Diffusion dialysis for NaCl and NaAc recovery using Polyelectrolyte Complexes /PVA membranes

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Abstract:

Diffusion dialysis (DD) technique is nowadays mainly utilized for recovering acid or alkali solutions, but the recovery of salts such as sodium chloride (NaCl) and sodium acetate (NaAc) is much more difficult due to their low diffusivity. Polyelectrolyte complexes (PECs)/polyvinyl alcohol (PVA) membranes containing functional groups of -C-OH, -Si-OH, -N⁺(CH₃)₃ and -SO₃Na are pioneered for DD process of salts. The membranes have improved stability in water and salt solution. The dialysis coefficients of NaCl (U_{NaCl}) are in the range of 0.00196-0.00290 m/h, which are 6 - 30 times higher than the values of commercial DF-9010 and CJMCDD-1 membranes. The dialysis coefficients of NaAc (U_{NaAc}) are in the range of 0.00108-0.00503 m/h, which are 30 - 143 times higher than the value of CJMCDD-1 membrane, whereas DF-9010 membrane has poor stability in NaAc solution. Finally, PECs/PVA membranes are applied to NaCl/threonine (Thr) mixture and NaAc waste residue solution, showing their outstanding advantages for DD process of salts. The membranes show both high permeability and selectivity for NaCl/Thr mixture, with separation factor ($S_{\text{NaCl/Thr}}$) as high as 6.495 (DF-9010: 1.25; CJMCDD-1: 0.224). The U_{NaAc} values for NaAc waste residue solution are 0.000602 - 0.00120 m/h, higher than that of commercial CJMCDD-1 membrane.

Keywords: Polyelectrolyte complex; PVA; salt; dialysis coefficients; separation factor

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1. Introduction:

Large amount of salt waste is produced from industrial processes such as biochemistry, food and medicine. Direct discharge of the waste liquor not only wastes useful resources, but also hardens soil, burns plants and pollutes water resources [1]. The waste liquor is a research topic to be treated economically and efficiently. Brackish waters are widely desalinated by reverse osmosis (RO) [2]. Waste water from paper and textile industry containing abundant salt can be treated through nanofiltration and electrodialysis [3-5]. Salts are also introduced in fermentation or acidolysis processes for production of amino acids. For instance, NaCl, $(\text{NH}_4)_2\text{SO}_4$, KH_2PO_4 or MgSO_4 is introduced in fermentation broth for production of threonine (Thr) [6], while as high as 4 mol/L NaCl is produced after neutralization of the remaining acidolysis liquid of pig hair during production of cystine [1]. Crystallization, distillation or ED processes have been tried for treatment of this kind of amino acid/salt mixtures [1, 7]. Wastewater containing NaAc, dimethyl sulfoxide, naphthalene, anthraquinone and pigment is produced in the industrial manufacturing process of dithianon, from which the NaAc has been utilized to produce NaOH and HAc through bipolar membrane electrodialysis (BP-ED) [8].

However, the common means for treating salt solution such as crystallization, RO, NF and ED are of high energy consumption, and membrane fouling is serious for NF and RO [9]. Diffusion dialysis (DD), on the other hand, utilizes concentration difference as the driving force and has the advantages of simple operation, low energy consumption, low membrane pollution, no pollution to the environment, low installation and operating cost [10]. Hence DD has received a lot of applications in the field of acid or alkali recovery.

In the organism, kidney dialysis is a common process for treating salt, and hollow-fiber dialysis membranes have been researched for the ions permeability during hemodialysis [11]. However, DD process is scarce in dealing with industrial salt waste water. The diffusivity of salt is much lower as compared with common acid or alkali, such as HCl and NaOH. What's more, conventional ion exchange membranes (IEMs) contain mono-functional groups. That is, cation exchange membranes (CEMs) have cation exchange groups such as $-\text{SO}_3\text{Na}$, and allow the passage of cations (counter ions) but reject anions (co-ions). Anion exchange membranes (AEMs), on the other hand, embody anion exchange groups such as $-\text{NR}_3^+$, which allow the passage of

anions but reject cations. Hence, the permeation of co-ions is critical for the diffusion process [10, 12]. For dialysis of HCl or NaOH, the co-ion of H^+ or OH^- has small size and high diffusivity and can diffuse through the membrane along with the counter ion to remain electric neutrality. For dialysis of salts such as NaCl and NaAc, their transport through AEMs is low since Na^+ as the co-ion has larger size and lower diffusivity as compared with H^+ . Similarly, the transport of salts through CEMs is also low due to the low activity and large size of anions (Cl^- or Ac^-).

