

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/272380963>

Computational Study of CO₂ Absorption in Aqueous and Non-aqueous Solutions Using MEA

ARTICLE *in* ENERGY PROCEDIA · DECEMBER 2014

DOI: 10.1016/j.egypro.2014.11.144

READS

18

2 AUTHORS, INCLUDING:



[Z. X. Zhang](#)

Xi'an Jiaotong University

69 PUBLICATIONS 611 CITATIONS

SEE PROFILE

GHGT-12

Computational study of CO₂ absorption in aqueous and non-aqueous solutions using MEA

Tingting Zhang^{a,b}, Zaoxiao Zhang^{a,b} *

^aState Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University,
No.28 Xianning West Road, Xi'an 710049, P.R. China

^bSchool of Chemical Engineering and Technology, Xi'an Jiaotong University,
No.28 Xianning West Road, Xi'an 710049, P.R. China

Abstract

Chemical absorption using Ethanolamine to capture CO₂ is considered to be an effective way to cover the large reduction of the greenhouse gas emissions. As the absorption capacity is different between aqueous and non-aqueous solutions, in this work, the reaction processes about monoethanolamine (MEA) absorbing CO₂ in aqueous and non-aqueous (take methanol as the medium) solvation effect without solvent molecular are studied using density functional theory (DFT), respectively. The result shows that the reaction mechanism is same both in aqueous and non-aqueous solutions and a two-step reaction process can demonstrate it well. The main effect of the different solvent on the reaction is the relative energy of the optimized configurations. The energy shows that stable configurations have lower relative energy in methanol than in water, which demonstrates that the configurations are more stable in non-aqueous solutions than those in aqueous solutions.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: CO₂ absorption; DFT; MEA; water; methanol; solvation effect

1. Introduction

The large amount emission of CO₂ has aroused big environmental issue, the Greenhouse effect [1]. Much method had been discussed to alleviate this phenomenon, among all the method, chemical absorption that using

* Corresponding author. Tel.: +86-29-82660689; fax: +86-29-82660689.

E-mail address: zhangzx@mail.xjtu.edu.cn.

aqueous alkanolamine solutions to absorb CO_2 is an important industrial method for capturing CO_2 from the flue gas of power plants [1,2]. Among the alkanolamines available, extensive studies have been done on monoethanolamine [MEA, $\text{HO}(\text{CH}_2)_2\text{NH}_2$] for its ability of quickly absorbing CO_2 in the form of a stable carbamate. However, most of the studies focus on aqueous solutions and 30 percentages mass aqueous solution of MEA have good performance at the temperature range of 0-150°C and pressure range of 0.001-20 MPa. However, water has large latent heat and will cost a lot of energy in the desorption process. In contrast, non-aqueous systems comprising a methanol solution of alkanolamine have been commercially employed for absorption of CO_2 , H_2S , and COS , etc., because of their high solubility and capacity of acid gas, low corrosiveness and low energy consumption during generation of used liquor. Thus non-aqueous solutions will have potential in absorbing CO_2 with low energy consumption [3].

Several works were done on theoretical analysis about the reaction path and possible products on MEA and CO_2 [4-6]. Da silva proposed that in the formation of carbamate, a single-step mechanism may account for the reaction process, for the ion pair is unstable [4]. Bjørnar Arstad studied the reaction of ammonia, monoethanolamine (MEA) and diethanolamine (DEA) respectively in absorbing CO_2 using water as solvation effect medium [5]. Also, the existence of extra reactant molecular was discussed about the effect on the activation energy of the reaction process. AMP and aniline were also discussed to investigate the reaction mechanism about absorbing CO_2 . Though there are extensive experimental and theoretical studies about the reaction mechanism about MEA and CO_2 , controversial conclusion of it still exists. The reaction intermediate is always the discussion focus. Three reaction styles were proposed among the studies [7],

- (1) **Single-step reaction mechanism.** Two MEA molecular and one CO_2 molecular react at the same time and finally produce the MEACOO^- and MEAH^+ .
- (2) **Zwitterion mechanism.** First, one MEA molecular react with CO_2 to form the ion pairs (MEA^+COO^-) as intermediate, then the intermediate react with another MEA, and finally produce the zwitterions MEACOO^- and MEAH^+ .
- (3) **Carbamic acid reaction mechanism.** First, one MEA molecular react with CO_2 to form the carbamate (MEA^-COOH) as intermediate, then the intermediate react with another MEA, and finally produce the MEACOO^- and MEAH^+ .

