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# Swelling behavior of polyethylenimine–cobalt complex in water

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**Abstract**

Polyethylenimine (PEI) was cross-linked by polyepichlorohydrin (PECH) and the swelling behavior of cross-linked PEI–Co complex membranes in water was studied. The equilibrium swelling ratio of PEI–Co complex membranes is lower and the swelling rate is slower than that of cross-linked PEI membranes without cobalt ion complexation. Both the equilibrium swelling ratio and swelling rate of PEI–Co complex membranes increase with increasing the molar ratio of PEI to PECH. The equilibrium swelling ratio of PEI–Co complex membranes remains almost constant with the change of the membrane thickness or temperature. The diffusion mechanism of water through PEI–Co complex membranes was also discussed, and it is found that the diffusion of water primarily obeys Fickian's law, and the activation energy of diffusion is calculated to be 40.4 kJ/mol.


*Keywords:* Polyethylenimine–cobalt complex; Water; Swelling; Diffusion

## 1. Introduction

The sorption and diffusion of solvents in and through polymers has been widely investigated from both theoretical and technological points of view. From swelling properties of polymers, the diffusion coefficients of solvents through polymers and other parameters can be obtained, which show great importance to membranes, ion exchangers, etc. [1]. The transport properties of solvents through polymers depend on a number of factors, such as chemical structure of polymer, species of solvents, and temperature, etc. [2–6].

Franson investigated the effect of the composition of poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) (HEMA/MMA) and poly(2-hydroxyethyl methacrylate-co-*N*-vinyl-2-pyrrolidone) (HEMA/NVP) on the transport properties of water, indicating that the diffusion of water gradually deviates from Fickian's law with increasing the content of the hydrophilic component in co-polymers [7]. However, the swelling mechanism of hydrophilic polymers in water is complicated due to the strong interaction between hydrophilic polymers and water, such as hydrogen bonding [4]. Therefore, there are few reports about the sorption and diffusion of water in and through hydrophilic polymers.

Polyethylenimine–cobalt (PEI–Co) complex is one of the most familiar metal complexes with reversible oxygen-binding properties. PEI–Co

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complex that reversibly binds and releases oxygen in response to the oxygen concentration is the candidate for the oxygen-enriching material. Recently, Nishide and his coworkers reported that PEI–Co complex in aqueous electrolyte solutions efficiently acted as the oxygen-enriching material, and that the reduction current of oxygen at an electrode significantly increased in comparison with the control electrode without the cobalt complex. Furthermore, a cobalt complex with a cross-linked PEI can provide an insoluble and swellable oxygen-enriching membrane to modify the electrode surface, which can operate even in pure electrolyte solutions [8,9].

While PEI is a hydrophilic polymer [10] and a cross-linked PEI membrane is swellable in water. Karlsson found that the water content affected the oxygen transport in poly(vinyl alcohol), and the existence of water did favor to the oxygen transport [11]. Kucukpinar indicated that high water content results in a noticeable increase in the oxygen permeability of poly(ethylene-co-vinyl alcohol) [12]. Therefore, the swelling behavior of PEI–Co complex membranes in water is significantly important. This work mainly focuses on the equilibrium and dynamic swelling behavior of PEI–Co complexes in water, as well as factors that affect the swelling behavior. Diffusion mechanism of water through PEI–Co complex membranes was also investigated according to the swelling results, and the activation energy of diffusion was estimated.

## 2. Experimental

### 2.1. Materials

Polyethylenimine ($M_n = \sim 6 \times 10^4$, 50% aqueous solution) was obtained from Aldrich. Polyepichlorohydrin ($M_n = \sim 1.2 \times 10^5$) was supplied by Wuhan Chem. Co., and dissolved in benzene, then purified by precipitation using methanol. Cobalt chloride was of analytical pure, supplied by Shanghai Hengxin Chem. Co.

### 2.2. Preparation of cross-linked PEI membranes

A solution of PEI and PECH (2 g in total) in DMF (30 mL) was heated to 60 °C slowly to prevent gelation, and stirred for 3–4 h. The hot solution was casted on a glass plate and cross-linked at 110 °C for 2 h, followed by drying under vacuum for 20 h to afford the transparent membrane of the cross-linked PEI ligand [13]. Membranes with various molar ratio of PEI to PECH were prepared. The thickness of the resulting membrane was calculated based on the density of the polymer ($\sim$1 g cm$^{-3}$).

