



# Ionic conductivity threshold in sulfonated poly (phenylene oxide) matrices: a combination of three-phase model and percolation theory

Xu Tongwen<sup>a,\*</sup>, Yang Weihua<sup>a</sup>, He Binglin<sup>b</sup>

<sup>a</sup>Department of Applied Chemistry, University of Science and Technology of China, Hefei 230026, China

<sup>b</sup>The State Key Laboratory of Functional Polymer Materials for Adsorption and Separation, Nankai University, Tianjin 300071, China

Received 4 July 2000; received in revised form 9 March 2001; accepted 28 May 2001

## Abstract

In this paper, both the percolation theory and the three-phase model (TPM) are employed to study the ionic transport behavior in sulfonated poly(phenylene oxide) (SPPO) series membranes. The conductive fraction was obtained from TPM, which had considered contributions of both the functional group and the neutral electrolytes impregnated in the polymer gel. The critical threshold at which the ions can be transported through the membrane or the membrane transit from insulator to a conductor, was calculated by the experimental data of membrane conductivities with different sulfonation degrees. The results showed that the threshold changed slightly from 0.14 to 0.19 when the concentration ranges from 0.01 to 0.1. Since the threshold is mainly determined by the active group zone and distribution, so a geometrically average value 0.16 is reasonably assumed here. This assumption coincides with the TPM which states that inter-gel fraction is not related with external concentration but related with the membrane properties. This experimental threshold is a little greater than the ideal value of 0.15 for a complete random system, suggesting that these ion cluster phases containing functional groups are not randomly dispersed in a practical SPPO membrane. If contribution of inter-gel is not considered, we will get a slightly larger value 0.18 as described in the previous paper. Therefore, a combination of TPM and percolation theory can bring us more precise information on ionic transport in SPPO matrices. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Poly (phenylene oxide) polymer; Ionic transfer; Ion exchange membrane; Percolation threshold; Three-phase model; Conductivity

## 1. Introduction

In recent years, one of the most important advances in separation science has been the development of ion exchange membranes. Such a membrane consists of a polymer network with positively or negatively charged groups (functional groups) anchored to it. The characterizations and applications of this kind of membrane have been well established in recent publications. However, few of them have reported the transport mechanism of the ions through an ion exchange membrane except for descriptions of the Nernst–Planck equation and non-equilibrium thermodynamics. In general, the transport of ions through an ion exchange membrane or a charged membrane is

controlled by two main factors (Dudek, Trochimczuk, & Wycisk, 1992). The first one is the interaction between the ions and the functional groups of the membrane and the second is the internal geometry of the membrane, which in many cases has a random fractal-like structure (Gefen, Aharony, & Alexander, 1983). This process is somewhat similar to the transport properties in a disordered medium. Thus, the concept of percolation theory often becomes a powerful tool for the description of such a process (Stauffer, 1985).

In this paper, we intend to study the transport characteristics of ions through a sulfonated poly (phenylene oxide) (SPPO) membrane. This kind of material possesses extraordinary electrochemical and mechanical properties and has been used widely in many industrial processes (Chludzinski, Austin, & Enos, 1971). Its unique transport characteristics is closely associated with a spontaneous

\* Corresponding author. Fax: +86-551-3601587.

E-mail address: twxu@ustc.edu.cn (X. Tongwen).

phase separation which occurs in hydrated SPPO polymer: the conductive aqueous phase due to sulfonation segregates into ion cluster phases containing functional groups which are dispersed in an insulating PPO matrix. Modern percolation theory is used in this paper to gain insight into the transport process occurring in this system and identify an ionic conductivity transition in such an SPPO membrane. Percolation theory was once used by Hsu, Barkley, and Meakin (1980) to discuss the analogous behavior of ion transport in a Nafion membrane. But they only considered volume fraction of aqueous phase in a given sample as the available conductive fraction (Hsu et al., 1980). In this paper, both the neutral electrolyte solution and functional group sites are considered as the available conductive sites. A three-phase model (TPM) will be used to estimate this conductive fraction. In addition, a very concise exposition of the most basic percolation concepts and results is provided and their utilities in transport of ions through an SPPO membrane system are evaluated based on the calculated conductive fraction.

## 2. Theoretical developments

### 2.1. Percolation concepts

Percolation theory derives its name from a problem in the study of flow through porous media (Stauffer, 1985). It differs essentially from diffusion. Percolation involves the movement of the permeate through the medium by ways of the relatively permeable pathways or pores, no matter how spongy, devious or small they are, while diffusion is regarding the movement of the molecules in both medium and permeate, and the pathways may be transient on a molecule scale. Percolation requires a statistically defined minimum fraction of open volume, which is to be distributed in concentrations and dimensions enough to allow for the desired transport. Diffusion does not have these limitations.