Until now, almost all of the theoretical studies about the simulation works on the reaction mechanism are mainly in gas phase and liquid phase which were taken water as solvent [4,8]. As the aqueous and non-aqueous solutions have different absorption capability [3,9,10], in order to know the difference of the solvent effect on the reaction mechanism of CO_2 absorbing by alkanolamine, the study of MEA absorbing CO_2 in water and organic solvent (methanol) will be discussed in this paper, respectively. As the reaction scheme proposed before, we would like to discuss the reaction process that involves MEA and CO_2 without solvent molecular.

2. Computational detail

The calculations were performed using Gaussian software. The reaction process of MEA absorbing CO_2 in aqueous (take water as solvent) and non-aqueous (take methanol as solvent) solvation medium are studied. The optimized geometries and frequencies of the reactants, products and transition states were obtained at the B3LYP/6-31G level. Single-point energy calculations for important configurations were performed. The Reaction energies equation is shown as: $\Delta E_{\text{reaction}} = E_{\text{products}} - E_{\text{reactants}}$, where $\Delta E_{\text{reaction}}$ is the energy difference between products and reactants for the corresponding reaction process, here E_{products} and $E_{\text{reactants}}$ are the energy of products and reactants, respectively [8].

3. Results and discussions

In this paper, we focus on the different solvent that affects the reaction process between MEA and CO_2 . And no analysis about solvent molecular taking part in the reaction is discussed. Learnt from the discussion of other researchers, MEA and CO_2 molecular have two different spatial configurations, one is the relative position of MEA and CO_2 in ring structure (circle configuration), and the other one is straight chain [5,7]. The two configurations are shown in Fig. 1.

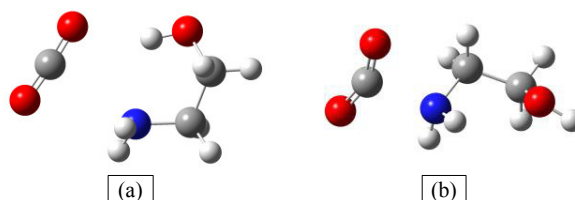


Fig. 1. (a) the ring structure, (b) the straight chain structure.

The reaction processes of the two configurations are considered separately. The process contains two parts, the first part is one MEA molecular reacts with one CO_2 molecular, the second part is another MEA molecular reacts with the product obtained at the first stage. The reaction process between one MEA molecular and one CO_2 molecular, it shows that they can react to form ion pair or the carbamate as mentioned before,



then the product reacts with a second MEA molecular to form the final products.

To analysis the different solvent effect between water and methane, we would like to discuss the whole reaction process with different solvent effect. In the following discussions, different reaction types with different solvent effect are shown.

3.1. MEA+ CO_2

In this part, the reaction types between one MEA molecular and one CO_2 molecular in liquid phase with different solvent were discussed.

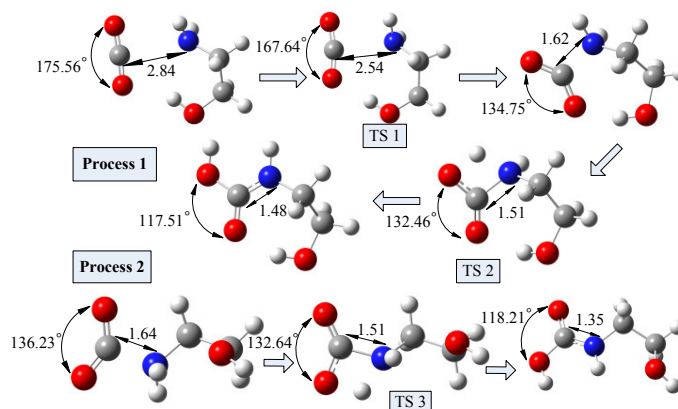


Fig. 2. The atom movements during the reaction process of MEA+ CO_2 .

