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Combination of OH^- ions and –OH groups within QPPO/PVA hybrid membranes for acid recovery

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ABSTRACT

Hybrid membranes are prepared from quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO), polyvinyl alcohol (PVA), monophenyl triethoxysilane, and tetraethoxysilane through sol–gel process. QPPO contains the anion-exchange groups which can be in the form of $–N^+(CH_3)_3OH^-$, $–N^+(CH_3)_3Cl^-$, or $–N^+(CH_3)_3Br^-$. The OH^- ions can combine with PVA–OH groups to form weak interactions such as hydrogen bonds, and thus enhance the compatibility between QPPO and PVA phases and membrane stability. Hybrid membranes with the combination of $OH^-/-OH$ are generally homogenous and compact, with the lower water uptake of 57.6–67.4%, methanol content of 38.3–40.2%, and swelling degrees of 223–500% in 65˚C water. The ion-exchange capacities are similar in the range of 1.04–1.08 mmol/g. Diffusion dialysis (DD) of $HCl/FeCl_2$ solution shows that as the temperature increases from 15 to 55˚C, the dialysis coefficients of HCl (U_H) increase from 0.008 m/h to 0.014–0.018 m/h, while the separation factors decrease from 61–67 to 41–50. The U_H values are similar to that of commercial membrane DF-120 (0.009 m/h at 25˚C), and the separation factors are higher than those of reported membranes (lower than 48). The U_H values can remain 87–95% after the erosion of $HCl/FeCl_2$ system, with no significant reduction of selectivity. Hence, the combination of OH^- ions and PVA–OH groups is effective to elevate membrane stability and selectivity, and the QPPO/PVA hybrid membranes can be potentially applied in DD process for acid recovery.

Keywords: Hybrid membrane; PPO; PVA; Diffusion dialysis (DD); Acid recovery

1. Introduction

Waste solutions containing inorganic acids and metal ions are largely produced from metal extracting [1], electroplating [2], and other processes [3]. The acidic solution can be effectively separated by diffusion dialysis (DD) process. The DD is a membrane separation process driven by concentration gradient [1]. During static DD process, the acidic solution and water are filled into a two-compartment cell and separated by a membrane. The membrane allows the transport of acid such as HCl, but impedes the transport of other components such as $FeCl_2$. Hence, acid (HCl)

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can be recovered after a period of time, and the membrane is a key factor to determine the DD efficiency.

Organic–inorganic hybrid membranes can combine the advantages of both organic and inorganic phases [4], such as high flexibility and strength, low density and favorable stability. Hybrid membrane generally contains a single organic phase and a single inorganic phase. The organic phase is often used as membrane matrix and thus controls membrane performances. The inorganic phase, which can be regarded as "additive", can improve membrane properties but generally has no significant effects on membrane functional groups. For example, as polyvinyl alcohol (PVA) contains plenty of –OH groups but no ion-exchange groups, PVA-based hybrid membranes are often highly hydrophilic and relatively difficult to achieve ion-exchange properties [5]. Another example is sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO). As SPPO contains ion-exchange groups but no –OH groups, hybrid membranes based on SPPO exhibit low permeability in DD process (0.002 m/h for NaOH [6]). Hence, the functional groups such as –OH and ion-exchange groups need to be combined from different polymer materials, and thus hybrid membranes with double organic phases need to be developed.

Though the polymer-blending methods are often used to prepare organic membranes [7,8], the combination of two organic phases is more difficult to prepare hybrid membranes. The two organic phases not only need to be compatible, but also can be cross-linked with inorganic phase [9], or can form some weak interactions such as acid–base pairs [10,11]. The hybrid membranes also need to be supported [9] or cross-linked with aldehyde [10] in some cases, which would reduce membrane permeability in DD process [12]. In our previous work, hybrid membranes were prepared from SPPO and PVA with the cross-linking of tetraethoxysilane (TEOS). The membranes have favorable DD performance for alkali recovery (0.007–0.010 m/h, 13–181), but the phase separation between SPPO and PVA is significant. The silica network cannot be continuous due to the "impediment effect" of SPPO phase, and thus the membrane is swelling seriously in water (water uptake, i.e. W_R is 95–470%) [12]. In our following work, quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) and PVA were blended, which were cross-linked with monophenyl triethoxysilane (EPh) and TEOS correspondingly. The double cross-linking agents (TEOS and EPh) can overcome the "impediment effect" and form continuous silica network. However, as the QPPO and PVA phases have different polarities but no significant interactions, membrane with high dosage of PVA (60%) is still highly hydrophilic (W_R of 205% [13]).

The QPPO contains anion-exchange group of $N^+(CH_3)_3Br^-$, which is designated as QPPO–Br^-. The $N^+(CH_3)_3$ ion is connected to the polymer chain through covalent bond, while the Br^- ion is regarded as "counterion" and can be exchanged with other anions such as Cl^- or OH^-. The counterions have different polarity in the sequence of $Br^- < Cl^- < OH^-$. For example, QPPO/SiO_2 membranes in the Br^- form have the W_R of 2–178%, while in the OH^- form have the W_R of 34–1,000% [14]. PVA-based anion-exchange membranes in the Cl^- form have the W_R of 75–175%, while in the OH^- form have the W_R of 90–240% [15].

Hence in this work, the QPPO with the counterions of Br^- will be changed into Cl^- or OH^-. The counterions of Cl^- or OH^-, due to higher polarity, can enhance their compatibility with PVA. More importantly, the OH^- ions may interact with PVA–OH groups through weak interactions such as hydrogen bonds, which would further enhance the compatibility between QPPO and PVA phases. The favorable compatibility may enhance the continuity of silica network within the hybrid membranes. Besides, as the OH^- ions and –OH groups interact with each other, they should have less chance to be combined with water or eroded by other regents.

