 Hz) dielectric measurement, and the frequency range was extended up to 10^5 Hz in recent works. Furthermore, this group has given original theoretical derivations on the dielectric behaviors of dipolar and conducting membranes, and also given detailed description on the mechanism of low-frequency dielectric response of membrane/solution systems [15,16]. The group of Mafé in Spain established a simple model for analyzing ac impedance spectra in bipolar membranes [28,29], by which the bipolar junction structure and its influence on the characteristic parameters involved in the field-enhanced water dissociation phenomenon were investigated [30,31]. Benavente's group successfully applied impedance measurement to study and monitor many artificial membranes used in industrial separation processes [9-11], and developed a novel analytical method to directly determine actual carrier content in a working membrane based on the linear correlation between the electric resistance of the membrane and the carrier content [9]. Martinsen *et al*. [32,33] investigated the contribution from the electrical properties of the sweat ducts to the total electrical properties of the epidermal stratum corneum, where they employed the long cylinder dielectric model proposed by Takashima [34] to describe the dielectric behavior of sweat ducts, so as to interpret the mechanism of low frequency dielectric relaxation of porous membranes. Strict theories for the dielectric behavior of various membrane systems including multilayer composite membranes were proposed by Zholkovikij [35]. Raudino *et al*. [36] developed a dynamic mean-field model through which the dielectric behavior of undulated lipid membranes was simulated. Bordi *et al*. [37] carried out impedance measurements on self-assembled lipid bilayer membranes on the tip of an electrode, and a simple equivalent circuit of the metal-supported lipid bilayer was employed to characterize their dielectric behaviors.

   Except for the above mentioned works, Hanai's group also exploited the application of DS on membrane systems by means of their unique dielectric analysis method, mainly focusing their DS investigations on the interfacial polarization response of layered membrane systems that generally occurs at frequency around 10^4 Hz [38-46]. Since the beginning of 1990s, Zhao *et al*. have emphasized their DS study on modeling and setting up dielectric analysis method with respect to membrane/solution systems, by taking advantage of the outstanding sensitivity of DS method to heterogeneous systems, and established a set of systematic analysis method to obtain the structural and electrical information of membrane and membrane/solution interface [13,14,41-47]. We will give this method an expanding introduction by taking some actual systems as examples in section 3.

1.3. Advantage and significance of dielectric study on membrane/solution system

It is well known that most functional polymer membranes used in material separation are working in aqueous solutions, the properties of these membranes in humid state thus are very important in understanding the separation processes. Although most methods used in the characterization of membrane, e.g. scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), etc., may provide useful information including the surface morphology and the size and distribution of pores in membrane [48,49], the information only represents the properties of membranes in dry state instead of humid state, and thereby has no direct correlation with the membranes' separation performance. Now that membrane of this kind is generally in humid state when in practical use, and it swells when immerged in aqueous solutions, it is very necessary to carry out in-situ study on a swelled membrane so as to obtain its properties in humid state. Besides, biological cell membranes have to exist in aqueous solutions, and some artificial membranes that are used as models of biological cell membrane such as lipid bilayer membranes have to be formed in aqueous solution and will not be stable without water, studies on these membranes, undoubtedly, also have to be carried out in aqueous solutions. On the other hand, although some other methods, say measuring membrane potential or salt permeability [21,50], can be used to study membranes in humid state, they can only give information on the properties or the behavior of the whole membrane but are incapable of detecting the inner structure of the membranes. Consequently, a method that is not only able to in-situ detect the properties of a membrane under working conditions but also sensitive to the change of the inner structure of the membrane is rather desirable. Fortunately, DS method is just such a method that can meet all these requirements. It should be emphasized that, nonetheless, in order to obtain the inner information of membrane, just carrying out dielectric measurement by simply adding instruments to the system is far from enough, and it is the numerical dielectric analysis based on reasonable dielectric theory and an appropriate model that counts most.

2. Theory, model and method
2.1. A summary of dielectric theory of interfacial polarization

For a heterogeneous system with planar structure comprised of an artificial membrane and solutions at both sides, when an AC electric filed is applied, its dielectric behavior in the frequency range around 10^4 Hz can be considered to be attributed to interfacial polarization from the viewpoint of Maxwell-Wagner theory [51,52]. Since the membrane domain and solution domain have different dielectric constant and electrical conductivity, when an

electric filed is applied, spatial charges will accumulate on the interfaces and produce an inductive field to keep the continuity of the electric current, similar to that in the multilayer capacitor. When this inductive field can not keep up with the change of an applied ac field, interfacial polarization relaxation occurs. Generally, for planar systems having n $(=1,2,\ldots,i,..)$ dielectric slabs with different dielectric constant (ε_i) and electrical conductivity (κ_i), if only the following condition is satisfied, n-1 relaxation processes with different characteristic relaxation times would be observed [53]:

$$\frac{\varepsilon_1}{\kappa_1} \neq \frac{\varepsilon_2}{\kappa_2} \neq \cdots\cdots \neq \frac{\varepsilon_i}{\kappa_i} \neq \cdots\cdots \neq \frac{\varepsilon_n}{\kappa_n} \tag{2}$$

This principle has been observed in many membrane/solution systems, and has been validated by a lot of experimental and theoretical studies [53]. Compared with the polarization processes due to dipolar polarization of constructing molecules and even with interfacial polarization in dispersion systems, the slow polarization processes in membrane/solution systems generally occurs in a lower frequency range and shows higher relaxation intensity because of the thin membrane layer and large surface area. For these reasons, although the number of dielectric relaxations observed in systems like biological cell or spherical particle suspensions with n phases is sometimes less than n-1, this principle is always hold in membrane/solution systems without exception.

In line with Maxwell-Wagner theory and within the scheme of the above principle, a variety of dielectric models have been proposed to interpret the dielectric behavior of different membrane systems. Among these models, electric equivalent circuit model is the most basic and widely used one, based on which, many more comprehensive models were also proposed by considering the special properties of actual membrane/solution system or its performing circumstance. Some of these models are simply introduced as follows.

