TRANSPORT OF IONS INSIDE POLYMER GEL IN AN ELECTRIC FIELD

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The transport of ions inside polymer gel in an electric field was investigated experimentally and theoretically using two kinds of nonionic gels of different bridge formation, containing electrolyte (salt) solution (Na_2SO_4 or KNO_3). The change of pH, concentration of salt and electric potential distribution inside the gel were measured. A mathematical model of diffusion and migration of ions was developed to predict the behavior of ions inside the gels in an electric field. Experimental results were well predicted by this model. The diffusion coefficients of ions inside the gels were also determined by fitting the results of calculation with experimental data, and the values were smaller than those in solution. It is considered that the decrease in diffusion coefficients in the gels depends on the tortuosity of diffusion path based on the tridimensional network structure of the gels. The tortuosities of polyacrylamide (PAcAm) and polyvinyl alcohol (PVA) gels were calculated as 2.8–3.1 and 2.5–2.6 respectively.

Introduction

There are some ionic polymer gels which swell or shrink in an electric field. It is considered that their properties are of great use in engineering fields, such as in switches, memories, mass exchange devices like water-absorbing and desorbing materials[9,10] and

mechanochemical transducers[11,12,13]. These gels can be used in liquid and/or in air. In liquid, such behavior of the gels is accompanied by mass exchange between outer solution and gel interior. Tanaka *et al.*[13] attributed the volume-phase transitions of an ionized polyacrylamide gel in water-acetone solvent in an electric field to electrostatic attraction between the positive electrode and negatively charged gel, leading to an imbalance of equilibrium swelling pressure.

Osada and Hasebe[8] tentatively ascribed the shrinking behavior of some ionic polymer gels to electrostatic interactions between electrode and gel. De Rossi *et al.*[3] attempted to interpret contractile phenomena of thermally crosslinked polyvinyl alcohol-polyacrylic acid gel in NaCl solution by mechanical rearrangement of the gel network caused by spatio-temporal pH gradients due to electrode reactions. Seida[10] *et al.* reported that the shrinkage occurs by both ion exchange between protons generated by electrode reaction at the anode and sodium ions dissociated from the ionic group in the gel and an increase of ionic strength on the cathode side. In the air, there is no mass exchange between gel interior and surrounding phase. Hirose *et al.*[6] reported the behavior of ions inside ionic and non-ionic gels in an electric field qualitatively and pointed out its significance in understanding the behavior of ions in developing these gels for engineering use. However, the kinetic behavior of ions inside gel in liquid and in air has not been published to date although they play a significant role in this phenomenon. In the present study, the transport process of freely mobile ions inside non-ionic polymer gels in an electric field were investigated experimentally and theoretically. There being no ionizable groups present in the polymer network, these gels show no drastic volume changes in response to stimulation and are chemically inactive. Therefore, non-ionic gel is useful for considering the influence of an electric field on the transport of ions on the basis of ionic valence, concentration and physical properties such as diffusion coefficients. The pH, salt concentration and electric potential distribution inside gels were measured. A mathematical model was developed to solve the transport process of ions numerically. The apparent diffusion coefficients of ions in the gel were estimated and compared with those in the solution.

