Quantum chemistry calculation and experimental study of CO_2/CH_4 and functional group interactions for the design of solubility selective membrane materials

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A B S T R A C T

The separation of CO_2 from CH_4 in the natural gas sweetening process would benefit from a membrane material which has a high solubility selectivity between these two molecules. In this study, quantum chemistry calculations were used to screen a set of twelve representative functional groups by comparing their CO_2 and CH_4 binding energies, as well as the binding energy differences. The calculation results indicate that non-base groups, such as acids and their salts, may help improve the solubility selectivity of polymeric membrane materials for CO_2 over CH_4. Experimental measurements of CO_2 solubility in polyacrylic acid (PAA) confirmed that acid groups can help absorb CO_2 and enhance the selectivity over CH_4. However, the selectivity increase due to the acid functional group is not exceptional. Further quantum chemistry study of functional group interactions reveals that strongly polar functional groups can have self-interactions and form "dimers" in the polymer. The formation of functional group dimers may decrease the solubility of CO_2 because of their weaker interactions with CO_2 than isolated functional groups. In addition, our calculations show that water can interact more favorably with polar functional groups than CO_2. Therefore the presence of water may decrease CO_2 solubility.

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1. Introduction

Natural gas sweetening is one of the most important gas separation processes in the energy industry because the acid gases, mostly carbon dioxide (CO_2) and hydrogen sulfide (H_2S), can corrode the distribution pipeline and CO_2 does not have heating value [1–3]. In comparison to the amine scrubbing technology, membrane separation seems to be more environmentally friendly because there is no amine solution loss to the atmosphere [2,4]. For membrane technologies to be more competitive, highly selective and permeable functional membrane materials have to be designed. The permeability (P) of a solute in a membrane material can be approximated as the product of its diffusivity (D) and solubility (S) [5,6]. The design of functional materials to increase carbon dioxide (CO_2) solubility selectivity over methane (CH_4) would require a good understanding of the interactions between CO_2/CH_4 and the potential functional groups. Experimental determination of these interactions is costly and time-consuming. Often, it is difficult to identify and isolate these interactions. Quantum chemistry calculations, however, can assist the study of such interactions in a fast and quantitatively accurate manner. With the choice of the right level of theory and a good

basis set, these calculations often give accurate results on the binding energies of molecules [7–9]. In fact, quantum chemistry screening has become a common practice in the scientific research for materials innovation, such as drug discovery [10] and design of functional materials [11,12].

Carbon dioxide is a Lewis acid gas. Therefore it is quite natural to design polymers with basic groups, such as amine, while excluding polymers with acidic groups, such as carboxylic acid. However, we have to realize that CO_2 has two types of atoms: C is an electron acceptor (Lewis acid) and while O is an electron donor (Lewis base). Most functional groups have both electron donors and acceptors at the same time. The absorption of CO_2 to a functional group usually happens through two or more interactions, so even an acid group could have affinity for CO_2 [13]. The absorption strength strongly depends on the polarities of the absorbates and the absorbing functional groups. As such, functional groups with high polarity may have strong interactions with, and may help absorb, CO_2. For CO_2/CH_4 separations, it is preferable to have functional groups that have strong interactions with CO_2 and weak interactions with CH_4, however interactions that are too strong might interfere with CO_2 diffusion through the polymer. To that end, quantum chemistry calculations have been conducted to obtain the CO_2 and CH_4 binding energies with a series of chemical structures (or functional groups). The binding energies of CO_2 and CH_4 for a total of twelve functional groups attached to hexane were calculated. Hexane was used instead of polyethylene for the following reasons: first, hexane

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reduced the effect of neighboring atoms on the binding energy calculations; second, studying the binding of CO_2 in a bulk system is not computationally feasible because of the number of atoms involved and the large number of systems that may be needed for statistical averaging. After the initial screening, solubility measurements were performed with two polymers, polyacrylic acid (PAA) and sodium polyacrylate (Na-PAA). The results were then compared with polyethelene, polyester amide (PEA) and poly(ethylene glycol) diacrylate. Finally, to explain our experimental results, the effects of functional group self interactions and water contamination on CO_2 absorption were studied.

