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Utilization of Molecular Simulation Software Gaussian 03 to Design Absorbent for CO_2 Capture

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Abstract

A preliminary study on the interaction between molecules of absorbent for CO_2 absorption was undertaken using Gaussian 03 molecular simulation software. The results indicate that the molecular interaction energy has strong correlations with Henry's constant. The lower interaction energy between molecules, solvent molecules form an "associated complex" more stability, and therefore the worse the effect of CO_2 absorption.

Keywords: ***Gaussian 03, molecular simulation, CO_2 capture, Henrys constant***

1 Introduction

In an effort to mitigate CO_2 emissions, a result of the world-wide consumption of fossil fuels [1], the United States Department of Energy is expected to develop commercial fossil fuel conversion systems by the year 2020, which would remove at least 90% of CO_2, and keep the increase in the cost of electricity below 10% [2]. One vision of such innovative clean energy is to produce power from coal using the integrated gasification combined cycle (IGCC) [3]. IGCC combined with "Carbon dioxide Capture and Storage (CCS)" technology has attracted wide attention in the field of CO_2 emission reduction. However, the cost of existing CO_2 capture technologies is still too high. Utilization of large-solubility and low-cost absorbent for CO_2 capture in IGCC can effectively reduce the electricity price increase caused by addition of CO_2 removal unit. As it needs to trap CO_2 before combustion under high pressure in IGCC, physical absorption is considered to be a better choice [4]. A large number of physical solvents have been developed, such as H_2O [5-7], methanol [8-11], propylene carbonate [12.13] and polyethylene glycol dimethyl ether[14.15], but the absorption performance of these solvents is not very good and capture cost is still very high.

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How to choose an excellent absorbent is the key of reducing capture cost. As screening only depending on experiments is time-consuming it is urgent to develop the effective theoretical model to guide the screening of absorbent. In the past more than 30 years, several theories and approaches have been presented, such as solubility parameter model [16-19], excess Gibbs free enthalpy model [20, 21].

However the above models are always semi-empirically obtained through thermodynamic correlations and lack of support of basic molecular interaction theory. This makes application of the theory by a certain degree of limitation. It is necessary to explore further in prediction of absorbent based on microscopic interaction.

Molecular interaction is always a hot research area in chemistry sciences [22]. It also is the basis revealed physical and chemical properties of substance. In early 30’s London classified the molecular interaction into four parts, electrostatic interaction, dispersion, exchange-repulsion and induction, referred to as Van der Waals interaction. In 1935, with the proposal of “hydrogen bond” the molecular interaction study entering into a new stage of development. Theoretically exact calculation of molecular interaction has become the most important tools revealing the physical and chemical properties of substances. Gaussian simulation approach is one of theory of the fastest growing in recent years [23-27]. Based on molecular orbital theory of electron motion and through solution of Schrodinger equation it can reveal the information of molecular structure, charge distribution, binding energy between atoms, etc.

Due to the better predicting results in this paper Gaussian approach is used to simulation and study the absorption performance of absorbent for CO_2.

2 Simulation and Experimental

It is reported that [16] solubilization of gas solute in a physical solvent accompanied with the de-construction of solvent molecule association. The stronger interaction of solvent molecule and the more stable association, the more gas is not dissolved into solvent. So study on interaction of solvent molecule can provide the assistance for screening of absorbent.

Molecular interaction ΔE is calculated as:

$$\Delta E = E_T - \sum_i E_i \quad (1)$$

Where, E_T is the total energy of association system, Ei is the energy of sub-system, $\sum_i E_i$ is the sum of all sub-system energy.

In this paper in order to simplifying calculation the total energy of solvent is approximated by interactions between two molecules. So, formula (1) can be rewritten as

$$\Delta E = E(2A) - 2E(A) \quad (2)$$

In the above calculation, balance calibration method (CP) [41] is used to eliminate the basis function overlap errors (BSSE). After correction formula (3) is rewritten as

$$\Delta E = E(2A) - 2E(A) + BSSE \quad (3)$$

On this basis, through explore the correlation between the interaction energy and the Henry’s constant obtained by experiments, it will provide assistance to predict the absorption performance of absorbents.

