

Preparation of Polyelectrolyte Complex Membranes Based on Sodium Cellulose Sulfate and Poly(dimethyldiallylammonium chloride) and Its Permeability Properties

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ABSTRACT: In this study, polyelectrolyte complex (PELC) membranes prepared by the simultaneous interfacial reaction between aqueous solutions of sodium cellulose sulfate (NaCS) as polyanion and poly(dimethyldiallylammonium chloride) (PDMDAAC) as polycation were proposed. The preparation conditions were optimized. The influence of two important factors, molecular weight (*MW*) of PDMDAAC and reaction time on the membrane formation procedure and permeability was investigated. Membranes with the preparation conditions as NaCS 3.5% (w/v), PDMDAAC (*MW* = 200–350 kDa) 7.0% (w/v), the reaction time 30 min, hold a favorable performance, and steady state in water flux experiment. To testify the feasibility of the membrane used in salt separa-

tion, membrane performances and selectivity of the inorganic salts as well as their relations to the preparation conditions, the operation parameters, the species of inorganic salts, etc., were investigated in the pressure-driven experiments. The results showed that this single-layer PELC membrane afforded higher rejections of divalent ions (SO_4^{2-}) to that of monovalent ions (Cl^-), which indicated the potential application of this membrane system in the salt rejection process. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 402–409, 2009

Key words: polyelectrolyte complex membrane; membrane separation; sodium cellulose sulfate; poly(dimethyldiallylammonium chloride); permeability

INTRODUCTION

Polyelectrolytes with counterion groups can form the aggregates by ionic interaction. The combination of aqueous solutions of polyanions with polycations results in water-insoluble precipitates called polyelectrolyte complexes (PELC).¹ As a new type of polymer materials, PELC have been proposed for the design of drug delivery systems, protein separation, microcapsules, anticoagulant coatings, and membranes for separating materials or even as skin substitutes, among other applications, because of their nontoxicity, bioabsorbability, high hydrophilicity, combined with considerable mechanical strength in the swollen state.² In the recent years, PELC membranes prepared by interfacial reaction of polyanion

and polycations have been developed as new kinds of polymer separation membranes. Their preparation consists of casting a layer of either the polyanion or the polycation aqueous solution onto a layer of the other. At the interface of both layers, a PELC forms a membrane with a thickness of less than 10 μm in the dry state. When the reaction is complete, the unreacted polyelectrolytes are washed out in a water bath, and the membrane precipitates. For practical use, the membranes must be mechanically reinforced by fixation onto a supporting material.³ Many authors have described the formation of membranes by this procedure, as well as their application in membrane pervaporation (PV) process.^{4–11} Furthermore, this kind of composite membrane has showed high selectivity of monovalent/divalent ion. The selective transport of ions makes these membranes the attractive candidates for water purification. The ion separation is ascribed to the polar counterions structure of the membrane, the permeating ions being electrostatically rejected by the equally charged parts of the membrane (Donnan "exclusion") and attracted by the oppositely charged parts (Donnan "inclusion").^{12–15}

Water-soluble anionic cellulose derivatives [sodium cellulose sulfate (NaCS) or sodium salt of

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sulfoethyl cellulose (SEC)] are well known for their high affinity to water.^{6,16} Membranes based on cellulose-based polyanions and synthetic polycations have been shown to be suitable for the separation of water from organic solvents by the PV process^{17–19} because of their high permeability for polar organic compounds. It seems that the chemical structure, having polysaccharide chains with very high capability for hydrogen bondings interaction, gives the best explanation for excellent permeation rates and selectivity of these membranes.⁹ Lukáš et al.^{20,21} have reported a kind of PELC membrane based on NaCS and poly(dimethyldilallylammonium chloride) (PDMDAAC). The surface characteristics of membranes were investigated by means of X-ray photoelectron spectroscopy (XPS), contact angle and tangential streaming potential measurements. Furthermore, the separation performance and selectivity of the membrane were intensively studied under PV, and the results showed that the membranes prepared by NaCS and PDMDAAC were especially suited for water separation from water–alcohol mixtures by PV with high separation efficiency and high permeation rates. Also, the interactions in macroscopic homogeneous reaction systems and phase transition by polysalt precipitation were investigated from the thermodynamic and kinetic points of view.²

However, the present literatures relating to the PELC membrane based on NaCS and PDMDAAC mentioned earlier mostly refer to the applications in the dehydration of organic solvents by PV process. Because the membranes behave like weak anion exchange membranes from the concentration potential investigations point of view,²² they can also be the potential choice in the salt separation; however, few investigations in this aspect have also been achieved.