The QPPO/PVA hybrid membranes will be used in DD process to recover acid from HCl/$FeCl_2$ solution. The combination between –OH groups and OH^- ions during membrane formation may be effective for DD process. The combination may be beneficial to the transport of HCl, but restricts the transport of Fe^{2+} ions. Hence, the membrane selectivity would be elevated for separating HCl/$FeCl_2$ solution.

2. Experimentals

2.1. Materials

Monophenyl triethoxysilane (EPh) was purchased from Dalian Yuanyong Organosilicon Plant (China). Tetraethoxysilane (TEOS) was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd (China). Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) were kindly supplied by Tianwei Membrane Co., Ltd, Shandong of China. The other regents were from domestic chemical reagents company and of analytical grade. Distilled water was used throughout.

Quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO–Br^-) solution was prepared from brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) through quaternization. The procedures were similar to those of our previous reports but without the hydrolysis process [16].

PVA was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd (China). The average degree of polymerization was 1,750 ± 50. PVA (5 wt%) aqueous solution was firstly prepared through dissolving. 42.4 g PVA was immersed in 760 mL water at room temperature for one day, then heated to 102℃ at the rate of 8℃/h and kept at 102℃ for around 2.5 h.

2.2. Preparation of QPPO/PVA hybrid membranes

QPPO/PVA hybrid membranes were all prepared from QPPO–Br^- (8.5 g), PVA (6 g, 120 mL), TEOS (1.08 g), and EPh (1.24 g). However, the counterions of QPPO and sol–gel process were different to prepare membranes Q–Si–Cl, Q–OH–Si, and Q–Si–OH, as shown in Scheme 1.

For the preparation of membrane Q–Si–Cl, QPPO–Br^- solution was mixed with TEOS and EPh, and taken sol–gel reaction at 65℃ for 12 h. The solution was then cast onto glass plate, dried at room temperature under adequate aeration for 2 d. The formed film was peeled off from the glass plate and designated as QPPO/SiO_2. The sol–gel reaction should be incomplete due to no heat treatment afterward, which is essential to the following sol–gel process with PVA. The QPPO/SiO_2 film was immersed in 1 M NaCl solution for 24 h, washed with water for 4–6 times, and redissolved in 25 mL of dimethyl formamide (DMF) and 10 mL of ethanol. The redissolved solution was dropped into 65℃ PVA solution within 1 h. The mixture was continued to stir at 65℃ for 24 h to obtain homogenous casting solution. The casting solution was cast onto glass plate, and dried at room temperature under adequate aeration. The formed film was peeled off from the glass plate, heated from 60 to 130℃ at the rate of 10℃/h, and kept at 130℃ for 4 h.

For the preparation of membrane Q–OH–Si, QPPO–Br^- solution was dried under adequate aeration, and then heated at 60℃ for 5 h. The formed film was immersed in 0.5 M NaOH solution for 3 h, washed with water for 6 times within 5 h, and redissolved in 25 mL of DMF and 10 mL of ethanol. The redissolved solution was designated as QPPO–OH^-. The solution was mixed with TEOS and EPh, and taken sol–gel reaction at 50℃ for 1 h, during which the viscosity of the sol–gel solution was increased significantly. The sol–gel solution was dropped into 50℃ PVA solution within 1 h, and continued to stir at 50℃ for 24 h to obtain homogenous casting solution. The casting solution was cast onto glass plate, dried and heated following the same procedures as above.

For the preparation of membrane Q–Si–OH, QPPO–Br^- was taken the same sol–gel process with TEOS and EPh as above. The obtained QPPO/SiO_2 film was immersed in 0.5 M NaOH solution for 3 h, washed with water for 4–6 times, and redissolved in 25 mL of DMF and 10 mL of ethanol. The redissolved solution was dropped into 50℃ PVA solution within 1 h. The mixture was continued to stir at 50℃ for 24 h to obtain homogenous casting solution. The casting solution was cast onto glass plate, dried and heated following the same procedures as above. The membrane thicknesses are in the range of 105–125 μm.

2.3. Membrane characterizations

Fourier transform infrared spectroscopy (FTIR) was recorded using FTIR spectrometer (Nicolet 67, Thermo Nicolet) with a resolution of 0.9 cm^{-1} and a spectral range of 4,000–400 cm^{-1}. Membrane cross section was observed through scanning electron microscopy (SEM, SU8020, Hitachi Company of Japan). The membranes were firstly cryogenically fractured in liquid nitrogen to obtain fresh cross sections, and then coated with gold and observed through SEM.

Linear expansion ratio (LER) was determined by the difference between wet and dry dimensions of membrane sample, which was cut into 3 cm × 1 cm. LER was calculated as $\text{LER} = (L_2 - L_1)/L_1 \times 100\%$, where L_2 and L_1 are the lengths of wet and dry membranes, correspondingly [17].

Ion-exchange capacity (IEC) was determined using the Mohr method [18]. Dry membranes was converted to Cl^- form in 1.0 M NaCl for 2 d. Excessive NaCl was washed off and then the membrane was immersed in 0.5 M Na_2SO_4 for 2 d. Anion-exchange capacities were obtained by determining the amount of the exchanged Cl^- through titration with 0.1 M $AgNO_3$.

Water uptake (W_R) was measured to investigate membrane hydrophilicity [19]. The dry membrane sample was immersed in water at 25℃ for 2 d. The wet sample was taken out and wiped with a filter paper. W_R was calculated as the relative weight gain per gram of the dry membrane sample.

