



Anionic surfactant-doped Pebax membrane with optimal free volume characteristics for efficient CO₂ separation



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ABSTRACT

Calcium lignosulfonate (CaLS) is an organic anionic surfactant, which has been used for the first time as a charged additive to improve the performance of Pebax membranes for CO₂ separation. Owing to the abundant hydrophobic groups and low charge density of lignosulfonate ion (LS²⁻), CaLS was found to efficiently interrupt the chain packing of Pebax 1657 matrix via both metal-organic complexation and hydrophobic interaction, endowing membranes with tunable fractional free volume (FFV). For dry membranes, CaLS could slightly enlarge membrane FFV without forming highly crosslinked structures. For humidified membranes, water-induced swelling led to a remarkable enhancement of FFV, while the hydrophobic interaction between CaLS and Pebax avoided excessive swelling. With the coexistence of CaLS and water, optimal FFV and moderate salting-out effect were acquired, resulting in very high CO₂ permeability (3585 Barrer) and fairly good CO₂/gas selectivity (29 for CO₂/CH₄ and 71 for CO₂/N₂). The separation mechanism was discussed by analyzing the relationship between salting-out effect and the well-known solution-diffusion mechanism. Based on the performance comparison of Pebax–CaLS membrane with the previously reported Pebax–salt membranes, the guideline about the design of polymer electrolyte membranes for CO₂ capture was tentatively proposed.

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1. Introduction

In recent years, exponential growth of global CO₂ emission arising from the escalating energy consumption, largely from the combustion of fossil fuels, has become one of the most challenging environmental and energy issues for human beings [1,2]. Among the mainstream technologies for CO₂ capture, membrane gas separation has attracted growing attentions due to the benefits from small footprint, low operating cost and easy scalability [3–7]. Currently, polymer-based membranes with excellent processing repeatability and scale-up simplicity constitute the most promising candidates for commercialization. Nevertheless, the bottleneck of polymer-based membranes that lies in the “trade-off” relationship between permeability and selectivity has not been well addressed [8–10]. In particular, considering the huge annual CO₂

emission required to be captured, polymeric membrane materials with super high CO₂ permeability and adequate CO₂/gas selectivity are urgently required [3,11].

Nowadays, the high-permeability polymeric membrane materials suitable for CO₂ separation are typically categorized into three groups: (1) polyether-based copolymers, especially poly (ethylene oxide) (PEO)-based ones [7]; (2) 6FDA-based polyamides [12]; (3) polymers of intrinsic microporosity [13,14]. These membrane materials possess high fractional free volume at dry state, and CO₂ separation is primarily dependent on solution-diffusion mechanism. On the other hand, hydrophilic polymers with intrinsically low fractional free volume have also been found highly permeable at the water-swollen state [15,16]. This fact is important for the rational development of CO₂ separation membranes, owing to the following three reasons. *Firstly*, the abundant polar groups of hydrophilic polymers allow preferential dipole–quadrupole interactions with CO₂ and thus solubility-dependent separation [17–19]. *Secondly*, the presence of water allows other efficient separation mechanisms (e.g. facilitated transport, salting-out effect), which is likely to overcome the inherent limit of the solution-diffusion

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mechanism [20–22]. In particular, “salting-out effect” for CO₂ separation membrane is a recently proposed concept, which means that water molecule surrounding ion is capable of decreasing the solubility of non-condensable gases (e.g. N₂, CH₄) and thus to disrupt the continuity of their transport pathways [21]. *Last but not the least*, many hydrophilic polymers are easy to be obtained, which is technologically attractive to develop a high-performance, low-cost membrane.

Owing to the aforementioned attributes, hydrophilic polymer membrane doped with a water-soluble salt is emerging as a potential candidate for efficient CO₂ capture [22–25]. The abundant amount of salt ions can strongly adsorb water from humidified gas environment to “salt out” the non-condensable gases and the fast transport of HCO₃[−] produced from CO₂ hydration. Furthermore, the ion–dipole interactions between ions and the polar groups on polymer chains can bring out “ionic crosslinking” effect, so as to avoid excessive swelling. In our previous study, a series of inorganic salts containing alkali and alkaline-earth metal cations have been adopted to fabricate membranes for CO₂ capture [22,25]. Both the cation and anion of salts were found to enable salting-out effect and ionic crosslinking effect, and thus high CO₂/gas selectivity was achieved. However, hydrophilic membranes containing organic salts have been scarcely reported for CO₂ separation. Actually, the presence of functional groups in organic salts may render multiple interactions between polymer matrix and salt ions, which provides more opportunities to optimize the free volume of membranes. Notably, anionic surfactant (AS), as one important type of organic salts, usually possesses abundant hydrocarbon groups, which are expected to weaken the ionic crosslinking effect of membranes by introducing hydrophobic interactions. In this manner, replacement of the inorganic salts by AS is envisaged to further enhance membrane permeability. Besides, the hydrophobic body of AS does not favor excessive water-induced swelling of membrane matrix.