In this work, we attempt to prepare and characterize the PELC membranes obtained by the interaction of NaCS as polyanion and PDMDAAC as polycation. The separation performance of the membrane is primarily determined by the chemical properties of the polyelectrolytes and the structure and morphology of the membrane. The parameters involved in the membrane formation procedure affect the membrane structure. So the conditions of preparing the PELC membranes will be optimized. Membrane performances and selectivity of the inorganic salts, as well as their relations to the preparation conditions, the parameters of operations, etc., will be investigated in the pressure-driven experiment. For better mechanical stability, the PELC membranes will be fabricated on poly(vinylidene fluoride) (PVDF) ultrafiltration (UF) membranes, which had a high chemical resistance.

EXPERIMENTAL

Materials

NaCS (molecular weight (*MW*) = 350–400 kDa) was prepared in laboratory scale by heterogeneous sulfation of cotton cellulose²³ with a degree of substitution (*DS*) = 0.42; PDMDAAC (*MW* < 100 kDa, 35 wt %; *MW* = 100–200 kDa, 20 wt %; *MW* = 200–350 kDa, 20 wt %). All the three kinds of PDMDAAC were in water) purchased from Aldrich (St. Louis, MO). All the chemicals were of analytical grade and used without further purification. Double distilled water was used throughout the study. PVDF UF membranes were used as supporting materials.

Membrane preparation

The concentrations of aqueous solutions of individual components for membrane preparation were in the range: 1.0–4.0% NaCS (w/v), 3.0–20% PDMDAAC (w/v). Membranes were prepared in two manners: first on a glass plate and second by using the so-called dip-coating method. The formation on a glass plate yields only the PELC membrane in the first step, which is the active layer in the separation process. However for improvement of the chemical stability, a composite system is preferred. The dip-coating method on the other hand yields directly composite membrane, which is the combination of the active layer with a porous support. Usually, the membranes without support were used for analytical measurements, whereas the membranes formed with supports were applied for permeability experiments.

Membrane formation on a glass plate

An aqueous solution of NaCS was cast on a glass plate with a thickness of 0.2 mm.¹⁹ Subsequently, the plate was immersed into a aqueous counterion solution PDMDAAC, and a layer of PDMDAAC was distributed on the film. The simultaneous reaction between two charged polyions led to the PELC membrane formation. After a period of reaction time, the glass plate was dipped into a water bath where the unreacted components were washed out. The resulting membrane was loosened from the glass plate, intensively soaked in distilled water and dried. All these steps were performed under the ambient conditions.

Dip-coating method

The membrane formation occurred immediately on the porous PVDF supports.⁶ The first layer consisted of NaCS and the second layer of PDMDAAC. Depositions were performed at room temperature. The

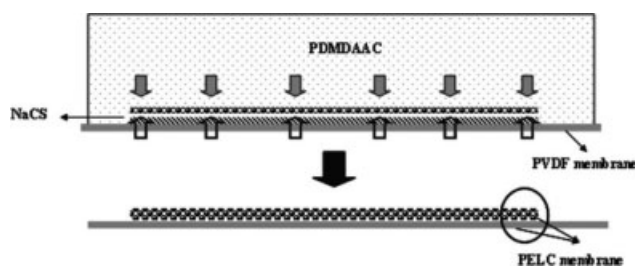


Figure 1 The formation of PELC membrane based on NaCS and PDMDAAC on supporting PVDF membrane.

second layer was applied subsequently onto the first wet layer. Both the two layers were not dried at all. When the interfacial reaction finished, the resulting composite membrane was washed by the distilled water. After being air-dried at 40–60°C for 30 min, the composite membrane could be used for permeability experiments without any further treatment. The thickness of the resulting composite membranes consisting of the active PELC layer and the porous PVDF support was in the range of 190–195 μm . The porous support alone was about 187–190 μm thick. Figure 1 shows schematically the formation of PELC membrane based on NaCS and PDMDAAC on a microporous PVDF membrane.

