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B.ENG. (HONS) CHEMICAL ENGINEERING

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SCREENING OF AMINE FOR CO_2 CAPTURE USING COSMO-RS MODEL

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by

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14766

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

____

(AP. Dr. Mohamad Azmi B Bustam @ Khalil)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AMIR AIMAN BIN ABD RAZAK

ABSTRACT

The significant and rapid reduction of greenhouse gas emissions is recognized as necessary to mitigate the potential climate effects from global warming. The postcombustion capture (PCC) and storage of carbon dioxide (CO_2) that produced from the use of fossil fuels for electricity generation and from contaminant presented in natural gas are a key technologies needed to achieve these reductions. The most mature technology for CO_2 capture is reversible chemical absorption into an aqueous amine solution. Although, amine-based solvents became promising solvents in CO_2 absorption process, the selection of appropriate amine for specific process is impossible without a prior screening. This work presents the screening technique to identify the potential amine for CO_2 capture using COSMO-RS model. To achieve this target we investigated 57 tertiary amine based CO_2 absorbents with different chemical structures. Screening procedures were carried out based on their CO_2 absorption rate and loading amount. The screening starts with the optimization of the amine compound geometry using TURBOMOLE. Then, we proceed with the prediction of the basicity of every amine candidates using COSMO-RS. The basicity were then compared with experimental results to check the reliability of the prediction. The correlation between predicted basicity value and amine performance in absorbing CO_2 was established. Several high performance amine absorbents for CO_2 capture were recommended for future studies.

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1. Background of Study

Scientific findings have shown that, if global warming keep on rising until it reach 2°C or more above the pre-industrial temperature, the risk of irreversible and catastrophic environmental change such polar ice melting will be unstoppable [1]. This global warming effect is attributed to increasing concentrations of CO_2 and other greenhouse gases in the earth's atmosphere. To overcome this problem, there are a number of initiatives to reduce CO_2 emissions around the world currently being carried out. Worldwide, there are more than 8,000 large stationary CO_2 sources whose cumulative emissions in 2005 were reported as being 13,466 $MtCO_2$/year [2]. This problem become even worst as the population keeps growing with increasing demands for more energy intensive lifestyles. Based on the study, it is well accepted that fossil fuels will continue to become the most important source of both heat and power generation and also in heavy industrial manufacturing operations for years to come [3]. According to the United Nation-Intergovernmental Panel on Climate Change (IPCC) and the IPCC projects global warming will keep increasing between 1.8 to 4°C in this century. This can be avoided if international community acts to cut down greenhouse gas (GHG) emissions.

Through the Kyoto Protocol (1997), developed countries agreed to reduce their CO_2 emissions by 5.2% below their 1990 levels. European Union (EU) has even agreed in 2008 to reduce GHG emissions to 20% below 1990 levels by 2020. Malaysia, as a party of the UNFCCC and has ratified the Kyoto Protocol, has already committed to formulate, and implement programs to mitigate climate changes [17]. However, given the increasing fossil energy consumption, the CO_2 emission level is likely to continue increasing, so even greater reductions in the CO_2 emissions will be required in the future. It was calculated that, for example, emissions of CO_2 may need to be reduced by more than 60% by 2100, in order to stabilize the atmospheric concentration of CO_2 at no more than 50% above its current level [4].

The largest contributor to emission of CO_2 is the use of fossil fuel which produce around 21.3 billion tonnes of CO_2 per year [36]. Apart from being generated as a product of fuel combustion, CO_2 also come in the form of contaminant gas inside natural gas. Due to relatively low emission, natural gas was currently one of the most attractive and fastest growing fuel of world primary energy consumption. The major contaminates present in natural gas feeds is CO_2 which must be removed as it reduces the energy content of the gas, affect the selling price of the natural gas and it becomes acidic and corrosive in the presence of water which has a potential to damage the pipeline and the equipment system.

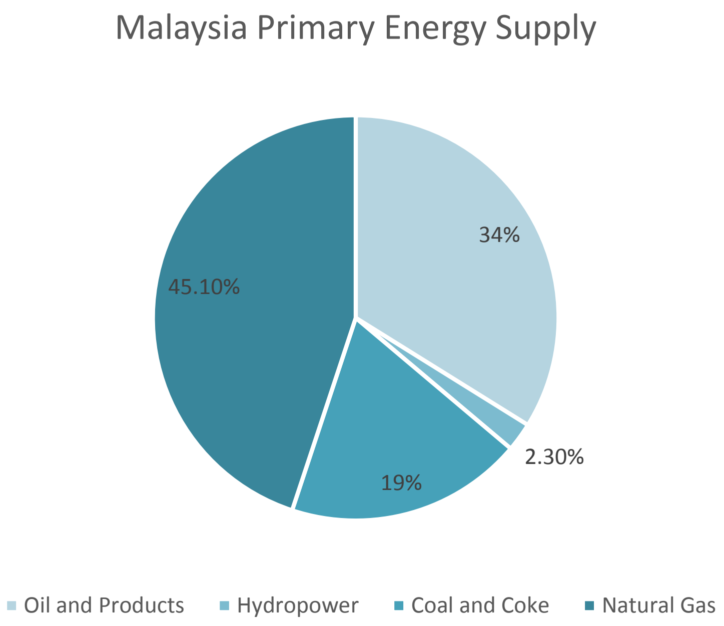


Figure 1: Malaysia Primary Energy Supply (Suruhanjaya Tenaga).

Figure 1 showing natural gas' share of Malaysia's primary energy mix in 2011. Since natural gas was introduced to the Malaysia power sector, it continuously become the most preferred fuel for power generation.

Carbon capture and storage (CCS) technologies are a promising route to achieve a meaningful reduction in CO_2 emissions in the near-term. CCS is defined as a system of technologies that integrates CO_2 capture, transportation and geological storage. Emission reduction targets such as 80- 90% of CO_2 emissions from fixed point sources are routinely discussed in the context of targets achievable by CCS technologies. Each stage of CCS is in principle technically available and has been used commercially for many years (IEA 2008). However, various competing technologies, with different degrees of maturity, are competing to be the low-cost solution for each stage within the CCS value chain. It is vital to select methods of CO_2 capture that are optimal not only in terms of their capital and operating cost, but also in terms of their environmental impact. There are numerous different technologies are being used by industry to remove CO_2 from gas streams, where it was an undesirable contaminant needed to be separated as a product gas. There are three technology options that are generally accepted as being suitable for commercial deployment in the near to medium term; post-combustion CO_2 capture using amine solvents, oxy-fuel combustion and calcium looping technologies. Post-combustion amine-based CO_2 capture is seen to be the most promising alternative because it is an “end of pipe” technology which means it can be installed either to the existing plant or to a new plant without affecting the current plant configuration.

However, due to unlimited possible candidates of amine-based solvent, the evaluation of amine for CO_2 capture is time consuming and expensive if carried out experimentally. The opportunity to select new amine may also be missed. Hence, to effectively select the best amine with desired properties, all possible amines must be preliminary screened in a systematic way. A predictive method for quantitative evaluation which is applicable to a range of solutes or solvents is desired to avoid the screening of a large amount of candidates. For this purpose, a quantum chemical approach combined with a solvation model is promising because it is applicable to a variety of chemical species that need to be investigated with the same parameters by just changing the molecular structure [19]. In this method, molecular geometries are optimized and the free energy of each species in solution is calculated. On the basis of these calculated free energies, we can estimate the species distribution at equilibrium in the solution [20]. The conductor-like screening model for real solvents (COSMO-RS) has been developed as a general and fast method for the a prior prediction of thermodynamic data for liquids such as activity coefficients, pK_a values, partition coefficients, vapor pressures, and solubility [21]. COSMO-RS is based on cheap quantum chemical calculations followed by statistical thermodynamics to give the free energies of all species in solution. The COSMO-RS method, among others, employs a density functional theory (DFT) at the BP/TZVP level and has been shown to be fast and accurate in various systems [22]. An important advantage of the COSMO-RS model is that it predicts the properties of component in a mixture without using any experimental data. In this work potential amines were screened to estimate its pK_a value using COSMO-RS and the relationship between the estimated pK_a value and the performance of amine which in this case is the absorption rate and absorption amount were established. It is found that, generally the performance of amine is directly proportional to its basicity.

1.2. Problem Statement

Carbon capture and storage is one of the promising ways to reduce CO_2 emission to the air either from burning of fossil fuel or from the contaminant inside natural gas. Currently, the most matured technology in this field is postcombustion amine-based solvent. However, there are unlimited types of amine-based solvent being discovered worldwide but to evaluate the capabilities for every single amine for CO_2 capture is time consuming and expensive if carried out experimentally. The opportunity to select new amine may also be missed. Hence, to effectively select the best amine with desired properties, all possible amines must be preliminary screened in a systematic way.

1.3. Objective

The objectives of this work are as follow:

a) To optimize the structure of amine and generate COSMO file Using Turbomole to predict the pK_a values of amine candidates using COSMOthermX.
b) To validate the predicted pK_a values with the experimental literature data.
c) To establish the relationship between basicity of amine with it absorption rate and absorption amount.
d) To suggest promising amine candidate based on this findings.

1.4. Scope of Study

The scopes of study for this particular project are:

a) This work focused on the screening of amine that suitable for CO_2 capture.
b) The scope of this work was limited to only tertiary amine due to limitation of time.
c) The tool used to estimate the thermodynamic properties of the amine is COSMO-RS.
d) The tool used to optimize the structure of the amine geometry is TURBOMOLE.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1. CO_2 Capture Technology

Relating to the environmental concerns that have been addressed in the previous section, there is a need to develop technologies to reduce CO_2 emission. As stated before, there are three technologies option that generally acceptable which are post-combustion amine-based CO_2 capture, oxy-fuel combustion process and calcium looping technologies.

2.1.1. Amine based CO_2 capture process description

In amine-based CO_2 capture in figure 2, the gas stream with high CO_2 content is contacted with the “lean” amine-based solvent stream which flows from top of absorption column through a packing materials and during the contact, the amine-based solvent will absorb the CO_2 molecule from the CO_2 rich gas stream [1]. This amine solvent reacts with CO_2 and once the CO_2 has reacted with the aqueous amine solution, it forms a carbonate salt [1]. When the “rich” solvent stream reaches the bottom of the column, it is directed to a solvent regeneration process, which is another gas-liquid contacting column with a condenser at the top and a reboiler at the bottom. The purpose of the reboiler is to heat the incoming liquid stream to a suitable temperature in order to both break the chemical bonds formed and to provide a vapour stream to act as a stripping fluid. The purpose of the overhead condenser is both to provide a reflux liquid stream to the column and to ensure that the top-product stream is as pure as possible. The regenerated amine can be recycled whereas the CO_2 is compressed and transported away as a liquid. Given the reactive nature of the absorption, amine based solvent processes are well-suited to capturing CO_2 from dilute, low pressure streams. This makes this technology applicable to the majority of existing large, fixed-point sources of CO_2.