Percolation theory has been thoroughly investigated and extensively applied in explaining the movement of oil in subterranean structures as well as the electrical conductivity of mixtures of conductors and non-conductors.

Its salient features can be conveniently illustrated on a two-dimensional grid with some of its sites randomly occupied as shown in Figs. 1a–d. For our purpose, unoccupied (blank grids) and occupied sites (black grids) would correspond to the PPO matrix and the ion cluster phases containing functional groups and electrolyte solution, respectively. At low ion exchange capacities, i.e., low functional group concentrations, ion clusters are well separated into “islands” (cf. Fig. 1a), and thus macroscopic ion flow from one side of the grid to the other is impossible. At a higher exchange capacity, these “islands” grow in size and interconnect to form extended pathways (cf. Fig. 1b). However, crucial links (such as gray grids in Fig. 1b) are still missing here and there, thus, long range ion transport is still impossible. Eventually, above a threshold value of occupancy, some of these links have been filled to form conductive channels through which ions can now flow as shown in Fig. 1c. Therefore, an ionic insulator-to-conductor phase transition occurs at this threshold and simultaneously the average size of the extended pathways, which is the correlation length of our phase transition problem, becomes macroscopic. At even higher exchange capacities (cf. Fig. 1d), percolation channels crisscross the grid engulfing dead ends and fill the missing links, resulting in progressively higher conductivity. In this case, “isolated” ion clusters do not exist any longer.

The application of the percolation theory to diffusion problems was first used to describe the effective conductivity of composite materials (Stauffer, 1985). If we imagine a composite material composed of conducting sites (taking copper particles as an example) and non-conducting sites (particles of insulating material), it is easy to see that when a voltage is applied across such composite materials, current flows only between these sites occupied by the copper particles. There exists a limit volume fraction of conducting sites, i.e., percolation threshold, below which the composite acts as an insulator and above which it acts as a conductor. This threshold obeys the scaling law taking the form

$$\begin{aligned} \omega &= \omega_0(c - c_0)^\beta, & c > c_0, \\ \omega &= 0, & c \leq c_0, \end{aligned} \quad (1)$$

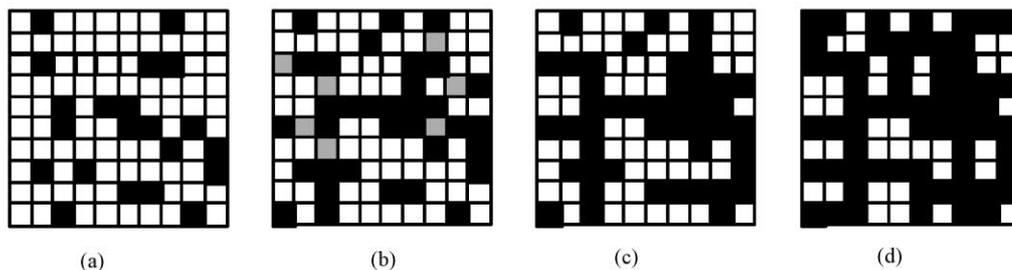


Fig. 1. A two-dimensional illustration for the concept of percolation: black areas—sites occupied; gray areas in (b)—to be occupied before the onset of ion transport.

where  $\omega$  is the relative conductivity and  $c$  is the volume fraction of conducting sites. The exponent  $\beta$  is a universal constant which depends only on spatial dimensions and is applicable to any percolation system regardless of its chemical, mechanical, structural morphological and statistical properties (Nelson, 1979). For a three-dimensional (3-D) system,  $\beta$  has been reported to range between 1.3 and 1.7 with 1.5 probably being the most reliable value (Kirkpatrick, 1973; Straley, 1977; Cohen, Jortner, & Webman, 1978). In contrast, the threshold volume fraction  $C_0$  depends on both the dimensionality and the manner in which the two components are dispersed (Straley, 1977; Cohen et al., 1978). For a 3-D continuous random system,  $C_0$  is 0.15 according to the previous investigations (Straley, 1977; Cohen et al., 1978; Scher & Zallen, 1970). However, it can be larger if ion clusters flocculate into several well-isolated regions (Cohen et al., 1978). Conversely, it may be smaller if they spread out into an extended network. Finally, the prefactor  $\omega_0$  depends on the details of the conduction mechanism and can only be computed from specific microscopic models. The important feature of our theory is that dimensional and topological information of cluster connectivity are contained in the factor  $(c - c_0)^\beta$ , whereas details of how ions move within a cluster have been separated out into the prefactor  $\omega_0$  which can be determined empirically.