In this study, anionic surfactant was doped into a hydrophilic polymer matrix for the first time, with the purpose of pushing the limit of CO₂ permeability for charged polymer membranes. Calcium lignosulfonate (abbreviated as CaLS, see the chemical structure in Scheme 1) was selected as the anionic surfactant due to the following considerations: (1) lignosulfonate (LS^{2−}) contains extra ether group and phenyl group on its hydrocarbon backbone, which ensures the high solubility of LS^{2−} in water without forming foams; (2) Ca²⁺ has been reported as an optimal cation for Pebax modification because of its capacity of triggering strong salting-out effect and ionic crosslinking effect [22,25]; (3) CaLS as a derivative of lignin is cost effective and environmental benign, which is important when being considered for commercialization. Pebax 1657 (Scheme 1) was selected as the hydrophilic polymer matrix

due to its preferential CO₂ sorption capacity, excellent film-forming ability and abundant availability [26–28]. Moreover, the non-ionic characteristic of Pebax allows the investigation of salting-out effect and ionic crosslinking effect caused by CaLS.

2. Experimental

2.1. Materials

Pebax(R) MH 1657 was purchased from Arkema (Paris, France). CaLS (purity > 96.0%) was purchased from Aladdin Reagent Co., Ltd. (China). Ethanol (AR) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). All chemicals were used without further purification.

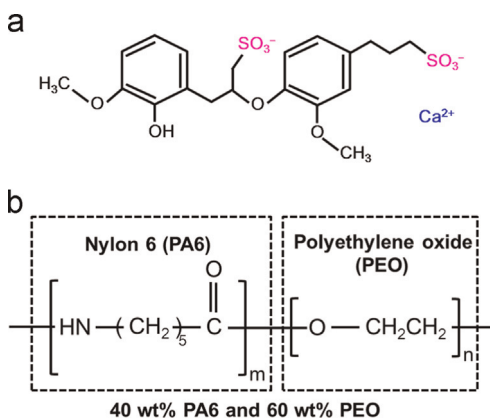
2.2. Membrane preparation

Pebax was dissolved in a mixed ethanol/water (70/30 wt%) solvent under mild mechanical stirring (with reflux) at 80 °C for 2 h to obtain 5 wt% homogeneous solution. After cooling the solution to ambient temperature, a certain amount of CaLS was added into the solution and allowed to be completely dissolved during 2 h stirring. The molar ratio of Ca²⁺ to ethylene oxide (EO) unit (abbreviated as Ca²⁺:EO) was controlled at 0, 1:60, 1:30, 1:15 and 1:7.5. After removing bubbles, the homogeneous solutions were cast onto Teflon petri dishes and then dried under ambient conditions for 24 h. The membranes were further annealed in a vacuum oven at 45 °C for three days to remove the residual solvent. The resultant membranes were designated as Pebax, where salt was absent, or Pebax–CaLS (X), where X means EO:Ca²⁺. The thickness of all membranes was controlled within the range of 80–90 μm. To ensure reproducibility, all the membranes above were repeated at least twice.

2.3. Membrane characterization

The morphology of Pebax–CaLS membrane and the distribution of CaLS in membrane were investigated by scanning electron microscope (SEM, Philips XL-30E) equipped with energy dispersive X-ray (EDX) spectroscopy. Thermal properties of samples were measured under N₂ atmosphere by Differential Scanning Calorimetry (DSC) module (DSC 200F3, NETZSCH), with the temperature rising from −70 to 250 °C at a heating rate of 10 °C/min. The chemical structure of membrane was characterized by a Nicolet-560 Fourier transform infrared spectrometer (FT-IR) with scan range of 4000–400 cm^{−1}. The crystalline structures of CaLS powder and the membranes were determined using wide-angle X-ray diffraction (WAXD) in the range of 10–50° at the speed of 10°/min (Rigaku D/max 2500 v/pc, CuK 40 kV, 200 mA, λ = 1.5406 Å). Young's modulus, break strength and maximum elongation of a sample were determined by a material testing machine (WDW-200 N) with the extension rate of 7 mm min^{−1}.

Membrane density was determined at 25 °C by the buoyancy method using an electronic balance (OHAUS®, CP224C) equipped with density determination kit. Fractional free volume (FFV) was calculated based on the density data following the previous method, [22] which is based on binary interaction principle. When there is only one additional component in polymer (the case of dry membrane measurement), the method is always available, because the difference between actual density and ideal density (calculated according to ideal mixing rule) is absolutely caused by binary interactions. When there is at least two additional components in polymer (the case of humidified membrane measurement), the method is only applicable when the interactions between/among the additional components are taken into consideration. In this



Scheme 1. Chemical structure of (a) calcium lignosulfonate and (b) Pebax 1657.

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