Morphology of membranes: Scanning electron microscope studies

The PELC membranes were immersed into the liquid nitrogen, broken into halves and then dehydrated in absolute ethanol. After the ethanol was evaporated, samples were observed by scanning electron micrographs (SEM) on a Philips XL-30M SEM instrument (Holland) with accelerative voltage of 20.0 kV. The thickness of the sample membrane could be measured from the cross-section micrograph.

Permeability experiments

The flux and separation experiments were carried out in a laboratory scale apparatus (Model SF-SC supplied by Superfiltration Membrane Tec, Hangzhou, China) with a membrane active area of 37.37 cm^2 . PELC membrane samples were fixed directly by two sintered glass plates. Each sample collection was preceded by a prerun time lasting from 15 min to 1 h, depending on the pressure and species of the feed, in which 25–50 mL of permeate was collected and discarded. When the flux became stable, about 30 mL permeate samples were collected, the corresponding periods cost in this experiment were recorded. Each run was repeated 2–3 times refilling the cell with fresh solution every time. Since the permeation setup was cross-flow filter, the con-

centration polarization would not be taken into consideration in the experimental discussion. The permeability of the PELC membranes was evaluated by two parameters, i.e., permeation flux J [$\text{L}/(\text{m}^2\cdot\text{h})$] and retention R , as shown in eqs. (1) and (2):

$$J = V/tS \quad (1)$$

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (2)$$

where V is the volume of permeate collected in time t , and S is the effective membrane area, c_f (wt % or mol/L) and c_p (wt % or mol/L) represent the concentrations of the feed and permeate, respectively.

Measurements of salt concentrations

When the concentration of the salt solution is extraordinarily low, it appears to be proportional to the conductivity. Hence, the salt concentrations of feed and permeate were determined by conductivity (model 105A, Thermo Orion, Beverly, MA), which has become the preferred method for quantifying salt in many laboratories.

RESULTS AND DISCUSSION

The formation of PELC membranes based on NaCS and PDMDAAC

The essential architecture of the PELC is based on highly polar counterions interactions by electrostatic bonds. During the PELC of NaCS and PDMDAAC formation, a pronounced arrangement of pairs of negative (sulfate groups of NaCS) and positive (quaternized amino groups of PDMDAAC) charges occurs, which results in a hydrophilic, relatively compact network in the PELC membrane. NaCl, as a reaction by-product is removed later during the rinsing procedure.

Many factors influence a membrane separation process: chemical structure and morphology of the membrane as well as parameters of the process itself, e.g., temperature, pressure, hydrodynamic conditions. Radically, a right diffusion of both components during the PELC membrane formation will have a direct effect on the final chemical structure. The main factors, which may limit the diffusion, are concentrations of polyanion and polycation in the interfacial reaction, and the reaction time.¹ Otherwise, the molecular weight of the components will also be taken into consideration in this experiment. By changing these parameters, the chemical structure of membranes might be optimized.

In this experiment, the PELC membranes were prepared on the glass plates, as previously described in detail in section "Membrane formation on a glass plate." By observing the appearance of the

membrane macroscopically, the ranges of concentrations of polyions, with which the integrated membranes may be formed without breakage, will be defined approximately. More precious optimization of the preparation conditions will be achieved in the following permeability experiments. When either of the component concentrations was extraordinary low (NaCS <2.0% or PDMDAAC <7.0%), it was almost impossible to form an intact PELC membrane, regardless of the other reactant's concentration. However, a high concentration of NaCS (>3.5%) would result in high viscosity, which would make itself difficult to be cast uniformly. Richau et al.¹⁹ concluded that NaCS practically predetermined the membrane charge density, also to a great extent the membrane performance; therefore, the variations in the PDMDAAC concentration could not have significant effect on the membrane properties. So in the range of concentrations restricted by the membrane formation, the maximum concentration of NaCS (3.5%), as well as the minimum concentration of PDMDAAC (7.0%) was adopted.