Methanol resistance was measured to evaluate the combination of QPPO and PVA phases, for pure QPPO was dissolvable in methanol. The dried membrane sample was weighed as m_1, and immersed in methanol at 25℃ for 2 d. The wet membrane was taken out, wiped with a filter paper and weighed as m_2. Then the membrane was dried again and weighed as m_3. The alcohol content was calculated as $(m_2 - m_3) \times 100\%/m_3$, and the weight loss percent was calculated as $(m_1 - m_3) \times 100\%/m_1$.

Swelling resistance was measured by membrane swelling behaviors in 65℃ water [13]. Pre-weighed membrane was immersed in 65˚C water, and then taken out at 6, 24, 48, 96, and 192 h. The membrane surface was wiped dry with a filter paper within 5 min and the wet membrane was weighed. The swelling degree was calculated as the weight gain per gram of dry membrane and recorded over the time.

The erosion of HCl–$FeCl_2$, though insignificant for short-term running, may become serious for long-term DD running. Commercial membrane DF-120 tends to become red and soft after several months, and even falls off from its fibers support during practical applications, according to the report of Tianwei Membrane Co., Ltd (Shandong of China). The erosion effects would be simulated as following [20]. Membrane sample was weighed, followed by immersion in HCl (1 M)/$FeCl_2$ (0.25 M) solution for 24 h, then taken out and wiped with a filter paper to remove residual solution on the surface. Subsequently, the sample was dried under adequate aeration for one day, and heated at 100˚C for 2 h. The above process was repeated again, during which the Fe^{2+} ions can be oxidized by air to form $FeCl_3$ and Fe_2O_3. Finally, the sample was washed with 1 M HCl and then with water for four times. The eroded sample was observed for the color-changing process, and taken for the measurements of weight loss percent, W_R and DD performance.

2.4. DD performance for HCl/$FeCl_2$ solution

DD running with HCl/$FeCl_2$ solution was carried out using a two-compartment cell separated by the membrane [16]. The membrane was firstly conditioned for 2 h in the feed solution (HCl/$FeCl_2$), and then located between two-compartment cell of equal effective volume (100 mL). The feed side of the cell was filled with the solution of HCl (1 M) and $FeCl_2$ (0.25 M), and the permeate side was filled with water. Both the two sides were stirred at identical rates to minimize concentration polarization effects during the diffusion test. Diffusion was allowed for 45 min, and then the feed/permeate solutions were removed from both sides of the cell.

The permeability was reflected from dialysis coefficients (U), which was different from the flux in pressure-driven process. The U can be calculated by the following formula:

$$U = \frac{M}{At\Delta C}$$

where M is the amount of component transported in moles, A the effective area in square meters (6.15×10^{-4} m^2), t the time in hours, and ΔC the logarithm average concentration between the two chambers in moles per cubic meters. ΔC was defined as below:

$$\Delta C = \frac{{C_f}^0 - (C_f - C_d)}{\ln[{C_f}^0/(C_f - C_d]}$$

where C_f^0 and C_f are the feed concentrations at time 0 and t, correspondingly, and C_d the diffusate concentration at time t. The HCl concentration was determined by titration with a standard Na_2CO_3 solution, while $FeCl_2$ concentration was determined by titration with a $KMnO_4$ solution. The separation factor (S) with respect to one species over another was given as the ratio of dialysis coefficients (U) of the two species present in the solution.

3. Results and discussions

3.1. OH^- ions is anticipated to enhance membrane compatibility and homogeneity

QPPO contains quaternary ammonium groups, which can be in the form of $-N^+(CH_3)_3Br^-$, $-N^+(CH_3)_3Cl^-$, or $-N^+(CH_3)_3OH^-$. The counterions of QPPO include Br^-, Cl^-, and OH^-, which are designated as QPPO–Br^-, QPPO–Cl^-, and QPPO–OH^-, respectively. The counterions affect membrane formation process and thus membrane structures and properties.

The counterions have different polarities in the sequence of $Br^- < Cl^- < OH^-$, and thus the polarity of QPPO is in the sequence of QPPO–Br^- < QPPO–Cl^- < QPPO–OH^-. The low polarity of QPPO–Br^- can reduce the swelling of QPPO phase, but may also reduce its compatibility with the PVA phase. Hence in this research, QPPO–Cl^- and QPPO–OH^- are utilized to enhance their compatibility with PVA. The favorable compatibility between QPPO and PVA may enhance membrane homogeneity and cross-linking degree.

Besides, QPPO–OH^- may interact with PVA–OH groups to from weak interactions such as hydrogen bonds. The weak interactions would further enhance the compatibility between QPPO–OH^- and PVA phases. The high compatibility is beneficial to the cross-linking among QPPO–OH^-, PVA and silica network within the hybrid membranes. The double organic phases of QPPO–OH^- and PVA may be regarded as "one organic phase," which breaks the previous "impediment effect" from double organic phases [12].

3.2. FTIR spectra prove membrane structure

The FTIR spectra of three membranes, together with material QPPO–Cl as comparison, are shown in Fig. 1. The membrane spectra show a large band between 3,100 and 3,700 cm^{-1}, which is ascribed to the stretching vibration of –OH groups and absorbed water. The bands in the 2,850–2,990 cm^{-1} region and at 1,470 cm^{-1} are from the stretching of CH_3–, –CH_2–, and =CH– groups (ν and δ). The band at 1,600 cm^{-1} is attributed to the C=C stretching vibration in phenyl groups ($\nu_{C=C}$); the peaks at 1,190 cm^{-1} are characteristic of C(=O)–O–C stretching, and 1,096 cm^{-1} is characteristic of –Si–O–Si– stretching [5].