### 2.3. Preparation of PEI–Co complex membranes

PEI–Co complex membranes were prepared by immersing cross-linked PEI membranes into the aqueous saturated solution of cobalt chloride for a sufficiently long time (3 days) at room temperature. The resulting membrane was washed with deionized water, then dried under vacuum for 20 h.

### 2.4. Swelling measurements

Dynamic swelling measurements were made primarily by gravimetric method. The membrane was immersed in deionized water at various temperatures, then the swollen membrane was taken out at an appropriate time interval, and the water adhered to the surface of the membrane was removed with filter paper, and quickly weighed on a Mettler analytical balance (Model AL 204, accuracy 0.0001 g), and then replaced into the water immediately. This procedure was repeated until the sample attained constant weight. The swelling results were analyzed in terms of number of moles of water absorbed ($Q_t$ mol%) per 100 g of polymer [1,14]

$$Q_t = \frac{W_t - W_0}{M_R} \times \frac{100}{W_0} \qquad (1)$$

where $W_0$ and $W_t$ is the weight of PEI–Co complex membrane before and after swelling in water at time $t$, respectively, and $M_R$ is molar mass of water.

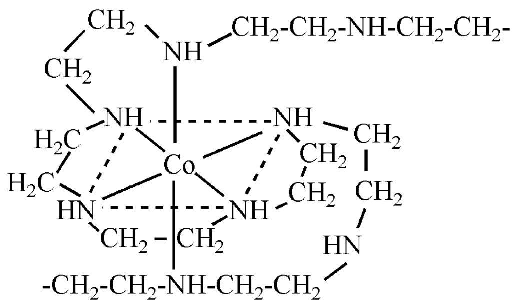
## 3. Results and discussion

### 3.1. Swelling behavior of PEI–Co complex membranes

As PEI is a hydrophilic polymer, a cobalt complex with a cross-linked PEI membrane can provide an insoluble and swellable oxygen-enriching membrane to modify the oxygen electrode that can operate even in pure electrolyte solutions. PEI membranes were prepared from DMF solution of PEI and PECH by casting and heating under nitrogen. The membrane has a cross-linked structure due to the reaction between secondary amino groups in PEI and chloromethyl groups in PECH. Cross-linked PEI membranes were extracted in methanol and benzene for a period of 48 h, respectively, to remove any uncross-linked molecules [13]. From the same weights of cross-linked PEI membranes before and after extraction, it indicates that almost all of the molecules have been cross-linked.

Cobalt ions were incorporated into the cross-linked PEI membrane by immersing the membrane in an aqueous saturated solution of cobalt chloride for 3 days. Swelling behavior of the PEI–Co complex membrane and PEI membrane without cobalt ion complexation in water was conducted for comparison. The change of the swelling ratio ($Q_t$) with time for both PEI and PEI–Co membranes in water is presented in Fig. 1. It is revealed that the swelling ratio for both PEI and PEI–Co membranes increased with time, and reached equilibrium after 20 min. During the swelling process, water penetrated into the cross-linked membranes and the volume of membranes expanded, resulting in the stretch of chain segments inside the cross-linking network. Meanwhile, cross-linking restricted the swelling of cross-linked membranes. Finally, the membranes in water reaches to the equilibrium swelling.

From Fig. 1, it is also found that the complexation of PEI with cobalt ions has a great effect on the swelling behavior. In comparison with that of the cross-linked PEI membrane, the equilibrium swelling ratio of the PEI–Co membrane is lower, and the time to reach the equilibrium swelling is longer, that is, the swelling rate decreases. After the complexation of imine groups in PEI with cobalt ions, the structure of PEI–Co complex is presented in Scheme 1 [8]. The complexation of PEI with cobalt ions will give additional cross-linking via donor–acceptor bonds along with the covalent cross-linking via PEI and PECH reaction so as to decrease the volume inside the network and swellability [15]. In addition, the hydrogen bonding between PEI and water is weakened owing to the complexation of PEI with cobalt ions [16]. These factors attribute to the decreases of the equilibrium swelling ratio of PEI–Co membranes in water, and of the swelling rate in comparison with PEI membranes.




Scheme 1. Structure of PEI–Co complex.

