Comparing Solvents for SO_2 Absorption by Molecular Dynamics Simulation

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Abstract
One of the 5 major air pollutants is SO_2 gas that is released to air, for example, with the exhausted gases from the Claus processes. Shell Cansolv® SO_2 Scrubbing System is an amine-based regenerable process that selectively absorbs SO_2 from a variety of gases, such as Claus tail gas. Since the solvent formulation of Cansolv process is not available and it has been patented by Shell company, in this paper, based on the related patent, the interactions between N,N',N'-(trimethyl)-N-(2-hydroxyethyl) (A) ethylenediamine and N,N-(dimethyl)-N',N'-bis-(2-hydroxyethyl) ethylenediamine (B) solvents with SO_2 are studied using molecular dynamics simulation. Molecular dynamics simulation shows interactions between solvents and SO_2 by use of nitrogen atoms is performed, as a result of which intraction in B solvent is stronger. In addition, Z-density profile (ρz) confirms that SO_2 gas is completely dispersed in B solvent. The energy absorption value of SO_2 gas in A and B solvents are -2.164 $kJ.mol^{-1}$ and -2.447 $kJ.mol^{-1}$ respectively. Therefore, stronger interactions, more dispersion and energy absorption performance of B solvent is more efficient in comparison with those of A solvent.
Keywords: SO_2 removal, Cansolv process, Diamine, Molecular Dynamics Simulation.

Introduction
SO_2 is one of the 5 major air pollutants. Its emission has devastating effects on human health and the environment. Reaction of SO_2 with eye moisture , lungs and other mucous membranes produces sulfuric acid that causes intense irritation. SO_2 exposure causes allergic reactions and exacerbates heart and respiratory diseases [1, 2]. Although SO_2 lifetime in the atmosphere is about one day, its harmful effect is enlarged by the conversion to tiny particles, liquid sulfuric acid and solid sulfate. Sulfuric acid is the main factor that contributes the acid rain and the acidic depositions, which destroys plants, mountains and buildings [3]. Therefore, SO_2 emision to the atmosphere must be prevented as much as possible. There are various methods such as seawater scrubbing, dual alkali method, amine-based processes, rinsing with cold water and SO_2 adsorption by activated carbon to remove SO_2 from flue gas in the oil and gas industry [4]. The subcategory of amine-based processes is Cansolv process which is the major of the common method [5]. Solvent formulation in Cansolv process is not available; from the other side of view, theoretical methods are able to shed light on the gas absorption.

Researchers have investigated the SO_2 absorption by amine solvents, alkanolamines and ionic liquids by molecular dynamics [6-8]. In this line, the present study considers N,N',N'-(trimethyl)-N-(2-hydroxyethyl) ethylenediamine, N,N-(dimethyl)-N',N'-bis-(2-hydroxyethyl) ethylenediamine solvents proposed by Shell company [9, 10]. Simulation is performed to get insight on the gas and solvent interactions.

Simulation Details

Figure 1 shows the optimized structure of solvents with their specific atomic lables.

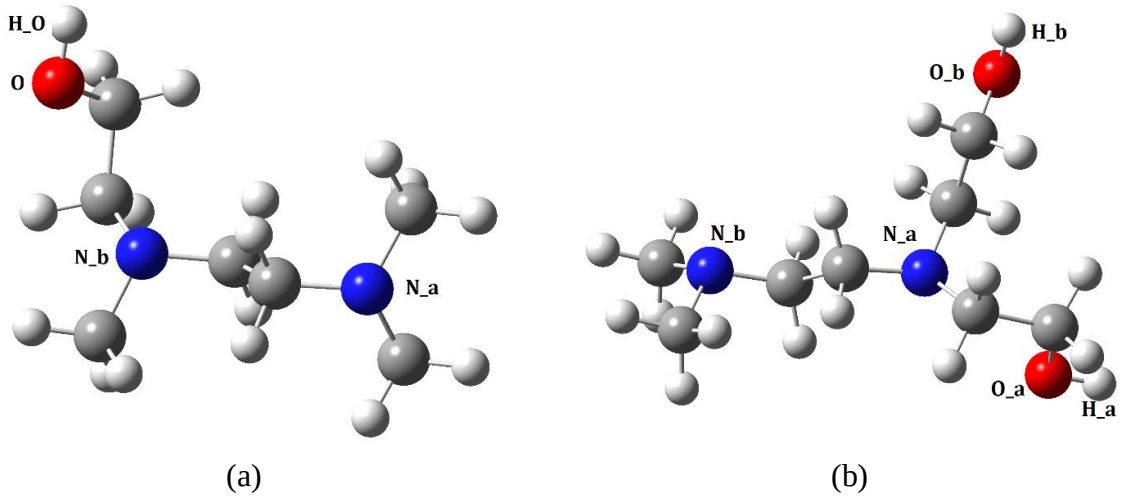

Figure 1: Structure of molecules. a) N,N',N'-(trimethyl)-N-(2-hydroxyethyl) ethylenediamine (A solvent), and b) N,N-(dimethyl)-N',N'-bis-(2-hydroxyethyl) ethylenediamine (B solvent)
Nitrogen, oxygen, carbon and hydrogen atoms are shown in blue, red, gray and light gray, respectively.