For improving the dialysis flux, our research group has designed IEMs with assistant functional groups. The groups such as $-Si-OH$ and $-C-OH$ can promote the transport of H^+ or OH^- groups through hydrogen bonding, and hence the flux of acid or base can be enhanced significantly [13-14]. Nevertheless, $-Si-OH$ and $-C-OH$ groups can not accelerate the transport of salt and hence may not be suitable for salt DD process. Later polyelectrolyte complexes (PECs)/PVA membranes are prepared from mixing of PVA with anion exchange and cation exchange multisilicon copolymers [15]. Polyvinyl alcohol (PVA) contains plentiful $-OH$ groups with high hydrophilicity, PECs with both $-N^+(CH_3)_3$ and $-SO_3Na$ groups can show improved stability and unique permeability, and the crosslinking of the $-Si-OH$ and $-C-OH$ groups can enhance the membrane stability. The membranes are utilized for DD of both acid and alkali, showing outstanding permeation flux. As the potential of polyelectrolyte complexes for salt permeation and separation through pressure-driven processes has been studied in previous researches [16-17], the PECs/PVA membranes are explored for DD process of salts in the present study.

Hence in this work, pure NaCl or NaAc solution is treated by DD process using PECs/PVA membranes, and the DD performances are compared with those of commercial membranes. Besides, amino acid/NaCl mixture and NaAc waste residue solution are processed to explore the membrane potential in treating actual industrial wastewater.

2. Experimentals

2.1. Experimental materials

Polyvinyl alcohol (PVA), with average degree of polymerization 1750 ± 50 , was supplied by Shanghai Yuanli Chemical Co., Ltd. (China). Pre-weighed PVA was immersed in water at room temperature for one day, then heated to around $95\text{ }^\circ\text{C}$ at the rate of $10\text{ }^\circ\text{C/h}$ and kept at $95\text{ }^\circ\text{C}$ for around 4 h. The homogeneous and transparent solution (5 wt%) was cooled to $60\text{ }^\circ\text{C}$ before use.

Commercial cation exchange membrane CJMCDD-1 was kindly supplied by Hefei Chemjoy Polymer Materials Co., Ltd. (China). Commercial anion exchange membrane DF-9010, which was also named as 9010 membrane [18], was supplied by Shandong Tianwei Membrane Technology Co., Ltd. (China). NaCl, NaAc and threonine (Thr) were of analytical grade and used without further purification. Sodium acetate waste residue was provided by a domestic agrochemical Co., Ltd. The waste residue (500 g) was dissolved in 1200 mL water through mechanical stirring. The accurate concentration of NaAc was determined by sodium ion concentration meter (DWS-51, Shanghai INESA Scientific Instrument Co., Ltd, China) and the organic impurities were analyzed by the Total Organic Carbon (TOC) analyzer (multi N/C 2100) from Analytik Jena AG, Germany. Deionized water was used throughout the experiments.

2.2. Preparation of the PECs/PVA membranes

The PECs/PVA membranes were prepared following previously reported procedures [15]. Firstly, cation exchange multisilicon copolymer was synthesized from the copolymerization of sodium styrene sulfonate (SSS) with γ -methacryloxypropyl trimethoxy silane (γ -MPS). Anion exchange multisilicon copolymer was synthesized from the copolymerization of vinylbenzyl chloride (VBC) with γ -MPS and quaternization with trimethylamine. Then the copolymer was dropped into 65 °C PVA solution and mixed to get the cation or anion exchange solution. Subsequently, the cation exchange solution was added dropwise into the anion exchange solution, stirred for 3 h, cast onto glass plates and dried at room temperature for two days. The formed film was peeled off from the plates, then heated from 50 °C to 130 °C, and kept at 130 °C for 4 h to obtain homogeneous and transparent PECs/PVA membranes. The dosage of the cation exchange solution with respect to the mixture solution increased from 0%, 20%, 40%, 60%, 80% to 100% and the membranes were recorded as M0, M20, M40, M60, M80 and M100, respectively. M20 - M80 were the PECs/PVA membranes. Membrane M0, the anion exchange membrane and membrane M100, the cation exchange membrane were used as references through the experiments.