Reaction time has a direct impact on the degree of the interfacial reaction. Too short reaction time would induce the insufficient formation of the PELC, which caused the friability and low mechanical strength, whereas too much time did little contribution to the reaction, if the reaction had been completed. Taking both experiments and literature into consideration, the suitable reaction time is in the range of 10–30 min.

Furthermore, the role played by the *MW* of PDMDAAC in the membrane formation was investigated. NaCS prepared by our laboratory has a uniform *MW* of 350–400 kDa, so it will not be discussed here. The lower the *MW* of PDMDAAC is, the shorter the length of polycation chain is; at the mean time, the size of PDMDAAC is smaller and its diffusivity in the membrane layer gets easier. We can conclude that low *MW* of the polyions may do benefit to the steady membrane formation.

SEM analysis

Figure 2 shows the surface and cross-section photographs of the homogeneous PELC membrane based on NaCS and PDMDAAC, the preparation conditions of which were 3.5% (w/v) NaCS, 7% (w/v) PDMDAAC (*MW* = 200 – 350 kDa), reacting for 30 min. It is obvious that a PELC membrane has formed with a thickness of about 1.4 μm on the microporous support. No appreciable pore and no phase separation in the membrane could be observed. It could be concluded that during the interfacial reaction of polyanion and polycation, a sufficient diffusion of both phases occurred, resulting in a homogeneous polymer network with a

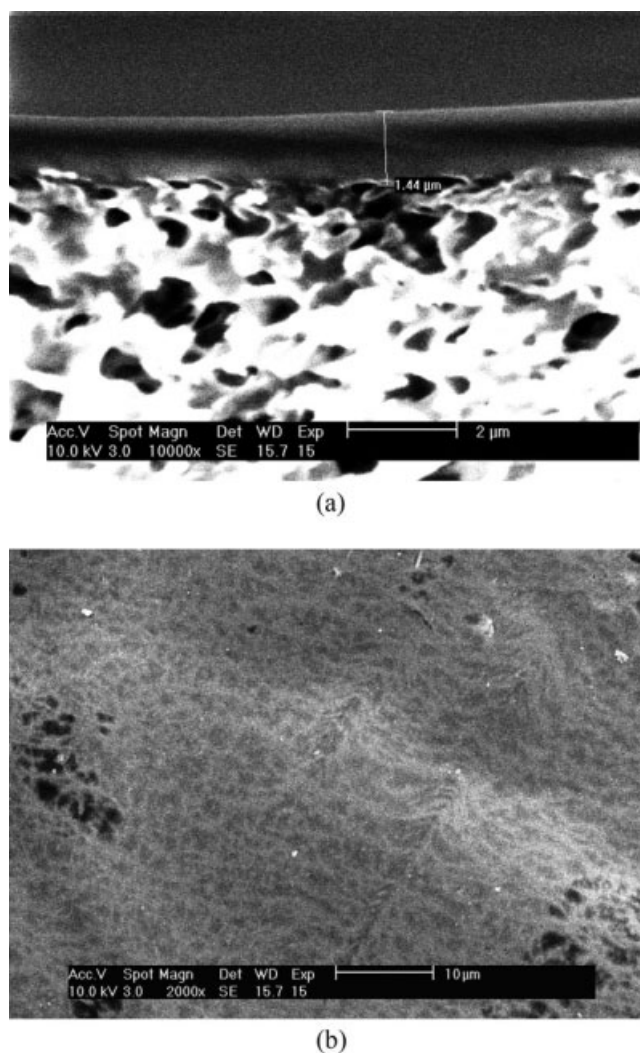


Figure 2 Micrographs of the PELC membrane: (a) cross section; (b) surface.

defined arrangement of positive and negative ions. In addition, the membranes did not dissolve in water, which confirmed the formation of PELC membrane.