The intensity of –Si–O–Si– (1,096 cm^{-1}) bands increases in the sequence of membranes Q–Si–Cl, Q–Si–OH, and Q–OH–Si when the intensity of C=C (1,600 cm^{-1}) is used as standard. The higher intensity of membranes Q–Si–OH and Q–OH–Si indicates that the OH^- ions can enhance the silica network during membrane formation. The highest intensity of membrane Q–OH–Si indicates that the OH^- ions can accelerate the sol–gel reaction of TEOS and EPh [21].

3.3. Higher compatibility proved by SEM images

The compatibility between two organic phases is compared among previous SPPO/PVA [12], QPPO–Br^-/PVA [13] and present QPPO/PVA membranes. The membrane SEM images are shown in Fig. 2.

Previous SPPO/PVA membranes are phase separated between SPPO and PVA phases. The SPPO phase, whose area ranges from 2 × 4 μm^2 to 3 × 6 μm^2, is like some "islands" dispersed in membrane matrix. The phase separation is partly attributed to the lower polarity of SPPO than that of PVA [12]. Previous QPPO–Br^-/PVA membranes are microporous with the diameter of 30–120 nm [13]. The membrane with 60% dosage of PVA has W_R of 205% and the swelling degree up to 426% in 65°C water [13]. The microporous structure and high hydrophilicity indicate the loose combination between QPPO–Br^- and PVA phases.

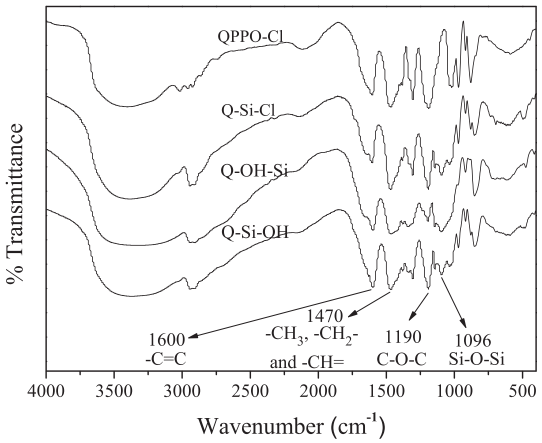


Fig. 1. FTIR spectra of material QPPO–Cl and membranes Q–Si–Cl, Q–OH–Si and Q–Si–OH.

Present QPPO/PVA membranes are generally compact without significant micropores (some interstices within membrane Q–OH–Si should be mainly attributed to the sample preparation in liquid nitrogen). The compact structure is different from those of previous hybrid membranes with double organic phases, which are phase separated [12] or microporous [13]. Besides, membrane Q–Si–Cl has some particles, while membranes Q–OH–Si and Q–Si–OH are more homogenous. The homogenous structure indicates the enhanced compatibility between QPPO and PVA phases.

3.4. Similar ion-exchange capacities (IECs)

Membranes Q–OH–Si and Q–Si–OH have similar IECs (1.04–1.08 mmol/g) to membrane Q–Si–Cl (1.13 mmol/g), indicating that though some quaternary ammonium groups ($-N^+(CH_3)_3OH^-$) may be lost during membrane formation processes such as heat treatment, most of the groups are generally stable.

Reports reflect that the $-N^+(CH_3)_3OH^-$ groups tend to be decomposed at elevated temperature. For example, the short-term thermal stability of alkaline anion-exchange membranes is in the range of 135–144°C [14] or 130°C [22]. Besides, the long-term thermal stability is much lower than the short-term thermal stability. For example, previous QPPO–Br^-/SiO_2 membranes have the short-term thermal stability all higher than 185°C, but their structure would be damaged after heated at 140°C for 3 h [14]. The present membranes Q–OH–Si and Q–Si–OH, though have been heated at 130°C for 4 h, are still stable in IECs. The stability indicate that the weak interactions between QPPO–OH^- ions and PVA–OH groups enhance the stability of $-N^+(CH_3)_3OH^-$ groups, for some of the weak interactions such as hydrogen bonds may still exist after the heat treatment [23].

3.5. Lower water uptake (W_R) and LER

The W_R and LER values are shown in Fig. 3. The values of membranes Q–OH–Si and Q–Si–OH (57.6–67.4%, 13.3–20.3%) are lower than those of membrane Q–Si–Cl (105.7, 26.7%). The lower values indicate the

