Steric Hindrance Effect Demonstrated in Polyvinylamine Facilitated Transport Membranes for CO_2 Separation

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This abstract consists of a brief description of CO_2 Facilitated Transport Membranes, Sterically Hindered Amine, and New Membranes based on Sterically Hindered Polyvinylamines in the following paragraphs for CO_2 separation.

CO_2 Facilitated Transport Membranes: CO_2 capture from flue gas (main component: N_2) is essential for eliminating greenhouse gas emission, and CO_2 separation from synthesis gas is effective for hydrogen purification. Due to the inherent advantages of membrane separation, e.g., high energy efficiency, operational simplicity, small footprint, and the elimination of thermodynamic equilibrium capacity limitations, membrane technology is receiving more and more attention for CO_2 separation. For most conventional polymer membranes, CO_2/N_2 separation follows the solution-diffusion mechanism. The key challenge of solution-diffusion membranes is the trade-off between permeability and selectivity, i.e., the Robeson's Upper Bound. However, for facilitated transport membranes, the non-reactive gas component, e.g., N_2, diffuses through the membrane via the solution-diffusion mechanism, whereas CO_2 follows the facilitated transport mechanism via its reversible chemical reaction with carriers (often amines). Therefore, CO_2 transport is facilitated, and both high CO_2 permeability and high CO_2/N_2 selectivity can be achieved.

Sterically Hindered Amine: Amine carriers are the key for the CO_2 separation performance of a facilitated transport membrane. Amine carriers exhibiting a high CO_2 loading capacity and reaction rate are always desirable. A sterically unhindered amine forms a stable carbamate ion with CO_2, as shown in Eq. (1), and the stoichiometric CO_2 loading is one mole of CO_2 per two moles of the unhindered amine. However, for a sterically hindered amine, its carbamate ion is not stable due to the incorporation of a bulky substituent group to the nitrogen atom and thus is converted to the bicarbonate ion as the sink for CO_2 with the resultant reaction shown in Eq. (2). Therefore, the stoichiometric CO_2 loading is doubled, with one mole of CO_2 per mole of the sterically hindered amine.

$$CO_2 + 2\,R\text{-}NH_2 \rightleftharpoons R\text{-}NH\text{-}COO^- + R\text{-}NH_3^+ \quad (1)$$

$$CO_2 + R\text{-}NH_2 + H_2O \rightleftharpoons HCO_3^- + R\text{-}NH_3^+ \quad (2)$$

A sterically hindered amine is defined as either a primary amine in which the amino group is attached to a tertiary carbon or a secondary amine in which the amino group is attached to at least one secondary or tertiary carbon. The effects of sterically hindered amines have been reported in a lot of literature on aqueous amine solutions for CO_2 absorption. Those works focus on the small molecules of sterically hindered amines in the aqueous phase. For solid membranes, amine carriers anchored to the polymer matrix are more desired, since it can eliminate the carrier loss. Zhao *et al.* in our group were the first to demonstrate the steric hindrance effect in solid polyamine-containing membranes. In that work, the polyallylamine was modified into sterically hindered amine, and the steric hindrance effect on separation performance was investigated for syngas purification applications.

New Membranes based on Sterically Hindered Polyvinylamines: The goal of this work on sterically hindered polyamines is to extend the research of steric hindrance effect demonstrated in polyallylamine-based membranes to other polyamines for the synthesis of

new, improved membranes for carbon capture applications. In this work, polyvinylamine was chosen as the amine carrier and modified into sterically hindered polyamines since it possesses the highest content of amino groups among all the common polyamines for CO_2 facilitated transport. The membranes synthesized in this work have been investigated mainly for CO_2 capture from flue gas in coal-fired power plants.

The amine modification reactions were conducted as follows: to synthesize poly(N-methyl-N-vinylamine), one equivalent amount of iodomethane as well as potassium hydroxide was added into the aqueous solution of polyvinylamine (PVAm) and reacted with the PVAm at 45^{o}C for 48 h. After the reaction, one methyl group should be attached onto the nitrogen atom of the amino group in each repeating unit of polyvinylamine to form poly(N-methyl-N-vinylamine), with one equivalent amount of potassium iodide salt and water generated as byproducts. The salt was removed from the polyamine solution by dialysis. Similarly, poly(N-isopropyl-N-vinylamine) and poly(N-tert-butyl-N-vinylamine) were synthesized by reacting PVAm with 2-bromopropane and 2-bromo-2-methylpropane, respectively, under the same reaction conditions. The steric hindrance degree can be quantitatively described by Taft's steric hindrance parameter, $\sum E_s$, which is determined by the group contribution method. The $\sum E_s$ values of polyvinylamine, poly(N-methyl-N-vinylamine), poly(N-isopropyl-N-vinylamine) and poly(N-tert-butyl-N-vinylamine) were calculated to be 0.93, 1.00, 1.86 and 2.67, respectively. The obtained sterically hindered polyamine solutions were concentrated by N_2 purging to have an appropriate viscosity for coating onto nanoporous polyethersulfone (PES) substrates and dried in the fumed hood at ambient conditions.

The membranes were all tested at 57^{o}C, the typical flue gas temperature. The dry feed gas consisted of 20% CO_2 and 80% N_2, and the sweep gas was purified argon. Both feed gas and sweep gas were humidified and saturated by water vapor at the testing temperature (the saturated water vapor content in each of the feed and sweep sides was 17 mol% at 57^{o}C). The pressure of the feed side was controlled at 1.5 psig while the sweep side pressure was maintained at 1.4 psig. Under the testing conditions, polyvinylamine membranes demonstrated an average CO_2 permeability of 213.9 Barrers and CO_2/N_2 selectivity of 48.5. Although the content of amino groups reduced by incorporation of alkyl groups, CO_2 permeability was improved by 24% and CO_2/N_2 selectivity was increased by 14% by modifying polyvinylamine into poly(N-methyl-N-vinylamine). These results have demonstrated the effect of steric hindrance on CO_2 separation performance with the incorporation of the methyl group for enhancing CO_2 loading capacity. Poly(N-isopropyl-N-vinylamine) and poly(N-tert-butyl-N-vinylamine) membranes showed 15% and 11% improvements on CO_2 permeability, respectively, with no significant changes in CO_2/N_2 selectivity. The improvement on selectivity was not as significant as CO_2 permeability, which could be attributed to the reduced polarity caused by the incorporation of bulky alkyl groups, thus increasing the solubility of N_2 in the membranes. Comparing the CO_2 separation performances of the above polyamine membranes and their corresponding steric hindrance degrees, we found that the CO_2 permeability increased first significantly with increasing the steric hindrance degree and then less pronouncedly with further increasing the steric hindrance degree. This could be explained by the reduced amino group content in the membranes and the lower reaction rate due to the incorporation of bulky groups onto amino groups. It should be noted that the new poly(N-methyl-N-vinylamine) membrane can give higher CO_2 permeability than the best sterically hindered polyamine membrane, i.e., poly(N-isopropyl-N-allylamine), reported in the literature.