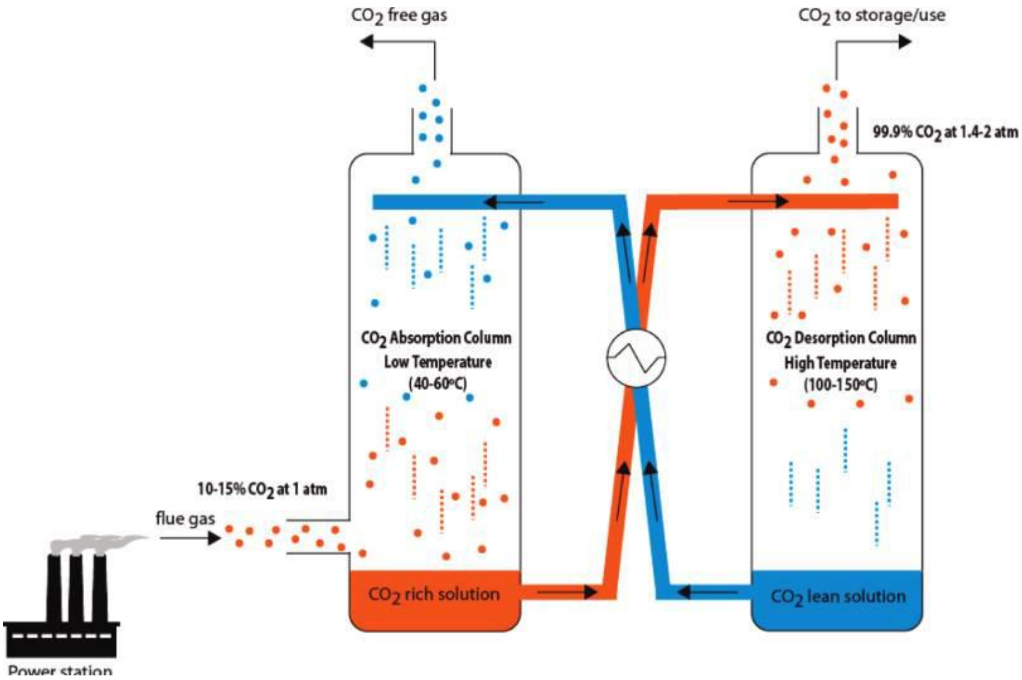


Figure 2: The chemical absorption and desorption of CO2 in postcombustion process

There are always pros and cons in using any technologies. In case of amine-based CO_2 capture, the advantage is, it is an “end of pipe” technology which means it can be installed either to the existing plant or to a new plant without affecting the current plant process [5]. However, this technology have distinct disadvantage over their cost either capital cost or operational cost. It is expected that by using this technology, it will reduce the thermal efficiency of a modern power plant from approximately 45% to approximately 35% [6]. This is due to the cost for compressing the CO_2 before it can be transported, costs related to transportation of flue gas and cost for solvent regeneration [1]. In addition, these processes are expected to consume between 0.35 and 2.0 kg of solvent per tons of CO_2 captured which will directly increase the cost to replace the lost solvent [7].

2.2. Amine

Chemical absorption technology is a matured technology which widely used on a large scale across several industries [8]. Therefore, it is assumed that no major innovation and improvement will occur in the design of both the column internals and the processor. Any new innovation or major scope for reducing the costs associated with these processes lies in the selection and design of new, advanced sorbent materials as it is the solvent which determines the thermodynamic and kinetic limits of the process [1]. The solvent chemistry also will determine the type and seriousness of any environmental and public health impacts because of the emissions of organic solvents, or their associated degradation or corrosion products. Therefore, the selection of appropriate solvents is not as simple. In terms of solvent selection, amines have traditionally been the solvents of choice, with a primary alkanolamine, monoethanolamine (MEA) typically considered to be the benchmark solvent with which alternative solvents must be compared. Other compounds which are often considered are sterically hindered compounds such as 2-amino-2-methyl-1-propanol (AMP), secondary amines such as diethanolamine (DEA) and tertiary amines such as methyldiethanolamine (MDEA) [1].

2.2.1. Types of Amines

Amines are organic compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are derivatives of ammonia, where in one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group. Amines fall into different classes depending on how many of the hydrogen atoms are replaced [23].

The first class of amine is primary amine. In primary amines, only one of the hydrogen atoms in the ammonia molecule has been replaced which means that the formula of the primary amine will be RNH_2 where "R" is an alkyl group. Secondary amine is amines with two of the hydrogen in an ammonia molecule have been replaced by hydrocarbon groups and tertiary amine is when all of the hydrogens in an ammonia molecule have been replaced by hydrocarbon groups [24]

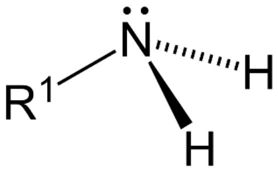
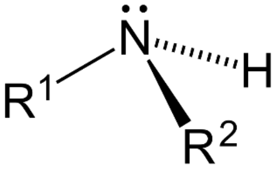
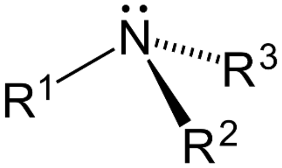
		
Primary Amine	Secondary Amine	Tertiary Amine

Figure 3: Basic types of amines

Amine can also be further classified into either sterically free or sterically hindered amine. Sterically hindered amine is amines for which either a primary amino group is attached to a tertiary carbon atom or a secondary amino group is attached to a secondary or tertiary carbon atom [24]. Polyamine, as in figure 4, in the other hand is another type of amine which is an organic compound having two or more primary amino groups (NH).

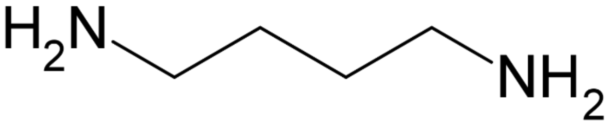


Figure 4: Structure of polyamine

2.2.2. Amine Reaction with CO_2

The reactive nature of the aqueous solutions of amines with CO_2 system is well known, and there is a large body of experimental and theoretical work in place detailing the mechanism and rates of these reactions. In addition to the ionic speciation equilibria owing to the disassociation of CO_2 and the amines in aqueous solution, the principal reaction of interest between CO_2 and a primary and secondary amine (in aqueous media) is the formation of a carbamate, which is typically considered to occur via the formation of a zwitterion, and subsequent base catalysed deprotonation of the zwitterion [4]. Generally, primary and secondary amines (represented as R1R2NH) can react with dissolved CO_2 to form a carbamic acid (R1R2NCOOH). Depending upon its acidity, it may then give up a proton to a second amine molecule forming a carbamate (R1R2NCOO$^-$) according to an overall stoichiometry of 2 as shown below [18].

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NCOOH$$

$$R_1R_2NCOO^- + H^+ \rightleftharpoons R_1R_2NCOOH$$

$$R_1R_2NH + H^+ \rightleftharpoons R_1R_2NH_2^+$$

Via this pathway two moles of amine are consumed per mole of CO_2 if the carbamic acid is acidic, which is generally assumed to be the case. Kinetically and thermodynamically this reaction pathway is generally favored for primary and secondary amines [25].

A second reaction pathway that also contributes to CO_2 absorption is CO_2 hydration to form bicarbonate. In this pathway an amine molecule (represented as R1R2R3N) simply acts as a proton accepting base, and possibly a catalyst, for the hydration of CO_2 [26].

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$

$$R_1R_2R_3N + H^+ \rightleftharpoons R_1R_2R_3NH^+$$

Via this pathway one mole of amine is consumed per mole of CO_2, so in terms of capacity it is more efficient. For tertiary and some sterically hindered primary and secondary amines this is the only pathway contributing to absorption. However, this pathway is generally less favorable kinetically than carbamate formation [25].

2.2.3. Parameters that affect performance of amine

In designing the absorption system, some parameters need to be properly selected to optimize the absorption process in terms of a cost-benefits analysis [11]. First parameter is the partial pressure of the CO_2 in the absorber. A high partial pressure of CO_2 in the absorber is beneficial to the absorption process, but raising the pressure of flue gases at the plant exit requires power for the blower. Thus, these two factors need to be properly determine in the selection of the absorption pressure. Since the flue gas has a large concentration of N2, while CO_2 concentration is only approximately 10 %, any increase of the total pressure only raise the CO_2 pressure by 0.1. Therefore the energy for flue gas compression should be the minimum possible and the pressure in the absorber should be the lowest possible, by using a low-pressure drop tray design in the packed column [4].

Secondly, another important factor in the design of both the absorber and the stripper is the solvent flow rate. The higher the flow rate, the lower the number of trays in the absorber and the stripper. The higher the flow rate, the higher is the solvent cost and the greater the diameter of the absorber and the stripper. Therefore, the optimum flow rate can be determined by the balance of these two competing factors: cost of solvent and number of trays in the absorber and stripper [4].

Next, the selection of the amine type is also a very important factor for the performance and cost of the capture system. Monoethanolamine (MEA) is the more reactive amine, and a 30 % amine solution allows the number of trays in the columns, and so the solvent flow rate, to be minimized, thus reducing the overall costs. Using secondary and tertiary amines is generally more expensive in terms of capital and operational costs compared to MEA. It must be noted that the energy required for regeneration is proportional to the sum of the heat of reaction and the latent heat of vaporization of the solvent [13]. By looking at the different solvents that can be used in CO_2 capture systems, it is possible to see that tertiary amines require less energy for regeneration. However, they have a very low absorption rate and thus a lower mass transfer rate and, ultimately, a larger equipment size for absorption and stripping will be required. For this reason, blending secondary and tertiary amines with primary ones or adding activators to MEA can reduce the heat of regeneration without significantly reducing the reaction rate. In order to increase CO_2 loading in the amine aqueous solution and reduce the regeneration heat, sterically hindered amines, such as those used by Mitsubishi Heavy Industries in their CO_2 recovery plants, have been tested and studied (Mimura, 1995, 1997). They have some very interesting properties capable of improving the performance of the system shows that sterically hindered amines such as KS-1 have a higher CO_2 absorption capacity than MEA (Mimura, 1995). This is mainly due to the fact that the chemical reactions do not produce the carbamate ion; this allows the CO_2 loading to be increased because 1 mol of CO_2 can react with 1 mol of amine rather than 0.5 mol.

2.2.4. Basicity of Amine

The dissociation constant (pK_a) is one of the key parameter that affects the performance of amine. It is an important factor in the selection of an amine based absorbent for acid gas removal and also serves as a first indicator of the reactivity of various amine-based absorbents towards CO_2 [4]. Dissociation constants provide the basic strength of the amine-based absorbent at a specific temperature. Their temperature dependency and reaction enthalpy will be reflected in the overall reaction enthalpy of CO_2 with the amine based solvent [4]. When the basic strength is reduced, the tendency to remove a proton from the intermediate zwitterions formed during the reaction with CO_2 will be lower.

Based on study by Puxty & Rowland [18], primary and secondary amines in general do not appear to show a strong correlation with pK_a. This is not surprising as carbamate formation has lower sensitivity to pH, and thus amine pK_a, is dependent on the carbamate stability constant which varies from amine to amine. The tertiary amines do show a strong dependence on pK_a consistent with bicarbonate formation being the dominant reaction pathway for CO_2 absorption. This is because the CO_2 hydration reaction is independent of the amine but is strongly pH dependent due to the small stability constant for bicarbonate formation. The mixed amines all contain primary or secondary functionality and also show little correlation with pK_a.

Based on this correlation, screening of amine as an absorption material for CO_2 capture can be done on the basis of its pK_a value.