2. Computational and experimental details

2.1. Computational method

The binding energies were calculated at the MP2 level of theory with a triple-zeta basis set 6–311++G(d,p) (except for a few, which used a smaller basis set as noted in the paper) using the Gaussian 09 [14] software. In our simulations, we found that it was necessary to use this large basis set to converge structures involving metal ions. Basis set superposition errors (BSSE) were subtracted for all binding energy calculations using the counterpoise method [15]. Binding energy ($E_{binding}$) of A with B was calculated as

$$E_{binding} = E(A+B) - E(A) - E(B).$$

Therefore, the more negative the binding energy, the stronger the interaction between A and B. The partial charges of atoms were obtained using the ChelpG [16] method as implemented in Gaussian, which fits the partial charge of atoms to the electrostatic potentials as derived from quantum chemistry calculations.
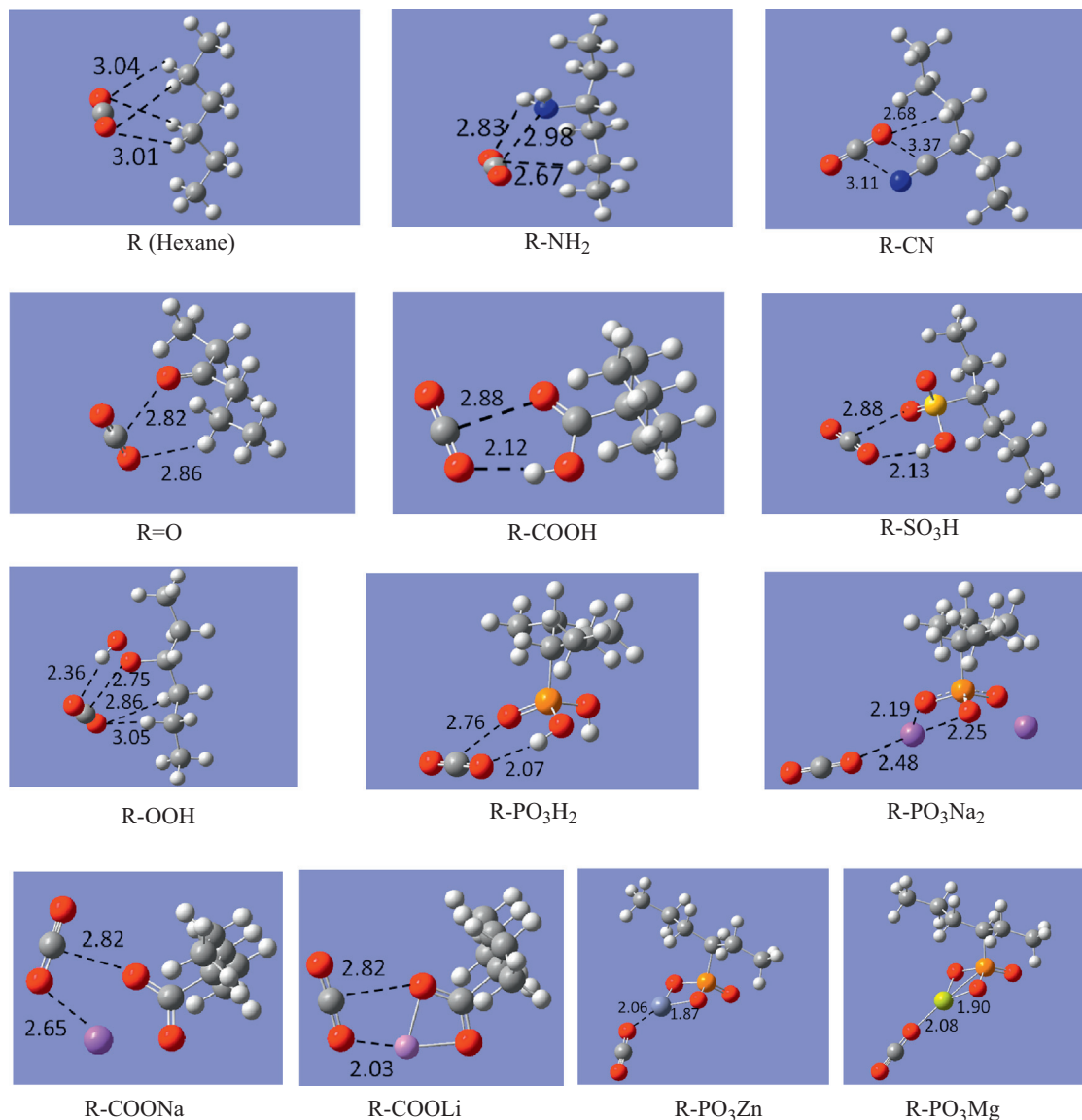
2.2. Materials

Fig. 1. The minimum energy configurations of CO_2–FG complexes (FG: functional group; attached to hexane). The unit of distance is Å. Red, gray, white, blue, orange, dark yellow, big purple, small purple, silver blue, and light yellow spheres represent O, C, H, N, P, S, Na, Li, Zn, and Mg atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)