2.2. Electrical model of planar multilayer structure
2.2.1. Equivalent circuit model for simple planar structure

For a membrane/solution system with planar multiphase structure, the electric property of one phase may be described by a parallel connection of a capacitor and a resistor, and a serial connection of each phase in the system forms the equivalent circuit model to simulate the whole system. In detail, an actual membrane/solution system in dielectric measurement is a membrane being sandwiched by aqueous solutions as schematically represented by Fig.1.(A), dielectric measurement on which will give us the frequency

dependent capacitance $C(f)$ and conductance $G(f)$ of the whole system. When a homogeneous membrane of complex dielectric constant ε_m^* separates two aqueous phases having the same complex dielectric constant ε_a^*, this system is actually composed of two phases because the properties of the liquid phases at both sides of the membrane are the same, as shown in Fig.1.(B), accordingly, the whole system can be thought to be having a two-layer structure and its complex dielectric constant can be represented by the following equation [17]:

$$\frac{1}{\varepsilon^*} = (1-\Phi)\frac{1}{\varepsilon_a^*} + \frac{\Phi}{\varepsilon_m^*} \tag{3}$$

Let S, l and d represent the membrane area, the length of the whole system, and the thickness of the membrane, respectively, and let $\Phi = d/l$, then Eq. (3) can be rewritten as:

$$\frac{1}{C^*(f)} = \frac{1}{C_a^*} + \frac{1}{C_m^*} \tag{4}$$

where $C^*(f)$, C_a^* and C_m^* are complex capacitances defined by $C^*(f) = \varepsilon_0\varepsilon^*(S/l)$, $C_a^* = \varepsilon_0\varepsilon_a^*[S/(l-d)]$, and $C_m^* = \varepsilon_0\varepsilon_m^*(S/d)$, respectively and the subscripts a and m denote the liquid phase and membrane phase, respectively. That is, this system may be represented by the equivalent circuit with two C/G units in series as shown in Fig.1.(B), from a dielectric point of view.

Similarly, a three-layer system, such as a homogeneous membrane immerged in asymmetric solutions or a membrane having two different layers immerged in a symmetric solution, may be expressed by a combination of three C/G circuit units in series as shown in Fig.1.(C), and the complex capacitance of the whole system can be represented by the following equation:

$$\frac{1}{C^*(f)} = \frac{1}{C_a^*} + \frac{1}{C_m^*} + \frac{1}{C_b^*} \tag{5}$$

where C_b^* is the complex capacitance of the third layer, which may be a solution layer that is different from the other liquid layer (layer a) or one of the membrane layers, resting with the actual composition of the system.
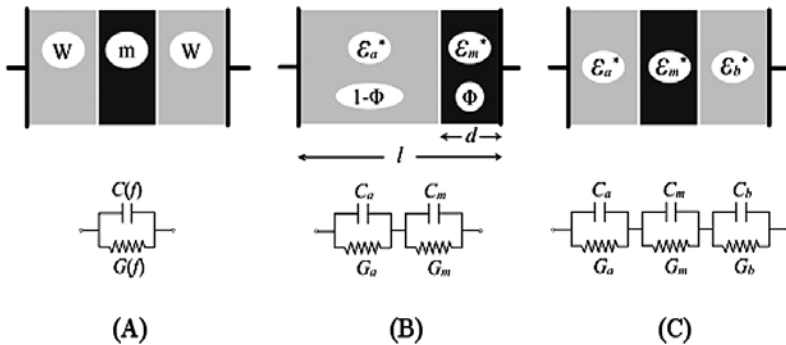
Figure 1. Electrical models of membrane systems expressed by equivalent circuit models. (A) actual measured system, (B) two-layer system and (C) three-layer system. For detail, see text.

Dielectric measurements on these two-layer or three-layer membrane systems will give us corresponding dielectric spectra, which are actually frequency dependent capacitance $C(f)$ and conductance $G(f)$ of the whole system [38]. While the objective of dielectric analysis is to quantitatively obtain the values of the parameters that represent the properties of each layer through the models mentioned above. Starting from the electrostatic law, Zhao and co-workers have derived expressions for the dielectric response of systems with planar multilayer structure, proved that the expressions are consistent with those derived from equivalent circuit model, and established a strict dielectric analysis method for three-phase membrane/solution systems [41,54]. This dielectric analysis method has been successfully applied to weakly-charged membrane systems such as reverse osmosis membrane and nanofiltration membrane, and important parameters including the conductive property of the membrane, the surface charge density and those correlated with ion permeation were obtained [13,46].

It should be noted, however, that the dielectric spectra expected from equivalent circuit models are simply represented by the sum of relaxations with a single relaxation time, namely Debye-type relaxation, whereas actual membrane systems generally show much broader spectra with a distribution of relaxation time, due to certain reasons such as the nonuniformity of one of the constituent phases. Therefore, it is inadequate to describe the dielectric spectra of most actual membrane/solution systems just with the electric circuit model, and more comprehensive models that take the detailed properties of each constituent phase into account should be established.

2.2.2. Dielectric model of concentration polarization

The phenomenon of concentration polarization (CP) is highly concerned in membrane separation industry due to its remarkable influence on the efficiency and cost of membrane separation processes, studies on this phenomenon, such as exploiting control technique on it, thereby are also extensively concerned in the field of membrane science. Therefore, if a study can obtain the values of the parameters in connection with the concentration polarization layer (CPL), it will undoubtedly offer a positive reference for theoretically resolving problems related with CPL. For CPL in a typical membrane system, since it is characterized by a conductivity distribution and hence is different from bulk solution, it should be treated as an independent layer and can be represented by a dielectric model as shown in Fig.2.
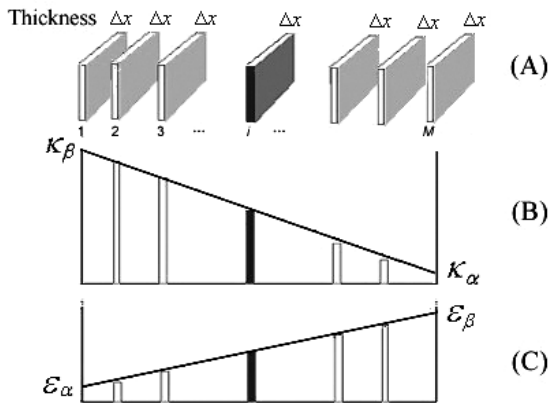

Figure 2. Illustration of dielectric model for the medium with varying dielectric constant and conductivity. (A) Assemble of thin-plate dielectrics, (B) Distribution of conductivity, and (C) Distribution of dielectric constant.