2.3. Characterizations of PECs/PVA and commercial membranes

2.3.1. Water uptake (W_R)

Water uptake (W_R) was measured to investigate the membrane hydrophilicity. The membrane samples were dried and weighed. Then they were immersed in water at room temperature for two

days and weighed after removal of surface water with filter paper. W_R was calculated according to the following equation:

$$W_R = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

where W_w and W_d were the weight of the wet and dry membrane samples respectively.

2.3.2. Apparent transport number of the counter ions

The membrane samples were conditioned for around 12 h in 0.15 mol/L KCl solution prior to the test, and then fastened between a two-compartment cell. One side of the cell was filled with 0.2 mol/L KCl solution, the other side with 0.1 mol/L KCl solution and multimeter electrodes were separately set in the two sides of the solution. The stable numerical value of membrane potential (E_m , mV) was read, from which apparent transport number of the counter ions was calculated [13, 19].

$$Em(mV) = \frac{1000RT}{F} (\bar{t} - 1) \ln \frac{c_1}{c_2} \quad (2)$$

where $\bar{t}$ was the transport number of ions, T (K) was the temperature, R was 8.314, F was 96485, and c_1/c_2 was 2.

2.3.3. Membrane stability in salt solutions

Membrane sample was dried and weighed as m_0 with the area of S_1 . The sample was immersed in 1.0 mol/L NaCl or NaAc solution at room temperature for 36 h. Subsequently, the sample was immersed in water for 4 days with changing of fresh water for 5 times and the area measured as S_2 . The weight was measured as m_2 after drying at 60 °C till constant weight. The weight loss percent and swelling degree as reflected by the area expansion ratio were calculated according to the following equation [20]:

$$\text{weight loss percent} = \frac{m_0 - m_2}{m_0} \times 100\% \quad (3)$$

$$\text{swelling degree} = \frac{S_2 - S_1}{S_1} \times 100\% \quad (4)$$

2.4. Diffusion dialysis (DD)

The DD was running at room temperature. The membrane sample, with an effective area of 6.15 cm², was fastened between a two-compartment cell [14]. One compartment was used as

diffusate side and filled with water, while the other compartment was used as dialysate side and filled with the solution of NaCl (1.0 mol/L), NaAc (1.0 mol/L), NaCl/Thr (20.00 g/L NaCl + 2.5 g/L Thr) mixture or NaAc waste residue solution. NaAc concentration was 1.525 mol/L and TOC of impurities was 20.54 g/L for NaAc waste residue solution.

The membrane was conditioned for around 2 h in the dialysate solution prior to the test. The running time of DD was fixed at 5 h, because the DD performance was generally stable with the time [13]. Both compartments were stirred at identical rates to minimize concentration polarization effects. The solutions were then removed from both sides of the cell. The concentrations of NaCl or NaAc were determined by sodium ion concentration meter (DWS-51), while the concentration of threonine was determined by Amino Acid analyser (S7130 Amino Acid Reagent Organizer, SYKAM from Germany). The organic impurities were analyzed by the TOC analyzer.

The separation factor (S) with respect to one species over another is given as the ratio of dialysis coefficients (U) of the two species present in the solution. U can be calculated by the following formula:

$$U = \frac{M}{At\Delta c} \quad (5)$$

M in Eq. (5) is the amount of the component transported in moles, A is the effective area in square meters, t is the time in hours. ΔC is expressed as following [21-22]:

$$\Delta c = \frac{c_f^0 - (c_f - c_d)}{\ln \frac{c_f^0}{c_f - c_d}} \quad (6)$$

where c_f^0 and c_f are the feed concentrations at time 0 and t , respectively, and c_d the dialysate concentration at time t .