2.3. COSMO-RS as Tools to Predict the Basicity of Amine

2.3.1. COSMO-RS

Conductor-like Screening Model for Real Solvents (COSMO-RS) is quantum chemistry based statistical thermodynamics model for the prediction of thermodynamic properties of fluids and liquid mixtures. COSMO-RS predicts thermodynamic properties of liquid mixtures, such as, activity coefficient, vapor pressures, and solubility by using the molecular structure of solute and solvent as initial inputs.

2.3.2. Modeling

Yamada, Shimizu, Okabe, Matsuzaki, Chowdhury & Fujioka in 2010 [20] and Scientific Computing & Modeling website [28] have come out with a model to predict amine basicity. In an aqueous solution, amine B reacts with H+ as a base and the species distribution in the equilibrium is related to its basicity.

$$BH^{+} + H_2O \leftrightharpoons B + H_3O^{+} \cdots (1)$$

$$pK_a \ - \ log_{10}\left(\frac{[B][H_3O^{+}]}{[BH^{+}]}\right) \cdots (2)$$

In this model, molar concentration is used in units of moles per litre instead of activity and the concentration of H2O is assumed to be constant. The Gibbs free energy of reaction (1) is the difference between the total free energies of the reactants and products.

$$\Delta G_{R1} = \ G(B) + \ G(H_3O^{+}) - \ G(BH^{+}) - \ G(H_2O) \cdots (3)$$

From the relation between the reaction free energy and the equilibrium constant, ΔG_R = -RT ln K, where R is the gas constant, the following equation is given at T = 298.15 K using energy units of kilocalories per mole.

$$pK_a = \ 0.733\Delta G_{R1} \ - \ 1.74 \cdots (4)$$

In aqueous amine solutions, CO_2 is absorbed by the formation of carbamate or bicarbonate anions

$$2B + CO_2 \leftrightarrow B'COO^- + BH^+ \cdots (5)$$

$$B + CO_2 + H_2O \leftrightarrow HCO_3^- + BH^+ \cdots (6)$$

where B′ implies the deprotonation of the neutral amino group. It should be noted that the species in the above relations are also involved in other reactions in the system. However, we assume that the equilibrium constants of reactions (5) and (6) are independent of other reactions. Hence, a ratio between carbamate and bicarbonate anions at equilibrium is represented by the equilibrium constants as follows.

$$r = \frac{[B'COO^-]}{[HCO_3^-]} = \frac{[B]K_{R5}}{[H_2O]K_{R6}} = \frac{[B]}{[H_{2O}]} \times \exp\left(\frac{-(\Delta G_{R5} - \Delta G_{R6})}{RT}\right) \cdots (7)$$

The experimental data in this work were obtained under conditions that simplify the treatment of the above equation. Under these conditions, we ignore the presence of CO_3^{2-}, H_3O^+ and OH^- ions in the charge balance equation.

$$[B'COO^-] + [HCO_3^-] = [BH^+] \cdots (8)$$

Using eqs (2) and (8), eq (7) may be adjusted to evaluate the calculation results of ΔG_{R5} and ΔG_{R6} using measurable parameters

$$\log_{10}\left(\frac{[B'COO^-]}{[HCO_3^-]}\right) = pH - pK_a + \log_{10}\left\{\frac{[B'COO^-] + [HCO_3^-]}{[H_2O]} \exp\left(\frac{-(\Delta G_{R5} - \Delta G_{R6})}{RT}\right)\right\} \cdots (9)$$

Where pH is defined as $-\log_{10}[H_3O^+]$.

CHAPTER 3

METHODOLOGY

3. METHODOLOGY

In the COSMO-RS method, the free energy of each species in solution is obtained by calculating its chemical potential with a statistical thermodynamics algorithm in which a measure of the system affinity to molecular surface polarity is calculated iteratively. COSMO-RS method to predict the thermodynamic properties of fluids and liquid mixtures is a unique way for priori prediction of behavior of pure fluids in their mixtures on the basis of unimolecular quantum chemical calculations [30]. Original work from Klamt et al. has already described the COSMO-RS theory comprehensively [31]. One main advantage of COSMO-RS model is that it is capable to predict the thermodynamic properties of any component in a mixture without using any experimental information. It uses the molecular structure of the solute/component as single initial input. Thus, it can be used to predict the basicity of amine solution in water.

The reliability of COSMO-RS to predict the pK_a value of organic bases has been shown by Eckert and Klamt in their work [31]. Therefore, in this work, COSMO-RS was used to predict the basicity of amine solution in water and finally develop the relationship between amine basicity with its performance in CO_2 capture.

Based on literature [20], standard procedure for COSMO-RS calculations of the pK_a values consist of two steps. In the first step, continuum solvation COSMO calculations of electronic density and molecular geometry optimizations were carried out at the B3-LYP/TZVP level using the resolution of identity (RI) approximation [29]. The structures are fully optimized and the quantum chemical calculations performed for each molecule with TURBOMOLE program package.

Then, the optimized geometries were used for a single-point COSMO calculation at the BP/TZVP level with the RI approximation. COSMO-RS calculation was performed using COSMOthermX program.

Predicted basicity values generated were then compared and plotted against the experimental results to confirm for the reliability of the prediction. Finally, the relationship between predicted basicity versus the absorption rate and absorption amount was established. Based on that relationship, we have suggested few amine candidates that potentially good candidates for CO_2 capture.

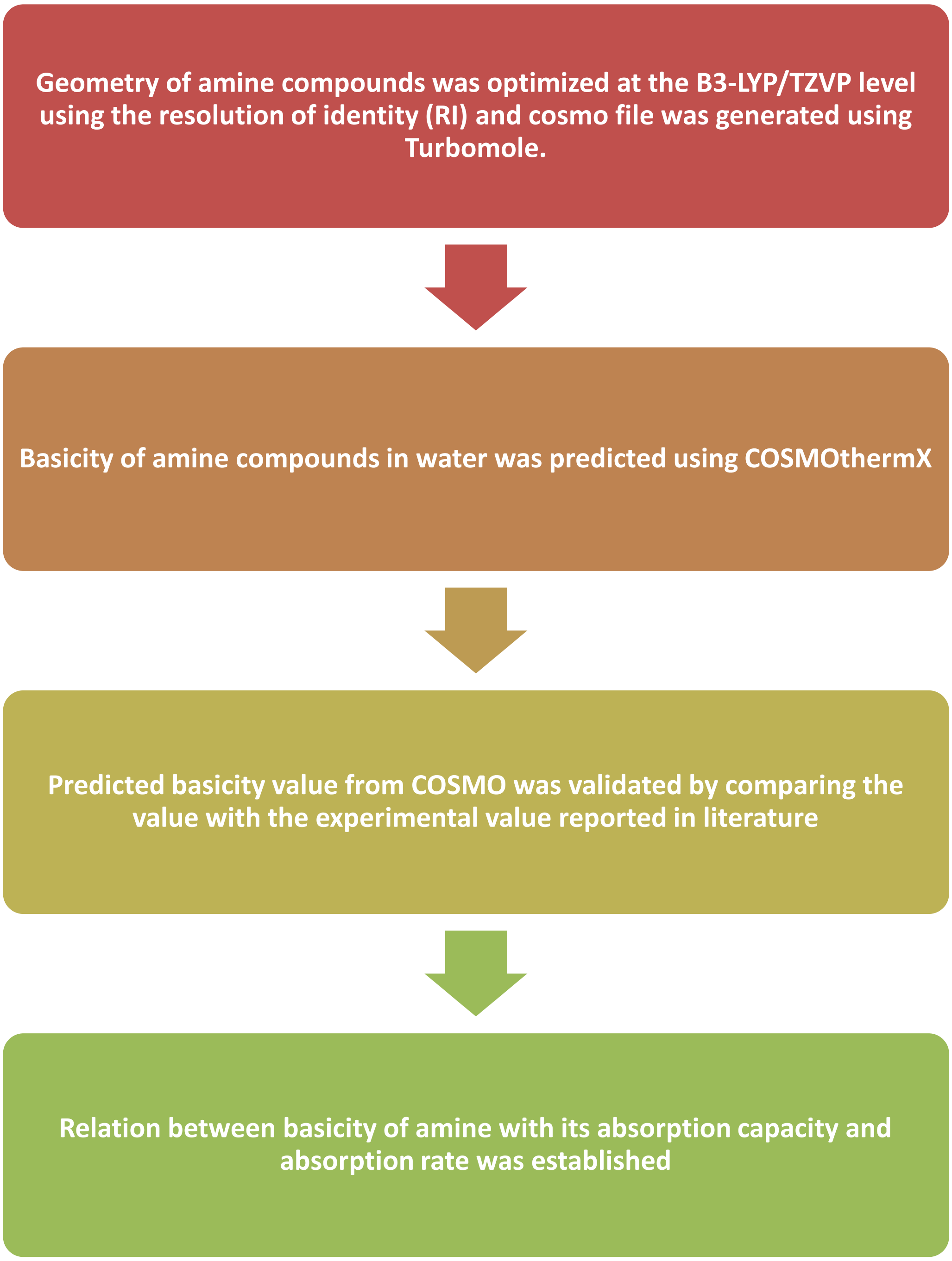
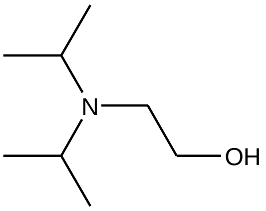


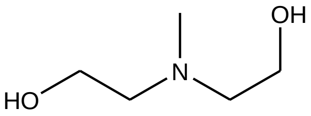
Figure 5: Summary of the methodology.

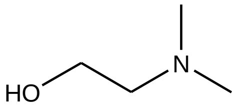
3.1. Identification of amine candidates

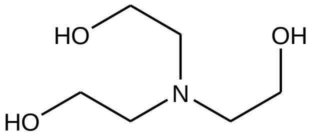
We selected 57 tertiary amine based absorbents with broad range of structures. They are illustrated as below.