The whole CPL with a thickness of t is composed of a series of infinitesimal thin plates, each with a thickness of Δx, homogeneous dielectric constant ε_i and conductivity κ_i (Fig.2(A)). The conductivity of CPL decreases linearly from κ_β to κ_α, as shown in Fig.2 (B) where the left side of CPL is the side near the membrane and the right side is the side far from the membrane, and it is this conductivity decrease in CPL that gives rise to the P-relaxation that we will discuss in detail later. While the dielectric constant of CPL keeps invariable. According to the Maxwell-Wagner theory, the whole capacitance and conductance of the CPL derived from the model are as follows [42]:

$$C_P = \frac{S(\kappa_\beta - \kappa_\alpha)}{t} \cdot \frac{B/\omega}{A^2 + B^2}$$

$$G_P = \frac{S(\kappa_\beta - \kappa_\alpha)}{t} \cdot \frac{A}{A^2 + B^2}$$

(6)

where A and B are complex expressions which are functions of κ_α, κ_β, and angular frequency $\omega \ (= 2\pi f)$. As a result, the capacitance and conductance of the CPL are functions of concentration gradient $(\kappa_\beta - \kappa_\alpha)/t$ and frequency f. By substituting Eq. (6) to the theoretical formula (Eq.(4)) that is derived from equivalent circuit model described above, the expression of the complex capacitance of the whole membrane/solution system can be derived, which includes the electrical properties of the CPL, the membrane phase, and the solution phase, denoted by the subscript p, m, and a, respectively (Eq.(7)):

$$C^* = F\left[C_p^*(\kappa_\beta, \kappa_\alpha, t, f), C_m^*, C_a^* \right]$$

(7)

Since complex capacitance has the following correlation with the measured capacitance and conductance: $C^* = C + G/j\omega$, Eq.(3) can be used to curve-fit the dielectric spectra of the membrane/solution system with a CPL, and phase parameters ($\kappa_\beta, \kappa_\alpha, t, C_m, G_m, C_S, G_S$) representing the properties of each phase of the system thus can be obtained through dielectric analysis [45].

These theoretical formulas coupled with the dielectric analysis method for planar multilayer system have been successfully applied to simulate the electrodialysis processes of anion- and cation-exchange membrane/solution systems [43,44]. Recently, the result of dielectric study on the nanofiltration membrane/solution system showed that [14], a wealth of information such as the structure of the membrane, the ion distribution in each layer, and the fixed charge density of the membrane can be revealed through the combination of this model with the theories of Donnan exclusion and dielectric exclusion. This will be elaborated as an example of dielectric analysis later on.

2.2.3. Dielectric model of concentration polarization with varying dielectric constant and conductivity

It is assumed in above dielectric model that the dielectric constant of CPL is invariable, which is apparently reasonable for CPL in aqueous solutions because the dielectric constant of water has little change with the variation of the concentration of the electrolyte solution wherein at a certain temperature. For systems with non-aqueous medium or with a special layer structure, however, Eq.(2) may not result in accuracy. For example, for a composite

membrane that contains a porous support layer filled with water, since the looseness of the porous support layer may have a distribution, as shown in Fig.3, namely there exists a gradient of water content in the layer, the dielectric constant of this layer may also have a distribution, and the CPL model that only considers the distribution of conductivity is obviously not enough to describe the dielectric behavior of such systems [14-16]. In this case, the dielectric model that takes account of the distribution of dielectric constant, as shown in Fig.2 (C), should be employed. According to this model, the theoretical expressions that quantitatively relate the measured capacitance and conductance to the electrical parameters of the system were derived, which take both the varying capacitance and conductance into account. The theoretical expression for the complex impedance of the phase with simultaneously varying dielectric constant and conductivity is detailed in Appendix. Accordingly, the complex capacitance of the whole membrane/ solution system is a function of more parameters as simply represented by the following expression [47]:

$$C^* = F \left[C_p^*(\kappa_\beta, \kappa_\alpha, t, \varepsilon_\beta, \varepsilon_\alpha, f), C_m^*, C_a^* \right] \tag{8}$$
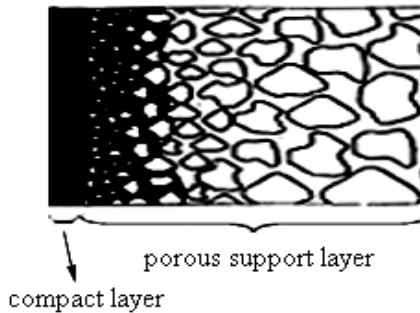

Figure 3. Schematic diagram of a composite membrane with a compact layer and a porous support layer.

here the subscripts m and a still denote a homogeneous membrane layer and solution phase, respectively. However, different from Eq.(7), the subscript p denotes a phase with simultaneously varying dielectric constant and conductivity, e.g. a porous support layer filled with solution. Apparently, this expression involves more information, and the information can be extracted in principle through analyzing more complex dielectric spectra from dielectric measurements although there are no actual example can be enumerated here. In

order to give an image about the spectra, we show a result of theoretical simulation.

Fig. 4 shows the results of numerical calculations by means of Eq. (8) and a set of parameters that is actualized in actual nanofiltration membrane/solution systems under working conditions. It can be seen from Fig. 4 that, only one dielectric relaxation is observed for composite membrane and porous support layer in the frequency range of interest. Both capacitance and conductance of composite membrane are smaller than those of porous support layer, while the relaxation frequency is higher of the former than the latter. When comparing the dielectric behavior of composite membrane with that of layered composite membrane/solutions system, it can be seen that the layered system exhibits two distinct dielectric relaxations. The lower frequency relaxation of layered system is almost totally overlapping with that of composite membrane, indicating that this dielectric relaxation is attributed to the inner structure of the composite membrane. In the higher frequency range, however, dielectric behavior of layered system is remarkably different from that of composite membrane, which signifies that the high frequency dielectric relaxation of layered system has no bearing on the inner structure of the composite membrane but is closely connected to the remarkable difference of electric properties between the solution and the composite membrane.
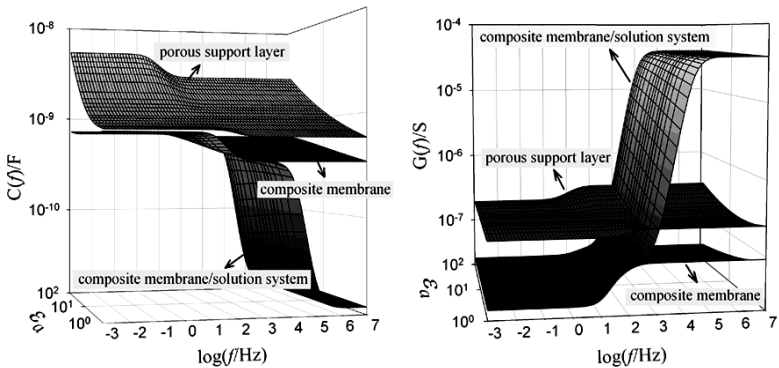

Figure 4. Frequency dependences of capacitance and conductance of porous support layer, composite membrane and layered system containing composite membrane and solutions. Taken from [47] with permission.