PERMEABILITY EXPERIMENTS

Permeability of pure water

During the formation of PELC membrane, *MW* of PDMDAAC and reaction time both have more distinct influence on the degree of the interfacial reaction than other parameters, consequently changing the permeability of the membrane. From this point of view, we put emphasis on the effect of this two preparation parameters in the pure water permeate experiments. Basic characters of the prepared membranes are presented in Table I with NaCS 3.5%, PDMDAAC 7% in common. The thickness of the PELC membrane increased with decreasing PDMDAAC *MW* because of the more adequate

TABLE I
PELC Membranes Based on NaCS and PDMDAAC Studied

Membrane No.	MW of PDMDAAC (kD)	Reaction time (min)	Thickness ^a (μm)
1	200–350	30	1.5
2	100–200	30	2.3
3	<100	30	2.8
4	200–350	10	0.5
5	100–200	10	0.7
6	<100	10	0.8

^a In the dry state.

diffusion of PDMDAAC into the network structure of the PELC. Also, the membrane thickness decreased when reaction time was shorter because of the insufficient formation of the PELC. The distinctness of membrane thicknesses can bring on the different performances in permeability experiments, which will be discussed in the following section.

Effect of preparation conditions on the pure water flux. The effect of the PDMDAAC MW on the water flux of the PELC membranes (No. 1–No. 3) were measured and shown in Figure 3. The water permeability increased with increasing PDMDAAC MW. When the operating pressure was less than 0.15 MPa, the water fluxes of membrane No. 2 and No. 3 were both approximately zero. When the pressure was 0.20 MPa, the flux of No. 1 was about 213.6 L/($\text{m}^2\cdot\text{h}$), while the fluxes of No. 2 and No. 3 were only 21.1% and 11.9% of that of No. 1, respectively. There is a significant difference among the membranes prepared by different PDMDAAC, mostly due to the role of the PDMDAAC MW in the interfacial reaction, as discussed in the previous section. When the interfacial reaction takes place, it is favorable to PDMDAAC with lower MW to diffuse into the film formed at the interface of two reactants comparatively. More probability of PDMDAAC getting into contact with NaCS will lead to greater reaction degree, which facilitates the thicker and more compact membrane structure. This may discourage the water from diffusing through the PELC membrane and cause the water flux to decrease dramatically.

Besides the MW of PDMDAAC, the reaction time also has a close relationship with the water permeability. Membranes No. 4–6 were prepared with 10-min reaction time. The pure water flux of No. 4 was about 10 times greater than that of No. 1, whereas, the insufficient reaction time induced the unstable state of the PELC membrane. In the permeability experiments, all three membranes No. 4–6 inclined to be fragmented round the edges along with the increasing of pressure, which would terminate the

achievement of further pressure experiment. According to the results, membrane No. 1 was in possession of better water permeability and would be the membranes studied in the experiments in succession, if not stated otherwise.

Effect of the operating parameters on the pure water flux. Figure 3 also shows the influences of the operating pressure on the water fluxes of both PELC membrane and the supporting PVDF membrane. It could be observed that for both membranes, the water permeability performed a similar behavior, increasing with a rise in the operating pressure. Compared with the PVDF membrane, the water flux of No. 1 appeared to show a distinct decrease, which attributed to the existence of compact NaCS/PDMDAAC membrane on the surface of the PVDF membrane.

The PELC membrane is inclined to break down when exposed for too much time to the high-pressure environment, which will shorten the life of application of the membrane. Figure 4 shows the water flux of one membrane (No. 1) in a long-term permeability experiment. The water flux was kept approximately constant when the operation time was less than 5 h. The result of this experiment revealed the steady performance and good reproducibility of PELC membrane based on NaCS and PDMDAAC in the permeability experiment.

Salt permeability experiments

Several recent reports showed multilayer PELC membranes affording high rejections of inorganic salts, as well as separation of small neutral molecules.^{24–29} For NaCS/PDMDAAC system, more researches focused on the applications in