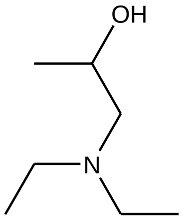
Alkanolamine

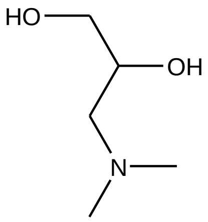

2-(diisopropylamino)ethanol

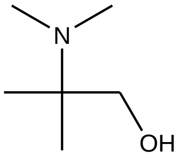

methyldiethanolamine


2-(dimethylamino)ethanol


triethanolamine


1-diethylamino-2-propanol


3-(dimethylamino)-1,2-propanediol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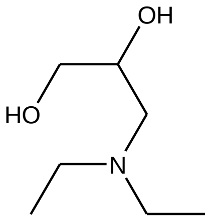
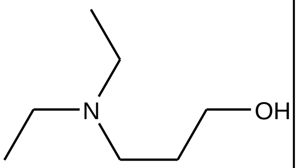
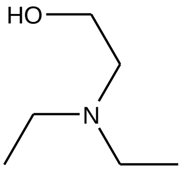
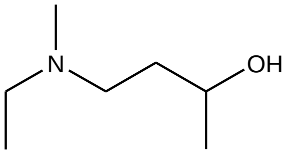
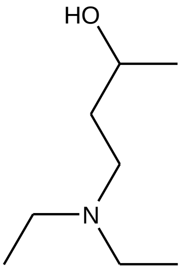
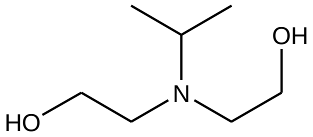

3-diethylamino-1,2-propanediol

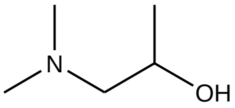

3-diethylamino-1-propanol

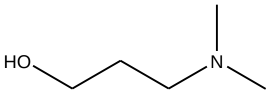

2-diethylaminoethanol


4-ethyl-methyl-amino-2-butanol

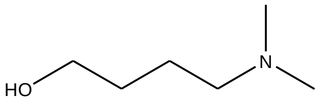

4-diethylamino-2-butanol


N-isopropyldiethanolamine

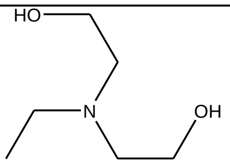

1-dimethylamino-2-propanol



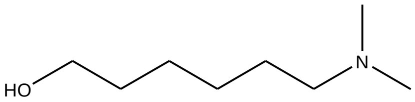
3-dimethylamino-1-propanol



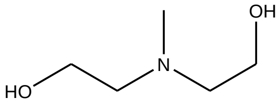
4-(Dimethylamino)-1-butanol



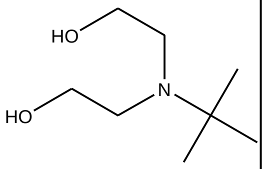
N-ethyldiethanolamine



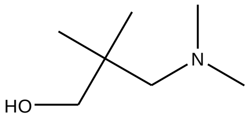
6-dimethylamino-1-hexanol



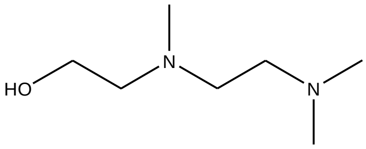
N-methyldiethanolamine



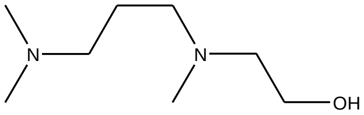
N-tert-butyldiethanolamine



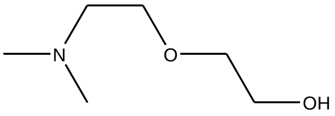
3-dimethylamino-2,2-dimethyl-1-propanol



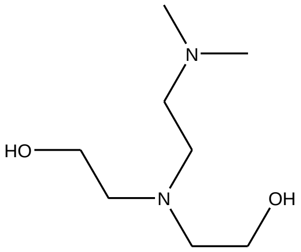
N- methyl -N- (N, N- dimethylaminoethyl) ethanolamine



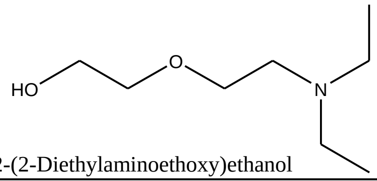
N- methyl -N- (N, N- dimethylaminopropyl) ethanolamine



2-[2-(Dimethylamino)ethoxy]ethanol

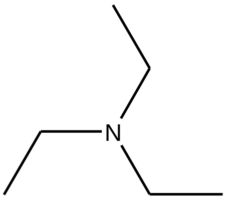


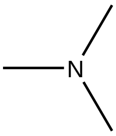
N- (N, N- dimethylaminoethyl) diethanolamine

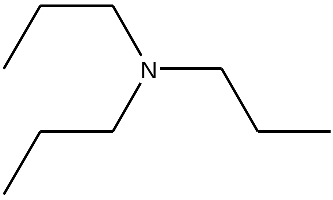


2-(2-Diethylaminoethoxy)ethanol

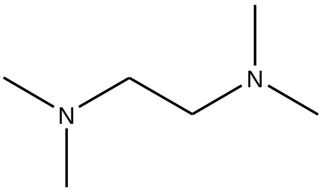
Alkylamine

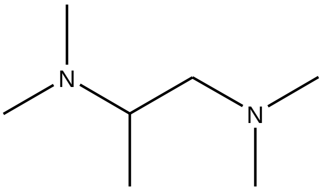

Triethylamine


Trimethylamine


1-Dipropylaminopropane

Diamine


N,N,N',N'-Tetramethylethylenediamine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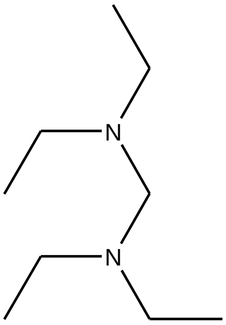
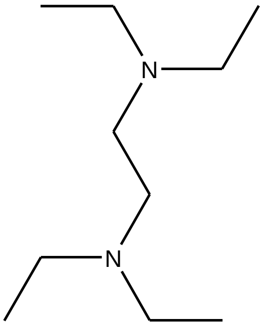
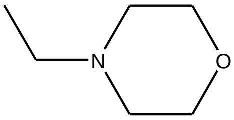
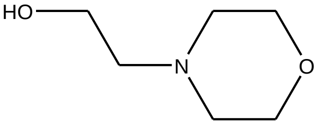

N,N,N',N'-Tetraethylmethanediamine


N,N,N',N'-tetraethylethylenediamine

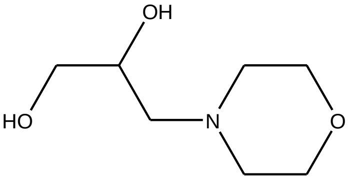
Cyclic Amine



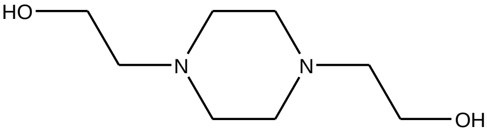
4-ethylmorpholine



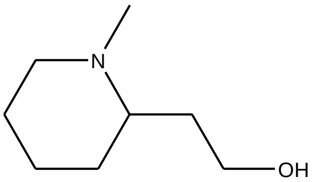
2-morpholinoethanol



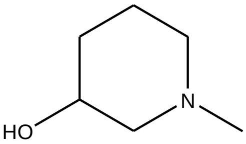
3-morpholino-1,2-propanediol



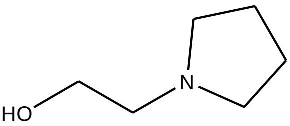
1,4-bis(2-hydroxyethyl)piperazine



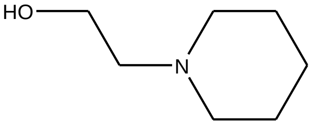
1-methyl-2-piperidineethanol



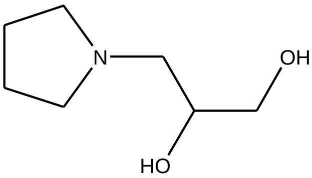
3-hydroxy-1-methylpiperidine



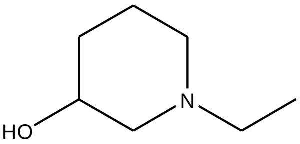
1-(2-hydroxyethyl)pyrrolidine



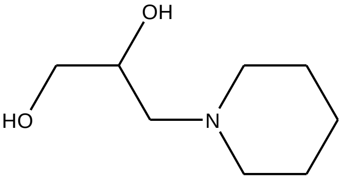
1-(2-hydroxyethyl)piperidine



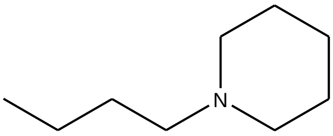
3-pyrrolidino-1,2-propanediol



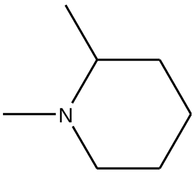
1-ethyl-3-hydroxypiperidine



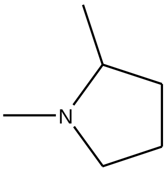
3-piperidino-1,2-propanediol



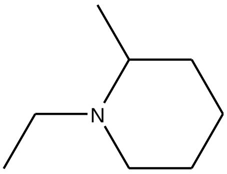
1-n-Butylpiperidine



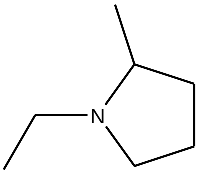
1,2-Dimethylpiperidine



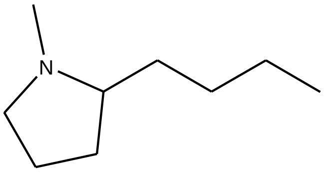
1,2-Dimethylpyrrolidine



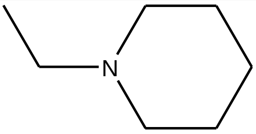
1-Ethyl-2-methylpiperidine



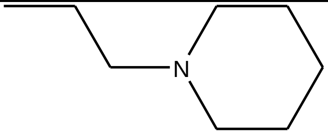
1-Ethyl-2-methylpyrrolidine



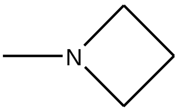
1-Methyl-2-n-butyl-pyrrolidine



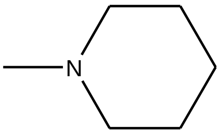
N-Ethylpiperidine



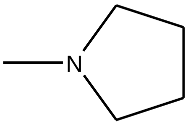
1-n-Propylpiperidine



N-Methyltrimethyleneimine

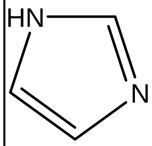


N-Methylpiperidine

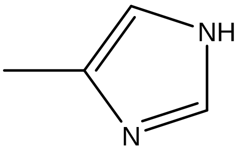


N-Methylpyrrolidine

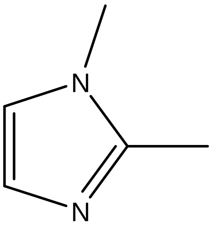
Aromatic Amine



imidazole



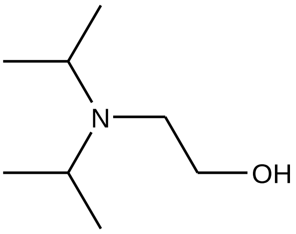
4-methylimidazole



1,2-dimethylimidazole

3.2. Optimization of amine geometry using TmoleX

In order to optimize the structure inside the Turbomole, first, we have to draw the structure for each amine candidates. Then, the drawing will be transfer into the 3D Molecular Builder inside the TmoleX software. Below is the example of the 2-(diisopropylamino)ethanol structure that have been redraw inside the TmoleX.