As showed in Fig.4, the above-mentioned model is applicable for a composite membrane composed of a compact layer and a porous support layer, such as nanofiltration membrane and reverse osmosis membrane, and much more information is expected to be obtained when this model is applied to

actual membrane systems. It is noteworthy that, due to the nonuniformity of the looseness of the polymer materials ($\varepsilon < 10$) in the porous layer, dielectric constant of an actual composite membrane will have distribution, no matter it is in the dry state when mixing with air that has a much lower dielectric constant ($\varepsilon = 1$) or in the humid state when immersed in water with a much larger dielectric constant ($\varepsilon \approx 80$). This will result in different energy barriers and hence different membrane permeation performance, characterized by a distribution of the membrane conductivity. In other words, for such systems both the conductivity and dielectric constant of a certain layer are not uniform. Accordingly, using the expressions that derived from this dielectric model to analyze the dielectric spectra of such membrane systems, undoubtedly, is rather worthy of expectation.

2.3. Dielectric analysis (the calculation of phase parameters)

The so-called dielectric analysis here means calculating phase parameters, which represent the properties of each phase of a heterogeneous system, from dielectric parameters that characterize dielectric relaxation spectra, based on an appropriate dielectric model. Hence, accurately determining dielectric parameters from dielectric spectra is an indispensable precondition. To this end, the Cole-Cole equation [55] (Eq. (9)) and its derivative empirical formulas are usually used:

$$\varepsilon^*(\omega) = \varepsilon_h + \sum_{i}^{n} \frac{\Delta\varepsilon_i}{1 + (j\omega\tau_i)^{\beta_i}} \tag{9}$$

where n denotes the number of dielectric relaxation, $\Delta\varepsilon_i$ and $\tau_i \left(= 1/(2\pi f_0) \right.$, f_0 is the characteristic relaxation frequency) denote the relaxation intensity and relaxation time of ith dielectric relaxation, respectively, and β_i ($0 < \beta_i \leq 1$) is the Cole-Cole parameter of ith dielectric relaxation, denoting the width of the distribution of relaxation times (when $\beta = 1$, this relaxation is a Debye type relaxation resulting from a single polarization mechanism). Curve-fitting the dielectric relaxation spectra by means of these empirical formulas will determine corresponding dielectric parameters such as the number of relaxation, the limiting values of capacitance and conductance in low-, middle, and high- frequency range, the relaxation intensity, and so on (see Fig.5). Among these dielectric parameters, relaxation intensity reflects the accumulation of electrical charges, while characteristic relaxation frequency and β_i may be used to judge the mechanism and the complexity of the relaxation, which are related to the inner conformation of the system under
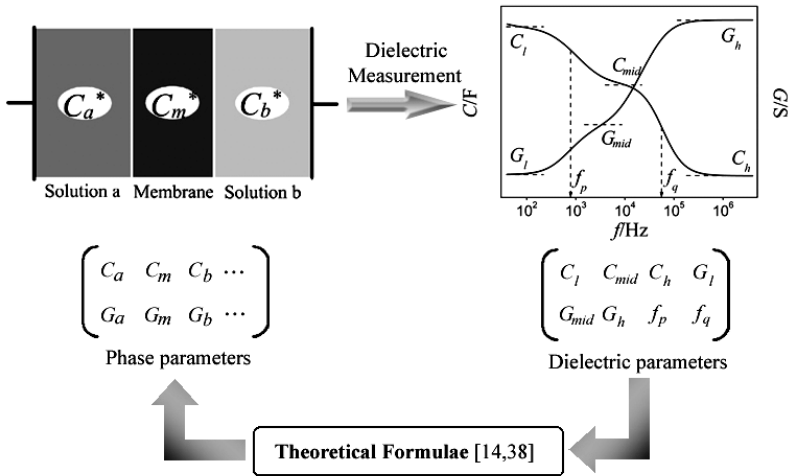
Figure 5. Diagrammatic representation of the dielectric analysis process.

investigation. For membrane systems, since the dielectric relaxation is generally obvious, the dielectric parameters can be directly extracted from the spectra even without curve-fitting.

After the needed dielectric parameters are determined, phase parameters that represent the properties of each constituent phase can be calculated by means of theoretical formulae [14,38]. Fig.5 shows a simple representation of the dielectric analysis process, where the dielectric parameters and phase parameters will vary with different membrane/solution systems. In what follows we will exhibit this process through some examples, and the calculation processes also vary with different systems.

3. Examples of dielectric analysis on different membrane systems
3.1. Ion-exchange membranes system (concentration polarization)

As an important and fundamental phenomenon in membrane science and a notorious effect in industrial application, concentration polarization (CP) has been extensively studied in connection with membrane separation processes such as electrodialysis, filtration and reverse osmosis. What follows is an actual example [43,44] which shows what kind of dielectric spectra will be observed when dielectric measurement is carried out on ion-exchange

membrane/solution system, how to carry out dielectric analysis and what information can be obtained through dielectric analysis.

In the absence of DC voltage, the membrane/solution systems shown in Fig.1.(A) did not show any dielectric relaxation because the ion-exchange membrane with high density fixed charges has high conductivity values and hence no charge will be accumulated on the membrane/solution interface. While in the presence of DC bias voltage, two-step dielectric relaxation including two relaxation terms (P-relaxation at lower frequency and Q-relaxation at higher frequency) can be observed. As an example, Fig.6 shows the dielectric spectra of cation-exchange membrane CMV immerged in distilled water under the application of different DC bias voltages. It has been confirmed through well-designed experiments that P-relaxation is a result of concentration polarization in the presence of DC bias voltage, and the Q-relaxation is mainly attributed to the concentration difference of the aqueous solutions on both sides of the membrane, which is caused by the application of DC bias voltage [43,44].
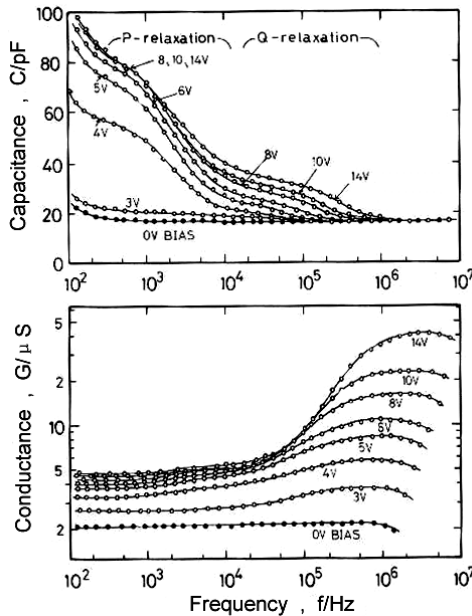

Figure 6. Frequency dependence of the capacitance and conductance of CMV membrane/distilled water system under application of different DC bias voltages. Taken from [43] with permission.