### 3.2. Effect of the composition on the swelling behavior of PEI–Co complex membranes

Although a larger feed ratio of PEI to PECH endowed membranes with a higher complexation capacity for cobalt ions, the mechanical properties of cross-linked PEI membranes decrease with the increase of the PEI content. The maximum molar ratio of PEI to PECH was reported to be 0.9 in considering the mechanical properties [13]. The effect of the molar ratio of PEI to PECH on the swelling behavior of PEI–Co complex membranes is presented in Fig. 2. From the figure, it is found that

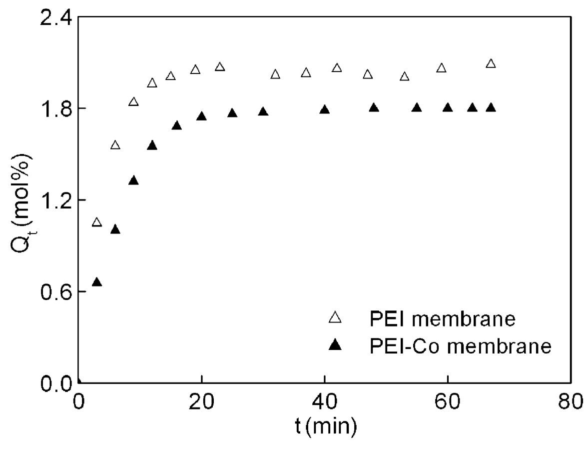



Fig. 1. Change of swelling ratios for PEI and PEI–Co membranes with time (molar ratio of PEI to PECH = 0.90).

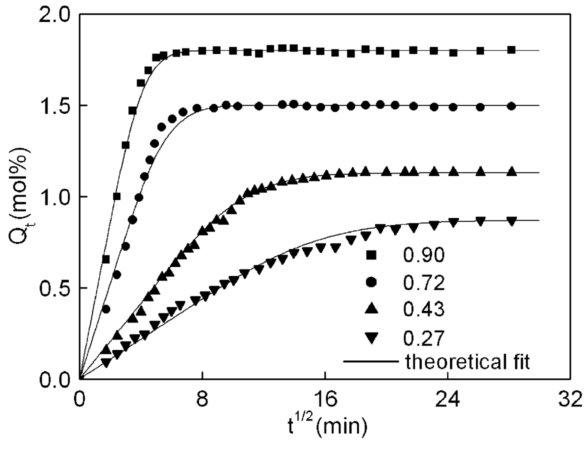



Fig. 2. Swelling behavior of PEI–Co complex membranes with various molar ratios of PEI to PECH.

increasing the PEI content increases not only the equilibrium swelling ratio of PEI–Co complex membranes in water, but also the swelling rate due to stronger intermolecular interactions between water and hydrophilic PEI.

In order to elucidate the mechanism of swelling, the experimental data (for a short time period or $Q_t/Q_\infty \leqslant 0.6$) was fitted into an empirical equation [14,17]

$$\frac{Q_t}{Q_\infty} = kt^n \quad (2)$$

where $Q_t$ and $Q_\infty$ are the solvent uptake (mol%) at time $t$ and at equilibrium, $k$ is a constant which depends both on the interaction between solvent and polymer and on the structure of polymer. The value of exponent $n$ gives an idea about the diffusion mechanism of solvent through polymer. If $n = 0.5$, the mechanism of swelling is termed as Fickian transport. This occurs when the diffusion rate of solvent is smaller than polymer segmental mobility. If the value of $n$ is not 0.5, then the transport is considered as non-Fickian, especially as case II transport for $n = 1$ and as anomalous transport for $n = 0.5$–1.0. For anomalous transport, the diffusion and relaxation rate are comparable.

For a flat sheet of a polymer membrane with uniform thickness and equal concentrations on both sides, according to Fickian's law the diffusion coefficient ($D$) can be calculated from the following equation [14,17]

$$Q_t/Q_\infty = 1 - 8/\pi^2 \sum_{n=0}^{n=\infty} \frac{1}{(2n+1)^2} \times \exp[-D(2n+1)^2\pi^2 t/h^2] \quad (3)$$

where $t$ is the time, $h$ is the initial thickness of the membrane, and $n$ is the integer ranging from 0 to $\infty$. For a short period of swelling, a modified short time expression can be used [1,14,17]

$$D = \pi(h\theta/4Q_\infty)^2 \quad (4)$$

where $\theta$ is the slope of the initial linear portion of the curve $Q_t$ versus $t^{1/2}$.