3. Results and discussion

3.1. Properties of the commercial and PECs/PVA membranes

Membranes M0 - M100 have thickness of 50-55 μm (Table 1), lower than the thickness of previous membranes (62 - 67 μm) [15] and hence the W_R values (36.7 – 252.9 %) are higher than

previously reported values (25.3 – 216.2 %). Membrane M0 prepared from PVA and anion exchange multisilicon copolymer has the highest W_R value, mainly because of the hydrophilic ion exchange groups $-N^+(CH_3)_3$ and the $-OH$ groups. PECs/PVA membranes (M20-M80) have lower W_R value than M0, and M60 has the lowest value of 36.7%. Therefore, formation of PECs can enhance membrane swelling resistance, because the membrane structure becomes condenser [16] when the cation and anion exchange copolymer chains are twisted and approached to form the polysalts. The bursting strength of M60 membrane has been measured as 0.17 MPa. As comparison, commercial CJ-EDC145 and CJ-EDA200 membranes (Hefei Chemjoy Polymer Materials Co., Ltd., China) without support and with thickness of ~ 0.145 and ~ 0.20 mm have bursting strengths higher than 0.35 MPa [23], and the values of the membranes based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (0.1 – 0.2 mm thick) with polyvinyl chloride substrate are higher than 0.8 MPa [24]. The lower strength of our membranes is partly due to the low thickness and absence of substrate or support. Besides, PVA material is of higher flexibility but lower strength than PPO material, since PPO contains benzene ring skeleton.

The ion transport numbers are also influenced by the formation of polysalts in PECs/PVA membranes. M60 and M40 have the lowest values of 0.67 and 0.78. The low selectivity towards counter-ions also means that the transport of co-ions is relatively easy. Take M40 as an example, the ratio of $-N^+(CH_3)_3$ to $-SO_3^-$ groups is around 6 : 4. The counter ions (Cl^-) can diffuse through the $-N^+(CH_3)_3$ groups, while the presence of zwitterionic or charge neutralization micro-phase in membrane matrix [15] can provide the passage for the co-ions (Na^+). The transport of both counter ions and co-ions may be advantageous for the diffusion of salts.

3.2 Stability in NaCl or NaAc solution

The different interactions, including the covalent bonding, the electrostatic and the hydrogen bonding should all influence the membrane stability, among which the electrostatic interaction is important since it can lead to dense membrane structure. The PECs are formed from $-N^+(CH_3)_3$ and $-SO_3Na$ groups through electrostatic interaction, resulting into zwitterionic or charge neutralization micro-phase [15], which can enhance membrane stability [25]. Accordingly, the swelling degrees of PECs/PVA membranes (M20-M80) are lower than membrane M0 and M100, and M40 and M60 have the lowest values of 11.3% and 11.6%, as shown in Table 2. The anion

exchange membrane M0 has the highest weight loss mainly because of the highest hydrophilicity. Commercial membranes DF-9010 and CJMCDD-1, especially CJMCDD-1, show low weight loss and swelling degree values, which are attributed to more hydrophobic polymer matrix (PPO and PVDF) and the presence of non-woven support.

Membrane M0 has the highest weight loss percent (37.0 %) in NaAc solution (Table 3), indicating its low stability. Membranes M20 - M80 have the weight loss percents of only 1.9 – 9.9%, indicating their significantly enhanced stability. DF-9010 membrane also shows high weight loss percent of 21.9%. Experimental observation shows that the NaAc solution became turbid after immersing DF-9010 membrane, and the membrane surface slags off significantly. Hence, DF-9010 anion exchange membrane has poor stability in NaAc solution. The instability should be caused by the degradation of the polymer material rather than the swelling of membrane matrix, since the swelling degree of DF-9010 is very low (1.4%). Commercial membrane CJMCDD-1, on the other hand, shows both low swelling degree and weight loss percent in NaAc solution and hence the stability is high.

3.3 DD performance for NaCl solution

M20 - M100 and commercial membranes are used for DD of NaCl solution. M0 membrane shows poor stability in NaCl solution and hence is not tested. The dialysis coefficients of NaCl (U_{NaCl}) are shown in Fig. 1. The values of PECs/PVA membranes (M20-M80) are from 0.00196 m/h to 0.0029 m/h, significantly higher than those of DF-9010 and CJMCDD-1 membranes. The values are also higher than that of NF115 ($\sim 10 \times 10^{-8}$ m/s, that is ~ 0.00036 m/h), CR65 ($\sim 2.2 \times 10^{-8}$ m/s, that is ~ 0.0000792 m/h) and MK40 ($\sim 0.7 \times 10^{-8}$ m/s, that is ~ 0.0000252 m/h) membranes for NaCl aqueous solution [26]. Therefore, PECs/PVA membranes have higher potential to treat NaCl solution.