For such a system, dielectric analysis based on the CPL model mentioned above and the theoretical expression (Eq. (5) and (6)) has calculated the values of capacitance and conductance of the solution on both sides of the membrane, the CPL parameters $(\kappa_\alpha,\ \kappa_\beta)$, the thickness of CPL (d_{cp}), and the conductivity gradient $(\kappa_\beta - \kappa_\alpha)/d_{cp}$. The value of κ_α, which denotes the conductivity of the solution near the membrane surface and is generally assumed to be zero in other CPL studies, is estimated through dielectric analysis to be 0.04 μS/cm. This value is very approximate to 0.055 μS/cm that is calculated from ion product of ultrapure water under the condition of pH=7. It was also found that the thickness of CPL has no bearing on the added DC bias voltage, and its value, about 0.83 mm, is consistent with what obtained from other methods [56] considering that the adopted models are different. Similar results were also obtained in the dielectric study on anion-exchange (AMV) membrane systems [44].

3.2. Bipolar membrane systems

Bipolar membrane or double fixed charge membrane, which is composed of a negatively charged layer and a positively charged layer joined in series, is able to ensure an electrochemical water splitting process at the interface separating the two layers. As a consequence of this important phenomenon, the use of bipolar membranes attracted much attention in scientific research and industrial application. Recently, Osaki *et al*. successfully employed the above-mentioned dielectric analysis method based on the three-layered dielectric model [12], as shown in Fig.7 (A), to investigate this phenomenon of bipolar membranes. The theoretical curves in line with the three-layered dielectric model are in well agreement with experimental curves, as shown in Fig.7 (B). They interpreted that the observed double dielectric relaxation profile is due to the heterogeneous construction of the membrane under dc bias voltage. By changing the properties of the membrane and surrounding electrolyte solution, each phase was identified by the phase parameters that derived from dielectric analysis, and it was found that one of the compositions of the heterogeneous structure is situated at the membrane interface region between the negatively and the positively charged membrane with a thickness of less than several micrometers, which has an extraordinarily large electric capacity with a magnitude of sub-microfarads.

Besides, Coster *et al*. carried out dielectric study on the α-dispersion (relaxation) of bipolar membrane systems [25], which occurs at rather lower frequency range and originates from geometrical properties of a structure that develops in the membrane as a consequence of the presence of fixed charges, and derived expressions for the membrane capacity and conductance as a
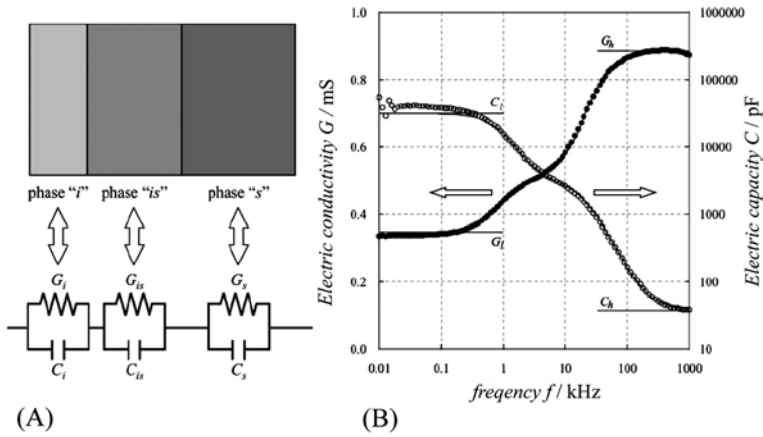
Figure 7. (A) Schematic diagram of the three-layered dielectric model and corresponding equivalent circuits for the dielectric spectra of a bipolar membrane. (B) Typical dielectric spectra of dipolar membrane/solution system (symbols) and theoretical curves (solid lines) in line with the three-layered dielectric model. Taken from [12] with permission.

function of frequency by solving the Nernst-Planck-Poisson equation. Through these expressions, the dielectric properties of central depletion layer were theoretically investigated.

3.3. Reverse osmosis membrane system

Reverse osmosis membrane, generally made up of an ultrathin, compact skin layer with a porous support layer underneath, is extensively used in sea and brackish water desalination, and the evaluation of the structure and the electrical properties of the skin layer is important for understanding the mechanism of reverse osmosis and also for improving the efficiency of desalination. Asaka studied dielectric relaxation of asymmetric cellulose acetate membranes in various aqueous electrolyte solutions [57]. In his study on commercial DRS series membranes, he found distinct dielectric relaxations, as shown in Fig.8, from which the capacitance C_m and conductance G_m of the membrane were determined through dielectric analysis based on the tree-layered dielectric model described in section 2.2.1. The thickness of the membrane estimated from C_m(=1.24 μF) was 26 nm, being different from the nominal thickness of the membrane but the same order of the thickness of the skin layer determined by electron microscopy.

The result suggested that C_m is attributed to the skin layer, and that the support layer does not contribute to the dielectric relaxation because the
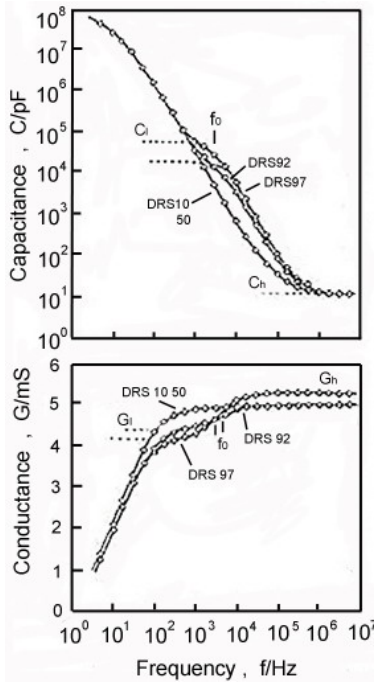
Figure 8. Frequency dependence of the capacitance and conductance of cell systems composed of DRS membrane immersed in NaCl solution. Taken from [57] with permission.

support layer is a porous layer containing much water and thus its dielectric constant and conductivity are nearly equal to those of the aqueous phase. Furthermore, the conductivity of the skin layer that was estimated from G_m is very close to the conductivity of the homogeneous cellulose acetate membrane in the humid state that was measured independently. On the other hand, the ratio of G_m/C_m for different types of electrolytes has been obtained by means of dielectric analysis on the DS of reverse osmosis membrane in different types of electrolyte solutions. The sequence of this ratio reflects the ion permeation ability, the smaller the ratio is, the fewer can this kind of ion permeate the membrane and the better the separation efficiency of the membrane is. This result was the same as the solute separation sequence determined by Matsuura *et al*. [58]. In a word, dielectric analysis method that can be completed within a short period of time is very effective in the comparison of the intensity and size of ion selectivity of reverse osmosis membranes.