## 2.2. Three-phase model (TPM)

A charged membrane has been considered as a micro-heterogeneous system. To theoretically describe such a system, many models have been proposed in the literature (Garba, Taha, Gondrexon, & Dorange, 1999; Bownen, Filipov, & Starov, 1999; Hsu & Kuo, 1999; Gnusin, Zabolotsky, Nikonenko, & Urtenow, 1986; Zabolotsky & Nikonenko, 1993). A typical one has been proposed by Gnusin et al. (1986) and developed by Zabolotsky and Nikonenko (1993). It is stated that the membrane was composed of two phases: one is named a “gel phase” with a relatively uniform distribution of ionogenic groups and hydrophilic parts of the matrix polymer chains impregnated with the charged solution compensating the charge of the fixed group and another is called as “inter-gel phase” with an electro-neutral solution filling the interstices between the elements of the “gel phase”. Starting from their microheterogeneous model, the membrane conductivity  $k_m$  was deduced as (Gnusin et al., 1986; Zabolotsky & Nikonenko, 1993; Elattar, Elmidaoui, Pismenskaia, Gavach, & Pourcelly, 1998):

$$k_m = (f_1 k_1^\alpha + f_2 k_2^\alpha)^{1/\alpha}, \quad (2)$$

where  $\alpha$  is a structural parameter, which reflects the reciprocal arrangement of the phase elements in the membrane (Dudek et al., 1992);  $f_1$  and  $f_2$  are the volume fractions

of the gel phase and the inter-gel phase, respectively;  $k_1$  and  $k_2$  are the conductivities of the gel phase (the active region) and the inter-gel phase (the interstitial region), respectively. Under the conditions of  $|\alpha| \ll 1$  (Gnusin et al., 1986; Zabolotsky & Nikonenko, 1993) and  $f_1 + f_2 = 1$ , Eq. (2) can be simplified as (Elattar et al., 1998):

$$k_m = k_1^{f_1} k_2^{f_2}. \quad (3)$$

Therefore, from this equation, linear regression can be achieved between  $\ln k_m$  and  $\ln k_2$ . We can easily acquire the volume fraction of the charged solution filling the interstices from the slope of the regressed lines.

When a charged membrane contains a volume fraction of inert phase, i.e., in the case that not all the polymer units are occupied by functional groups, Zabolotsky and Nikonenko (1993) used again the two-phase model by combining the pure gel phase (fixed group zone) and the inert phase (hydrophobic polymer) into a coherent region which can be considered as quasi-homogeneous and named “the joint-gel phase”. This “joint-gel phase” is characterized by volume fraction,

$$f_1 = f_{11} + f_{12}, \quad (4)$$

where  $f_{11}$  is the volume fraction of “the pure gel phase” free of inert inclusions and  $f_{12}$  “the inert phase”. Therefore, a charged membrane can be considered from the viewpoint of a TPM, where the membrane consists of hydrophobic polymer with a volume fraction  $f_{11}$ , an active ion exchange zone with a volume fraction  $f_{12}$  and an interstitial zone comprising neutral electrolyte solution with a volume fraction  $f_2$ .

## 2.3. Available conductive sites

For a practical charged membrane, its geometry can be modeled with the help of an  $n$ -dimensional lattice, where there are two kinds of lattice sites: conducting ones (available ones) and non-conducting ones (Hsu et al., 1980; Xu, Yang, & He, 1998). Following the above analyses, the conducting sites in a charged membrane, taking a membrane prepared from SPPO polymer as an example, correspond to both the active functional groups (i.e. the active gel phase) and the neutral electrolyte solution which have been filled between the matrices, i.e. the inter-gel phase, while the non-conducting sites imitate the unsulfonated PPO matrix, i.e. the inert polymeric phase. Therefore, the same behavior as the composite materials can be observed in a real charged membrane when a voltage is applied and there is a direct parallel relationship between the conductivity and the concentration of conductive sites. For an SPPO membrane, the sulfonation degree has a substantial effect on the volume of conductive sites, because it affects not only the volume fraction of active gel phase in the membrane but also the water content which is directly connected with the inter-gel phase. Following the composite materials, the

conductivity of an SPPO membrane can also be described by similar scaling law as Eq. (1) (Xu et al., 1998):

$$k_m = k_0(f_c - f_0)^\beta, \quad f_c > f_0, \\ k = 0, \quad f_c \leq f_0, \quad (5)$$

where  $f_c$  and  $f_0$  are, respectively, the total conductive fraction and threshold conductive fractions in an SPPO membrane. Following the above analyses,  $f_c$  will include two parts: the “pure-gel phase” partly in “joint-gel phase”  $f_{11}$  and the “inter-gel phase”  $f_2$ . Eq. (5) elucidates that percolation phenomena exist in an SPPO membrane. The threshold fraction of conductive sites will be calculated in this paper in accordance with the percolation parameters and concepts, and from which the threshold sulfonation degree will be determined. In addition, this method can also be applied in the investigations of other charged membrane systems that are now used in different industrial operations, such as ultrafiltration, nanofiltration and electro dialysis.