Table 1
Values of $n$, $k$ and $D$

| Molar ratio of PEI/PECH | 0.27 | 0.43 | 0.72 | 0.90 |
|---|---|---|---|---|
| $n$ | 0.52 | 0.56 | 0.59 | 0.61 |
| $k$ ($s^{-n}$) | 0.008 | 0.009 | 0.011 | 0.015 |
| $D$ ($cm^2/s$) | $7.3 \times 10^{-10}$ | $1.4 \times 10^{-9}$ | $4.2 \times 10^{-9}$ | $7.2 \times 10^{-9}$ |

The estimated values of $n$ and $k$ by regression analysis from the plot of $\lg(Q_t/Q_\infty)$ versus $\lg t$ are given in Table 1. The correlation coefficient is found to be 0.98. The values of $k$ increases with increasing the PEI content, indicating the faster swelling rate corresponding to the more hydrophilic content. The values of $n$ range from 0.52 to 0.61, suggesting that the mechanism of transport was close to Fickian for all samples. The values of $n$ increase with the increase of the hydrophilic content in the membranes, indicating that the diffusion of water gradually deviated from Fickian law. This behavior can be explained on the basis of the strong interaction between the hydrophilic component and water. Similar results have also been observed for HEMA/MMA and HEMA/NVP co-polymers by Franson and Peppas [7].

Estimated values of $D$ according to Eq. (4) are listed in Table 1. As we expected, the values of $D$ is found to be increasing with the increase of PEI content in PEI–Co complex membranes.

### 3.3. Effect of the membrane thickness on the swelling behavior of PEI–Co complex membranes

The effect of the membrane thickness on the swelling behavior of PEI–Co complex membranes in water was also studied (Fig. 3). From this figure, it is shown that the time to reach the equilibrium swelling becomes shorter with the decrease of the membrane thickness, whereas the ratio of equilibrium swelling remains unchanged.

The experimental diffusion results were compared with the theoretical predictions using Eq. (3). This equation clearly represents a Fickian mode of trans-

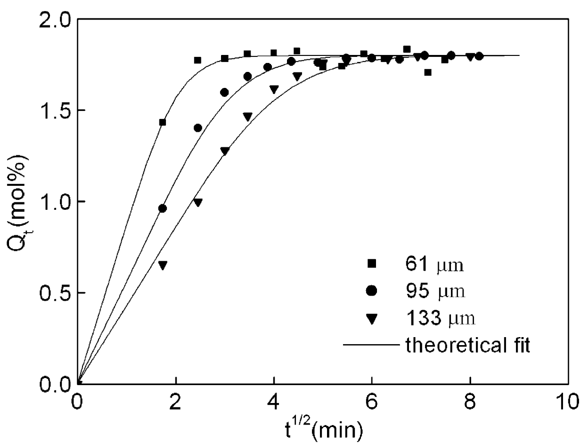



Fig. 3. Swelling behavior of PEI–Co complex membranes with various thickness (molar ratio of PEI to PECH = 0.90).

port. Experimental value of diffusion coefficient ($D = 7.2 \times 10^{-9}$ cm$^2$/s) at the same molar ratio of PEI to PECH is substituted into Eq. (3) to get theoretical curves of PEI–Co complex membranes with different thickness. The resulting curves are shown in Fig. 3. To the whole swelling process, all of the PEI–Co complex membranes with various thickness show fairly good agreement between experimental and theoretical diffusion profiles. This indicates that the system obeys a Fickian mode of transport.

### *3.4. Effect of temperature on the swelling behavior of PEI–Co complex membranes*

The effect of temperature on the swelling behavior varies significantly for different systems. George found that the ratio of equilibrium swelling of styrene–butadiene rubber membranes in *n*-octane increased with increasing temperature [14]. On the contrary, Graham pointed out that for cross-linked poly(ethylene glycol) urethane network in water the equilibrium swelling gradually decreases as the temperature is varied from 25 to 60 °C [18]. Lee and Chen investigated the swelling behavior of poly(2-hydroxyethyl methacrylate-co-3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate) gels in water, and found that the gels exhibited a minimum swelling ratio at 55 °C [19]. Swelling studies were conducted at 20, 40, and 60 °C and the results are presented in Fig. 4. It is obvious that the swelling rate of PEI–Co complex membranes in water increases with the increase of temperature. This is not surprising as diffusion rates increase with temperature. The ratio of equilibrium swelling is found to be almost constant with the change of temperature. When the temperature increased, the chain segments tend to move more easily and the free volume inside the network increased, meanwhile, the hydrogen bonding between PEI and water is weakened. Taken the two factors above into account, the ratio of equilibrium swelling does not change significantly with the variation of temperature [19].

