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Novel polyelectrolyte complex membranes containing free sulfate groups with improved pervaporation dehydration of ethanol



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ABSTRACT

Novel polyelectrolyte complexes containing free sulfate (SO₃) groups (PECSs) were synthesized, with the sulfation of NH₂ groups in the soluble chitosan (CS)/sodium carboxymethyl cellulose (CMC) complexes, and their membranes (PECSMs) were subjected to pervaporation dehydration of ethanol. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy were employed to characterize the chemical structure and the composition of PECSs. Zeta (ξ) potential and field emission scanning electron microscopy were used to investigate the surface charge density of the PECS particles and the morphology of their membranes. The effects of the chemical composition on the swelling degree, the hydrophilic property, and the pervaporation dehydration performance of PECSMs were determined. It was found that free SO₃ groups were successfully incorporated into PECSMs. Both the flux and the separation factor of PECSMs increased with increasing SO₃ groups. The permeation flux of PECSMs increased, and their selectivity was almost invariable with increasing temperature. A high separation performance of PECSMs was achieved in the dehydration of 10 wt% water–ethanol mixtures at 70 °C, yielding a flux and a separation factor for the PECSM-20 at 1385 g/m² h and 1571, respectively. These results indicated that the introduction of free SO₃ groups into PECSMs was an effective strategy to improve the pervaporation dehydration performance of PECSMs.

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1. Introduction

Pervaporation utilized as a membrane separation technology has advantages over the traditional distillation or adsorption process, especially for separating an azeotropic mixture or a mixture of liquids with close boiling points [1]. Pervaporation features energy-saving characteristics and high efficiency in separating liquid–liquid molecules, and has been attracting growing interests [2]. There is a wide range of applications for pervaporation, such as the dehydration of organics, the recovery of organics, and the separation of organic mixtures. The dehydration of organics is always viewed as a major part of industrial usage [3]. Polymeric materials are excellent candidates for the dehydration of organics, and their membranes are lower-cost and improved process-ability [4]. A variety of polymeric materials, including poly (vinyl alcohol) [5–7], thin-film composite membranes [8], organic–inorganic hybrids [9–11], and charged

polymers such as chitosan (CS) and other synthetic polyelectrolytes as well as their corresponding complexes [12–14], have been subjected to pervaporation dehydration of alcohols.

Polyelectrolyte complexes (PECs) have been considered as a promising candidate for pervaporation dehydration due to their ionic-crosslinking structure and highly hydrophilic property [15]. PEC membranes (PECMs), including multilayered PECMs [16,17], two-ply PECMs [18], and blend PECMs [19,20], were prepared by different methods and used for pervaporation dehydration. Homogenous PECMs were prepared with weak poly-carboxylate (COO[−]) and positively charged polyelectrolytes in acidic conditions, and dispersed in alkaline solutions [21]. The homogenous PECMs exhibited good performance in the dehydration of aqueous alcohols, which was arisen from the unique water channel structure contributed by the charged PEC particles, based on the positron annihilation lifetime spectroscopy (PALS) analysis [22]. Due to the higher hydrophilicity of sulfonate or sulfate groups compared with carboxylate groups [23], PECMs containing sulfonate groups exhibited a better pervaporation dehydration performance than those containing carboxylate groups [24–26]. These homogenous PECMs composed of complexed sulfate (SO₃) groups were also

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prepared by complexing sulfated sodium carboxymethyl cellulose containing SO_3^- and COO^- groups with polycations in acidic conditions, and then dispersed in alkali solutions. Complexed SO_3 groups improved the pervaporation performance of PECMs for the ethanol dehydration [27]. However, homogenous PECMs containing free SO_3 groups have not been prepared yet. This is because SO_3^- units pair with ammonium (NH_3^+) groups prior to COO^- when the co-existence of the dual anionic groups occurs, owing to the stronger binding interaction between SO_3^- and NH_3^+ [28]. Moreover, free SO_3 groups exhibit a higher affinity with water than with the ion-pairs between SO_3^- and NH_3^+ [29]. It is readily anticipated that free SO_3 groups could enhance the hydrophilicity of the water channels embedded in PECMs leading to the effective improvement of the permeation flux, while maintaining the ionic-crosslinking characteristic of the PECMs, which inhibits excessive swelling and assures high selectivity.

Aiming at introducing free SO_3 groups into PECs, our approach in this study was through the sulfation of NH_2 groups in PECs. CS containing NH_2 groups and CMC containing carboxylate (COONa) groups were used as polyelectrolyte substrates, and their soluble CS/CMC complexes were prepared based on the previous “acid protection” strategy. PECs containing free SO_3 groups (PECSs) and their homogenous membranes (PECSMs) were prepared by the sulfation of NH_2 in the soluble CS/CMC under alkaline conditions. The characterization of the structure and the pervaporation performance of PECSMs were systematically discussed. It was confirmed that free SO_3 groups were capable of effectively improving the performance of PECSMs in the dehydration of ethanol and rendering PECSMs to have high pervaporation performance.