### 3. Experimental

#### 3.1. Materials and reagents

Poly (phenylene oxide) (PPO) of intrinsic viscosity equal to 0.53 dl/g in chloroform at 25°C was imported from Asash Co., Japan. Chloroform, Chlorosulfonic acid and N,N-dimethyl-formamide (DMF) are all analytical reagents and used as received.

#### 3.2. Sulfonation of PPO (Huang & Kim, 1984)

PPO was stirred at room temperature for 0.5–1.0 h with a solvent of chloroform to form an 8% solution. Prior to PPO sulfonation, the small quantity of sulfonable materials (ethanol and water) in the solution was determined and removed by neutralization with additional chlorosulfonic acid. The PPO batches were then sulfonated by adding proper amount of chlorosulfonic acid. The products were in liquor form at low sulfonation degree or precipitated from the solutions at high sulfonation degree. Then, the liquors were stored for use and the precipitated polymers were washed with distilled water and dried at room temperature. If sodium form is preferred, SPPO with hydrogen form is allowed to make contact with an aqueous salt, preferably a base solution such as sodium or a potassium hydroxide solution. After equilibrating the polymer with the solution, the solid is rinsed with distilled water to remove the excess electrolytes and dried in use.

#### 3.3. Preparation of SPPO membranes

An SPPO polymer in sodium form was exhaustively dried for at least 2 days at 50°C in vacuum state. It was then dissolved in DMF to form a casting solution of about

15 wt% and cast onto a glass plate to form a film of 0.2 mm dried thickness (if at low sulfonation degree, the above reaction liquors were directly cast onto a glass plate). This film was dried for a minimum of 2 h under cover and kept overnight without cover at ambient conditions. The dried membrane was removed from the glass plate and stored wet in a 10 wt% NaCl aqueous solution.

#### 3.4. Determination of sulfonation degree of SPPO (Kruczek & Matsuura, 1998)

Sulfonation degree ( $x$ ) was defined as the molar ratio of sulfonated units to the total basic units and calculated from the ion exchange capacity (IEC) measurements.<sup>1</sup> The IEC of SPPO was determined by the acid–base back titration with phenolphthalein as an indicator.

#### 3.5. Determination of the specific conductivity of the membranes

Membrane conductivities were calculated from membrane impedance measurements which was determined by a fast a.c. technique with high frequencies (> 104 Hz) as reported in the literature (Mo & Liu, 1986). The experiments were carried out for solution concentrations ranging from 0.01 to 0.10 M at 25°C.

#### 3.6. Water content

The water content ( $W_R$ ) was determined after equilibrating a sample of membrane in sodium ion with deionized water at room temperature. The membrane samples were removed from water and weighed immediately after blotting the free surface water. Then they were dried in vacuum state for at least 24 h at  $60 \pm 5^\circ\text{C}$ . The water content was deduced from the difference in weight between the wet ( $W_1$ ) and the dry ( $W_2$ ) membrane in unit  $\text{g H}_2\text{O g}^{-1}$  wet membrane (in the form of sodium) based on the following formula.

$$W_R = (W_1 - W_2)/W_1. \quad (6)$$

#### 3.7. Measurement of film density (Kruczek & Matsuura, 1998)

The density of polymeric films was determined by comparing the weight of the polymer films in air and in a non-swelling liquid–water. Experiments were conducted using a 10 ml hydrometer flask and the density  $\rho_p$  was

<sup>1</sup>  $x = \text{IEC}/1000 / ((1 - M_{\text{SPPO}} \times \text{IEC}/1000) / M_{\text{PPO}} + \text{IEC}/1000)$ , where IEC is in unit:  $\text{meq g}^{-1}$  dry sodium polymer and  $M_{\text{SPPO}}$  and  $M_{\text{PPO}}$  denote the molecular weight of SPPO (Na form) and PPO, respectively.

calculated from the following equation:

$$\rho_p = \frac{(H_3 - H_1)\rho_L}{(H_2 - H_1) - (H_4 - H_3)}, \quad (7)$$

where  $H_1$  is the weight of flask,  $H_2$  the weight of flask + water,  $H_3$  the weight of flask + polymeric film,  $H_4$  the weight of flask + water + polymeric film and  $\rho_L$  the density of water.

## 4. Results and discussion

### 4.1. Determination of available conductive sites

The conventional measurements of the tested membrane samples were collected in Table 1 except that their conductivities versus the concentration of solution are depicted in Fig. 2. It can be clearly seen that samples with low sulfonation exhibit very poor wettability (or low water content) and low electrical conductivity. On the contrary, samples with high sulfonation degrees give very good wettability and high conductivity. A sharp jump for the conductivities is also observed in the considered samples.