2.1 Simulating approach

(1) Optimization of molecular structure

Continuously adjust dihedral angles of bond orbit until interaction minimum, the optimum molecular structure is achieved.

(2) Calculation of interaction energy

Moller-Plesset （MP）approach is used in calculation of interaction energy in formula (3). MP method is a high-level molecular orbital theory based on quantum chemical calculation methods.This

method is based on Hartree-Fock self-consistent field theory can provide the approximate solution of multi-electron system with adapting of micro perturbation theory. As considering fully the electro impacts MP approach has been used widely in studies of molecular interactions [28-37].

In above calculation, 6-311++G(d，p) basis sets including dual-polarization functions and diffuse functions were chosen as the basis functions. The final results were calculated by Gaussian 03.

2.2 Experimental

CO_2 of 99.99 (vol. %) purity was supplied by BeiWen Gas in Beijing. The solvent, Ethylene glycol mono-ethyl ether acetate (EGEA), 2,3-pentane-dione, 2,3–butanedione, 2-heptanone, butyl acetate, propyl acetate, ethyl acetate, Dimethoxy methane, 2 – Pentanone, Diethyl carbonate, methyl acetate, 2-butanone, Dimethyl malonate, dimethyl carbonate, acetone, Diethylene glycol mono-ethyl ether(DGME), Diethylene glycol monomethyl ether (DGMM), Propylene carbonate, Ethylene glycol monoethyl ether (EGME), ethylene glycol mono-methyl ether (EGMM), n-Butanol, iso-propanol, n-propanol, 1,3-Propylene glycol,ethylene glycol, were all purchased from Aladdin-reagent Company in Shanghai with the same weight fraction of 0.999. All components were used without further purification.

Apparatus and data procedure in this work was based on the constant volume method and reported in previous work [38].

3 Results and Discussion

The molecular interaction energy calculated of solvents by Gaussian 03 and Henry's constants of solvents are listed in Table 1.

Table 1 Molecular interaction energy and Henry's constants of solvents (25°C)

Solvents Name	Molecular formula	$E_{solvent}$ /kcal mol^{-1}	$E_{solvent\text{-}Solvent}$ /kcal mol^{-1}	△E/kcal mol^{-1}	Henry's constant/25℃
EGEA	C6H12O3	-460.031628	-920.071025	-0.007769	3.8136
2,3-Pentane-dione	C5H8O2	-344.663571	-689.335333	-0.008191	4.13
2,3- Butane-dione	C4H6O2	-305.519286	-611.047142	-0.00857	4.64
2-Heptanone	C7H14O	-349.113624	-698.236129	-0.008881	5.0127
Butyl acetate	C6H12O2	-385.012402	-770.033728	-0.008924	5.02
Propyl acetate	C5H10O2	-345.85888	-691.726853	-0.009093	5.1803
Ethyl acetate	C4H802	-306.690174	-613.389511	-0.009163	5.372
Di-methoxy methane	C3H8O2	-268.664262	-537.337734	-0.00921	5.4561
2 - Pentanone	C5H10O	-270.804838	-541.618968	-0.009292	5.5744
Diethyl carbonate	C5H10O3	-420.89244	-841.794252	-0.009372	5.6851
Methyl acetate	C3H6O2	-267.499132	-535.007859	-0.009595	5.9125
2-Butanone	C4H8O	-231.65029	-463.310268	-0.009688	6.0576
Dimethyl malonate	C5H8O4	-494.758441	-989.526648	-0.009766	6.1375
Dimethyl carbonate	C3H6O3	-342.573596	-685.157018	-0.009826	6.1823
Acetone	C3H6O	-192.497978	-385.005758	-0.009802	6.2091
DGME	C6H14O3	-461.152038	-922.314271	-0.010195	7.45
DGMM	C5H12O3	-421.999548	-844.009407	-0.010311	8.13
Propylene carbonate	C4H6O3	-380.572929	-761.156354	-0.010496	8.3451