2-(diisopropylamino)ethanol

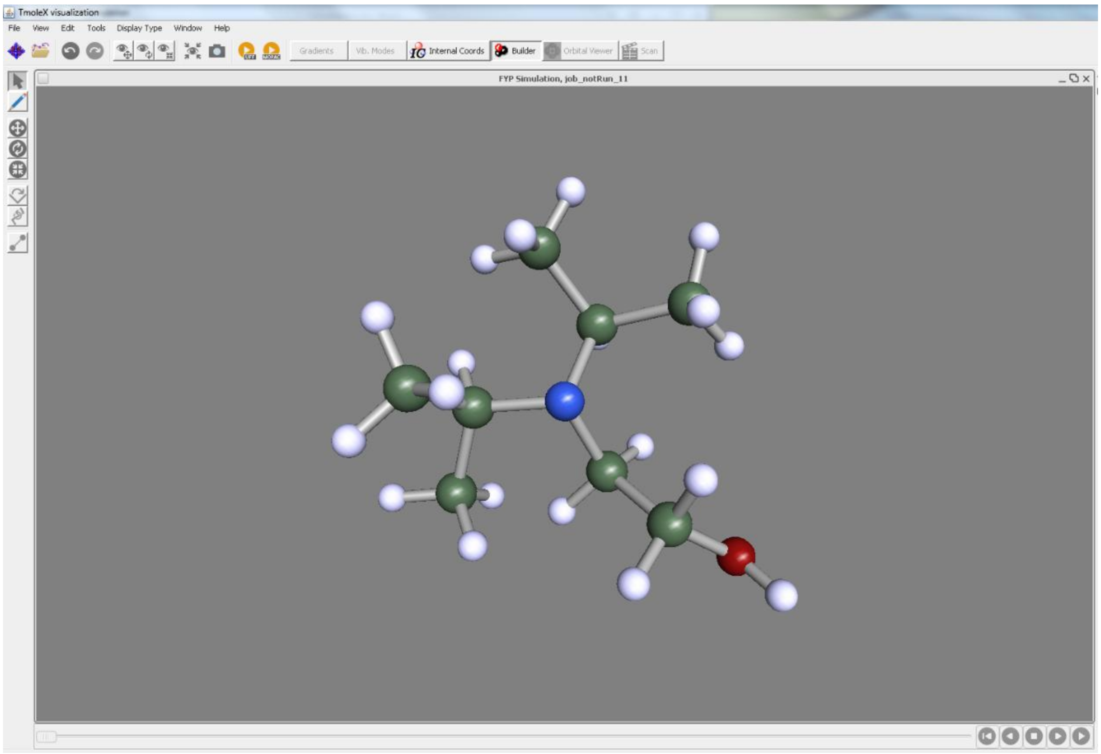
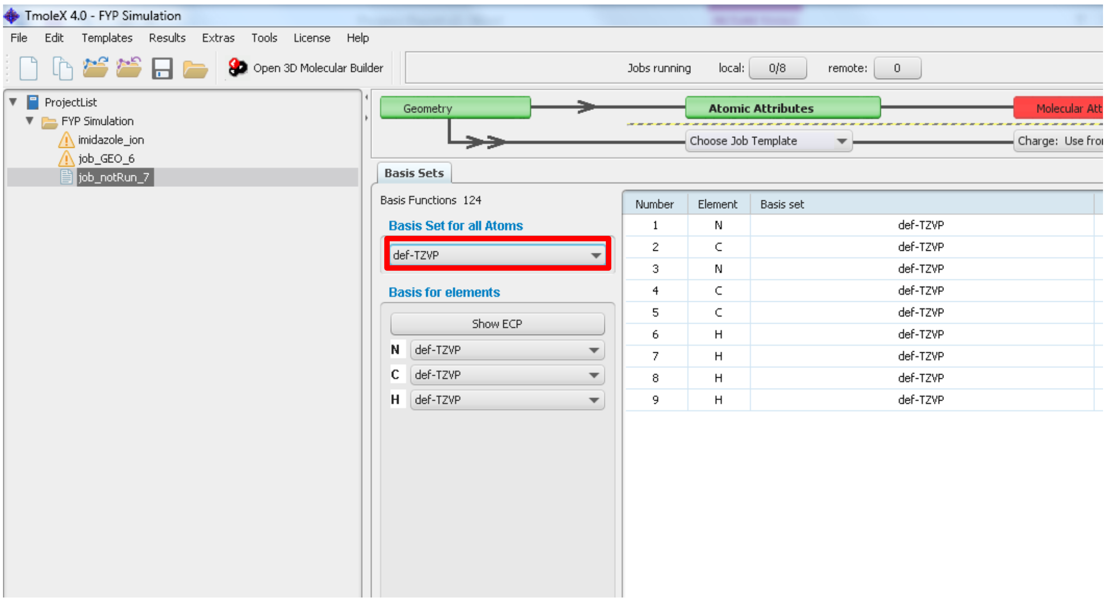


Figure 6: 2-(diisopropylamino)ethanol molecular structure drawn inside TmoleX



Jobs running local: 0/8 remote: 0

Basis Functions 124

Basis Set for all Atoms

def-TZVP

Basis for elements

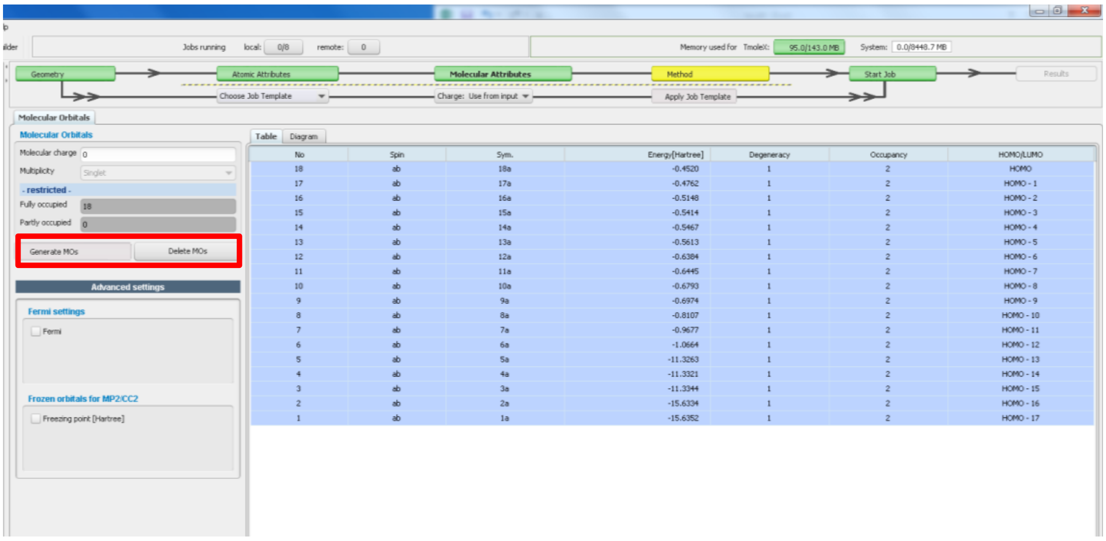
N def-TZVP

C def-TZVP

H def-TZVP

Number	Element	Basis set
1	N	def-TZVP
2	C	def-TZVP
3	N	def-TZVP
4	C	def-TZVP
5	C	def-TZVP
6	H	def-TZVP
7	H	def-TZVP
8	H	def-TZVP
9	H	def-TZVP

Figure 7: Geometry optimization was set on TZVP atomic basis



Jobs running local: 0/8 remote: 0

Memory used for TmoleX: 95.0/143.0 MB System: 0.0/8448.7 MB

Molecular Orbitals

Molecular charge 0

Multiplicity Singlet

- restricted -

Fully occupied 18

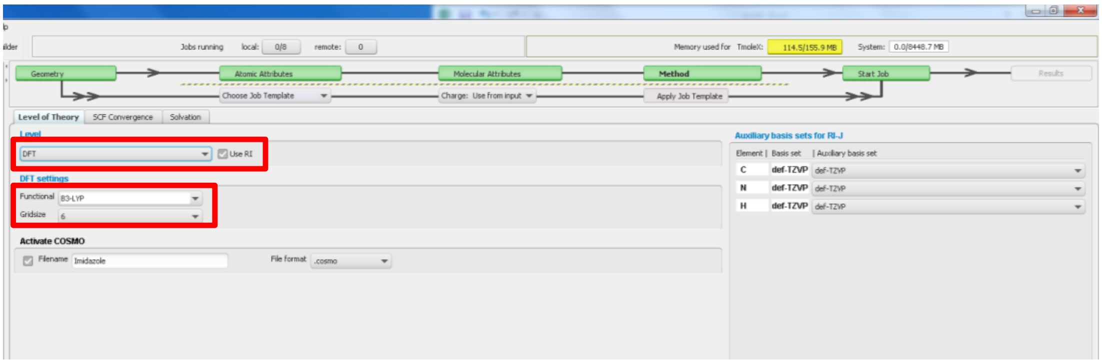
Partly occupied 0

☐ Fermi

☐ Freezing point [Hartree]

No	Spin	Sym.	Energy[Hartree]	Degeneracy	Occupancy	HOMO/LUMO
18	ab	18a	-0.4520	1	2	HOMO
17	ab	17a	-0.4762	1	2	HOMO - 1
16	ab	16a	-0.5148	1	2	HOMO - 2
15	ab	15a	-0.5414	1	2	HOMO - 3
14	ab	14a	-0.5467	1	2	HOMO - 4
13	ab	13a	-0.5613	1	2	HOMO - 5
12	ab	12a	-0.6384	1	2	HOMO - 6
11	ab	11a	-0.6445	1	2	HOMO - 7
10	ab	10a	-0.6793	1	2	HOMO - 8
9	ab	9a	-0.6974	1	2	HOMO - 9
8	ab	8a	-0.8107	1	2	HOMO - 10
7	ab	7a	-0.9677	1	2	HOMO - 11
6	ab	6a	-1.0664	1	2	HOMO - 12
5	ab	5a	-11.3263	1	2	HOMO - 13
4	ab	4a	-11.3321	1	2	HOMO - 14
3	ab	3a	-11.3344	1	2	HOMO - 15
2	ab	2a	-15.6334	1	2	HOMO - 16
1	ab	1a	-15.6352	1	2	HOMO - 17

Figure 8: Molecular orbitals for the molecule was generated



Jobs running local: 0/8 remote: 0

Memory used for TmoleX: 114.5/155.9 MB System: 0.0/8448.7 MB

Charge: Use from input

Level

DFT ☑ Use RI

DFT settings

Functional: B3-LYP

Gridsize: 6

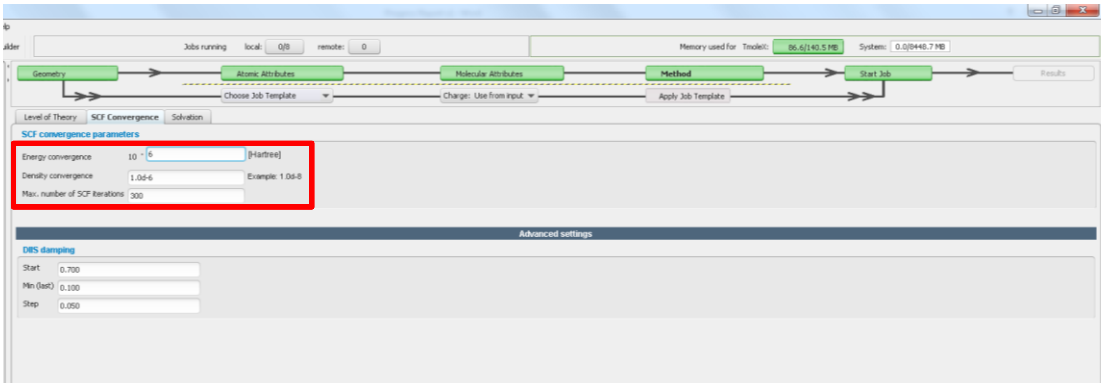
Activate COSMO

☑ Filename: Imidazole File format: .cosmo

Auxiliary basis sets for RI-J

Element	Basis set	Auxiliary basis set
C	def-TZVP	def-TZVP
N	def-TZVP	def-TZVP
H	def-TZVP	def-TZVP

Figure 9: Calculation were performed on the density functional theory (DFT) at the B3-LYP/TZVP level with resolution of identity (RI)



Jobs running local: 0/8 remote: 0

Memory used for TmoleX: 86.6/140.5 MB System: 0.0/8448.7 MB

Charge: Use from input

SCF convergence parameters

Energy convergence: 10⁻ 6 [Hartree]