All the stuctures were optimized using density functional theory at B3LYP/6-31G(d,p) level of theory. The atomic charges, as well as bond lengths and bond angles of target components were computed by Gaussian 09 [13]. Bond, angle and dihedral angle constants in addition to the van der Waals potential parameters were extracted from CHARMM force field [14]. Morover, all force field parameters of SO_2 gas were taken from Morganti et al. [15].
In this study, the temperature and the pressure are 410 K and 1 atm, respectively, and they are kept constant during the simulation by Nose–Hoover thermostat and barostat [11]. The simulation control conditions are listed in table 1.

Table 1: Simulation control conditions

Simulation time (ns)	Production (ns)	Equilibration (ns)	Time step (fs)	Ensemble	Cutoff distance (Å)
1	0.2	0.8	1	NPT	17

The cubic simulation box containing 216 solvent molecules and 5 SO_2 molecules were simulated by molecular dynamics package DL_POLY 2.17 [12].

Radial distribution function (RDF) clearly shows the local structure of a substance and expresses organization of atoms around each other [16].

Potential of mean force (PMF) is used to evaluate the SO_2 gas absorption energy in solvent. PMF is calculated by the following relation:

$$PMF = -RTln(RDF) \quad (1)$$

where *R*, *T* and RDF are gas constant, temperature and the radial distribution function, respectively. According to Figure 2, the difference between the minimum energy (solid line) and the average energy in solution (dashed line) is the absorption energy [17].

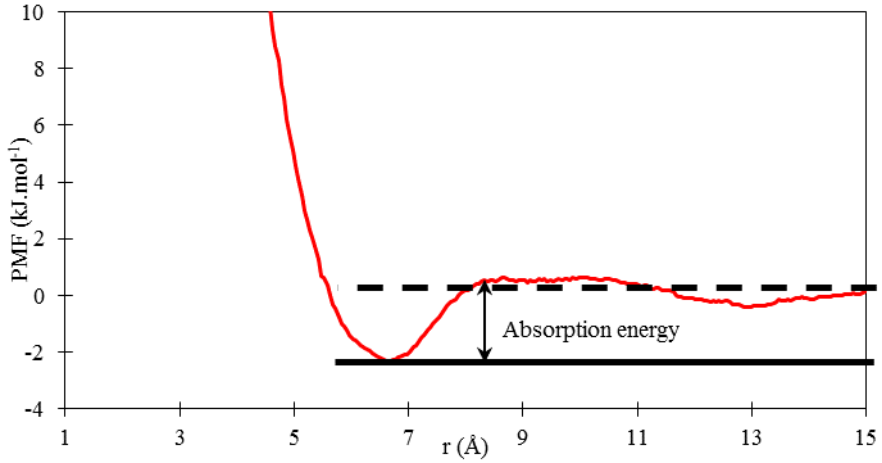

Figure 2: Diagram of calculating SO_2 absorption energy from PMF at 410 K and 1 atm.

Results and discussion

Among all interactions between SO_2 and solvent atoms, N_a…S and N_b…S in A and B solvents are the strongest, see Figure 3 for details.

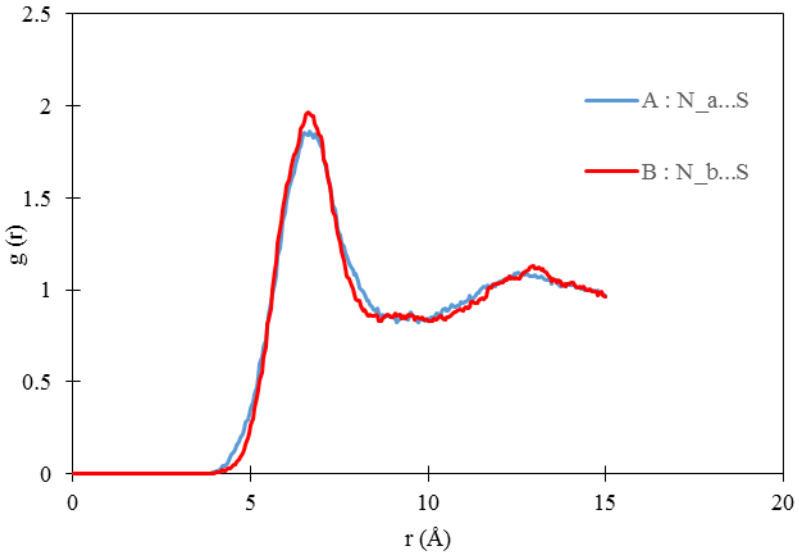

Figure 3: RDF between the nitrogen of A, B solvents and SO_2 gas at 410 K and 1 atm.

