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Prediction of CO_2 loading of amines in carbon capture process using membrane contactors: A molecular modeling

Bijan Rezaei, Siavash Riahi*

Institute of Petroleum Engineering, Faculty of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

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ABSTRACT

Separation of carbon dioxide from gas streams with respect to CO_2 negative environmental effects is one of the most significant parts of gas separation processes. For this purpose, using membrane contactors is a promising technology and finding high performance solvents is crucial to development of this technology. Aqueous solutions of amines are the most employed solvents for this aim. The fact that performance of amines in carbon capture is greatly affected by variation in their molecular structure has been proven. Quantitative structure property relationship (QSPR) is a technique which employs molecular structure related variables known as descriptor for modeling. In this paper, QSPR method is employed for modeling and predicting CO_2 loading of different amines after absorption and desorption steps in carbon removal process using membrane contactors. Physico-chemical and theoretical descriptors were calculated for a data set including sixteen amines. Variable selection and model development were performed by genetic algorithm-multiple linear regression (GA-MLR) method. Developed models could predict CO_2 loading of amines' solutions after absorption and desorption by coefficient of determination of 0.986 and 0.989 and standard error of the estimate equal to 0.0572 and 0.0496, respectively. In comparison between desorption and absorption model, desorption model is more accurate and absorption model provides simpler descriptors. Validity of the developed models were confirmed by different statistical tests and models showed high predictability power. Furthermore, mechanistic interpretation was applied in order to explain the relation between CO_2 loading and descriptors which appeared in the models. It was found out that steric hindrance effect has a more significant influence on desorption than absorption.

1. Introduction

Nowadays, reduction of CO_2 emissions as a greenhouse gas has great importance to mitigate global warming effect. Considering the fact that 25 percent of carbon dioxide production is related to the fossil-fuel fired power plants, carbon capture and storage from flue gas is a vital process to develop. Currently, CO_2 capture and release by a cyclic chemical absorption/regeneration process using aqueous solutions of amines is the most applied and developed technology for this purpose (Chowdhury et al., 2013; Puxty et al., 2009). However, this process has disadvantages such as thermal degradation of amines, corrosion due to degradation products, volatile loss of absorbents and high energy consumption in regeneration step. Amine regeneration could involve 70 percent of the total operational cost of carbon removal process (Karadas et al., 2010). In a large number of studies, using membrane contactors instead of packed beds in amine cyclic process has been suggested as a promising alternative (Chowdhury et al., 2013; Fang et al., 2009; Khaisri et al., 2011; Okabe et al., 2008; Teramoto et al., 2003). This technology has the ability to reduce energy consumption for CO_2 desorption by employing a low temperature regeneration process. Reduction of regeneration temperature decreases thermal degradation and volatile loss of amines. Furthermore, membrane contactors are free from operational problems of packed beds including flooding, channeling and entrainment. Frequently, vacuum or inert gas sweeping are applied to increase low desorption kinetics caused by low temperature (Cui, 2013; Wang et al., 2013).

Detecting high performance absorbents is a key step in the development of carbon capture by membrane contactors. Consequently, Wang et al. have tried to find the most effective absorbents by investigating on sixteen different amine-based absorbents

* Corresponding author.
E-mail address: riahi@ut.ac.ir (S. Riahi).

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which have shown proper regeneration performance in packed bed process (Wang et al., 2013). To the best of author's knowledge, this has been the most comprehensive study in this area.

In order to properly identify high performance amines, experiments on a larger set of amines is required. By developing reliable models to predict main parameters of absorption and desorption in carbon capture using membrane contactors, effective molecular characteristics of absorbents could be detected. Using these characteristics as a criterion for amine selection or synthesis will be time-saving and more economical.

Wang's study confirmed the presence of a relationship between amine's molecular structure and performance of carbon removal using membrane contactors (Wang et al., 2013). Although, Wang determined only negative or positive effects of structural characteristics qualitatively and did not derive any numerical relationship. However, his achievements are enough to show that QSPR methodology is a proper approach to estimate parameters of interest in the membrane process. QSPR approach is based on the assumption that the differences in molecular structure are the reasons for macroscopic properties variation. QSPR studies aim to find a mathematical relation between parameter of interest and a set of descriptive parameters called descriptors which are mathematical expressions of molecular structure. The so called descriptors employed in a QSPR study may be molecular properties or theoretical, i.e. computed based on the molecular structure. Descriptors can be as simple as number of a specific functional group or complicated as highest occupied molecular orbital energy. After calculation of the descriptors, next steps are generally as follows: 1) Selecting the most efficient subsets of descriptors (variable selection) and model development based on these subsets, 2) Analyzing developed models statistically and selecting the best model and 3) evaluation of predictability and validity of the selected model (Berhanu et al., 2012; Le et al., 2012). QSPR technique has been employed in a wide range of fields (Mavaddat and Riahi, 2016; Riahi et al., 2009, 2008). The possibility to calculate all of the essential parameters for prediction, using three-dimensional structure of molecule, without any need to do experiments is a major advantage of this method.