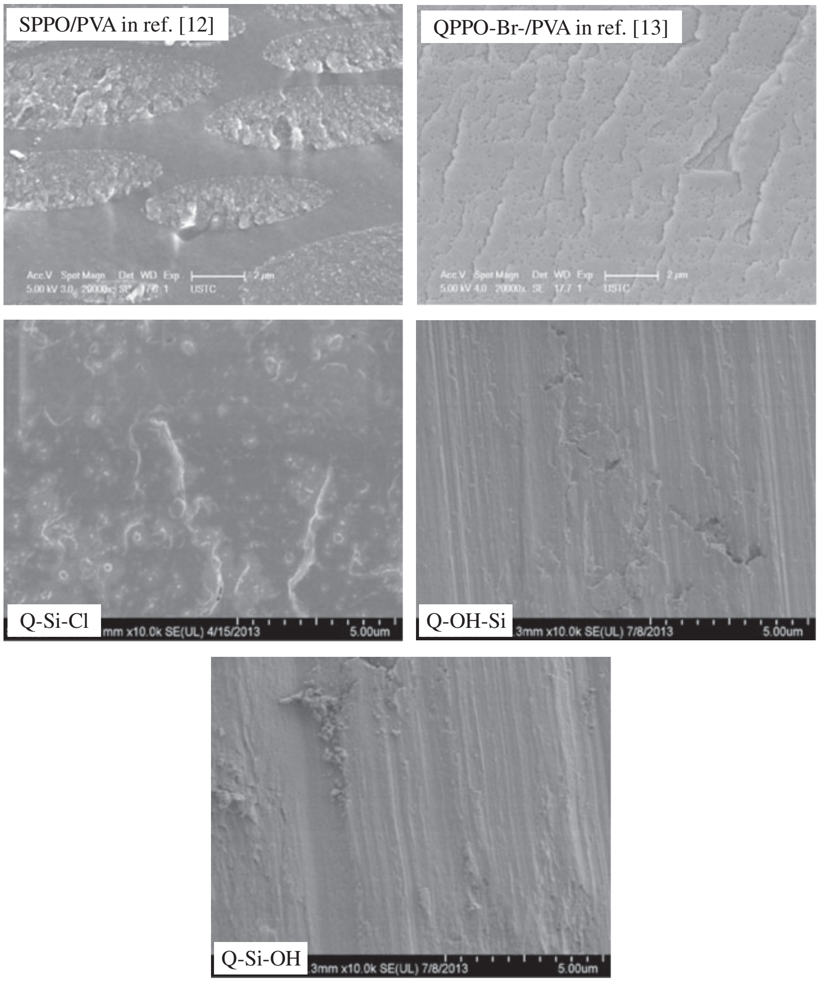


Fig. 2. SEM images for the reported SPPO/PVA [12] and QPPO–Br$^-$/PVA hybrid membranes [13] and the present QPPO/PVA hybrid membranes.

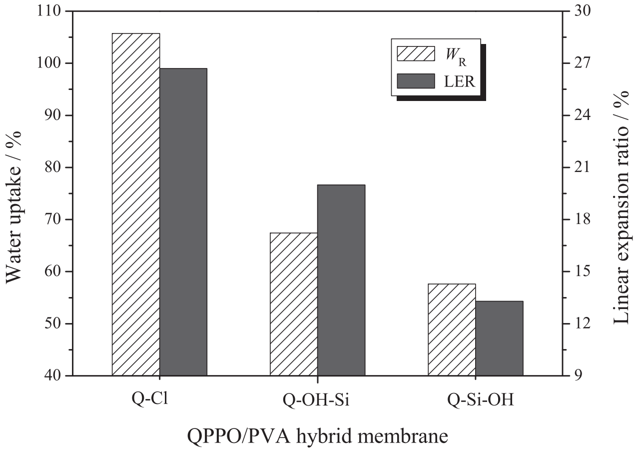


Fig. 3. Water uptake (W_R) and LER of QPPO/PVA hybrid membranes.

weak interactions between OH$^-$ ions and PVA–OH groups reduce membrane swelling in water. The $N^+(CH_3)_3OH^-$ groups, if without the weak interactions, should have higher hydrophilicity than $N^+(CH_3)_3Cl^-$ [15]. However, the combination of OH$^-$ ions and PVA–OH groups not only enhances membrane cross-linking degree, but also reduces their chances to bond with water. This can be further supported by the lower W_R and LER values of membrane Q–Si–OH than those of membrane Q–OH–Si. Membrane Q–Si–OH is prepared from the QPPO/SiO_2–OH$^-$ and PVA, and the OH$^-$ ions can combine with PVA–OH groups directly without the sol–gel process of TEOS and EPh, as shown in Scheme 1. Hence, the combination of OH$^-$ ions and PVA–OH groups should be more sufficient, which enhances the membrane stability.

3.6. High methanol resistance

Methanol resistance is measured to investigate the combination of QPPO and PVA phases. QPPO is dissolvable in methanol or ethanol, while PVA is dissolvable in water. Methanol resistance can be reflected from the methanol content and weight loss percent, which are shown in Fig. 4. The methanol content is in the range of 38.3–58.3%, and the weight loss percent is in the range of 14.0–19.1%. The low methanol content indicates that the QPPO phase is protected by PVA phase and silica network, which reduces the chances of QPPO being eroded by methanol. The PVA phase, which is stable in alcohol [24], can protect membrane from being eroded by alcohol.

The protection of PVA phase seems to have two modes. One is that the PVA phase packets the ion-exchange component, which is like an "island" encapsuled in the PVA phase [12]. The "island" mode seems to be more effective to protect the ion-exchange component, for the ethanol content is only in the range of 1.3–21.3% [12]. The other mode is the homogenous blending of PVA and QPPO phases in this study. The PVA phase can reduce the chances of erosion, but may not be able to impede the methanol or ethanol permeating into the membrane matrix. Though the homogenous blending mode may be less effective to alcohol resistance, it is beneficial to swelling resistance in water, as proved by W_R.

The methanol content and weight loss percent are in the sequence of membrane Q–Si–Cl > Q–OH–Si > Q–Si–OH. This also proves the effective combination between OH^- ions and PVA–OH groups.

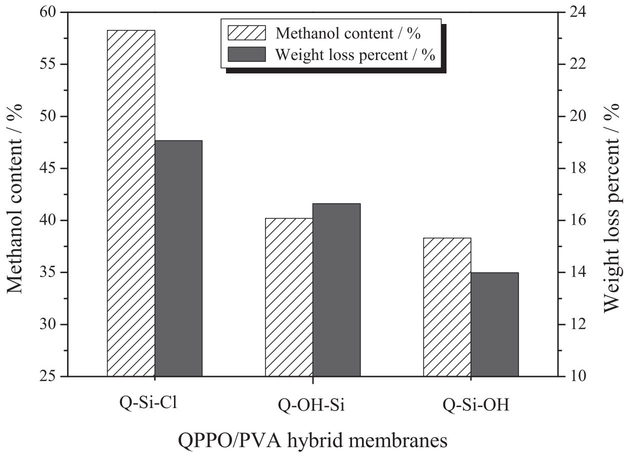


Fig. 4. Methanol content and weight loss percent after immersion in methanol for 48 h.