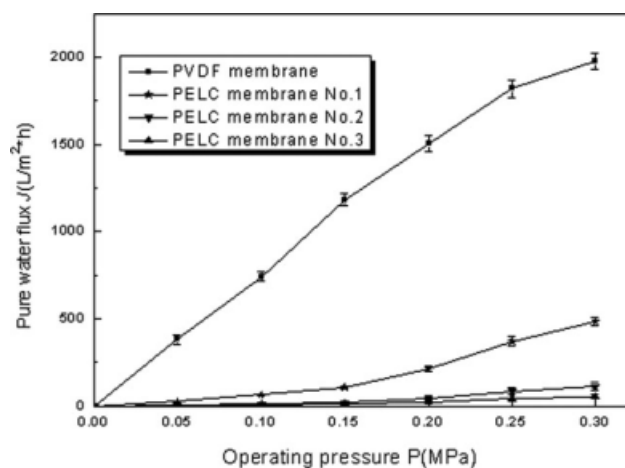


Figure 3 Pure water fluxes of PELC membranes with different PDMDAAC MW (Membranes No. 1–3) and supporting PVDF membrane.

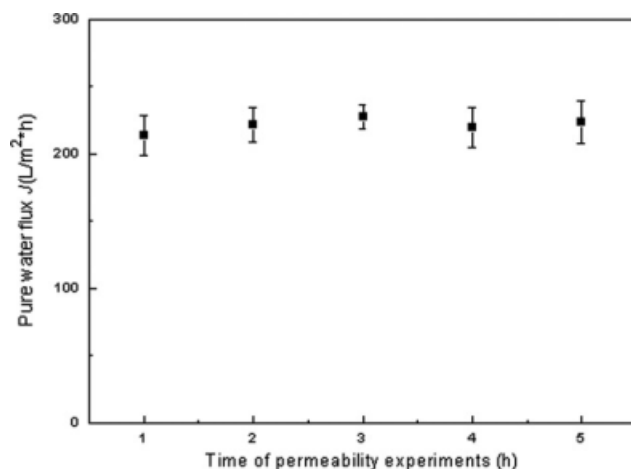


Figure 4 Pure water flux at different times of permeability experiment (Membrane No.1; 0.20 MPa).

dehydration of organics by PV process. In this section, the potential capability of the PELC membrane based on NaCS and PDMDAAC in the salt separation will be discussed from the perspective of a single-layer membrane, and the effect of different factors on the membrane performance in this salt rejection process will be described, which could be the ground of further research of multilayer PELC membrane.

Effect of operating parameters on salt permeability. In this experiment, six different kinds of inorganic salts were adopted: sodium chloride (NaCl), sodium nitrate (NaNO_3), potassium chloride (KCl), sodium sulfate (Na_2SO_4), calcium chloride (CaCl_2), and magnesium chloride (MgCl_2). The concentrations of the former three salts were 0.01 mol/L while the others were 0.005 mol/L, so that they could have the same ionic strength. For each sample, a prerun time was also decided at the beginning of the permeation. The salt flux curves remain in a similar trend regardless of variety and valence, increasing with the increase of operating pressure [see Fig. 5(a)]. There was distinctness among the different kind of salts because of their charge and size, which will be analyzed in detail in the following section.

Figure 5(b) illustrates a types of pressure-separation relationship of the PELC membrane in the salt separation. For all the six different salts, the retention curves followed the same pattern that increased up to a pressure of 0.25 MPa and then leveled off. This shape of the curve is typical of that expected for a nanofiltration membrane.³⁰ According to the space charge model for the electrolyte transport through charged capillaries developed by Osterle and coworkers^{31–33} and applied by Wang et al.³⁴ to nanofiltration membranes, salt rejection is a function of the capillary (pore) radius, charge density, feed

concentration, and the Peclet number (Pe) in the system. The space charge model shows that salt rejection increases with decrease in the capillary radius, decrease in feed concentration and increase in charge density. For a membrane of constant thickness, the volume flux, which depends on pressure, is directly related to the Pe number. For a defined membrane and constant feed solution, the salt rejection will initially increase with the Pe number and then level off.³⁴

Effect of feed concentration on the salt permeability. The role of salt concentration in the permeability is complicated because of the double-acting influence of the ions' amount and ionic strength. Figure 6 illustrates the effect of NaCl concentration varying from 0.01 to 0.05 mol/L on the performance of the PELC membrane No. 1. With the increase of NaCl concentration in the feed, the flux increased tardily and reached zenith at 0.04 mol/L. The retention