As mentioned above, the fraction of the available conductive sites in an SPPO  $f_c$  in Eq. (5) contains two sides: the “pure-gel phase” part in “joint-gel phase”  $f_{11}$  and the “inter-gel phase”  $f_2$ , which, respectively, represent the contributions of functional group and the contained electrolyte solution to the membrane conductivity. Here, we will use two steps to calculate the total conductive fraction. Firstly, Eq. (3) is used to estimate  $f_1$  and  $f_2$  from the conductivity measurements at different solutions. Then we evaluate  $f_{11}$  from IEC measurements.

To evaluate these parameters, Fig. 2 was replotted in ln–ln coordinates as shown in Fig. 3. The approximately linear relationship between  $\ln k_m$  and  $\ln k_2$  effectively shows that the theoretical approach agrees with the experiment. The slopes of this dependence give the volume fraction of the inter-gel phase  $f_2$  whose values are collected in Table 2. The value of the volume fraction of

joint-gel phase can thus be calculated ( $f_1 = 1 - f_2$ ). As previously mentioned, for a practical SPPO membrane, the sulfonated groups or chains, which are conductive, will contribute to pure-gel phase, while the unsulfonated PPO units, which are almost insulating, contributed to inert gel phase. It can also be reasonably assumed that volume fraction of polymer chains will be proportional to the number of their units and thus based on the definition of the sulfonation degree  $x$  (which is defined as the molar ratio of sulfonated units to the total basic units in the polymer chains, cf. Section 3.4). We can easily obtain that the volume fraction of pure-gel phase is equal to the sulfonation degree multiplied by the total joint-phase, i.e.  $f_{11} = x f_1$ . Thus, fraction of the total available conductive sites can be finally decided and collected in Table 2.

To check the validity of this method further, the values of  $f_1$  has also been calculated from the magnitudes of the intersection  $K$ . Based on Eq. (3),  $K = f_1 \ln k_1$ . We can substitute  $\ln k_1$  at one point into the formula to get  $f_1$  value. Of course, point of interest is the iso-conductance point at which the conductivities of membrane and the solution are equal, i.e.  $k_m = k_1 = k_2 = k_{\text{iso}}$ .  $k_{\text{iso}}$  can be easily obtained from the intercept of curves drawn in  $k_m - C$ ,  $k_2 - C$  coordinates (Fig. 2) or from  $\ln k_m - \ln k_2$  dependence (Fig. 3), which are accumulated in Table 2 for different membrane samples. Obviously,  $f_1$  values obtained in this manner are quite similar to those directly calculated from the formula  $f_1 = 1 - f_2$ .

In addition, the volume fraction of inter-gel phase,  $f_2$ , can also be simply calculated from the measurements of water content and polymer density as shown in Table 1. Values of  $f_2$  for different samples determined in this manner were shown in Table 2. It is observed that at low sulfonation region, values calculated from TPM and calculated from densities are almost consistent. A slight deviation exists in a relatively high sulfonation degree region. It should be emphasized, however, that the weight of film in a non-swelling liquid required for determination of experimental density was measured in water. An increase in IEC results in an increase of the hydrophilicity

Table 1  
The preliminary properties of the considered membrane samples

Membrane samples	Membrane thickness (mm)	IEC meq g <sup>-1</sup> dry membrane	Sulfonation degree	Water cont. g H <sub>2</sub> O g <sup>-1</sup> wet membrane	Density, g cm <sup>-3</sup>	Conductivity $k^a$ (μs cm <sup>-1</sup> )
M1	0.05	0.029	0.003	0.048	1.01	0.001
M2	0.06	0.037	0.004	0.068	1.01	0.001
M3	0.07	0.54	0.069	0.14	1.02	0.007
M4	0.07	1.07	0.144	0.22	1.10	1591.7
M5	0.08	1.14	0.155	0.24	1.12	1860.5
M6	0.10	1.19	0.163	0.29	1.14	2295.5
M7	0.10	1.35	0.188	0.46	1.15	6562.4
M8	0.10	1.92	0.287	0.69	1.16	15204.4

<sup>a</sup>Calculated from impedance measurements when the samples were equilibrated with 0.1 M NaCl.

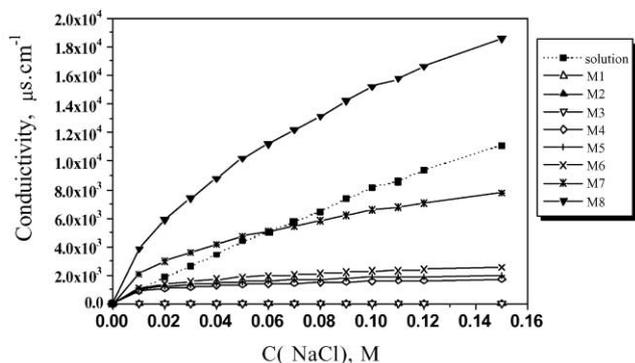


Fig. 2. Electroconductivity of the SPPO membranes in contact with NaCl salt solutions.