Fig. 2 shows the atom movement of the whole reaction process with solvation effect of water in the simulation study. When MEA and CO_2 molecular are in circle configuration, they first form an ion pair through a transition state, then one hydrogen atom shifts from MEA to CO_2 , finally form the carbamate product. Process 1 in Fig. 2 shows the reaction diagram. When MEA and CO_2 molecular are in straight chain configuration as process 2 shows, the reaction are simplified to be a carbamate formation process, and no transition state is found before the ion pair formation process. The energy change about this process is shown in Fig. 3. Here the zero point is the energy sum of the separately optimized geometry of MEA and CO_2 . The black line shows the energy change of process 1, and the

red line is for the process 2. From Fig. 2, we can see that in the reaction process, during the formation of ion pair, the bond length of N-H shortens and the dihedral angle of C=O=C decreases. In the formation of carbamate, TS 2 and TS 3 are the transition state geometries for different spatial configurations. The atom movement of hydrogen, the bond length of N-H and the dihedral angle of C=O=C have the same variation trend. As shown from Fig. 3, despite the different spatial configuration, the energy change of the hydrogen transfer process (TS 2, TS 3) is almost the same, and the activate energy barrier is 160 kJ/mol. As for TS 1, the forward energy barrier is not large but could not be ignored.

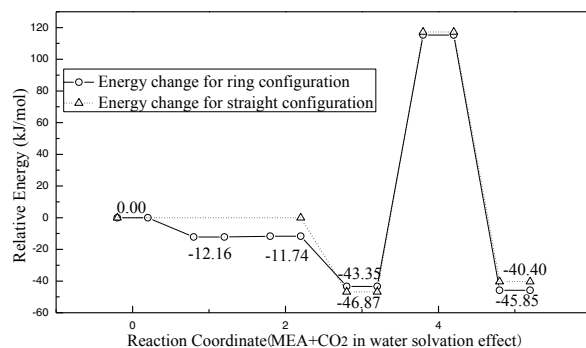


Fig. 3. The energy change of the process of MEA+CO₂ in water.

To investigate the solvation effect of methanol, the simulations on the same reaction process are studied, and the atom movements are the same as those in water solvation effect. The energy changes of the whole process are shown in Fig. 4. The energy changing trend is consistent with that in water, but the numerical value is different which could be explained by the different solvation effect. The energy comparison between that in water and methanol shows that for the optimized initial configurations, it is more stable in methanol for the energy of them are lower than that in water.

Seen from the energy value in Fig. 3 and Fig. 4, during the hydrogen transfer process, the circle configuration has lower energy barrier than the straight configuration, and for the last carbamate product, the circle configuration has lower relative energy and is much more stable.

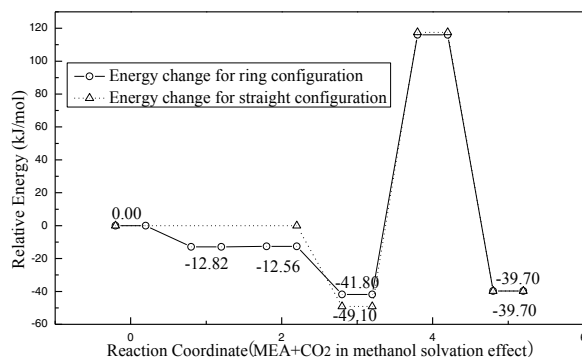


Fig. 4. The energy change of the process MEA+CO₂ in methanol.