EGME	C4H10O2	-307.829947	-615.670416	-0.010522	8.3775
EGMM	C3H8O2	-268.667585	-268.689019	-0.010717	9.5669
n-Butanol	C4H10O	-232.806437	-465.62377	-0.010896	12.3107
Iso-Propanol	C3H8O	-193.660937	-387.333067	-0.011193	12.5717
n-Propanol	C3H8O	-193.652959	-387.317177	-0.011259	12.8466
Ethanol	C2H6O	-154.499799	-309.011395	-0.011797	13.2959
Methanol	CH4O	-115.340861	-230.693673	-0.011951	13.621
1,3-Propylene glycol	C3H8O2	-268.693717	-537.400626	-0.013192	38.123
Ethylene glycol	C2H6O2	-229.532702	-459.079782	-0.014378	47.6813

Interaction energy data in Table 1 are correlated with the Henry's constant and shown in Fig.1.

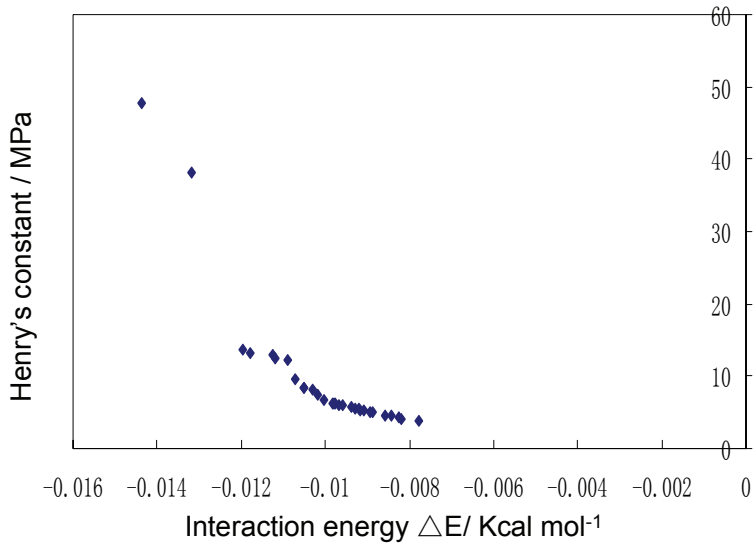

Fig 1 Correlation between interaction energy with Henry's constant

It is indicated that the interaction energy quantifying calculated by Gaussian 03 without any empirical parameters can predict the absorbent performance. As shown in Fig.2, Solvent interaction energy the higher the absolute value, the worse the effect of solvent absorption, As hydrogen bond interaction is stronger, alcohols have the high molecular interaction energy and poor absorption effects. While ethers, esters have significantly smaller molecular interaction, therefore these solvents are more suitable for capture CO_2 as an absorbent.

4 Conclusions

A preliminary study on the interaction between solvent molecules was undertaken using Gaussian 03 molecular software. The results indicate that the relevance between molecular interaction energy and Henry's constant is very high. The lower interaction energy between molecules, solvent molecules form a "polymer" more stability, and therefore the worse the effect of CO_2 absorption.This means that the Gaussian 03 software can provide the reference framework for prediction of CO_2 absorbent.