Another point that should be noted is the influence of membrane thickness. The membrane performances can be affected by their thickness in some cases. For instance, membranes with lower thickness can be quaternized to a higher extent when immersed in trimethylamine (TMA), leading to higher ion exchange capacities (IEC) and W_R , and higher acid permeability [27]. Another example is commercial membranes DF-120 and 9010, which are both based on quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO). DF-120 membrane with thickness

of 0.32 mm and W_R of 42% exhibits H^+ dialysis coefficient of 0.009 m/h [28]. Meanwhile, 9010 membrane with thickness of 0.129 mm and W_R of 19.7% shows H^+ dialysis coefficient of 0.014 m/h [18].

IEC values of PECs/PVA membranes should not be influenced by their thickness, since the ion exchange groups ($-SO_3^-$, $-NR_3^+$) are pre-introduced before the membrane casting process. The membrane thickness is around 50 μm , which is much lower than those of commercial membranes. However, the commercial membranes contain non-woven fibers as the supports, and the active membrane layer is only about half of the whole thickness [29]. Therefore, the difference of membrane thickness is lower than that apparently appeared. On the other hand, the NaCl permeability can be 6 - 30 times higher than the values of commercial membranes. Hence, the superior permeability of PECs/PVA membranes is mainly due to the membrane composition such as the presence of both $-SO_3^-$ and $-NR_3^+$ groups and large amount of $-OH$ groups, rather than the thickness.

Anion exchange membrane DF-9010 (0.00034 m/h) has higher U_{NaCl} value than cation exchange membrane CJMCDD-1 (0.000095 m/h). The reason can be found in the view point of the membrane swelling and NaCl transport mechanism. DF-9010 exhibits higher swelling degree in NaCl solution, which can accelerate the ions diffusion. Meanwhile, the functional $-N^+R_3$ groups permit the transport of Cl^- ions as counter ions. The radius of Na^+ ion (0.98 or 0.95 Å) is lower than that of Cl^- ion (1.81 Å) [30] and hence its migration as the co-ion is easier, leading to relatively higher U_{NaCl} value. CJMCDD-1 membrane, on the other hand, has $-SO_3^-$ group and permits the migration of Na^+ ions, while Cl^- ions are more difficult to transfer through the membrane due to the static electro repulsion and the larger radius. The disadvantage of cation exchange membrane can also be confirmed by the lower U_{NaCl} value of M100 than those of M20-M80, despite the significantly higher swelling degree in NaCl solution.

Among the PECs/PVA membranes (M20-M80), M40 and M60 have highly dense structure and the swelling degrees are the lowest, which should hinder the transport of NaCl. Nevertheless, their U_{NaCl} values remain high, even higher than M80, illustrating the merit of more fully formed PECs for accelerating NaCl diffusion. Review of previously reported PECs membranes shows somehow contradictory results in electrolyte separations. On one hand, salt ions with low valence such as Na^+ and Cl^- can successfully pass through the membrane containing polysalts. For instance, the

permeability of NaCl can remain higher than 90% as the weight ratio of N-methylene phosphonic and quaternized chitosan changes from 0 : 1 to around 1 : 1 [16]. On the other hand, the PECs membrane from layer-by-layer (LBL) deposition are capable of rejecting ions with both low and high valences [31-32]. For instance, membranes from alternating electrostatic LBL adsorption of polyvinylamine (PVA) and polyvinyl sulfate (PVS) show NaCl and Na₂SO₄ rejections of 84 and 96% at 5 bar, and 93.5 and 98.5% at 40 bar, respectively [32]. We conclude that the structure of PECs may also be the key for influencing salt permeability. PECs from mixing of polyanions and polycations have inter-connected and twisted chains, and hence the functional groups such as -NR_3^+ , -SO_3^- and -PO_3^{2-} are dispersed in the membrane matrix to form zwitterionic structure [16], which provides passage of both anion and cation. The PECs from LBL process, on the other hand, consist of positively and negatively charged polyelectrolyte layers in alternating sequence [32]. The charged layers can strongly reject the equally charged ions in aqueous solution and hence the transfer of salts can be hindered, as illustrated in Fig. 2.

3.4. DD performance for NaAc solution

The dialysis coefficients of NaAc (U_{NaAc}) are also shown in Fig. 1. The U_{NaAc} values of PECs/PVA membranes are from 0.00108 m/h to 0.00503 m/h, higher than that of commercial CJMCDD-1 membrane (0.000035 m/h). DF-9010 membrane has low stability and hence is not suitable for DD of NaAc solution.