The energy change shows that during the MEA+CO₂ reaction process, it is more likely to form ion pair instead of carbamate product, that is,



3.2. 2MEA+CO₂

During the reaction process, when MEA and CO₂ react to form the intermediate (ion pair), another MEA molecular involves in and acts as a base. Then the hydrogen atom moves from N atom of the first MEA molecular to the N atom of the second MEA molecular. The schematic diagram is shown as Fig. 5. Finally zwitterions are formed as MEACOO⁻ and MEAH⁺. The atom movements of different configurations reaction process are shown as process 3, 4, 5 in Fig. 5. Process 3 is the circle configuration reacting with MEA, and process 4 and 5 are the straight configuration reaction process, and the difference between 4 and 5 is the relative structure of the second MEA. With different configuration, the same hydrogen transfer process has different energy change as shown in Figs. 6 and 7. Fig. 6 is the energy change of the reaction process in water solvation effect. The black line represents the energy change of process 3, the red line represents the energy change of process 4, and the blue line represents that of process 5. The zero point is the energy sum of the separately optimized molecular of two MEA and one CO₂. Seen from the data of the energy, the blue and the black line have same energy changing trend where there exists a small but cannot be ignored forward energy barrier. For the red line, the forward energy barrier is the same with that of the backward. Process 4 and 5 which is corresponding to the red and blue line, those two geometries is of the straight chain configuration, and their initial energy of the optimized geometry is similar. But for the circle geometry, the initial energy of the optimized geometry is lower than that of the straight chain geometries. Compared the corresponding energy between Fig. 6 which represents the water solvation effect and Fig. 7 for methanol solvation effect, the energy in methanol is lower than that in water, which demonstrates that the geometries are more stable in methanol than in water.

The energy change of the reaction process shows that the reaction mechanism of 2MEA+CO₂ prefer to be a formation of zwitterions no matter in water or in methanol solvation effect, that is based on the formation of ion pair, another MEA molecular reacts as a base to accept hydrogen proton and finally generate the zwitterions,

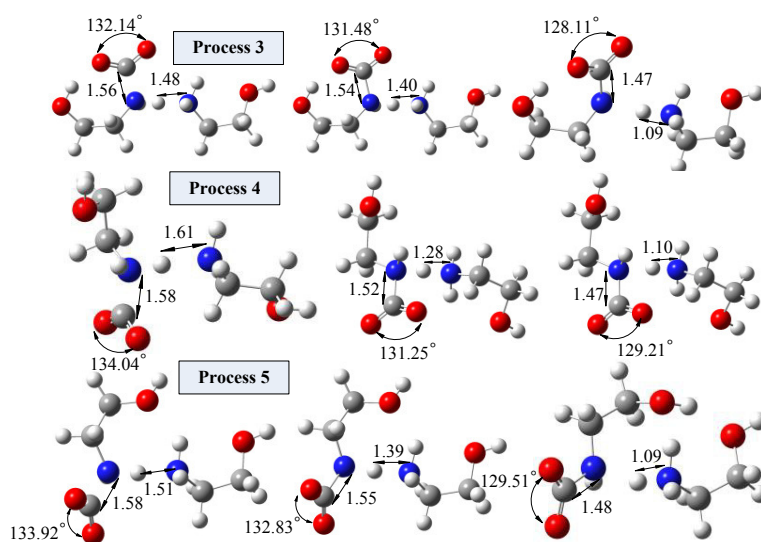
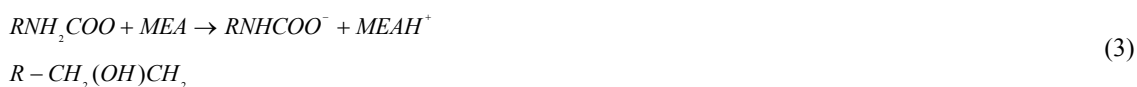


Fig. 5. The atom movements during the reaction process of the 2MEA+CO₂.

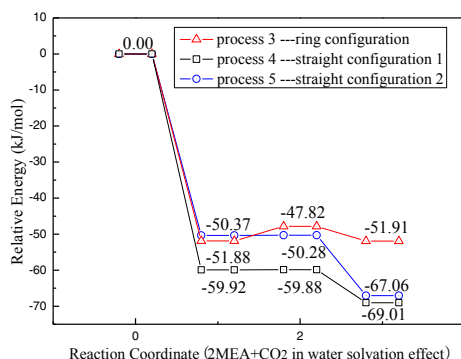


Fig. 6. The energy change of the process 2MEA+CO₂ in water.