1. Experimental

1.1 Sample preparation

Two kinds of gels were chosen as samples. One was polyacrylamide (PAcAm) gel having chemically bridged formation. This gel was synthesized by free-radical polymerization according to the following procedure. 4.569 g of acrylamide monomer (main component) and 0.150 g of N,N'-methylene-bis-acrylamide (crosslinking reagent) were dissolved in 50 ml of distilled water (Solution A). Solution B of an accelerator, N,N,N',N'-tetramethylethylenedi-amine (TEMED: 1.16 g), and solution C of an initiator, ammonium persulfate (1.71 g), were prepared in a manner similar to that for solution A. 14 ml of solution A was mixed with 2 ml of solution B and 4 ml of solution C. Polymerization took place in glass tubes ($d = 5.0 \times 10^{-3}$ m, $L = 3.0 \times 10^{-2}$ m) for one day at 298 K. The gels were immersed in a large amount
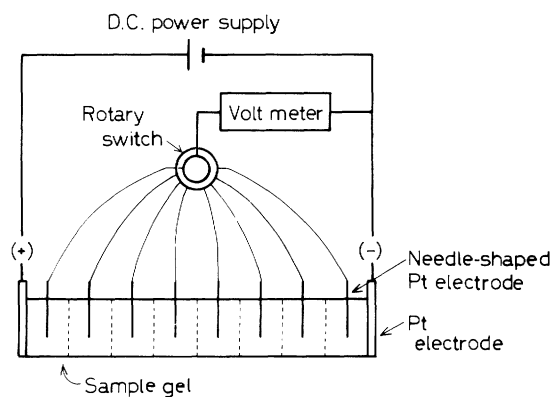
Fig. 1. Experimental Apparatus

of distilled water for two days at room temperature to remove unreacted substances in the gels. The other kind of gel was polyvinyl alcohol (PVA) gel having physically bridged formation (semi-crystalline structure)[7]. This gel was prepared in the following manner. 2 g of PVA (degree of polymerization: 2000; saponification value: 99.5 mol%) was dissolved in 16 g of distilled water. This solution was then mixed with 8 g of dimethyl sulfoxide. The pregel solution was frozen at 243 K for 6 hours in glass tubes and then slowly thawed at 298 K. The gels obtained were immersed in a large amount of distilled water for two days to remove unreacted substances.

These gels were washed and immersed in a large amount of concentrated salt (Na_2SO_4 or KNO_3) solution. The water contents of PAcAm and PVA gels were 95.4 wt% and 89.4 wt% respectively.

1.2 Apparatus and procedure

The experimental apparatus is shown in **Fig. 1**. A cylindrical gel containing electrolyte (salt) solution (Na_2SO_4, KNO_3) was placed between two platinum electrodes. A voltage of 10V was applied across the electrodes. The longitudinal distribution of electric potential in the gel was measured using eight needle-shaped platinum electrodes (Fig. 1). The platinum electrodes were set in the gel and measurements were carried out using a volt meter. The gel was cut in eight equal pieces soon after the experiment and the pH in each gel piece was measured using a needle-shaped pH electrode. After this procedure, the PAcAm gels were reserved in 4 ml of distilled water for two weeks, while the PVA gels were heated at 373 K for an hour to allow the gel to decompose into solution. These solutions were analyzed by atomic adsorption spectrometry and ICP plasma emission spectrochemical analysis to estimate the amount of cation (Na^+) and anion (SO_4^{2-}) in each piece of the gel.

2. Theoretical Analysis

We describe the transport model of freely mobile

ions inside a gel containing electrolyte (salt) solution as follows. Ions originating from the salt were initially distributed uniformly in the gel. When an electric potential was applied between the two Pt electrodes, cations migrate toward the cathode and anions toward the anode, resulting in an increase of cations at the cathode side and of anions at the anode side. The surplus or deficit charge can be compensated by taking up H^+ and OH^- ions generated by the electrode reaction to satisfy electrical neutrality. Thus the transport process in this system can be described by migration and diffusion of ions inside the gel[4]. The system equation can be written as

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + \frac{\partial}{\partial x}\left(u_i C_i \frac{\partial \phi}{\partial x}\right) + r_i \quad (i=1\text{--}4) \quad (1)$$

where the subscript 1: cation originated from the salt, 2: anion originated from the salt, and 3: H^+, 4: OH^-. D, u, ϕ and r are apparent diffusion coefficient, electrochemical mobility, electric potential and reaction rate respectively. The electrical neutrality can be written as Eq. (2). Since cation and anion originated from salt are chemically inactive and the net rate of charge generation in a homogeneous reaction must be zero, Eqs. (3) and (4) are obtained as follows.