References

[1] http://scifun.chem.wisc.edu/chemweek/pdf/CarbonDioxide.pdf
[2] Plasynski, S.; Deel, D.; Miller, L.; Kane, B. Carbon sequestration technology roadmap and program plan. U.S. Department of Energy, Office of Fossil Energy; National Energy Technology Laboratory. April 2007.
[3] Heintz, Y. J.; Sehabiague, L.; Morsi, B. I.; Jones, K. L.; Pennline, H. W. Novel Physical Solvents for Selective CO2 Capture from Fuel Gas Streams at Elevated Pressures and Temperatures. Energy & Fuels 2008, 22, 3824–3837.
[4] http://www.graz-cycle.tugraz.at/pdfs/co2_capture_strawman_feb2004.pdf
[5] Diamond, L. W.; Akinfiev, N. N. Solubility of CO2 in water from −1.5 to 100℃ and from 0.1 to 100 MPa: evaluation of literature data and thermodynamic modeling. Fluid Phase Equilibria 2003, 208, 265–290.
[6] Vorholz, J.; Harismiadis, V.; Rumpf, B.; Panagiotopolous, A.; Maurer, G. Vapor-Liquid Equilibrium of Water + Carbon Dioxide and the Binary System, Water + Carbon Dioxide from Molecular Simulation. Fluid Phase Equilibria 2000, 170, 203-234.
[7] Carroll, J. J.; Slupsky, J. D.; Mather, A. E. The solubility of Carbon Dioxide in water at low pressure. J. Phys. Chem. Ref. Data 1991, 20 (6), 1201-1209.
[8] Yoon, J. H.; Lee, H. S.; Lee, H. High-Pressure Vapor-Liquid Equilibria for Carbon Dioxide + Methanol, Carbon Dioxide + Ethanol, and Carbon Dioxide + Methanol + Ethanol. J. Chem. Eng. Data 1993, 38, 53-55.
[9] Bezanehtak, K.; Combes, G.; Dehghani, F.; Foster, N.; Tomasko, D. Vapor-Liquid Equilibrium for Binary Systems of Carbon Dioxide + Methanol, Hydrogen + Methanol, and Hydrogen + Carbon Dioxide at High Pressures. J. Chem. Eng. Data 2002, 47, 161-168.
[10] Joung, S. N; Shin, H. Y.; Kim, S. Y.; Yoo, K. P.; Lee, C. S.; Huh, W. S. Measurements and correlation of high-pressure VLE of binary CO2–alcohol systems (methanol, ethanol, 2-methoxyethanol and 2-ethoxyethanol). Fluid Phase Equilibria 2001, 185, 219–230.
[11] Robinson, D.; Peng, D.; Chung, S. The Development of the Peng-Robinson Equation and its Application to Phase Equilibrium in a System Containing Methanol. Fluid Phase Equilibrium 1985, 24, 25-41.
[12] Blanchard, F.; carré, B.; Bonhomme, F.; Biensan, P.; Lemordant, D. Solubility of carbon dioxide in alkylcarbonates and lactones, Can. J. Chem 2003, 81, 385-391.
[13] Ai, N.; Chen, J.; Fei, W. Y. Solubility of Carbon Dioxide in Four Mixed Solvents. J. Chem. Eng. Data 2005, 50, 492-496.
[14] Gainar, L.; Anitescu, G. The solubility of CO2, N2 and H2 in a mixture of dimethylether polyethylene glycols at high pressures. Fluid Phase Equilibria 1995, 109, 281-289.
[15] Aionicesei, E; Škerget, M; Knez, Ž. Measurement and Modeling of the CO2 Solubility in Poly(ethylene glycol) of Different Molecular Weights, J. Chem. Eng. Data 2008, 53, 185–188.
[16] Jolley, J.E.; Hildebrand, J.H. Solubility, entropy and partial molal volumes in solutions of gases in non-polar solvents. American Chemical Society -- Journal, v 80, n 5, p 1050-1054, Mar 5, 1958
[17] Ellis, S.R.M.; Spurr, M.J. New use of solubility parameter on binary systems.Petroleum Management, v 34, n 4, p 183-187, Apr, 1962
[18] Gardon, J.L. Influence of polarity upon solubility parameter concept. Journal of Paint Technology, v 38, n 492, p 43-57, Jan, 1966