Density convergence: 1.0d-6 Example: 1.0d-8

Max. number of SCF iterations: 300

DIIS damping

Start: 0.700

Min (last): 0.100

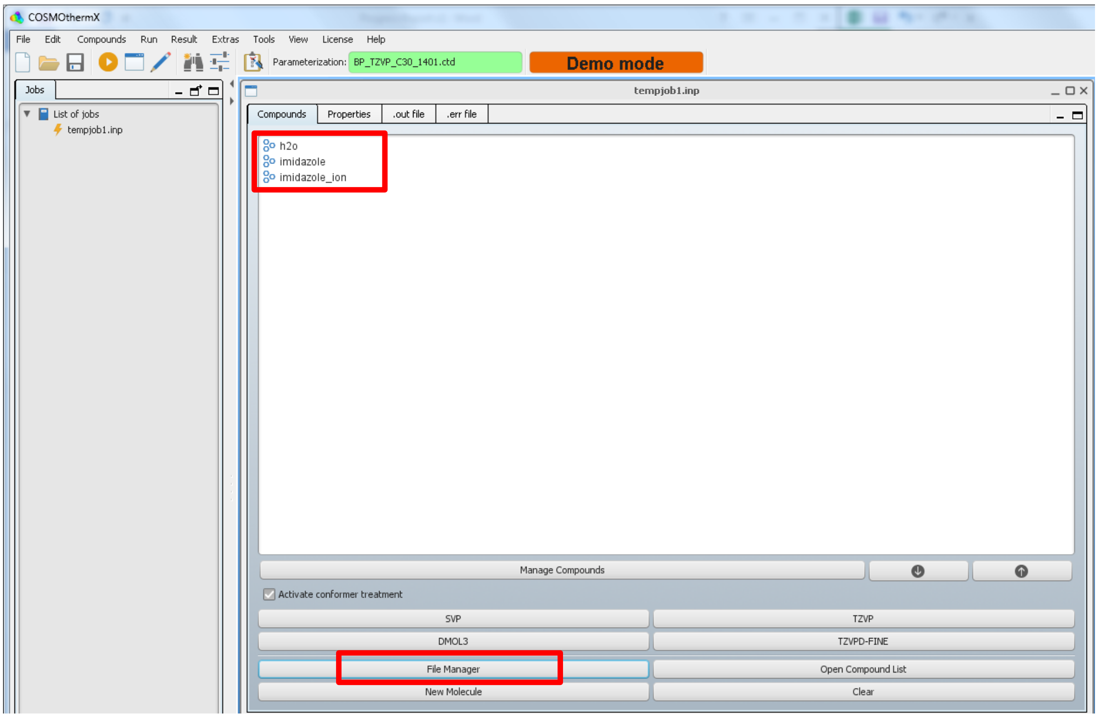
Step: 0.050

Figure 10: Setting of convergence parameter for the geometry optimization

Steps above was repeated for all of the amine candidates and its respective ions.

3.3. Prediction of basicity of amine compound in water using COSMOthermX

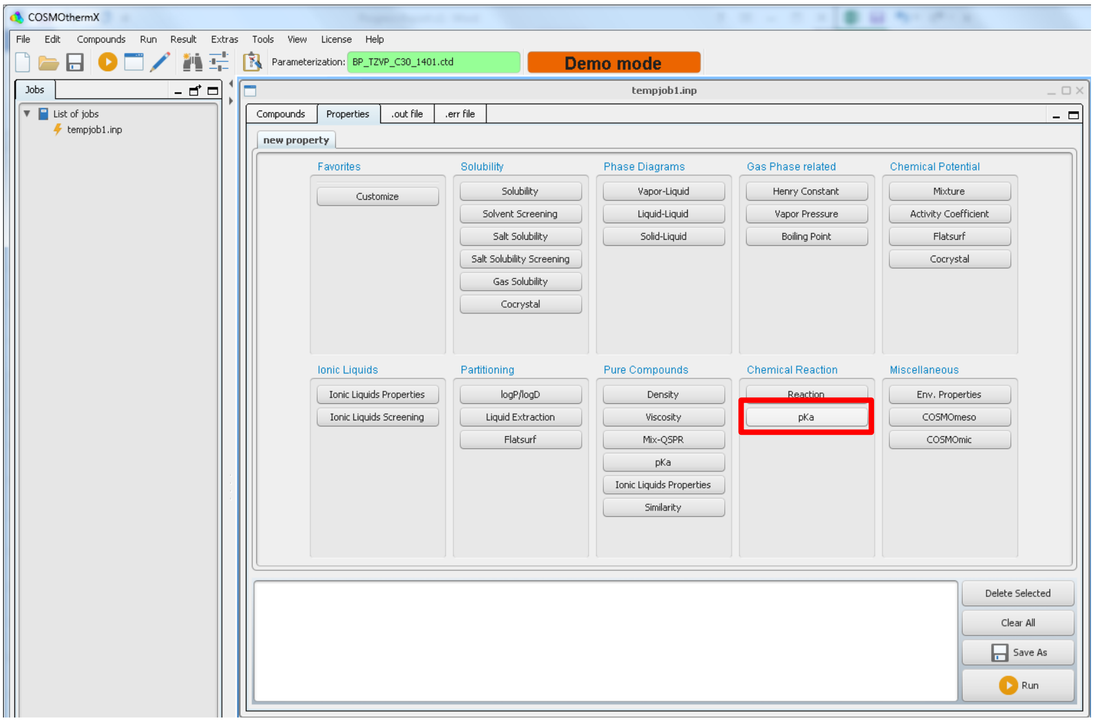
After the geometry optimization process for all of the amine was finished, the data was then imported into COSMOthermX to predict the basicity. COSMO-RS are capable to predict the thermodynamic properties of fluids and liquid mixtures by using the molecular structure of the solutes and solvents as initial inputs.



Parameterization: BP_TZVP_C30_1401.ctd

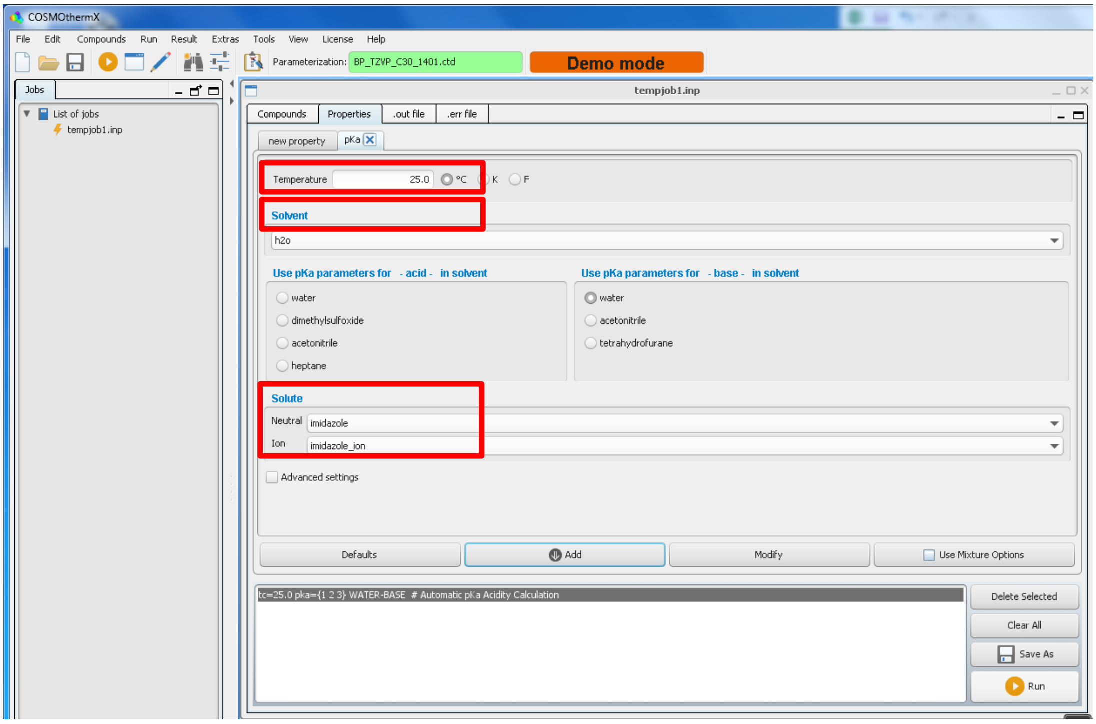
h2o
imidazole
imidazole_ion

Figure 11: The optimized imidazole molecule and ion was imported into COSMO



Parameterization: BP_TZVP_C30_1401.ctd

Figure 12: Prediction of basicity using COSMO-RS



Parameterization: BP_TZVP_C30_1401.ctd

tempjob1.inp

Temperature 25.0 ● °C ○ K ○ F

Solvent

h2o

Solute

Neutral imidazole

Ion imidazole_ion

```
tc=25.0 pka={1 2 3} WATER-BASE  # Automatic pKa Acidity Calculation
```

Figure 13: Prediction of pK_a value of amine solution in water at temperature of 25°C

3.4. Gantt Chart and Key Milestone (FYP II January Semester)

Table 1: Gantt Chart for the FYPII

No	Activties / Tasks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	**Project Work Continue**															
	Identification of amine candidates	🟦	🟦	🟦												
	Geometry optimization of amine	🟦	🟦	🟦	🟦	🟦										
	Basicity prediction using COSMO						🟦	🟦								
2	**Progress Report**								🟥							
3	**Pre Sedex**											🟥				
4	**Submission of Draft**												🟥			
5	**Submission**															
	Softbound													🟥		
	Technical Paper													🟥		
6	**Oral Presentation**														🟥	
7	**Submission of Hardbound**															🟥

CHAPTER 4

RESULT AND DISCUSSION

4. RESULT AND DISSUSION

4.1. Correlation between experimental and calculated pK$_a$

To validate the result, the predicted basicity of amines were compared with experimental results reported in literature. For comparison, 46 experimental data points over 24 to 27 degree Celsius were used. The experimental data is based on the literature.