3.7. Swelling resistance in 65˚C water

Swelling degrees in 65˚C water, defined as relative weight gain of the membrane, have been collected at different time and the results are shown in Fig. 5.

The swelling degrees increase rapidly in the initial 24 h, but then become balanceable in the following 24–192 h. The highest swelling degrees are in the range of 223–673%, which are about 4–6.5 times higher than the W_R values (57–105%). The high swelling degrees at 65˚C may indicate the limitation of the weak interactions between OH^- ions and PVA–OH groups. The weak interactions may be sensitive to the elevated temperature. However, the swelling degree of membrane Q–Si–OH is still lower than that of previous QPPO–Br^-/PVA membrane (426% of membrane M60 in Ref. [13]), indicating the enhanced membrane stability.

3.8. Higher resistance to the erosion of $HCl/FeCl_2$

$HCl/FeCl_2$ solution is often taken as an example to evaluate the acid recovery through DD [2,3,13,16]. The erosion of $HCl/FeCl_2$, though insignificant in short-term running, becomes serious after several months or one year for commercial membrane DF-120, according to the report of Tianwei Membrane Co., Ltd, Shandong of China. Here, the erosion effect is simulated at accelerating rate, and is investigated through the variations of membrane color, W_R, weight loss percent, and DD performance, as shown in Table 1.

The W_R values after the erosion are in the range of 74.4–133.2%, which are higher than the values before the erosion (57–105%). The weight loss percents are in the range of 13.9–16.5%. The increased W_R and

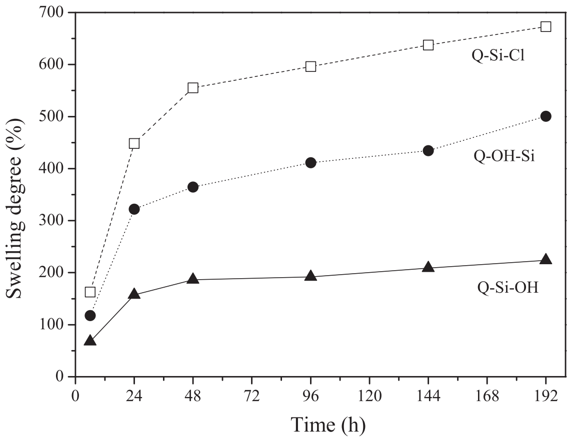


Fig. 5. Swelling degrees of QPPO/PVA hybrid membranes in 65˚C water.

significant weight loss percent indicate the erosion effect of HCl/$FeCl_2$. The Fe^{2+} ions can be changed into $Fe(OH)_2$ in neutral circumstance, and then become Fe^{3+} and Fe_2O_3 in air atmosphere [20]. The $Fe(OH)_2$ and Fe_2O_3, if precipitate within the membrane matrix, can swell and damage membrane structure. The erosion effect had been investigated by membrane performance, digital photos, and energy dispersive spectrometer (EDS) for QPPO–Br^-/PVA membranes [20]. Besides, the membrane color is changed from transparent to black, which may be attributed to the elimination of PVA–OH groups [20], a reaction favored by acid condition and high temperature [25].

The W_R and weight loss percents decrease from membranes QPPO–Br^-/ PVA [20], Q–Si–Cl to Q–OH–Si or Q–Si–OH, indicating the membrane stability is enhanced from Br^-, Cl^- to OH^- forms. The membrane stability can be further proved by the erosion effect on DD performance, which will be discussed in Section 3.9.

3.9. DD of HCl/$FeCl_2$ solution

3.9.1. Dialysis coefficient of HCl (U_H) with respect to the temperature

Waste solutions containing inorganic acids and metal ions may come from metal extracting, electroplating, and other processes [1–3]. Here HCl/$FeCl_2$ solution is taken as an example to evaluate the DD performance. The DD results are evaluated by U_H and separation factor (S). The U_H values with respect to the temperature are shown in Fig. 6.

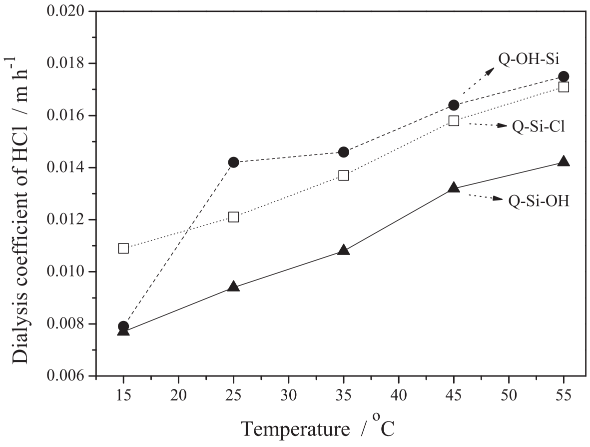


Fig. 6. Dialysis coefficient of HCl (U_H) with respect to temperature.

As the temperature increases from 15 to 55˚C, the U_H values increase from 0.008–0.011 m/h to 0.014–0.018 m/h. These values are only about 1/2–1/4 of previous QPPO–Br^-/PVA membranes (0.021–0.049 m/h at 25˚C [13]). The lower U_H values should be mainly attributed to three reasons. Firstly, the W_R values of present membranes are lower than those of previous QPPO–Br^-/PVA membranes (57–105% vs. 63–205% [13]). For example, the W_R of membrane Q–Si–OH is 50.8% after DD process at 25˚C. The lower hydrophilicity would reduce the transport rate of H^+ ions [16]. Secondly, present membranes are generally compact and homogeneous, while the previous membranes contain plenty of micropores, as proved by the SEM images. The compact structure would reduce the ion transport rate. Finally, the present IECs are lower than previous values, which would reduce the ion transport rate and thus U_H values. However, the present U_H values are still similar to those of commercial DF-120 membrane (0.006–0.025 m/h at 15–55˚C), indicating the values are acceptable in acid recovery.