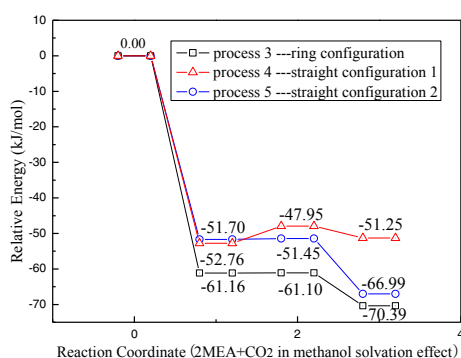


Fig. 7. The energy change of the process 2MEA+CO₂ in methanol.

4. Conclusions

The discussions above about the reaction process and energy change of MEA+CO₂ and 2MEA+CO₂ show that the whole reaction mechanism about MEA and CO₂ can be stated by a two-step reaction process better than other reaction mechanisms. That is, MEA and CO₂ prefer reacting to form ion pair first and then the obtained ion pair reacts with another MEA molecular to produce zwitterions. During the reaction process of MEA+CO₂, for different spatial configurations, the reaction path is different. And the ring spatial configuration has lower relative energy of the optimized structures than the straight configuration.

Compared the simulation study of the reaction process between MEA and CO₂ in water and methanol solvation separately, the results of the atom movements and the energy change show that without the involvement of solvent molecular, the reaction process of MEA and CO₂ are the same no matter in aqueous or non-aqueous(methanol) solutions. The main effect of the different solvent on the reaction is the relative energy of the optimized configurations. The energy shows that configurations have lower relative energy in methanol than in water, which demonstrates that the configuration are more stable in non-aqueous solutions than that in aqueous solutions.

The energy change shows that the forward reaction process has a small energy barrier, and the backward process has big energy barrier, that is why it is easier to absorb CO₂ and can be operated at a low temperature but the regeneration process need a large amount of energy and operate at high temperature.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (No. 51276141).

References

- [1] International Energy Agency (IEA), World Energy Outlook, 2009.
- [2] Li LT, Xie Q. Separation and Utilization of Greenhouse Gas CO₂ [J]. *Low Temperature and Specialty Gases*, 2005, 23(4).
- [3] Park SW, Lee JW, Choi BS et al. Absorption of carbon dioxide into non-aqueous solutions of N-methyldiethanolamine[J]. *Korean Journal of Chemical Engineering*, 2006, 23(5): 806-811.
- [4] Eirik FDS, Hallvard FS. Computational chemistry study of reactions, equilibrium and kinetics of chemical CO₂ absorption[J]. *International Journal of Greenhouse Gas Control*, 2007, (1): 151-157.
- [5] Arstad B, Richard B, Ole S. CO₂ Absorption in Aqueous Solutions of Alkanolamines: Mechanistic Insight from Quantum Chemical Calculations[J]. *The Journal of Physical Chemistry. A* 2007, (111): 1222-1228.
- [6] Roberto LR, Marco AM, Alejandro J. Molecular Dynamics Simulations of Aqueous Solutions of Ethanolamines[J]. *The Journal of Physical Chemistry. B* 2006, (110): 14652-14658.
- [7] Xie HB, Zhou YZ, Zhang YK, et al. Reaction Mechanism of Monoethanolamine with CO₂ in Aqueous Solution from Molecular Modeling[J]. *The Journal of Physical Chemistry, A* 2010, (114): 11844-11852.
- [8] Ismael M, Sahnoun R, Suzuki A, et al. A DFT study on the carbamates formation through the absorption of CO₂ by AMP[J]. *International Journal of Greenhouse Gas Control*, 2009, (3): 612-616.
- [9] Usubharatana P, Tontiwachwuthikul P. Enhancement factor and kinetics of CO₂ capture by MEA-methanol hybrid solvents[J]. *Energy Procedia*, 2009: 95-102.
- [10] Yu YS, Lu HF, Zhang TT, Zhang ZX. Determining the Performance of an Efficient Nonaqueous CO₂ Capture Process at Desorption Temperatures below 373 K[J]. *Industrial & Engineering Chemistry Research*, 2013, (52): 12622-12634.