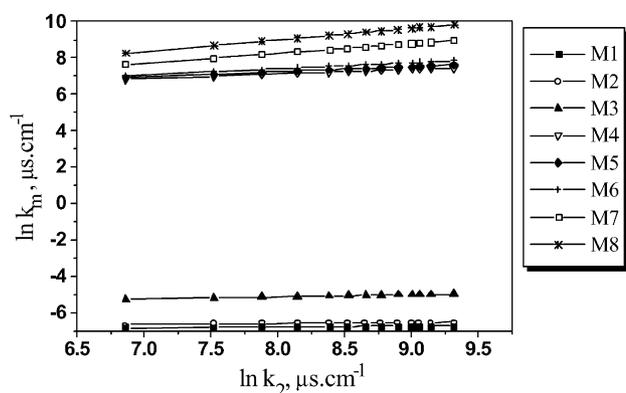


Fig. 3. ln–ln plots between the conductivities of the membranes and the external solution.

of polymer. Consequently, more water can penetrate into sulfonated polymer chains, thus increasing the apparent weight of the sample in water, and hence resulting in the inaccuracy of the experimental density at high sulfonation degree. It also should be stated that the data calculated from density are only based on the water content of membrane samples in pure water (cf. Section 3.6), while

the data calculated from TPM are based on the membrane conductivity in a concentration range from 0.01 to 0.1 M. Therefore, with the considerations of these factors and the results in the literature (Gnusin et al., 1986; Zabolotsky & Nikonenko, 1993; Elattar et al., 1998), it is stressed that data from TPM are close to the nature of the system investigated here and used in the following analysis.

#### 4.2. Determination of threshold in SPPO

To evaluate the threshold, conductivities of the membrane samples are depicted versus the total conductive fraction (Fig. 4). It is observed that there is an abrupt change in  $k_m - f_c$  curves for all considered concentrations at about  $f_c = 0.18$ . After this point, the conductivity of the membrane jumps abruptly from nearly zero (which is insulating for all practical purposes) to 1000 over. This implies that analogous percolation phenomena exist in an ion exchange membrane system. To precisely determine this threshold value, scaling law Eq. (5) is thus used. As mentioned above, the exponent  $\beta$  is a universal constant with 1.5 probably being the most reliable value, which does not change with the chemical, mechanical, structural, morphological and statistical properties (Nelson, 1979). Thus, a linear regression can be made between  $k_m^{2/3}$  and total conductive fraction  $f_c$  above the threshold to obtain  $k_0$  and  $f_0$  values. The regression conducted in this manner is plotted in Fig. 5 for different external solution concentrations (only three concentrations are shown for simplicity) and the results are accumulated in Table 3. Obviously, all the curves have good correlation factors above 0.99 (except 0.97 for  $c = 0.01$ ), implying that  $\beta = 1.5$  is suitable for the regressions. The percolation threshold  $f_0$  and the prefactor  $k_0$  are calculated from the interception and slope of these series regression lines are also collected in Table 3. It can be seen, for the concentration change from 0.01 to 0.1, that the threshold value is slightly changed from 0.14 to 0.19. This change is mainly

Table 2  
The evaluated parameters based on TPM

Membrane samples	$f_2$	$K$	$f_1 = 1 - f_2$	$f_c$	$k_{iso}^m$ ( $\mu\text{s cm}^{-1}$ )	$f_1^a$	$f_2^b$
M1	0.049	-7.169	0.951	0.052	0.0006	0.962	0.048
M2	0.062	-7.09	0.938	0.066	0.0006	0.945	0.068
M3	0.122	-6.10	0.878	0.182	0.001	0.892	0.142
M4	0.258	5.05	0.742	0.365	937.1	0.738	0.237
M5	0.282	4.99	0.718	0.393	1003.6	0.722	0.261
M6	0.332	4.75	0.668	0.441	1080.6	0.680	0.318
M7	0.532	4.00	0.468	0.620	5343.8	0.466	0.495
M8	0.642	3.85	0.358	0.745	33037.7	0.370	0.721

<sup>a</sup>Calculated from the slope  $K$  of  $\ln k_2 - \ln k_m$  curves as shown in Fig. 3.

<sup>b</sup>Calculated from water content.