$$\sum_{i=1}^{4} z_i C_i = 0 \quad (2)$$

$$r_1 = r_2 = 0 \quad (3)$$

$$\sum_{i=1}^{4} z_i r_i = 0 \quad (4)$$

The chemical equilibrium relation of water is

$$K_w = C_3 C_4 \quad (5)$$

Using initial concentration (C_0), applied electric potential (ϕ_0), gel length (L), and specific time (t_0) as the characteristic values respectively, Eq. (1) can be rewritten in dimensionless form as

$$\frac{\partial M_i}{\partial T} = P_{D_i} \frac{\partial^2 M_i}{\partial X^2} + P_{u_i} \frac{\partial}{\partial X}\left(M_i \frac{\partial \Phi}{\partial X}\right) + R_i \quad (i=1\text{--}4)(6)$$

where $M = C/C_0$, $T = t/t_0$, $X = x/L$, $\Phi = \phi/\phi_0$, $P_{D_i} = t_0 D_i/L^2$, $P_{u_i} = t_0 \phi_0 u_i/L^2$ and $R_i = r_i t_0/C_0$, are dimensionless number of concentration, time, length, electric potential, diffusion coefficient, electrochemical mobility and reaction rate, respectively. Eqs. (2) and (5) can be manipulated to yield

$$M_3 = \frac{2K'_w}{\theta + \sqrt{\theta^2 + 4K'_w}}, \quad \theta > 0$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (7)$$

$$M_3 = \frac{-\theta + \sqrt{\theta^2 + 4K'_w}}{2}, \quad \theta \leqq 0$$

$$\theta = z_1 M_1 + z_2 M_2, \quad K'_w = M_3 M_4$$

Multiplication of Eq. (6) by z_i and summing of the whole species with the help of Eq. (4) gives Eq. (8).

$$\sum_{i=1}^{4} z_i \left[P_{D_i} \frac{\partial^2 M_i}{\partial X^2} + P_{u_i} \frac{\partial}{\partial X}\left(M_i \frac{\partial \Phi}{\partial X}\right) - \frac{\partial M_i}{\partial T} \right] = 0 \quad (8)$$

Initial and boundary conditions can be written as

$$M_i = 1 \quad (T=0, 0<X<1)$$

$$N_i = 0 \quad (T>0, X=0 \text{ and } X=1) \quad (i=1,2) \quad (9)$$

The flux of chemically inactive species (N_i) is zero at the surface of the electrode (Eq. (9)). This system is described by Eqs. (6)–(9). These equations were rewritten in finite-difference form to solve them by the tridiagonal method[14]. The potential values at both ends of the gel $(\Phi_{X=0}, \Phi_{X=1})$ in computation were determined by the experimental measurements shown in Fig. 1. P_{u_i} was replaced by P_{D_i} using the Nernst-Einstein relation. In these equations, unknown parameters P_{D_1} and P_{D_2} were determined by fitting the results of calculation with experimental data. P_{D_3} and P_{D_4} were determined by Eq. (10).

$$P_{D_{i+2}\text{gel}} = P_{D_{i+2}\text{sol}} \times \frac{P_{D_i\text{gel}}}{P_{D_i\text{sol}}} \quad (i=1,2) \quad (10)$$

where the subscripts sol and gel denote aqueous solution and gel phase respectively. Equation (10) implies that the degree of decrease in diffusion coefficients of H^+ and OH^- ions in the gel was equivalent to those of the cation and the anion originated from the salt.