Table 2: Experimental and Predicted pK$_a$ data using COSMO-RS for 46 amines molecule

	Amine	**Experimental** pK$_a$ **value**	**References**	**Predicted** pK$_a$ **value**	
1	2-(dimethylamino)ethanol	9.23	*a*	8.9082	Alkanolamine
2	2-(diisopropylamino)ethanol	9.97	*a*	8.7145	
3	methyldiethanolamine	8.52	*a*	6.4864	
4	triethanolamine	7.76	*a*	4.9620	
5	1-diethylamino-2-propanol	10.18	*c*	7.8509	
6	2-(dimethylamino)-2-methyl-1-propanol	10.34	*c*	8.6800	
7	3-(dimethylamino)-1,2-propanediol	9.14	*c*	7.3381	
8	3-diethylamino-1,2-propanediol	9.89	*c*	8.8513	
9	3-diethylamino-1-propanol	10.29	*c*	9.1650	
10	4-diethylamino-2-butanol	9.94	*d*	9.6742	
11	4-ethyl-methyl-amino-2-butanol	9.82	*c*	7.5262	
12	N-isopropyldiethanolamine	9.12	*c*	7.8804	

13	N-tert-butyldiethanolamine	9.06	*c*	7.1598	
14	2-diethylaminoethanol	10.01	*c*	8.5663	
15	1-dimethylamino-2-propanol	9.76	*c*	10.5978	
16	3-dimethylamino-2,2-dimethyl-1-propanol	9.54	*c*	8.0679	
17	N-ethyldiethanolamine	8.86	*c*	6.6199	
18	3-dimethylamino-1-propanol	9.54	*c*	9.4595	
19	Triethylamine	10.78	*e*	8.8846	Alkylamine
20	Trimethylamine	9.80	*a*	9.8503	
21	1-Dipropylaminopropane	10.26	*f*	8.1489	
22	4-ethylmorpholine	7.71	*b*	6.3038	Cyclic Amine
23	2-morpholinoethanol	6.93	*b*	7.8087	
24	1,4-bis(2-hydroxyethyl)piperazine	7.70	*b*	5.6807	
25	3-morpholino-1,2-propanediol	6.76	*b*	5.3589	
26	1-methyl-2-piperidineethanol	9.89	*c*	8.8247	
27	3-hydroxy-1-methylpiperidine	8.49	*c*	8.2620	
28	1-(2-hydroxyethyl)pyrrolidine	9.86	*c*	8.8945	
29	3-pyrrolidino-1,2-propanediol	9.64	*c*	8.6909	
30	1-(2-hydroxyethyl)piperidine	9.76	*c*	7.9745	
31	1-ethyl-3-hydroxypiperidine	9.21	*c*	8.2004	
32	3-piperidino-1,2-propanediol	9.49	*c*	8.2366	
33	1-n-Butylpiperidine	10.47	*f*	9.7208	
34	1,2-Dimethylpiperidine	10.26	*f*	9.6359	
35	1,2-Dimethylpyrrolidine	10.26	*f*	10.4037	
36	1-Ethyl-2-methylpiperidine	10.70	*f*	10.0471	
37	1-Ethyl-2-methylpyrrolidine	10.64	*f*	10.2597	
38	N-Ethylpiperidine	10.40	*f*	9.7282	
39	N-Methylpyrrolidine	10.46	*f*	9.8118	
40	N-Methyltrimethyleneimine	10.40	*f*	9.9339	
41	1-n-Propylpiperidine	10.48	*f*	9.9376	

42	1-Methyl-2-n-butyl-pyrrolidine	10.24	*f*	9.6891	
43	N-Methylpiperidine	10.08	*f*	9.8125	
44	imidazole	6.99	*b*	6.9728	Aromatic Amine
45	4-methylimidazole	7.54	*b*	7.8610	
46	1,2-dimethylimidazole	8.00	*b*	7.9773	

[a] Data from Perrin [32]. [b] Data from Hedetaka [20]. [c] Data from Firoz [33].[d]

The experimental pK_a values that listed in the Table 2 above, and the values predicted by the COSMO-RS//B3P/TZVP method are plotted in the Figure 14.

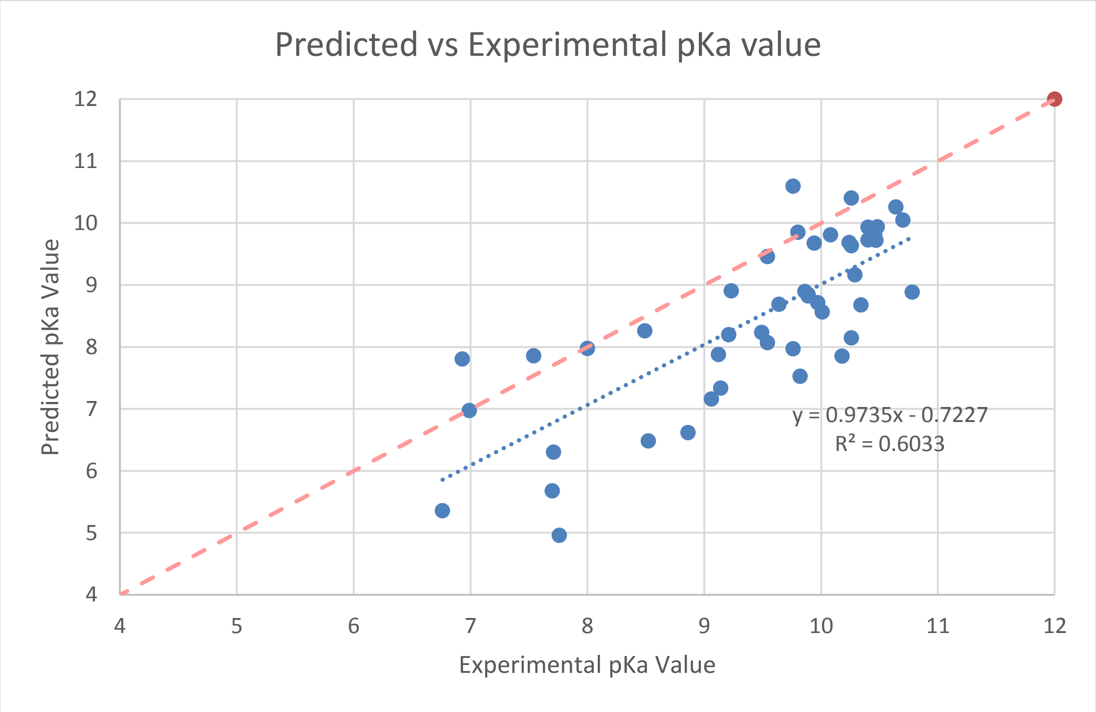


Figure 14: Graph of pK_a values calculated using COSMO-RS//BP/TZVP versus Experimental value

From the correlation above, pK_a values obtained with the COSMO-RS//BP/TZVP method showed a good correlation with experimental values. It can be notice that a plot of experimental pK_a value versus predicted value using COSMO-RS gives a linear trend with R^2 of 0.6. Therefore, COSMO-RS software can be used with reasonable confidence to estimate the pK_a values of tertiary amines of different structure. The regression slopes is 0.97 which is also consistent with the theoretical value of 1. This is considered to be a consequence of the COSMO-RS model that successfully treats hydrogen bonding with a simple description.

$$rmsd = \sqrt{\left(\frac{1}{N}\right)\sum_{1}^{N}(experimental - predicted)^2}$$

The root-mean-square deviation (rmsd) of basicity of the amine solution inside water is 1.2 pK_a-units. This agrees with the expected deviation from the work done by Eckert & Klamt [31] which is around 1.0 pK_a-units.

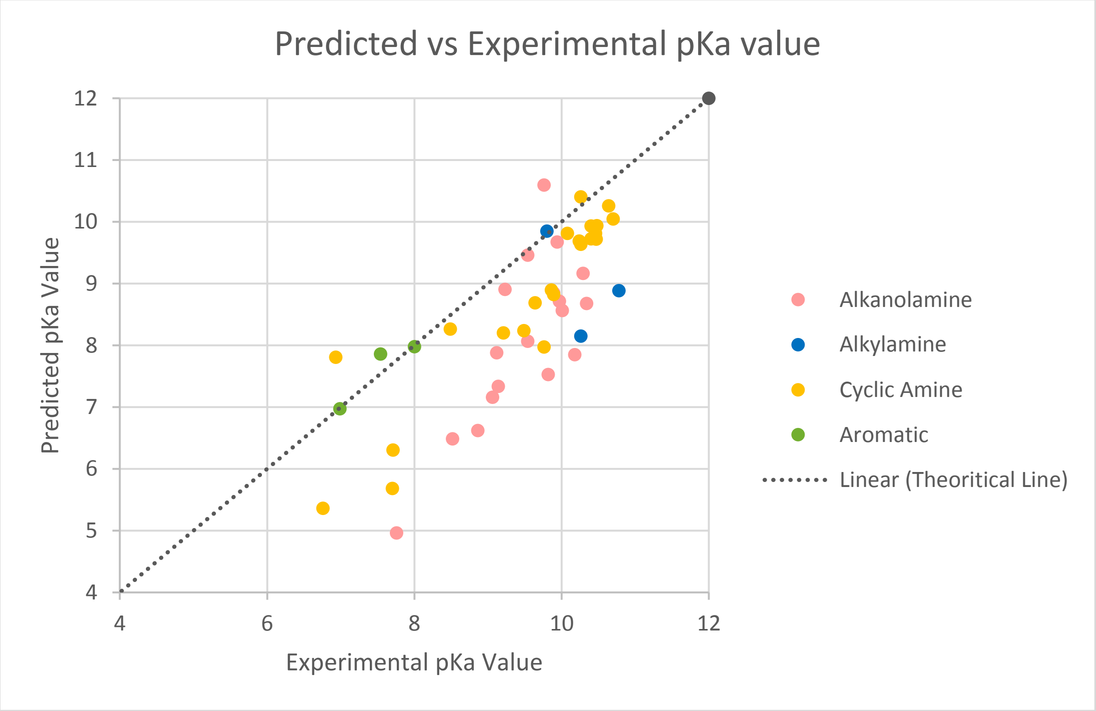


Figure 15: Distribution of pK_a value for different amine types

Figure 15 shows the distribution of experimental versus predicted pK_a value by COSMO-RS//BP/TZVP based on different tertiary amine structure. As can be seen from the distribution, most of the predicted value lies on the bottom of the theoretical (x=y) line which indicates that the overall predicted value was lower than it actual value. This can be explain based on the work described in the literature by Eckert and Klamt [31] as they demonstrated the pK_a prediction for organic bases and they found that tertiary aliphatic amine (i.e. alkanolamine, alkylamine, cyclic amine) require a systematic correction of 2 pK_a units because of problem faced by most of the quantum chemical continuum solvation models. This correction factor have not been adopted in this work. As for aromatic amine, it shows a good correlation with the experimental value with rmsd of 0.19.

Using COSMO-RS//BP/TZVP method to determine the thermodynamic properties of amine in H_2O system gives us advantage because of it has low computational cost due to RI approximation. Thus, this method is suitable for screening purposes.

4.2. Correlation between predicted basicity value with absorption rate and absorption amount.

After benchmarking, the absorption rate and absorption amount of the amine were examine to study the effect of basicity on the performance of amine. The pK_a value is an important fundamental property which affects the kinetics and possibly the mechanism of the capture process [34]. Many previous studies also reported on a Brønsted relationship between the rate constant of the reaction of amines with CO_2 and the basicity of such amines [35]. In tertiary amines, the rate shows a strong dependence on pK_a because of the base-catalyzed mechanism. Puxty et al.[18] studied a relation between CO_2 absorption rates and calculated pK_a values among 76 amines and found that the larger is the value of pK_a, the higher is the absorption rate, as a general trend. This trend was confirmed in Figure 18, where the absorption rates were plotted against the predicted pK_a values. However, based on its small R^2 value, Figure 16 indicates that the absorption rate is also governed by other factors such as steric hindrance around the amino moiety. Based on the Figure 17, it can also be generalize that the larger is the value of pK_a, the higher is the absorption amount.