Among PECs/PVA membranes, M60 membrane shows the lowest U_{NaAc} value and M20 exhibits the highest value. M60 has dense membrane structure and the lowest swelling degree in NaAc solution. Ac^- ion is of lower diffusivity and larger size as compared with Cl^- ion and hence the dense membrane structure is vital for hindering NaAc diffusion. Membrane M20, with higher swelling degree and the highest content of -NR_3^+ groups, can accelerate the transport of Ac^- ions and thus the NaAc diffusion is enhanced.

3.5 DD performances for NaCl/Thr solution

The DD performances, including dialysis coefficients of NaCl (U_{NaCl}) and Thr (U_{Thr}), and separation factors (S) for NaCl/Thr solution, are shown in Fig. 3. The data of commercial DF-9010 and CJMCDD-1 membranes are also shown for comparison.

The U_{NaCl} values of PECs/PVA membranes are in the range of 0.00084 - 0.00146 m/h, which are about 6 - 26 times higher than those of commercial membranes DF-9010 and CJMCDD-1 (0.000132 m/h and 0.000056 m/h correspondingly). Membranes M40 and M60 show the highest U_{NaCl} values, which is mainly due to the presence of zwitterionic or charge neutralization micro-phase in PECs/PVA membranes [15]. More importantly, the $S_{\text{NaCl/Thr}}$ values of M40 and M60 are also high, which should be due to the dense membrane structures. Overall, PECs/PVA membranes, especially M40 and M60 membranes show both high permeability and selectivity in NaCl recovery from amino acid/ salt mixture.

Diffusion dialysis (DD) is driven by concentration difference across the ion exchange membranes and hence the separation is achieved mainly based on the different permeability of different ions. Up to now, DD process of acid/salt and base/salt mixtures are widely reported, since the permeability of acid or base can be much higher than those of salts. However, the separation of salt/organics has been seldom reported. The present work is a trial of the possibility of PECs /PVA membranes for salt recovery from amino acid or NaAc waste residue solution, and the effect of multivalent ions on the membrane performances has not been tested.

Previous DD process about acid/salt mixture has revealed that the presence of salt such as NaCl, FeCl_2 , NiCl_2 , CuCl_2 , ZnCl_2 or AlCl_3 can influence the transport of Cl^- , which is called the "salt effect". The effect is different when different salts are used [33]. For instance, Cu^{2+} , Fe^{2+} and Ni^{2+} can promote the transport of Cl^- much more than Al^{3+} and Na^+ , whereas, Zn^{2+} shows apparent hindrance effect. The findings above may indicate that the transport of salts can be influenced by multivalent ions. For instance, threonine fermentation broth may contain Cl^- , NH_4^+ , SO_4^{2-} , CO_3^{2-} , Na^+ , Fe^{2+} , Mg^{2+} , Ca^{2+} , and other heavy metal ions. The transport of Cl^- ions may be facilitated due to the presence of Fe^{2+} and hence NaCl permeability might be increased. Meanwhile, the influence of other salts should be complex and needs more investigation.

3.6 DD for NaAc waste residue solution

The DD performances, including dialysis coefficient of NaAc (U_{NaAc}) and TOC values of the impurities after 5 h running, are shown in Fig. 4. The data of CJMCDD-1 membrane are also shown for comparison.

The U_{NaAc} values of PECs/PVA membranes are from 0.000602 m/h to 0.00120 m/h, about 13 - 26 times higher than that of commercial CJMCDD-1 membrane (0.0000469 m/h). M40 and M60 show relatively lower U_{NaAc} values, which is in accordance with the results for pure NaAc solution. The TOC values in water compartment are also relatively low as compared with M80 and M100, and hence dense membrane structure can retard the transfer of impurities in NaAc waste residue and increase the product purity. Overall, the PECs/PVA membranes can be potentially applied in treating industrial waste salt.

The U_{NaCl} and U_{NaAc} values decrease for most of the membranes in Fig. 3 and Fig. 4 as compared with Fig. 1, which may be due to membrane fouling and competition of other components with NaCl or NaAc. Amino acid in NaCl/Thr mixture and organic impurities in NaAc waste residue solution can be adsorbed at membrane surface or into the membrane cross-section, which can cause membrane fouling and hinder NaCl or NaAc transport through the membrane. The difference of M20 membrane in Fig. 3 and Fig. 4 as compared with Fig. 1 is much more significant as compared with the other membranes. Possible reason is that M20 membrane has higher W_R value than M40 - M80 membranes and can be more significantly swelled in aqueous solution. The adsorption of amino acid or organic impurities can be higher, leading to lower salt permeabilities.