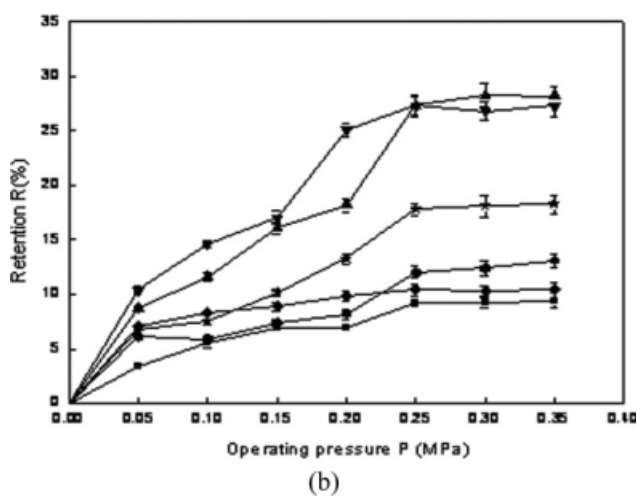
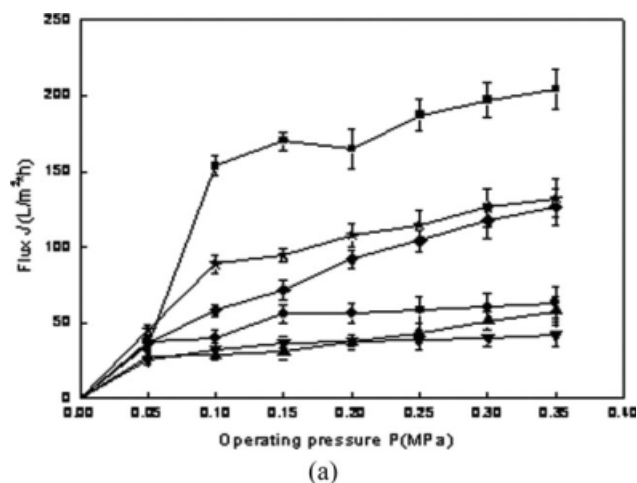


Figure 5 The effect of operating pressure on the salt permeability (■NaCl; ★ NaNO_3 ◆KCl; 0.01mol/L; ▲ Na_2SO_4 ; ▼ CaCl_2 ● MgCl_2 ; 0.005 mol/L): (a) salt flux; (b) salt retention.

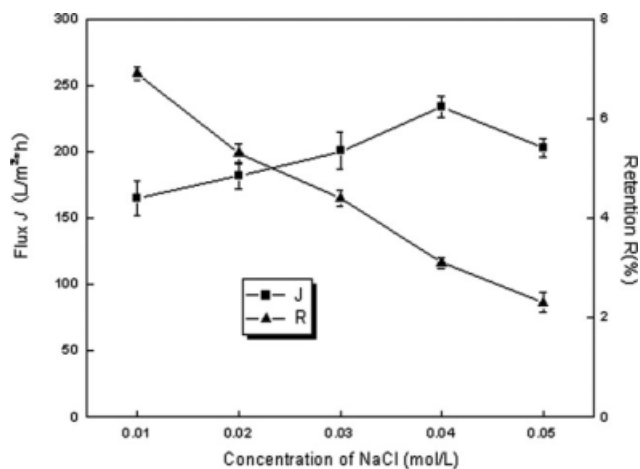


Figure 6 The effect of feed concentration on the salt permeability.

decreased with the increasing NaCl concentration, but the value was no more than 8%, which indicated that almost all the NaCl could get through the membrane. The phenomenon can be explained by the coupling effect of the amount of ions and ionic strength. Inorganic salts are known to weaken the Coulomb interaction between polyelectrolyte at higher concentration, leading to membrane dissolution and decreasing network density, while the increasing net amount of ions block off the flux through the membrane to some extent. When the NaCl concentration increased below 0.04 mol/L, the effect of the ionic strength was ascendant, the enhanced ionic strength made the compact arrangement of ion bonds in the membrane decrease, and the activity of polymer chains declined, the flux increased because structure of the membrane became incompact.