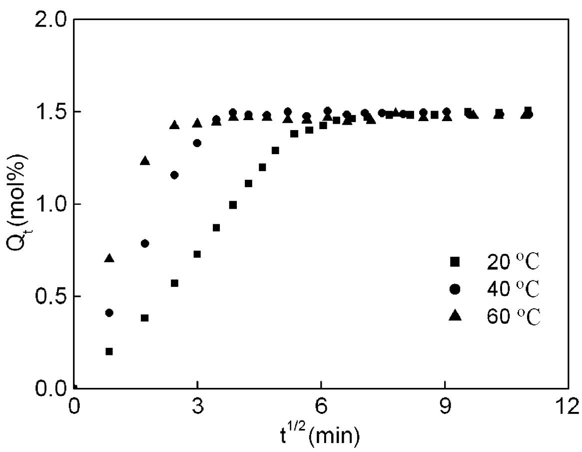



Fig. 4. Swelling behavior of PEI–Co complex membranes with various temperatures (molar ratio of PEI to PECH = 0.72).

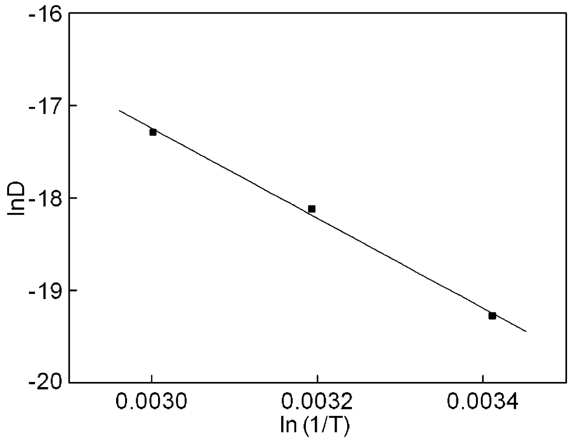



Fig. 5. Effect of temperature on the diffusion coefficient of water through PEI–Co complex membranes.

From the initial swelling data, the diffusion coefficient at various temperatures was obtained, and the activation energy of diffusion ($E_D$) was calculated from Arrhenius plot (Eq. (5)) of $\ln D$ against $\ln(1/T)$ [20]

$$D = D_0 \exp(-E_D/RT) \tag{5}$$

From Fig. 5, it is shown that $\ln D$ changes linearly with $\ln(1/T)$ and the correlation coefficient is 0.998, which indicates that the diffusion obeys Arrhenius's law and is temperature activated. The mobility of polymer segments is slower and the resistance to swelling is larger at lower temperature, while the mobility of polymer segments and water are enhanced so as to increase the diffusion coefficients at higher temperature. The activation energy of diffusion is calculated to be 40.4 kJ/mol from the slope of $\ln D$ versus $\ln 1/T$ curve.

## 4. Conclusions

Complexation of PEI with cobalt ions significantly influences the swelling behavior of the PEI–Co complex membranes in water. The equilibrium swelling ratio of PEI–Co complex membranes is lower than that of PEI membranes without cobalt ion complexation. Molar ratio of PEI to PECH, membrane thickness and temperature play important roles in the swelling behavior of PEI–Co complex membranes. As the PEI content increases in PEI–Co complex membranes, both the equilibrium swelling ratio and swelling rate increase. Temperature does not affect the equilibrium swelling, but enhances the swelling rate. The hydrogen bonding or the interaction between PEI and water not only affects the equilibrium swelling and swelling rate, but also plays a key role in the diffusion mechanism. The diffusion of water through PEI–Co membranes deviates from Fickian mode slightly when the PEI content increases, and the diffusion of water through PEI–Co complex membranes is temperature activated.

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