[19] Hansen, C.M. Three dimensional solubility parameter -- Key to paint component affinities – 1. Journal of Paint Technology, v 39, n 505, p 104-117, Feb, 1967
[20] Zheng, Danxing; Ji, Peijun; Qi, Janping.Maximum excess Gibbs function of working pairs and absorption cycle performance. International Journal of Refrigeration, v 24, n 8, p 834-840, December 2001
[21] Zheng, Danxing; Ji, Peijun; Qi, Jianping. Evaluation of absorption heat transformer performance by excess Gibbs function of working pairs. Journal of Chemical Engineering of Chinese Universities, v 14, n 5, p 409-414, Oct 2000(Chinese)
[22] Pople J A, Head-Gordon M, Fox D J, Raghavachari K and A.Curtiss L. Gaussian-1 theory : A general procedure for prediction of molecular energies [J].J Chem Phys,1989,0:5622.
[23] Curtiss L A, Raghavachari K, Trucks G W and Pople J A. Gaussian-2 theory formolecular energies of first- and second- row compounds[J].J Chem Phys,1991,94:7221.
[24] Curtiss L A, Raghavachari, K and Pople J A. Gaussian-2 theory using reduced Mφller- Plesset orders [J].JChem Phys,1993,98 :1293.
[25] Curtiss L A , Raghavachari K , Redfern P C, Rassolov V , and Pople J A. Gaussian-3(G3) theory for molecular containing first and second row compounds [J].J Chem Phys,1998,109:7764 .
[26] Curtiss L A, Redfern P C , K.Raghavachari and Pople J A. Gaussian-3 theory using reduced Mφller-Plesset order[J]. J Chem Phys,1999,110:4703.
[27] Curtiss L A , Redfern P C , Raghavachari K and Pople J A. Gaussian-3 theory : a variation based on third-order perturbation theory and an assessment of the contribution of core-related correlation[J].Chem Phys Lett,1999,313:600.
[28] Wang YIbo; Tao Fuming; Pan Yugang. Studies on initio-calculation of hydrogen bonding energy and its utilization in analysis for HF、H2O and NH3 molecule. [J]. SCIENCE(B Sets) 1995, 25(10): 1016-1025.
[29] ChalasinskiG，SZczesniaKMM. Origins of structure and energetics of van der waals clusters from ab Initio calculations [J] Cem.Rev.，1994，94:l723 一 1765
[30] Racine S C and Davidson E R. Electron correlation contribution to the hydrogen bond in (HF)2 [J]. J. Phys. Chem, 1993，97:6367-6372.
[31] Quack M，Suhm M A Potential energy surfaces，quasiadiabatic channels，rovibrational spectra，and intramolecular dynamics of (HF)2 and its isotopomers from quantum Monte Carlo calculations[J] J. Chem. Phys. 1991，95:28-59
[32] Scheiner S. Ab initio studies of hydrogen bonds: the water dimmer paradigm J] Annu. Rev. phys. Chem.，1994，45:23-56
[33] Chkravorty S J. The water dimer: Correlation energy caculations[J]J.Phys. Chem，1993，97:6373-6383
[34] Tao F M，Klemperer W. Ab initio search for the equilibrium structure of the ammonia Dimmer[J]. J.Chem.Phys.，1993，99:5976-5982
[35] Xantheas S S， Dunning T H. The structure of the water trimer from ab initio calculations [J]. J. Chem. Phys.，1993，98:8037-8040
[36] Reed A E，Curtiss L A，Weinhold F. Intermolecular interactions from a nature bond orbital donor-acceptor view point[J] .Chem.Rev.，1988，88:899-926
[37] Gwinner, B.; Roizard, D.; Lapicque, F.; Favre, E.; Cadours, R.; Boucot, P.; Carrette, P.L. CO2 Capture in Flue Gas: Semiempirical Approach to Select a Potential Physical Solvent. Ind. Eng. Chem. Res 2006, 45, 5044-5049.
[38] Gui, X.;Tang, ZH.G.;Fei,W.Y.; CO2 capture with physical solvent dimethyl carbonate (DMC) at high pressures J Chem. Eng. Data. 2010(559), 3736-3741.