Though membrane Q–OH–Si has lower W_R values than membrane Q–Si–Cl (67% vs. 105%), membrane Q–OH–Si has higher U_H value. The higher U_H value may indicate that proper combination of OH^- ions and PVA–OH groups is beneficial to the transport of HCl. As shown in Scheme 2, the OH^- ions and

Table 1
Membrane color, W_R, weight loss percent, and DD performance after the erosion of HCl–$FeCl_2$ system

Membrane	DF-120 [20]	M40 [20]	Q–Si–Cl	Q–OH–Si	Q–Si–OH
Composition	QPPO–Br^-	QPPO–Br^-/PVA	QPPO–Cl^-/PVA	QPPO–OH^-/PVA	QPPO–OH^-/PVA
Color	Yellow	Black	Black	Black	Black
W_R (%)	55.5	146.4	133.2	132.7	74.4
Weight loss percent (%)	11.3	19.0	16.5	14.1	13.9
U_H (m/h)	0.0057	0.0241	0.0062	0.0075	0.0067
S	13.9	33.2	49.7	68.1	68.8
DD temperature (˚C)	25	25	15	15	15
[a]Reduced ratio of U_H (%)	36.7	48.4	43.1	5.1	13.0

[a]The reduced ratio is calculated from the U_H values before and after the erosion, which can reflect the membrane stability.

PVA–OH groups are combined to form a cluster. The OH^- ions would be exchanged into Cl^- ions during DD process, but the cluster structure should still remain, which may be beneficial to the transport of HCl in the solution. The Cl^- ions in the solution can be transported by ion-exchange process, while the H^+ ions in the solution may be transported through PVA–OH groups by weak interactions such as hydrogen bonds. Hence, the transport rate of HCl can be accelerated through the combination of counterions and PVA–OH groups.

Membrane Q–Si–OH has lower U_H values than membrane Q–Si–Cl or Q–OH–Si, which should be attributed to the lower hydrophilicity and more compact combination of OH^- ions and PVA–OH groups. Membrane Q–Si–OH is prepared from the QPPO/SiO_2–OH^- and PVA, and the OH^- ions can combine with PVA–OH groups directly without the sol–gel process of TEOS and EPh (Scheme 1). Hence, the combination of OH^- ions and PVA–OH groups should be more compact. The high compact combination of OH^- ions and PVA–OH groups, though enhances membrane stability, may restrict the transport of HCl.

3.9.2. Separation factor (S) with respect to the temperature

Separation factor (S) is calculated from the U_H/U_{Fe}, which reflects the membrane selectivity on the transport of H^+ and Fe^{2+} ions. Fig. 7 shows as the temperature increases from 15 to 55°C, the S values decrease from 47.7–67.5 to 39.6–50.6. The reduced S values indicate the trade-off effect between permeability (U_H) and selectivity. However, the reduced ratio is only in the range of 17.0–32.4%, indicating the S values are less sensitive to the temperature than the U_H values, especially at 35–55°C. The S values at 55°C are still higher than those of the commercial membrane (17–32 at 15–55°C [16]) and reported membranes [5,13,16,26], as shown in Table 2.

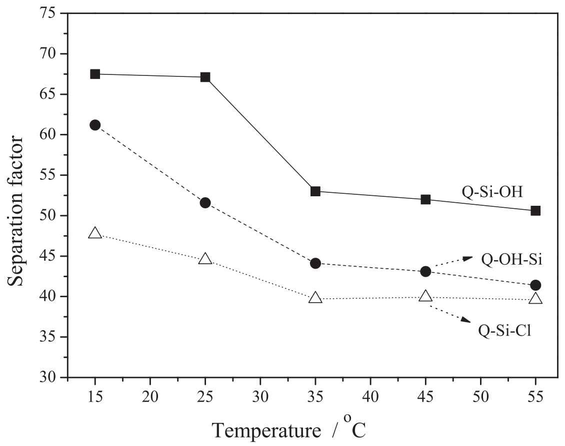
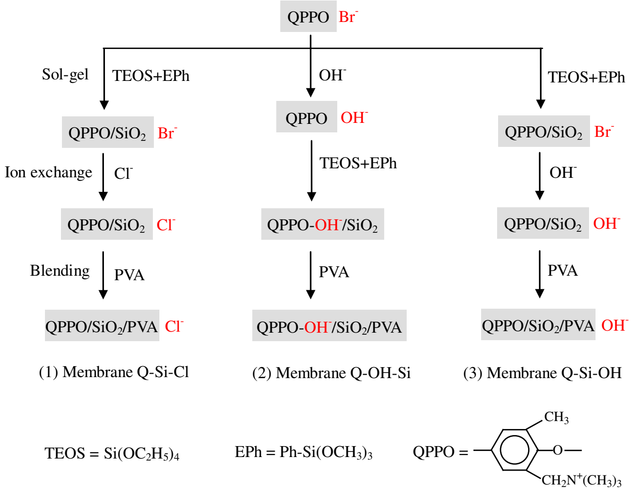
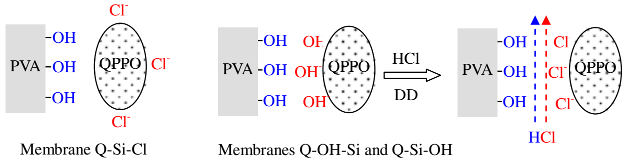


Fig. 7. Separation factor with respect to temperature.