3.4. Nanofiltration (NF) membrane system

Nanofiltration (NF) membranes, which possess nanoscale pores and are weakly charged in general, have an asymmetrical layered structure and have been widely used for material separation in electrolyte solution. NF membrane usually shows intermediate characteristics between ultrafiltration membrane and reverse osmosis membrane due to its composite structure that comprises both a micro porous support layer and a compact polymer layer. The large difference of dielectric constant between the membrane material and the bulk solution results in a dielectric exclusion effect, which hinders transport of ions through the membrane and hence achieves the separation of electrolytes from water; meanwhile, although the porous support layer is more permeable to solvents, the fixed charges on membrane polymer chains will give rise to Donnan exclusion effect and make the membrane permselective with respect to ion size and charge. These two effects as well as some other separation mechanisms simultaneously exist during the separation processes and interact with each other, enormously complicating the investigation of the NF processes. As similar systems to those mentioned above, the Maxwell-Wagner theory and the corresponding theoretical formulas are also suitable for the dielectric analysis on NF membrane/solution systems.

The authors recently studied the dielectric relaxation behavior of composite NF membrane (NTR7450) in different electrolyte solutions [13,14], and two distinct dielectric relaxations were observed as shown in Fig.9, where Fig.9.(A) and (B) shows the frequency dependence of capacitance and conductance of the system composed of the NF membrane and LiCl solutions with various concentrations, respectively, and Fig.9.(C) is the corresponding complex plane plots of complex capacitance, which is characterized by a semicircle in connection with a circular arc for each electrolyte concentration. These two dielectric relaxations showed different features when the environmental condition was changed, indicating that the mechanisms contributing to the low and high frequency dielectric relaxation are different.

To fully understand the mechanisms of the double dielectric relaxations, and then to obtain the information about the inner structure of the NF membrane and the membrane permselectivity to the ions, dielectric analysis based on an appropriate dielectric model should be carried out. First of all, the dielectric parameters should be accurately determined. Since the dielectric spectra shown in Fig.9.(C) imply that the low frequency relaxation has distribution of relaxation time and the high frequency one is of Debye type, the following formula, which combines the Cole-Cole equation with the Debye equation, was employed to fit the $C–f$ curves (Fig.9.(A)):

$$C(f) = \frac{(C_l - C_{mid})\left[1 + (f/f_p)^{1-\alpha}\cos\left(\frac{\pi}{2}(1-\alpha)\right)\right]}{1 + 2(f/f_p)^{1-\alpha}\cos\left(\frac{\pi}{2}(1-\alpha)\right) + (f/f_p)^{2(1-\alpha)}} + \frac{C_{mid} - C_h}{1 + (f/f_q)^2} + C_h \qquad (10)$$
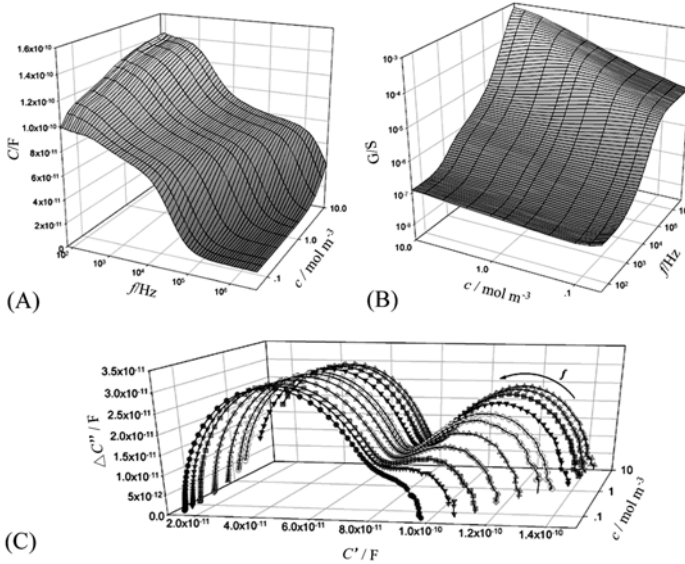

Figure 9. Dielectric spectra for the system composed of NF membrane and LiCl solutions. (A) Capacitance and (B) conductance vs frequency and bulk concentration, (C) complex plan plots of complex capacitance for the same system as a function of bulk concentration. Taken from [14] with permission.

The dielectric parameters including C_h, C_{mid}, C_l, f_p, f_q, and α thus can be determined through curve-fitting, where C_h, C_{mid}, and C_l are limit capacitance at the plateaus of the $C - f$ curve in the high-, middle- and low-frequency range, respectively; f_p and f_q are characteristic relaxation frequencies of the low- and high-frequency relaxations, respectively; and $\alpha(=1-\beta)$ is the Cole-Cole parameter denoting the distribution of relaxation time. While the conductance parameters G_h, G_{mid} and G_l, which denote the limit conductance at the plateaus of the $G - f$ curve (Fig.9.(B)) in the high-, middle- and low-frequency range, respectively, can be determined directly from the curves of $G - f$. Through analyzing the dependence of these dielectric parameters, especially the characteristic relaxation frequency and relaxation intensity (ΔC

and ΔG), on the concentration of electrolyte solution, it was concluded that the high-frequency dielectric relaxation is attributed to the membrane/solution interfacial polarization while the low-frequency one is a result of the double layered composite structure of the NF membrane.
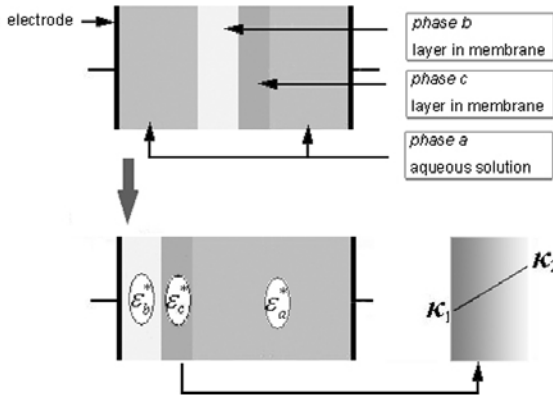

Figure 10. Dielectric model for the NF membrane/solution system composed of three phases with different complex dielectric constant. Conductivity of phase c is linearly distributed. Taken from [14] with permission.

Through the dielectric model for the multilayered composite membrane/solution system, shown in Fig.10, the quantitative relation between the dielectric parameters and the phase parameters was established. The complex dielectric constant of the solution and each layer of the composite membrane were given by this model, accordingly the inner information about the electric and structural properties of the membrane/solution system was obtained through dielectric analysis. By changing the condition of the solution including the species and concentration of electrolyte, the acidity, and so on (these factors undoubtedly have influence on the electric properties of the membrane), more dielectric spectroscopy data were obtained, through which the looseness, the materials, and fixed charge content of each layer of the NF membrane were estimated, and the permselectivity of the membrane to different species of ions was inspected [14]. The theoretical formula of membrane conductivity, Eq.(11), was derived in accordance with Donnan equilibrium principle, which not only takes the contribution of H^+ ion into account, but also gives a good description on its relationship with the concentration and mobility of free ions in the membrane [13,14].

$$\kappa_m = \left(U_{M^+}^m c_{M^+}^m + U_{A^-}^m c_{A^-}^m + U_{H^+}^m c_{H^+}^m \right) F \tag{11}$$

where, $U_{M^+}^m$, $c_{M^+}^m$, $U_{A^-}^m$, $c_{A^-}^m$, $U_{H^+}^m$, and $c_{H^+}^m$ denote mobility and concentration of cation, anion, and proton in the membrane, respectively, F is the Faraday constant.