In this paper, QSPR approach was used to develop models for prediction of amines' CO_2 loading after absorption and desorption steps in carbon capture process using membrane contactors. Best models were selected and developed by GA-MLR method. In addition to statistical tests, mechanistic interpretation was used to confirm developed models.

Although carbon dioxide separation from gas streams has been of a great importance, the only QSPR studies which have been done about it, is in conventional separation process (Momeni and Riahi, 2015, 2014). To the best of the author's knowledge, this paper is the first QSPR study on CO_2 removal by membrane contactors.

2. Methodology

2.1. Data set

CO_2 concentration in aqueous solutions of amines after absorption section (rich loading) and after regeneration section (lean loading) were extracted from Wang's paper (Wang et al., 2013). Absorption membrane contactor was operated at room temperature (298 K) and ambient pressure, while pressure and temperature of desorption membrane contactor were set at 20 kPa and 75 °C, respectively. Wang also calculated absorption capacity, amount of absorbed CO_2 and regeneration yield. Considering the fact that these parameters were calculated from rich and lean loadings, only CO_2 loadings were modeled. A list of the compounds and respective data and structures is provided in Table 1. Data set consists of primary, secondary, and tertiary amines; alkanolamines; polyamines; diamines; and sterically hindered amines.

2.2. Computational procedure

Generally, two types of physico-chemical and theoretical descriptors are used in QSPR. Physico-chemical descriptors consist of physical molecular properties such as log_(octanol/water), pK_a, and molar refractivity. Employing these descriptors in modeling is referred as Hansch analysis. Theoretical descriptors are more convenient and mostly calculated from 2D or 3D structure of molecule, mathematically (Consonni and Todeschini, 2010; Golbraikh and Tropsha, 2000). Considering many references about the relation between amine's pK_a and CO_2 loading in literature, both theoretical and physico-chemical descriptors were used in this paper (Chowdhury et al., 2013; Puxty et al., 2009; Wang et al., 2013).

Experimental pK_a values of amines in absorption step were extracted from literature (Burkett and Davis, 1995; De Robertis et al., 2001, 1993, 1992; Glasstone and Schram, 1947; Hamborg and Versteeg, 2009; Hamborg et al., 2007; Vacca and Arenare, 1967). Both rich and lean loadings represent CO_2 solubility in amines and their difference is due to different measurement conditions (temperature and pressure). In order to apply temperature effect on pK_a and estimate pK_a value in desorption temperature, suggested equation by Perrin was used as following (Perrin, 1964):

$$-\frac{d(pK_a)}{dT} = (pK_a - 0.9)/T \quad (1)$$

Therefore, by neglecting pressure effect on pK_a, lean and rich loadings predictions could be done by only one model. Since polyamines have one pK_a for each nitrogen in their structure, summation of pK_a values for the all of nitrogens in molecule was used for these amines. By doing so, not only pK_a is considered, but also number of reaction sites (nitrogens) with carbon dioxide is taken into account for polyamines.

To calculate a portion of theoretical descriptors, optimized geometry of the molecule is required. Thus, geometry of compounds was pre-optimized applying semi-empirical optimization method RM1. Final optimization was carried out by employing density functional theory (DFT) at the level of B3LYP and 6-31++G (d,p) basis set (Foresman et al., 2015). These calculations were performed using Gaussian software (Frisch et al., 1998). Electronic and quantum chemical descriptors including dipole moment, sum of the electronic and thermal free energies, HOMO energy (highest occupied molecular orbital energy) and LUMO energies (Lowest Unoccupied molecular orbital energy) were extracted from Gaussian output.

Then, geometrically optimized structure of each molecule was imported into Dragon software developed by the Milano Chemometrics and QSAR research group (Todeschini et al., 2011), and finally, dragon calculated 4885 descriptors for each molecule. The most efficient set of descriptors for developing MLR models was obtained using genetic algorithm. Since large search space (large amount of descriptors) would result in imprecise and slow performance of genetic algorithm, a number of descriptors were eliminated by applying the following criteria: (i) descriptors with constant or near-constant values were excluded (ii) one of the collinear descriptors (correlation coefficient >0.95) that had lower correlation with loading values was eliminated. A total of 459 descriptors were left for each molecule as an output of this procedure. Finally, calculated descriptors with addition of 31 descriptors, which were extracted from Gaussian, formed a (16 × 490) data matrix consisted of dragon and Gaussian descriptors. After