Scheme 1. Preparation procedures of membranes Q–Si–Cl, Q–OH–Si and Q–Si–OH, which are all prepared from QPPO, PVA, TEOS, and EPh.



Scheme 2. Interactions between counterions (Cl^- or OH^-) and PVA–OH groups within QPPO/PVA hybrid membranes.

The S values of membranes Q–OH–Si and Q–Si–OH are not only higher than that of membrane Q–Si–Cl, but also higher than those of all the other reported membranes. The high selectivity indicates the superior membrane structures. Membrane selectivity is not only controlled by W_R and IEC, but also affected by the content of –OH groups, which can be regarded as "assistant" functional groups [13].

The combination of –OH groups and OH^- ions would affect the arrangement of functional groups and polymer chains during heat treatment. The groups and chains may be more concentrated and compact, which is beneficial to repulse ions of high volume and valence. Though the OH^- ions would exchange with Cl^- ions during DD process, the compact and concentrated arrangement should still existed. The arrangement may be effective for the transport of HCl, but restricts the transport of Fe^{2+} ions.

Table 2
Separation factors (*S*) for commercial DF-120, reported and QPPO/PVA hybrid membranes

Membrane	Composition	W_R (%)	IEC (mmol g^{-1})	Temperature (°C)	*S*
DF-120 [16]	QPPO–Br^-	42	1.9	15–55	17–32
Ref. [16]	QPPO–Br^-/SiO_2	18–53	1.7–2.2	15–65	11–41
Ref. [5]	PVA/SiO_2	29–39	0.7–1.0	15	15–21
Ref. [26]	PVA/SiO_2	44–303	0.5–1.2	25–40	18–48
M60 in Ref. [13]	QPPO–Br^-/PVA	205	1.2	25	26
This research	QPPO–Cl^-/PVA	105.7	1.13	15 - 55	39.6–47.7
This research	QPPO–OH^-/PVA	57–105	1.0–1.1	15–55	41.4–67.5

3.9.3. DD performance after the erosion of HCl/$FeCl_2$

DD running at 15°C is also taken after the erosion of HCl/$FeCl_2$, as shown in Table 1. The U_H values are in the range of 0.0062–0.0076 m/h, and the *S* values are in the range of 49.7–68.8. The U_H values decrease when compared with those of membranes without erosion, but the *S* values are stable. The reduced U_H should be attributed to the damaged structure such as the loss of PVA–OH groups. The stable selectivity indicates that the damaged structure is also disadvantageous to the transport of Fe^{2+} ions. As the mechanism for the transport of Fe^{2+} ions is still ambiguous, we can only assume that the "activity points" for the transport of Fe^{2+} ions may also be damaged during the erosion of HCl/$FeCl_2$.

The reduced ratios of U_H after the erosion are 48.4, 43.1, 5.1, and 13.0% for membranes QPPO–Br^-/PVA [20], Q–Si–Cl, Q–OH–Si, and Q–Si–OH, respectively. The low reduced ratios of membranes Q–OH–Si and Q–Si–OH indicate that the combination between OH^- ions and PVA–OH groups is effective to enhance membrane stability in HCl/$FeCl_2$ system. The PVA–OH groups and the counterions are protected by each other, and thus have less chance to be attacked during the erosion. The high stability in HCl/$FeCl_2$ system is meaningful for practical application to enhance membrane life expectancy.

4. Conclusions

QPPO/PVA anion-exchange hybrid membranes are prepared from quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO), PVA, monophenyl triethoxysilane, and tetraethoxysilane. The QPPO phase contains quaternary ammonium groups which are in the form of $–N^+(CH_3)_3Cl^-$ (Cl^- form) or $–N^+(CH_3)_3OH^-$ (OH^- form). The $–N^+(CH_3)_3OH^-$ groups have the counterions of OH^-, which can combine with PVA–OH groups to form weak interactions such as hydrogen bonds.

The hybrid membranes in OH^- forms are compact and more stable. The stability can be reflected from the lower water uptake of 57–67%, swelling degrees of 223–500% in 65°C water, and methanol content of 38–40%. DD running of HCl/$FeCl_2$ solution shows that as the temperature increases from 15 to 55°C, the dialysis coefficients of HCl (U_H) increase from 0.008–0.011 m/h to 0.014–0.018 m/h, while the separation factors decrease from 48–68 to 40–51. The hybrid membranes in OH^- forms are less sensitive to the erosion of HCl/$FeCl_2$ system, whose U_H values only reduce 5–13% and separation factors are generally stable after the erosion. Hence, the combination of OH^- ions and PVA–OH groups cannot only enhance the membrane stability, but also elevate the membrane selectivity. The combination degree is worth to be investigated further for the transport of HCl.

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List of symbols

QPPO	—	quaternized poly(2,6-dimethyl-1,4-phenylene oxide), which is a type of anion-exchange material
QPPO–Br^-	—	QPPO contains quaternary ammonium groups in the form of $–N^+(CH_3)_3Br^-$
QPPO–Cl^-	—	QPPO contains quaternary ammonium groups in the form of $–N^+(CH_3)_3Cl^-$
QPPO–OH^-	—	QPPO contains quaternary ammonium groups in the form of $–N^+(CH_3)_3OH^-$
PVA	—	polyvinyl alcohol
EPh	—	monophenyl triethoxysilane
TEOS	—	tetraethoxysilane
DD	—	diffusion dialysis

U_H — dialysis coefficient of HCl
S — separation factor
DMF — dimethyl formamide
IEC — ion-exchange capacity
W_R — water uptake
SEM — scanning electron microscopy
LER — linear expansion ratio
M — mol L^{-1}

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