2. Experimental

2.1. Materials

Chitosan (CS) ($M_n=200,000$ g/mol, deacetylation degree=90%) was purchased from Yuhuan Chemical Company. Sodium carboxymethyl cellulose (CMC), with an intrinsic viscosity of 625.1 mL/g in 0.1 M sodium hydroxide (NaOH) aqueous solutions at 30 °C, was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Trim-ethylamine-sulfur trioxide complex ($(\text{CH}_3\text{CH}_2)_3\text{N}\cdot\text{SO}_3$) was purchased from Aldrich and used without further purification. All organic solvents (analytical grade), such as ethanol and acetone, were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used as received. Hydrochloric acid (HCl), sodium hydroxide (NaOH), and sodium carbonate (Na_2CO_3) were analytical reagents. Polysulfone ultra-filtration membranes were supplied by the Development Centre of Water Treatment Technology, Hangzhou,

China, which were used as membrane substrates. De-ionized water, with a resistance of 18 $M\Omega$ cm, was used in all experiments.

2.2. Preparation of sulfated CS/CMC complexes (PECSs) and their membranes (PECSMs)

As shown in Fig. 1, PECSs were prepared by using sulfur trioxide trim-ethylamine complex ($(\text{CH}_3)_3\text{N}\cdot\text{SO}_3$) to sulfate the NH_2 groups of the water-soluble CS/CMC complexes. This sulfation procedure was actual N-sulfated of NH_2 groups in CS/CMC complexes according to the method developed by Holme [30]. From Fig. 1, it could be observed that the prepared CS/CMC complexes contained some residual NH_2 on CS chains for sulfation reaction. The unionized carboxyl groups (COOH) entitled the CS/CMC complex with the ability to form homogenous solutions under alkali conditions. The water-soluble CS/CMC complexes were prepared based on the previously reported “acid protection” strategy, and dispersed in alkali aqueous solutions [31]. First, 400 mL negatively charged CMC solutions and 400 mL positively charged CS solutions were dissolved in 0.005 M HCl. Then, the molar concentration of both the CS and the CMC monomer unit was kept at 0.01 M. It was speculated that there was 50 mol% of residual NH_2 protonated to NH_3^+ groups on CS chains and 50 mol% COO^- groups protonated to COOH groups on CMC chains. In other words, the charge density of the CMC chains was 0.5, which was equal to that of the CS chains. Subsequently, the CS solutions were dropped into the CMC solutions under vigorous stirring at 600 rpm. Turbidity immediately occurred when the CS solutions were added, and the PECSs were precipitated out when the ionic complexation between CMC and CS was reached. It should be noted that the ionic complexation was reached when approximately 400 mL CS solutions were added into 400 mL CMC solutions. This result was attributed to CMC and CS chains having the same charge density. The obtained CS/CMC complexes were dried at 50 °C for 6 h. Finally, the dried CS/CMC complexes (1.6 g) were dispersed in Na_2CO_3 aqueous solution (80 mL) due to the existence of unionized carboxyl groups (COOH) in them, and then the sulfated agent ($(\text{CH}_3)_3\text{N}\cdot\text{SO}_3$) was added. The pH of this aqueous solution was kept at 9 by adjusting the molar ratio of Na_2CO_3 to $(\text{CH}_3)_3\text{N}\cdot\text{SO}_3$. After the reaction at 60 °C for 6 h, the product was precipitated in acetone, collected, and washed with acetone three times. The obtained PECSs were dissolved in 80 mL water, and then precipitated in ethanol, collected and washed with 80% (v/v) aqueous ethanol three times to remove the residual salts. The obtained PECSs were dried at 50 °C for 6 h. The compositions of PECSs were tuned by varying the ratio of the $(\text{CH}_3)_3\text{N}\cdot\text{SO}_3$ monomer to the monomer unit of CS. Three compositions of PECSs were prepared with the ratios of the $(\text{CH}_3)_3\text{N}\cdot\text{SO}_3$ monomer to the monomer unit of CS in CS/CMC complexes at 1, 2, and 3. The ratios of the Na_2CO_3 monomer to the monomer unit of CS were 0.5, 1.5,

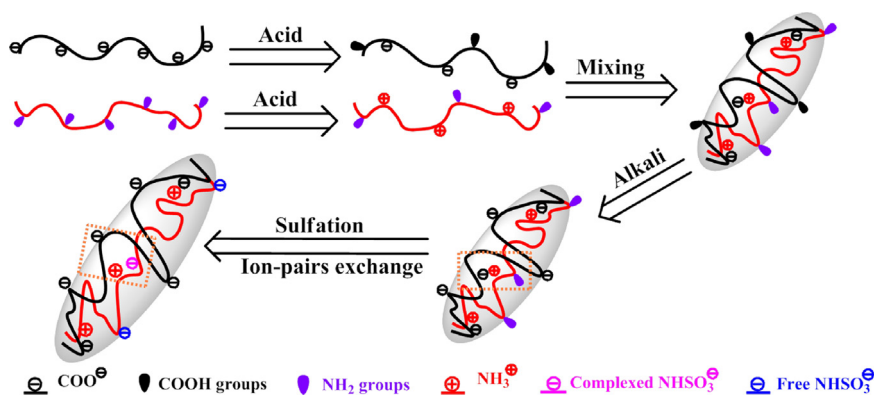


Fig. 1. Schematic diagram for fabricating PECs containing free SO_3 groups (PECSs).

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