3. Results and Discussion

3.1 pH distribution

Figures 2 and 3 show the experimental and theoretical results of pH distribution at each time for PAcAm gel containing 10^{-2} M Na_2SO_4 (Fig. 2) and PVA gel containing 0.4×10^{-2} M Na_2SO_4 (Fig. 3), respectively. In both figures the ordinate represents the dimensionless length of the gel. The numbers in the open circles represent the pH obtained by experiment. When an electric potential was applied across the electrode (for example, 10V), the pH in the gel began changing from the electrode side to the center of the gel. The pH increased at the cathode side $(X=1.0)$, while it decreased at the anode side $(X=0.0)$. A steep pH gradient was formed at $X=0.6$ after about 10 minutes in both gels (see the profile of pH distribution in the case of PVA gel in Fig. 4). The theoretical pH distribution shows good agreement with experimental one.

3.2 Potential distribution

The dimensionless potential (Φ) distribution inside the PAcAm gel is shown in Fig. 5. The numbers in the open circles represent the values obtained by experiment. Initially, the potential distribution was
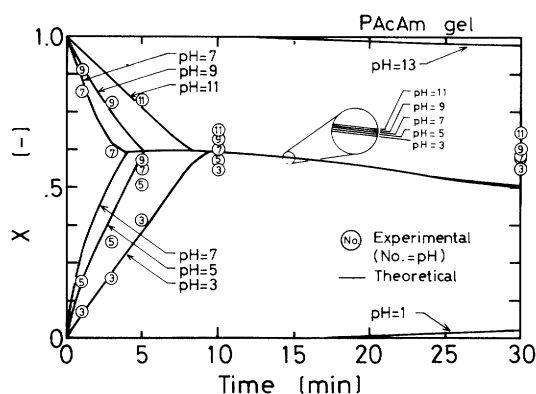
Fig. 2. Experimental and theoretical results of pH distribution inside gel in the case of PAcAm gel containing 10^{-2} M Na_2SO_4
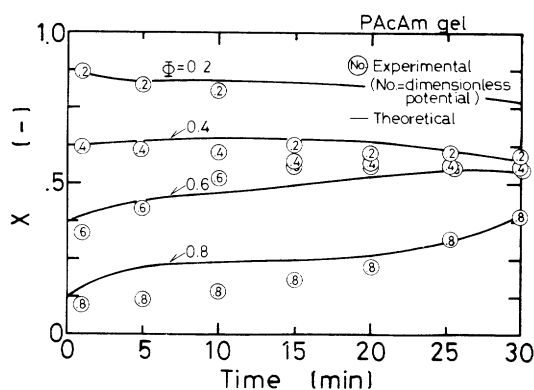

Fig. 3. Experimental and theoretical results of pH distribution inside gel in the case of PVA gel containing 0.4×10^{-2} M Na_2SO_4

Fig. 4. Distribution of pH and electric potential inside gel at (a) 10 and (b) 30 minutes