Effect of salt species on the performance of the PELC membrane. Separation of inorganic salts is quite different from that of neutral molecules because selectivity is based more on the charges of the analytes than on their size. However, the variation of polyelectrolyte systems will still affect the charge density and swelling of PELC membranes, having a significant effect on both selectivities and solution flux in the separation of salts.¹³ Figure 7 shows the solution flux and salt retention of different species of salt with the same ionic strength at 0.20 MPa. For NaCl, NaNO₃, and Na₂SO₄, the flux were 164.8 L/(m²·h), 107.9 L/(m²·h), 37.3 L/(m²·h), respectively, following the order of NaCl > NaNO₃ > Na₂SO₄. The salt retention also followed the same sequence. The remarkable difference of flux and retention was caused by the anion mainly because of the same cation Na⁺. Usually, a PELC membrane affords higher rejections of divalent ions to that of monovalent ions,¹⁵ and the result was in a good agreement with this conclu-

sion. On the other hand, for NaCl, KCl, CaCl₂, and MgCl₂, which processed same monovalent anion Cl⁻, the salt flux followed the order of NaCl > KCl > MgCl₂ > CaCl₂. There was no certain relationship found between the salt retention and cationic valence, and the retention of KCl was bigger than that of MgCl₂. The abnormal phenomenon could be attributed to the complicated surface properties of the PELC membrane. According to Lukáš et al.,²⁰ the concentration of quaternized groups of polycations PDMDAAC primarily determined the surface properties of PELC membrane, and specific adsorption of cations from the salt solution was another contribution to the surface charge for the NaCS/PDMDAAC membrane. Different degrees of adsorption process of the cations could more or less change the salt retention performance of the PECL membrane.

CONCLUSIONS

This article focused on the preparation and permeability of single-layer PELC membrane based on the simultaneous interfacial reaction between aqueous solutions of NaCS as polyanion and PDMDAAC as polycation. The preparation conditions were optimized. The effects of MW of PDMDAAC and the reaction time on the permeability of membrane were investigated. Membrane No. 1, the preparation condition of which was NaCS 3.5% (w/v), PDMDAAC (MW = 200–350 kDa) 7.0% (w/v), together with a reaction time of 30 min, processed a favorable performance in water flux experiment. The flux was about 213.6 L/(m²·h) when the operating pressure was 0.20 MPa, also, the membrane No. 1 had an excellent steady state in the repeating experiments.

The feasibility of the membrane No. 1 used in salt separation was also investigated. Membrane performances and selectivity of the inorganic salts as

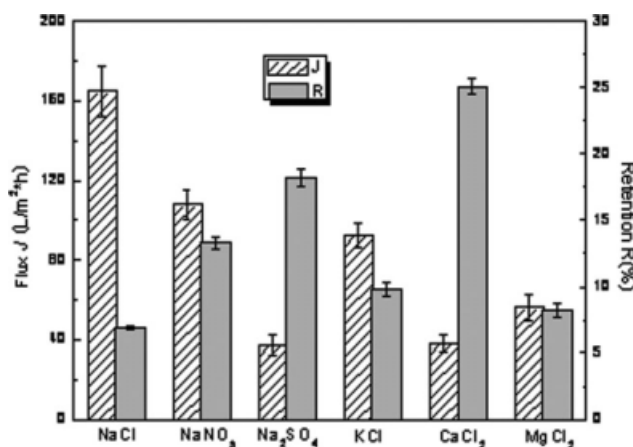


Figure 7 Permeability of different kinds of salts (the concentrations of Na₂SO₄, CaCl₂, and MgCl₂ were 0.005 mol/L while others were 0.01 mol/L; 0.20 MPa).

well as their relations to the various parameters were tested in the pressure-driven experiments. The complicated interaction between the salt and PELC layer should be taken into account when the flux and salt rejection were discussed. The membrane dissolution and cationic adsorption were two major factors that changed the membrane performances and selectivity. The obtained results showed that PELC membrane afforded higher rejections of divalent ions (SO_4^{2-}) to that of monovalent ions (Cl^-), which indicated the potential capability of this PELC membrane system in the salt rejection process. More research should be achieved on how to enhance the permeability and selectivity of the membrane in salt separation in the further experiments.

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