The ion transport rate of different concentration and species in the membrane was also interpreted very well by Eq.(11) [14]. Fig.11 gives the conductance of the membrane layer facing the solution as a function of the electrolyte concentration and species, where Fig.11.(A) shows the result of dielectric analysis and Fig.11.(B) shows a rough simulation with Donnan equilibrium principle for the concentration dependence of membrane conductance in NaCl solutions. As can be seen in Fig.11.(B), the simulation result agreed with the dielectric analysis result, indicating that the dielectric model employed here and the dielectric analysis method are rational. It should be pointed out that, although Fig.11 gave us a lot of information, it only represents one of the numerous parameters that can be derived from dielectric analysis. As a result of dielectric analysis, much more information that reflects the membrane structure, the ion distribution in each membrane layer, and the change of ion distribution with the electrolyte's species and concentration was also obtained. Through these parameters, the assumption that the membrane is composed of two layers with different electrical properties was confirmed, and the ion mobility in each layer as well as the permselectivity of the membrane to different electrolyte was estimated. And it was finally revealed that both layers play different roles in the salt separation processes according to the inner structure of NF membrane and the different permeation performance of ions in different layers.
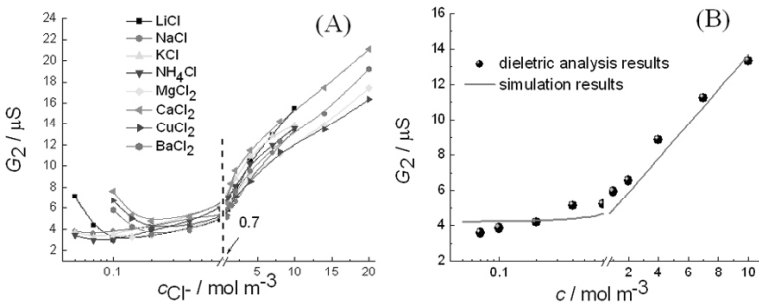

Figure 11. (A) G_2 vs electrolyte concentration and species; (B) A simulation with Donnan equilibrium principle for concentration dependence of G_2 of the membrane in NaCl solutions. Taken from [14] with permission.

It can be clearly concluded from the above mentioned four examples that, DS method has good efficiency that other methods may not have in the investigation of functional polymer membranes used in material separation, more importantly, it also has outstanding uniqueness in in-situ obtaining the information about the electric and structural properties of the membrane, the membrane/solution interface, and the solution under actual working condition.

According to the dielectric exclusion theory, when ions in electrolyte solution transfer from solution into a membrane it has to overcome an energy barrier. The magnitude of this energy barrier is mainly decided by the difference of dielectric constant between the membrane's and solution's or between different layers' in a membrane, and can be calculated from the Born effect [18], which may be expressed in terms of its latest form [59]:

$$\Delta G^{el} = \frac{z^2 e^2}{8\pi\varepsilon_0 a}(\frac{1}{\varepsilon_m} - \frac{1}{\varepsilon_w}) - \frac{z^2 e^2}{4\pi\varepsilon_0\varepsilon_m d}\ln(\frac{2\varepsilon_w}{\varepsilon_m + \varepsilon_w}) \qquad (12)$$

where ΔG^{el} denotes the energy barrier, a is the hydration radii of ion, ε_m and ε_w are the membrane's and solution's dielectric constant, respectively, which can be calculated from the capacitances of membrane and solution that derived from dielectric analysis, and the following relations: $\varepsilon_m = C_m(d/S\varepsilon_0)$ and $\varepsilon_w = C_w(L/S\varepsilon_0)$ (where d is the thickness of swollen membrane and L/S is the cell constant), z and e are valence of electrolyte solution and electric unit charge, respectively. According to Eq. (12), it can be predicted that the energy barrier would increase with increasing difference in dielectric constant between the membrane and the solution, and with increasing valence of the ions. Now, this theoretical prediction has been proved by the results of dielectric analysis on NF membrane/solution systems. Therefore, dielectric analysis method is not only able to explore the structure of membrane and the distribution of ions in membrane, but also able to help in essentially understanding the reason for the permeation and permselectivity of membrane, the understanding of the permeation and permselectivity from a microscopic viewpoint being closely related to the rejection in the nanofiltration and reverse osmosis processes.

4. Concluding remarks

For more details of the content in section 2 and 3, please refer to corresponding references. Evidently, the dielectric analysis method based on appropriate dielectric models in combination with basic membrane permeation theories is able to quantitatively determine many parameters that characterize the system under study. These parameters, generally speaking, would not be

obtained unless more than one physical method and many instruments were applied to a system. This indicates that DS method is unique and effective in obtaining the inner information of membrane systems, especially in in-situ charactering them under working conditions. The applicability of DS method to membrane/solution system has been validated theoretically, and a great number of works including the examples particularized above have proved that the key point to obtain more inner information about the system under study is analyzing dielectric spectra based on appropriate dielectric models, i.e. dielectric analysis.

A further development of DS method in its application to the characterization of membrane systems mainly relies on the progress of both of the following two aspects. One is the improvement of dielectric measurement method and measurement system design, where there is a large exploiting space. A more precise measurement is definitely the prerequisite of a more successful application. The other one is the improvement of dielectric theories, models, and analysis methods. In this regard, dielectric theories and models are deserved to be applied to more actual membrane systems, and then to improve these dielectric models according to the real properties of various actual systems, namely to make them more applicable to corresponding actual systems. As for the improvement on dielectric models, now what can be expected is, that the information that is more approaching to actual material separation processes could be obtained, if the geometrical factors of the pores in membrane and the dielectric constant difference between bound water and bulk water in the pores would be taken into account when set up dielectric models [20,21,59], because these factors are more accordant with the inner structure of actual membrane systems. Such a strict physical model, however, will enormously complicate mathematical processing. Although the development of computer fitting method has made more perfect curve-fitting to be possible, the increasing numbers of variable certainly will bring on the increase of fitting uncertainty, which doubtlessly is the biggest challenge in quantitative dielectric analysis.