Fig. 5. Experimental and theoretical results of electric potential distribution inside gel in the case of PAcAm gel containing 10^{-2} M Na_2SO_4
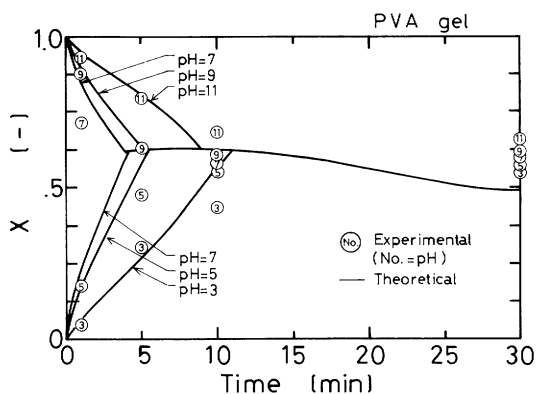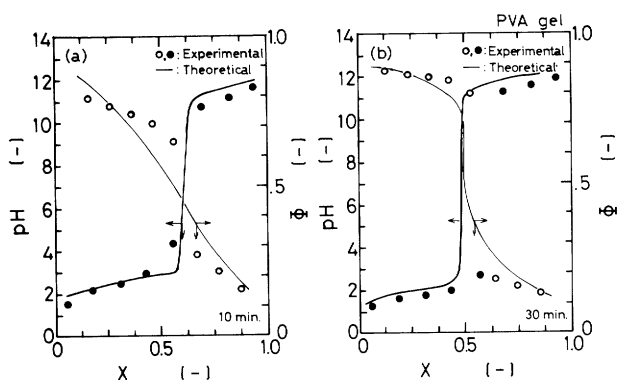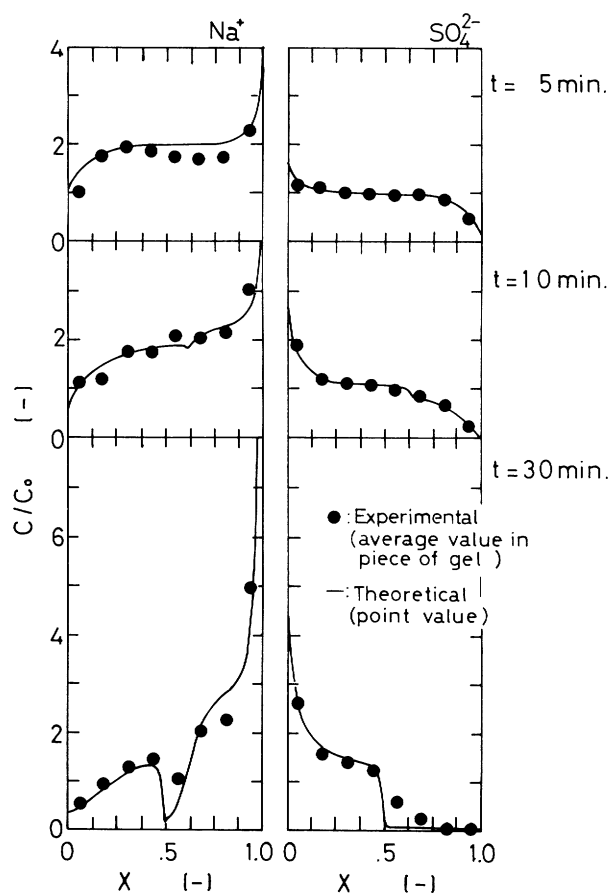

Fig. 6. Experimental and theoretical results of concentration distribution of ions inside gel in the case of PAcAm gel

linear. Once the electric potential was applied, a steep potential gradient was gradually formed with the lapse of time. The position of steepest potential gradient was the same as the steepest pH gradient shown in Figs. 4(a), (b). The steepest calculated potential gradient was established gradually compared with that shown by the experimental data in the initial stage (Fig. 4(a)). The experimental and theoretical changes of potential profiles in the case of PVA gel were similar

to those of PAcAm gel.

3.3 Concentration of salt

The amount of anion and cation originated from the salt in the PAcAm gel are shown in **Fig. 6**. The experimental results are represented in terms of average concentration in each piece of gel. The cation increased at the cathode side and decreased at the anode side with the lapse of time, while the anion behaved oppositely. The concentration of anion and cation at 30 minutes were decreased at the steepest

pH (potential) gradient formed. In calculation, the unknown parameters P_{D_1} and P_{D_2} were determined by curve-fitting of theoretical results (Fig. 6). The distributions of anion and cation on the basis of calculation predict the experimental data fairly well, showing the tendency of anion and cation to decrease at the steepest pH gradient formed.

3.4 Diffusion coefficient

The estimated diffusion coefficients of ions in the gel are tabulated in **Table 1**. The diffusion coefficients of ions in solution are also listed in the table[2]. The estimated values were somewhat small compared with those in solution. There exist some factors (tortuosity, constriction, retardation) which control the diffusion coefficient (mobility) of charged species in gel[1]. It is considered that the diffusion coefficients depend on the tortuosity because of the tridimensional network structure of the gel. The tortuosities of PAcAm and PVA gels were calculated in a manner[5] to yield 2.8–3.1 and 2.5–2.6 respectively.