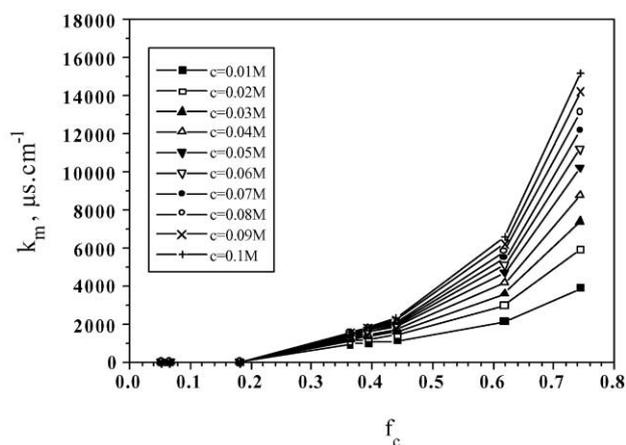


Fig. 4. Experimental conductivity values plotted against the total conductive fraction in the SPPO membranes in contact with different electrolyte concentrations.

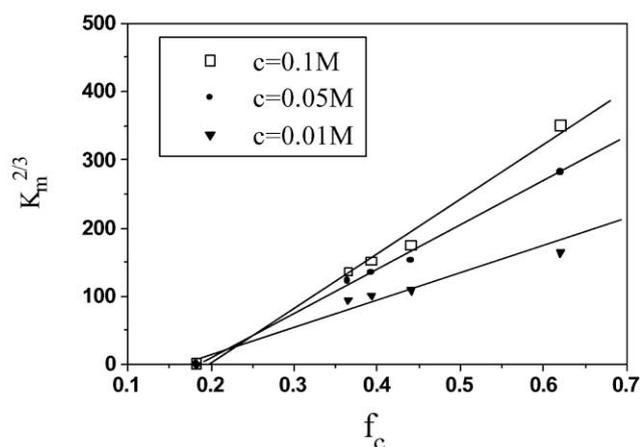


Fig. 5. Linear regressions between  $k_m^{2/3}$  and  $f_c$  for  $f_0$  and  $k_0$  under various external solution concentrations.

due to an increase in electrolyte concentration adsorbed in the membrane when an external concentration increases and thus an inter-gel phase contributes more to the conduction. In fact, the threshold is mainly determined by

the active group zone and distribution; so it is assumed here that the effect of external solution concentration is ignored. This assumption coincides with the TPM which states that inter-gel fraction  $f_2$  is not related with external concentration but related with the membrane properties. Therefore, with the consideration of the error possibly existing in the high sulfonation degree region (sulfonated membranes are easy to swell at this region), we assumed a value 0.16, which is geometrically averaged from the maximum value 0.19 and minimum value 0.14, as the experimental threshold for SPPO system. This value is a little greater than the ideal value of 0.15 for a complete random system, which suggests that these ion cluster phases containing functional groups are not randomly dispersed in a practical SPPO membrane. In our previous investigation, we obtained a threshold sulfonation degree value 0.067 (Xu et al., 1998). This sulfonation degree corresponds to the total conductive fraction  $f_c = 0.18$  based on the analysis in this paper (cf. Table 2, sample M3). This slight discrepancy of threshold in the same system is mainly because, in the previous calculation, the inter-gel zone has not been considered; so, the estimated threshold is larger than that in this paper. In fact, hydrophilicity of the membrane and the Donnan adsorption of salt ions, and many water-filled channels containing salt ions contribute to the ion cluster phases and thus to the conductivity. So, the determination of threshold based on TPM in this paper seems to be more precise.

### 5. Conclusions

The inter-gel zone, pure-gel zone and inert-gel phase are assumed and used to calculate the conductive fraction in an SPPO system. The percolative nature of the transport process, i.e. the conductivities of ions, and the importance of cluster connectivity as well as an ionic insulator-to-conductor transition has been identified for this series of membranes based on both TPM and percolation theory. The results showed that this system had

Table 3  
Regression results between  $f_c$  and  $k_m^{2/3}$

Concentration <i>M</i>	Slope	Intercept	Correlation factor	$k_0$	$f_0$
0.01	369.0	-54.0	0.979	7087.1	0.14
0.02	466.9	-76.3	0.993	10089.4	0.16
0.03	530.5	-91.1	0.996	12219.1	0.17
0.04	583.7	-103.8	0.997	14102.5	0.17
0.05	635.1	-116.1	0.997	16004.9	0.18
0.06	668.2	-124.1	0.997	17274.2	0.18
0.07	700.4	-132.0	0.996	18535.3	0.18
0.08	729.7	-139.2	0.995	19709.7	0.19
0.09	762.9	-147.4	0.995	21073.4	0.19
0.10	792.0	-154.6	0.994	22290.5	0.19

a threshold of about 0.16, which is a little greater than the ideal value of 0.15 for a complete random system, suggesting that these ion cluster phases containing functional groups are not randomly dispersed in a practical SPPO membrane. Compared with our previous studies, this value is a little less. This difference in threshold mainly results from a lack of consideration for the contribution of inter-gel to conductivity. In fact, this factor cannot be neglected because of the hydrophilicity of the membrane and the Donnan adsorption of salt ions. So, the determination of threshold based on TPM in this paper seems to be more precise and more conformable to practical processes.