As Figure 3 illastrates, the interaction between B solvent and SO_2 is stronger than that of A solvent and SO_2.

In addition, Z-density profile (ρ_z) is applied to find out the position of the SO_2 molecules at the z-axis of the simulation box. Figure 4 shows the density profiles of SO_2 gas at 410 K. The ρ_z indicates the distribution of the molecule or atom. In order to shed light to the distribution of gas in the solvent, the standard deviation (σ) was calculated. The greatest value confirms that SO_2 is slightly distributed in the solvent.

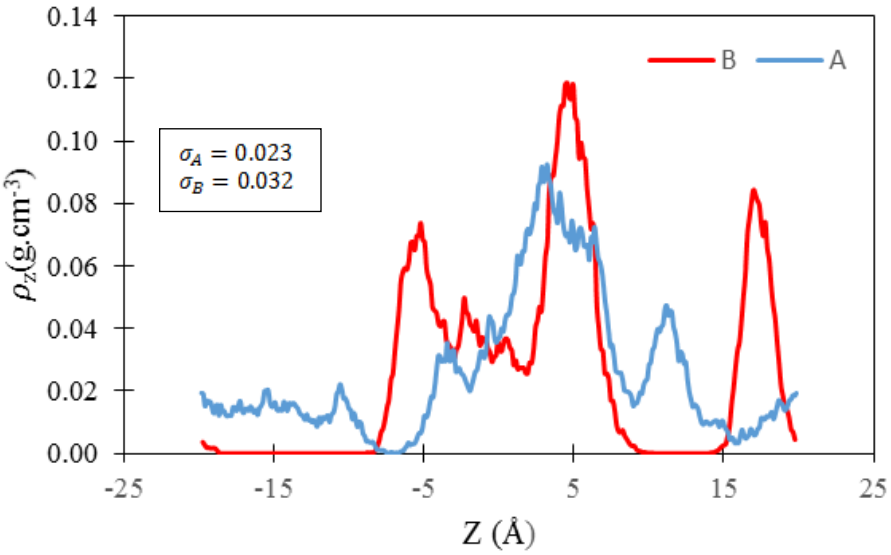

Figure 4: SO_2 density profile inside solvents A and B and its standard deviation values at 410 K and 1 atm.

In A solvent, there are three obvious peaks for SO_2 gas. Two SO_2 molecules are located at -5 and 11 Å of the center of the simulation box, and the other SO_2 molecules are in the range of 2.5 to 7.5 Å. It is expected the number of peaks in a completely distributed solution is equal to SO_2 gases. In the case of A solvent, there are three peaks with 0.12, 0.085 and 0.075 g.cm^{-3}, at 5, 17 and -5 Å. In contrast, a short peak is observed about 2.5 Å with 0.05 g.cm^{-3} for B solvent. The highest peak at 5 Å indicates two other SO_2 molecules. It can be said that SO_2 gases are distributed at the middle of the simulation box when equilibrium is reached. However, the standard deviation of SO_2 gas for B solvent is higher than that of A solvent. Therefore, B solvent has ability to dissolve SO_2. In addition, the absorption energy values confirm this result. The absorption energy values of SO_2 gas in A and B solvents are -2.164 and -2.447 kJ.mol^{-1}, respectively, at 410 K.

Conclusions

SO_2 gas absorption in A and B solvents was studied by molecular dynamics simulation. The interaction between SO_2 and B solvent is stronger than A solvent according to RDF results. Besides, SO_2 gas is more distributed in the B solvent and its solubility is considerable. As a result, the system containing B solvent and SO_2 gas is more stable than the system with SO_2 and A solvent. SO_2 absorption energy in A and B solvents was examined by PMF. The PMF values confirm that B solvent possesses greater absorption energy. Finally, the N,N-(dimethyl)-N',N'-bis-(2-hydroxyethyl) ethylenediamine absorbs SO_2 gas stronger than the N,N',N'-(trimethyl)-N-(2-hydroxyethyl) ethylenediamine. Notic that the first one contains two hydroxyl groups.

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