4. Conclusions

Polyelectrolyte complexes (PECs)/PVA membranes are prepared from blending of PVA, anion and cation exchange multisilicon copolymers. Zwitterionic or charge neutralization micro-phase from the combining of $-\text{N}^+(\text{CH}_3)_3$ and $-\text{SO}_3^-$ groups can not only enhance membrane stability, but also influence the diffusion dialysis (DD) performances of NaCl, NaAc, NaCl/Thr mixture and industrial NaAc waste residue.

PECs/PVA membranes have improved stability when compared with anion or cation exchange copolymer-PVA membranes. The permeability for NaCl or NaAc solution is much higher than commercial membranes. The dialysis coefficient of NaCl (U_{NaCl}) can reach up to 0.00290 m/h, higher than those of commercial DF-9010 and CJMCDD-1 membranes (0.00034 m/h and 0.000095 m/h). The formation of PECs can accelerate the NaCl diffusion, despite the dense membrane structure and low swelling degrees. The dialysis coefficient of NaAc (U_{NaAc}) can reach

up to 0.00503 m/h, also higher than that of CJMCDD-1 membrane (0.000035 m/h). Membrane anion exchange capacity and swelling behaviour play the key role in determining the permeability of NaAc. The PECs/PVA membranes show both higher permeability and selectivity than commercial membranes for NaCl/Thr mixture. For treating NaAc waste residue, the U_{NaAc} values are from 0.000602 m/h to 0.00120 m/h, higher than that of CJMCDD-1 membrane (0.0000469 m/h). Overall, the PECs/PVA membranes can be potentially applied in treating industrial waste salt.

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Captions of Tables and Figures

Tables

Table 1 Membrane thickness and properties

Table 2 Membrane stabilities in NaCl solution

Table 3 Membrane stabilities in NaAc solution

Figures

Fig. 1 The dialysis coefficient of NaCl (U_{NaCl}) and NaAc (U_{NaAc})

Fig. 2 Illustration of NaCl transport through PECs membranes from mixing or LBL method

Fig. 3 The dialysis coefficient of NaCl (U_{NaCl}) and separation factor ($S_{\text{NaCl/Thr}}$) for NaCl/Thr solution

Fig. 4 The dialysis coefficient of NaAc (U_{NaAc}) and TOC values of impurities in water compartment after 5 h diffusion dialysis running for NaAc waste residue. Note: TOC value of NaAc has been deducted.

Table 1 Membrane thickness and properties

Membrane	DF-9010	M0	M20	M40	M60	M80	M100	CJMCDD -1
composition	QPPO/SiO ₂	PVA-anion exchange copolymer		PECs/PVA			PVA-cation exchange copolymer	PVDF+S PPO
thickness (μm)	115 ^a	50	51	51	50	50	55	118 ^a
W _R (%)	20.3	252.9	81.2	48.3	36.7	45.6	47.4	26.26
transport number of Cl ⁻	0.83	0.86	0.91	0.78	-	-	-	-
transport number of K ⁺	-	-	-	-	0.67	0.84	0.88	0.98

^aThe thickness of DF-9010 and CJMCDD-1 membranes includes non-woven support.

Table 2 Membrane stabilities in NaCl solution

membrane	swelling degree (%)	weight loss percent (%)
DF-9010	1.9	3.5
M0	98.3	35.0
M20	29.3	6.0
M40	11.3	4.5
M60	11.6	4.4
M80	27.7	2.2
M100	36.5	2.5
CJMCDD-1	0.07	~0

Table 3 Membrane stabilities in NaAc solution

membrane	swelling degree (%)	weight loss percent (%)
DF-9010	1.4	21.9
M0	41.3	37.0
M20	59.0	9.9
M40	25.1	4.8
M60	11.7	3.3
M80	18.4	1.9
M100	38.4	2.4
CJMCDD-1	~0	2.0

Fig. 1

Fig . 2

PECs membrane
from mixing

(a)

PECs membrane
from LBL method

(b)

Fig.3

Fig . 4

The **Suggested Referees** are listed below.

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