A knowledge of the percolation threshold will be helpful for the design of an ion exchange membrane system with the proper conductivity. Percolation theory presented here is a very general one and can be expected to apply to other ionomeric systems as well.

### Acknowledgements

Tongwen Xu is grateful to the Japan Society for Promotion of Science and the financial support from the Natural Science Foundation of China (No. 29976040) for supporting his visit to the University of Tokyo. T.W. Xu is also indebted to Prof. S.-I. Nakao for his kind acceptance so that this manuscript can be prepared and revised in Tokyo University. Key Foundation of Educational Committee of Anhui Province (2000jl255zd), Natural Science Foundation of Anhui Province (99045431), the Foundation of Resources and Environments of University of Science and Technology of China and the Youth Foundation of USTC (1999) are gratefully acknowledged.

### References

- Bowern, W. R., Filipov, A. N., & Starov, V. M. (1999). A model of the interaction between a charged particle and a pore in a charged membrane surface. *Advances in Colloid and Interface Science*, 81(1), 35–72.
- Chludzinski, P. J., Austin, J. F., & Enos, J. F. (1971). Office of Saline Water Research and Development Progress Report No. 697. General-Electric Co., Lynn, MA.
- Cohen, M. H., Jortner, J., & Webman, I. (1978). Percolation conductivity in granular metal films. *Physics Review*, B17, 4555–4557.
- Dudek, M. R., Trochimeczuk, W. M., & Wycisk, R. (1992). Biased diffusion across ion-exchange membranes-percolation theory approach. *Journal of Membrane Science*, 67, 273–282.
- Elattar, A., Elmidaoui, A., Pismenskaia, N., Gavach, C., & Pourcelly, G. (1998). Comparison of transport properties of monovalent anions through anion-exchange membranes. *Journal of Membrane Science*, 143, 249–261.
- Garba, Y., Taha, S., Gondrexon, N., & Dorange, G. (1999). Ion transport modeling through nanofiltration membranes. *Journal of Membrane Science*, 160(2), 187–200.
- Gefen, Y., Aharony, A., & Alexander, S. (1983). Anomalous diffusion on percolating clusters. *Physics Review Letters*, 50, 77–80.
- Gnusin, N. P., Zabolotsky, V. I., Nikonenko, V. V., & Urtenow, M. R. (1986). Convective-diffusion model of electro-dialytic desalination. *Russian Journal of Electrochemistry*, 22, 273–277.
- Hsu, J. P., & Kuo, Y. C. (1999). Modified Gouy–Chapman theory for an ion-penetrable charged membrane. *Journal of Chemical Physics*, 111(10), 4807–4816.
- Hsu, W. Y., Barkley, J. R., & Meakin, P. (1980). Ion percolation and insulator-to-conductor transition in a Nafion<sup>1</sup> perfluorosulfonic acid. *Macromolecules*, 13, 198–200.
- Huang, R. Y. M., & Kim, J. J. (1984). Synthesis and transport properties of thin composite membranes. Synthesis of PPO polymer and its sulfonation. *Journal of Applied Polymer Science*, 29, 4017–4025.
- Kirkpatrick, S. (1973). Percolation and conduction. *Review of Modern Physics*, 45, 574–577.
- Kruczek, B., & Matsuura, T. (1998). Development and characterization of homogeneous membranes from high molecular weight sulfonated polyphenylene oxide. *Journal of Membrane Science*, 146, 263–275.
- Mo, J. X., & Liu, S. M. (1986). Determination of area resistance in an ion exchange membrane by a conductive electrode. *Technology of Water Treatment*, 12, 84–87 (in Chinese).
- Nelson, D. R. (1979). Recent developments in phase transitions and critical phenomena. *Nature*, 269, 379–383.
- Scher, H., & Zallen, R. (1970). Critical density in percolation processes. *Journal of Chemical Physics*, 53, 3759–3761.
- Stauffer, D. (1985). *Introduction to percolation theory*. London: Taylor and Francis.
- Straley, J. P. (1977). Critical exponents for the conductivity of random resistor lattices. *Physics Review*, B15, 5733–5737.
- Xu, T. W., Yang, W. H., & He, B. L. (1998). The insulator-to-conductor transition in SPPO polymer membranes: Percolation theory approach. *Chinese Journal of Chemical Engineering*, 6(4), 283–289.
- Zabolotsky, V. I., & Nikonenko, V. V. (1993). Effect of structural membrane inhomogeneity on transport properties. *Journal of Membrane Science*, 79, 181–198.