Due to the limited pages, this chapter only introduces the applicability of DS method in polymer membrane/solution systems, and the examples are limited to ion-exchange membrane, dipolar membrane, reverse osmosis membrane, and nanofiltration membrane. There is no doubt that fundamental research on the performing processes of all kinds of membranes is of great interest and significance, however deeper investigations on these processes are generally very complicated because a variety of background knowledge is involved in these processes. Therefore, it is definitely not a matter of membrane science itself to essentially resolve all fundamental problems of the field of membrane and then to benefit the application of functional membranes from them. In this connection, it is bound to be a tendency to combine many

other disciplines, especially colloid and interface science, into membrane science. Obviously, the further application of DS method in the field of membrane will confront big challenges, while multidisciplinary cooperation, at the same time, will provide large room for this application to development. The future for the application of DS method in membrane system appears to be unlimited, and it is particularly worthy of expectation, that DS method would be applied to more actual membrane systems and hence to gain more valuable information through dielectric analysis, as well as that it could be applied to the real time monitoring of actual material separation processes so as to provide direct evidence on the separation mechanism.

At the end of this chapter, we would like to point out that, the present review has omitted the part of dielectric measurement, which, nevertheless, does not mean that dielectric measurement itself (experimentally) is easy to carry out. In fact, an accumulation of many aspects of experience including the design of the measurement cell and measurement system is a prerequisite to obtain desirable data. In addition, we also would like to point out that, although the present review is mainly focused on the models and analysis methods established by the author's and Hanai's group, we do not mean to undervalue the significance and importance of other researchers' works. Readers may find a great number of enlightening original papers or reviews about the studies on membrane systems by using DS (or IS) method, from publications on membrane or colloidal and interface science and from the references introduced in this chapter, among which the review of Coster *et al.* [16] is particularly noteworthy.

Acknowledgment

Appendix

For a membrane/solution system including a layer with locally varying conductivity and dielectric constant, such as the one with a porous support layer filled with solution, the integral expression for the complex impedance of such a heterogeneous layer is as follows [47]:

$$Z_{\mathrm{p}}^{*}(f)S = \frac{1}{G_{\mathrm{p}}^{*}(f)}S = \int_{0}^{t}\frac{\kappa_{x}}{\kappa_{x}^{2}+\left(\omega\varepsilon_{0}\varepsilon_{x}\right)^{2}}dx - j\int_{0}^{t}\frac{\omega\varepsilon_{0}\varepsilon_{x}}{\kappa_{x}^{2}+\left(\omega\varepsilon_{0}\varepsilon_{x}\right)^{2}}dx = I_{1}-jI_{2} \qquad \text{(A-1)}$$

where

$$I_1 = \frac{\Delta \kappa}{2tA} \ln(\frac{A}{C}t^2 + \frac{B}{C}t + 1)$$

$$+ \frac{\kappa_\alpha/A - \Delta\kappa_\beta/2A^2 t}{\sqrt{C/A - (B/2A)^2}} [arctg \frac{t + B/2A}{\sqrt{C/A - (B/2A)^2}} - arctg \frac{B/2A}{\sqrt{C/A - (B/2A)^2}}]$$

(A-2)

where

$$I_2 = \frac{\omega\varepsilon_0\Delta\varepsilon}{2tA} \ln(\frac{A}{C}t^2 + \frac{B}{C}t + 1)$$

$$+ \frac{\omega\varepsilon_0\varepsilon_\alpha/A - \omega\varepsilon_0\Delta\varepsilon B/2A^2 t}{\sqrt{C/A - (B/2A)^2}} [arctg \frac{t + B/2A}{\sqrt{C/A - (B/2A)^2}} - arctg \frac{B/2A}{\sqrt{C/A - (B/2A)^2}}]$$

(A-3)

where

$$A = (\Delta\kappa/t)^2 + \omega^2\varepsilon_0^2(\Delta\varepsilon/t)^2$$

(A-4)

$$B = 2\kappa_\alpha\Delta\kappa/t + \omega^2\varepsilon_0^2 2\varepsilon_\alpha\Delta\varepsilon/t$$

(A-5)

$$C = \kappa_\alpha^2 + \omega^2\varepsilon_0^2\varepsilon_\alpha^2$$

(A-6)

List of symbols

a [m]	hydration radii of ion
C^* [F]	complex capacitance
C [F]	capacitance
C_l, C_{mid}, C_h [F]	limit capacitance at the plateaus in the high-, middle-, and low-frequency range, respectively
C_a^*, C_b^* [F]	complex capacitance of electrolyte solution on either side of the membrane

C_m^* [F]	complex capacitance of the membrane
$c_{M^+}^m$, $c_{A^-}^m$, $c_{H^+}^m$ [mol/m^3]	concentration of cation, anion, and proton in the membrane, respectively
d [m]	thickness of the membrane phase
$e = 1.602 \times 10^{-19}$ [C]	electric unit charge
$F = 96485.34$ [C/mol]	Faraday constant
G [S]	conductance
G_l, G_{mid}, G_h [S]	limit conductance at the plateaus in the high-, middle-, and low-frequency range, respectively
j	imaginary unit ($\sqrt{-1}$)
l [m]	length of the whole membrane/solution system, equal to the distance between both electrodes
S [m^2]	electrode surface area
t [m]	thickness of the concentration polarization phase p
$U_{M^+}^m$, $U_{A^-}^m$, $U_{H^+}^m$ [m/N/s]	mobility of cation, anion, and proton in the membrane, respectively
z	valence of electrolyte solution
ε^*	complex dielectric constant, complex permittivity
ε_a^*, ε_m^*	complex dielectric constant of, respectively, the electrolyte solution and membrane
ε	dielectric constant, relative permittivity
ε_i	dielectric constant of phase i for multiphase systems, $i = m, w..., m$ denoting membrane phase, w denoting water phase, etc.
$\Delta \varepsilon_i$	relaxation intensity of the ith dielectric relaxation
ε_α, ε_β	dielectric constant of a phase with varied dielectric constant at a side near the phase

	with, respectively, higher and lower dielectric constant
ε''	dielectric loss, the imaginary part of complex permittivity
$\varepsilon_0 = 8.854 \times 10^{-12} [\text{F/m}]$	dielectric constant of vacuum
κ [S/m]	electrical conductivity
κ_i [S/m]	conductivity of phase i for multiphase systems
κ_α, κ_β [S/m]	conductivity of the concentration polarization phase at a side, respectively, near and far from the membrane
ω [rad/s]	angular frequency given by $\omega = 2\pi f$, where f denotes frequency (sec^{-1})
Φ	volume fraction of the membrane given by $\Phi = d / l$
τ [s]	characteristic relaxation time, given by $\tau = 1/2\pi f_0$, where f_0 is characteristic relaxation frequency
$\beta = 1 - \alpha$	Cole-Cole parameter denoting the time distribution of a dielectric relaxation

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