3.5 pH distribution in the gel containing KNO$_3$

The change of pH distribution in the case of PAcAm gel containing 10^{-2} M KNO$_3$ was simulated to examine the validity of this model. The parameters P_{D_1} and P_{D_2} were determined in a similar way to those in the PAcAm gel containing 10^{-2} M Na$_2$SO$_4$ (Table 1). As the electrochemical mobility u_{K^+} is larger than $-u_{NO_3^-}$ (while $u_{Na^+} < -u_{SO_4^{2-}}$), cation migrates faster than anion in this system. The results are shown in **Fig. 7**, showing a tendency of pH distribution similar to that of gel containing Na$_2$SO$_4$. The simulated results agree well with experimental data.

From these results, this model was found to describe fairly well the pH, salt concentration and electric potential distribution inside the gel. This model is very useful for predicting the behavior of ions inside a gel in an electric field.

Conclusion

The transport process of ions inside a gel in an electric field was investigated experimentally and theoretically. A model based on the Nernst-Plank equations was developed to predict the behavior of ions inside the gel. This model was found to describe fairly well the pH, salt concentration and electric potential distribution inside the gel. The diffusion coefficients of ions inside gels were estimated by the method of curve-fitting of a theoretical curve. The estimated values were smaller than those for the aqueous solution. It is considered that the decrease in diffusion coefficients in the gel depends on the tortuosity of the diffusion path. The tortuosities of PAcAm and PVA gels were calculated as 2.8–3.1 and 2.5–2.6 respectively.

Table 1. Diffusion coefficients

Ion	$D_+ \times 10^9$ [m^2/s]		Ion	$D_- \times 10^9$ [m^2/s]	
	solution	gel		solution	gel
H$^+$	9.31	3.22 (PAcAm)	OH$^-$	5.26	1.59 (PAcAm)
	—	3.36 (PVA)		—	1.79 (PVA)
Na$^+$	1.33	0.46 (PAcAm)	SO$_4^{2-}$	1.06	0.32 (PAcAm)
	—	0.48 (PVA)		—	0.36 (PVA)
K$^+$	1.96	0.68	NO$_3^-$	1.90	0.57

Fig. 7. Results of simulation in the case of PAcAm gel containing 10^{-2} M KNO$_3$

Nomenclature

C	= concentration	[mol/m^3]
C_0	= initial concentration inside gel	[mol/m^3]
D	= diffusion coefficient	[m^2/s]
F	= Faraday's constant	[C/mol]
K_w	= dissociation constant of water	[mol^2/m^6]
K_w'	= dimensionless dissociation constant of water, K_w/C_0^2	[—]
L	= gel length	[m]
M	= dimensionless concentration, C/C_0	[—]
N	= mass flux	[mol/m$^2 \cdot$s]
P_D	= dimensionless diffusion coefficient, Dt_0/L^2	[—]
P_u	= dimensionless electrochemical mobility, $ut_0\phi_0/L^2$	[—]
r	= reaction rate	[mol/m$^3 \cdot$s]
R	= dimensionless reaction rate, t_0r/C_0	[—]
R	= gas constant	[volt$\cdot$C/mol$\cdot$K]
t	= time	[s]
t_0	= characteristic time	[s]
T	= dimensionless time, t/t_0	[—]
T_k	= absolute temperature	[K]
u	= electrochemical mobility	[m^2/volt$\cdot$s]
x	= coordinate along gel length	[m]
X	= dimensionless x coordinate, x/L	[—]
z	= valence	[—]
ϕ	= electric potential	[V]
ϕ_0	= applied potential difference	[V]
Φ	= dimensionless electric potential, ϕ/ϕ_0	[—]

<Subscript>

i	= species code
sol	= aquaous solution phase
gel	= gel phase

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