Table 3: Predicted pK_a value from this work is to be compare with the absorption rate and absorption amount

	Amine	**Predicted pK_a value**	**Absorption Rate (g-CO_2/L-soln/min)**	**Absorption Amount (g-CO_2/L-soln)**	**References**
1	2-(dimethylamino)ethanol	8.9082	1.70	73	c
2	2-(diisopropylamino)ethanol	8.7145	1.01	57	c
3	methyldiethanolamine	6.4864	1.56	55	c
4	triethanolamine	4.9620	0.75	22	c
5	1-diethylamino-2-propanol	7.8509	1.66	78	c
6	2-(dimethylamino)-2-methyl-1-propanol	8.6800	1.18	88	c
7	3-(dimethylamino)-1,2-propanediol	7.3381	1.28	70	c
8	3-diethylamino-1,2-propanediol	8.8513	3.40	73	c
9	3-diethylamino-1-propanol	9.1650	2.60	89	c

10	4-ethyl-methyl-amino-2-butanol	7.5262	1.37	69	c
11	N-isopropyldiethanolamine	7.8804	1.36	58	c
12	N-tert-butyldiethanolamine	7.1598	1.91	52	c
13	2-diethylaminoethanol	8.5663	2.49	94	c
14	1-dimethylamino-2-propanol	10.5978	2.24	92	c
15	3-dimethylamino-2,2-dimethyl-1-propanol	8.0679	1.08	57	c
16	N-ethyldiethanolamine	6.6199	0.70	39	c
17	3-dimethylamino-1-propanol	9.4595	1.47	71	c
18	1-methyl-2-piperidineethanol	8.8247	3.17	77	c
19	3-hydroxy-1-methylpiperidine	8.2620	1.08	55	c
20	1-(2-hydroxyethyl)pyrrolidine	8.8945	2.41	94	c
21	3-pyrrolidino-1,2-propanediol	8.6909	1.25	47	c
22	1-(2-hydroxyethyl)piperidine	7.9745	2.22	83	c
23	1-ethyl-3-hydroxypiperidine	8.2004	0.96	56	c
24	3-piperidino-1,2-propanediol	8.2366	3.33	57	c
34	4-(Dimethylamino)-1-butanol	9.2296	3.58	97	c
35	6-dimethylamino-1-hexanol	9.5948	3.97	80	c

[c] CO_2 *absorption rates were calculated at 50% of the 60 min* CO_2 *loading and 40 °C.* CO_2 *absorption amount at 60 min* CO_2 *loading at 40 °C [33].*

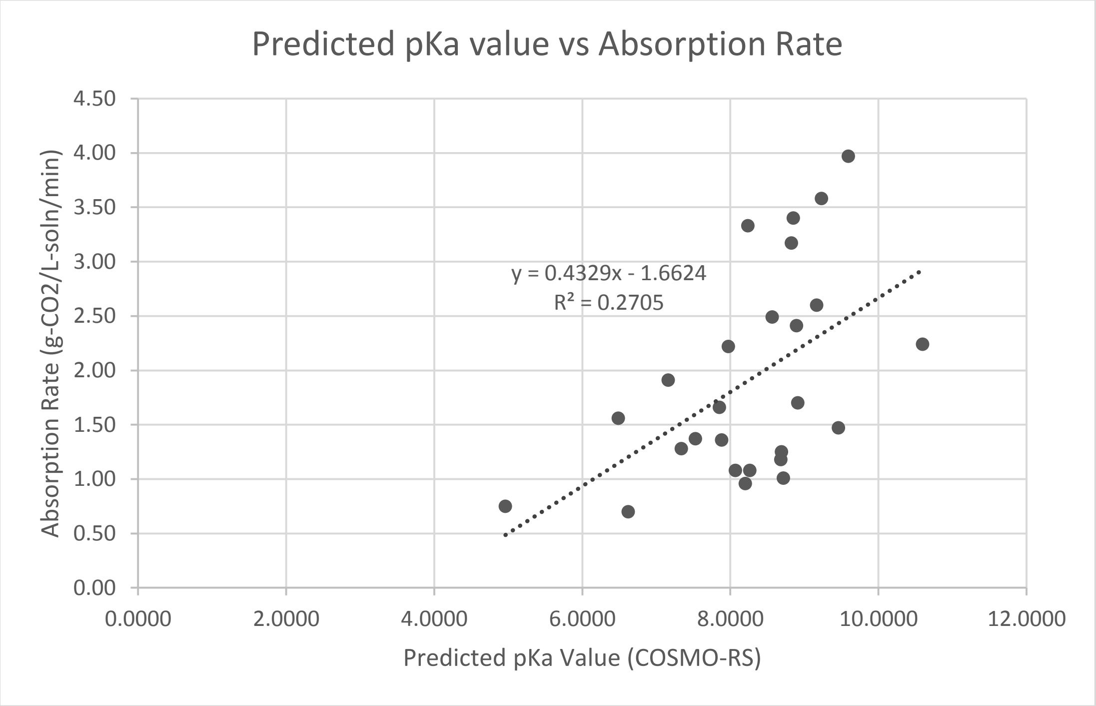


Figure 16: Predicted pK_a value vs Absorption Rate

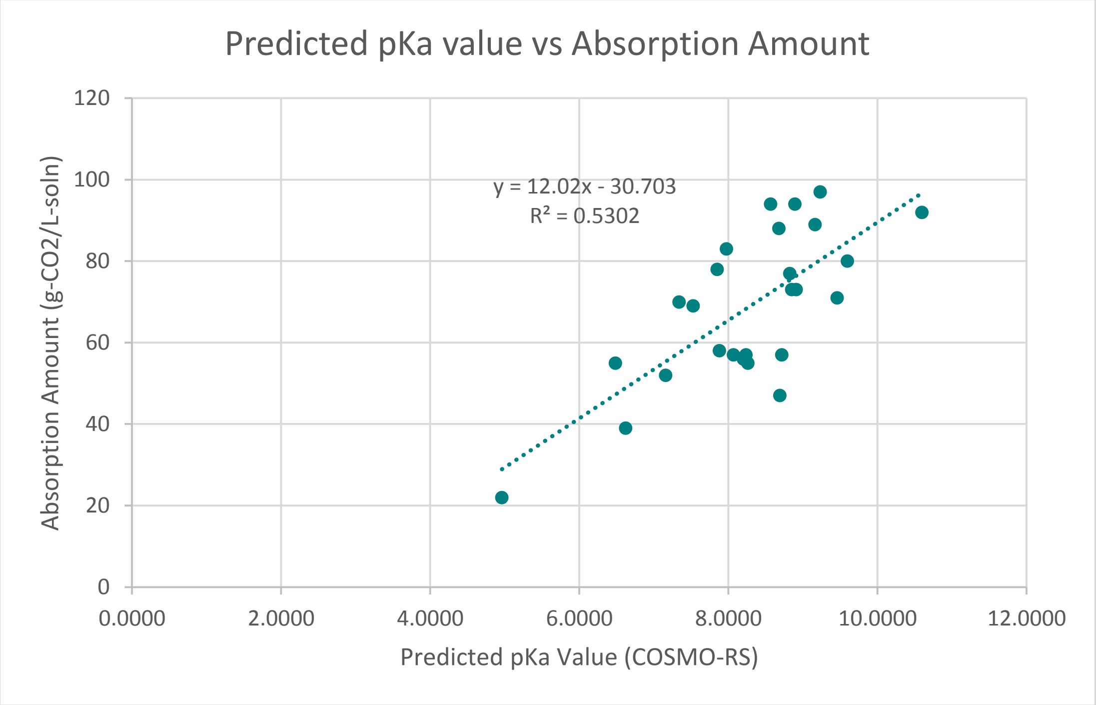


Figure 17: Predicted pK_a value vs Absorption Amount

By having this two generalization which relate the predicted pK_a value from COSMO-RS with absorption rate and absorption amount, we can roughly predict and quickly screen the performance of tertiary amine (in terms of absorption rate and capacity) by just having to simulate and predicted pK_a value for that particular molecule. Of course this screening technique was not perfectly accurate but at some point it can be a reliable screening technique to help reduce time and cost for screening unwanted amine candidate in the lab scale.

In this work, we have predicted the absorption rate and absorption capacity for 26 amines molecule by using this technique. Based on the equation of regression line obtained in the Figure 18 and Figure 19, we estimated the absorption rate and amount by using the equation below.

$$y = 0.4329x - 1.6624 \rightarrow for\ prediction\ of\ absorption\ rate$$

$$y = 12.02x - 30.703 \rightarrow for\ prediction\ of\ absorption\ amount$$

Table4: Prediction of absorption rate and absorption capacity

No	**Name**	**Predicted pK_a value**	**Absorption Rate (g-CO_2/L-soln/min)**	**Absorption Amount (g-CO_2/L-soln)**
1	1,2-Dimethylpyrrolidine	10.4037	2.84	94.349474
2	1-Ethyl-2-methylpyrrolidine	10.2597	2.78	92.6182334
3	1-Ethyl-2-methylpiperidine	10.0471	2.69	90.0630218
4	1-n-Propylpiperidine	9.9376	2.64	88.7471924
5	N-Methyltrimethyleneimine	9.9339	2.64	88.7028386
6	Trimethylamine	9.8503	2.60	87.6971252
7	N-Methylpiperidine	9.8125	2.59	87.24325
8	N-Methylpyrrolidine	9.8118	2.59	87.2344754
9	N-Ethylpiperidine	9.7282	2.55	86.2302044
10	1-n-Butylpiperidine	9.7208	2.55	86.140415
11	1-Methyl-2-n-butyl-pyrrolidine	9.6891	2.53	85.7597416
12	1,2-Dimethylpiperidine	9.6359	2.51	85.119917

13	Triethylamine	8.8846	2.18	76.0897718
14	1-Dipropylaminopropane	8.1489	1.87	67.2468982
15	1,2-dimethylimidazole	7.9773	1.79	65.18406222
16	4-methylimidazole	7.8610	1.74	63.78664647
17	2-morpholinoethanol	7.8087	1.72	63.15797655
18	imidazole	6.9728	1.36	53.11006538
19	4-ethylmorpholine	6.3038	1.07	45.06810938
20	1,4-bis(2-hydroxyethyl)piperazine	5.6807	0.80	37.57864258
21	3-morpholino-1,2-propanediol	5.3589	0.66	33.7104228

Based on Table 4, the five most outstanding amine candidates in terms of their absorption rate and absorption capacity are 1,2-Dimethylpyrrolidine, 1-Ethyl-2-methylpyrrolidine, 1-Ethyl-2-methylpiperidine, 1-n-Propylpiperidine, and N-Methyltrimethyleneimine. This estimation might not accurate, but at least it gives us insight that we might not want to go and spend our time to run a performance testing experiment on 3-morpholino-1,2-propanediol.

CHAPTER 5

CONCLUSION AND RECOMENDATION

5. CONCLUSION & RECOMENDATION

The basicity of amine based solvent were by the DFT-based COSMO-RS method. The agreement between the predicted and experimental result from literature indicates that COSMO-RS method is applicable to be used in this system as a tool for initial screening. It is expected that this work will be able to provide initial screening tool to systematically screen possible amine candidates for CO_2 capture using COSMO-RS. Using the model developed in this study, the performance of amine in terms of absorption rate and absorption capacity can be evaluated. The importance of this work is, it should be able to reduce time and cost in selecting appropriate amine especially from huge number of candidates. It should also increase the opportunity to select new amine candidates.

To further improve this work, there are some recommendation that can be implement in the future:

- This work is only valid for tertiary amine based solvent and may not be reliable to the other types of amine. Thus, for further improvement, the relationship between other types of amine with its respective thermodynamic properties should be study.
- Other than absorption amount and absorption rate, heat of reaction also one of the important parameter in evaluating the performance of amine because most of the cost in operating the amine based PCC comes from absorbent regeneration process. Thus, it is recommended to include also the assessment for heat of reaction in further study.

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