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# Improvement of carbon dioxide absorption technology using conductor-like screening model for real solvents (COSMO-RS) method

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Solvents with better properties than the ones presently in use for carbon dioxide (CO<sub>2</sub>) absorption processes would make absorption technology more attractive for large scale reduction of CO<sub>2</sub> emissions. In this work, more than 2000 solvents comprising of four groups were considered for screening. The groups are: amine solvents (primary, secondary, tertiary, sterically hindered, multiple amines and physical solvents), neutral solvents, mixed solvents and ionic liquids (ILs). Conductor-like screening model for real solvents (COSMO-RS) model was used in predicting thermodynamic properties, such as Henry's constant, octanol-water partition coefficient, solubility in water and vapour pressure of all the solvents. The best two solvents from each of the four groups were selected based on the criteria of high capacity and high selectivity of the solvent in comparison to a benchmark solvent (BS), that is, [methyl-diethanolamine (MDEA) + Piperazine]. All the eight selected solvents were found to be environmental friendly having very low octanol-water partition coefficient KOW, which is far less than the hazard limit of 10,000. Out of the eight selected solvents, sulfolane (S), (NMP + S), and ([N,N,N,N,N-Pentamethyl-N-IsopropylGuanidinium][Br]) were recommended for having better properties than the BS.

**Key words:** Henry's constant, conductor-like screening model for real solvents (COSMO-RS), carbon dioxide absorption, capacity, selectivity.

## INTRODUCTION

There is a steadily increasing interest in methods for reducing carbon dioxide (CO<sub>2</sub>) emissions as a measure for preventing global warming. Absorption with aqueous amine solvents is at present the most viable technology for CO<sub>2</sub> capture. Mixtures of alkanolamines with promoters has traditionally been used for the removal of CO<sub>2</sub> from natural gas and refinery gas and the same technology is an option for the treatment of exhaust gases. For high-pressure applications, methyldiethanolamine (MDEA) based systems have been

used successfully for many years (Eirik, 2005). For exhaust gases, the most common amine has been monoethanolamine (MEA). The high energy demand for regeneration and relatively high degradation rates for this amine solvents are however unfavorable for large fossil fuel power plants. Because of this, it is important to find solvents with better properties than the ones presently in use as an approach to improving CO<sub>2</sub> absorption technology which can be obtained from screening a large number of solvents to make it more attractive technology

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for large scale use to reduce CO<sub>2</sub> emissions.

There are a number of different solvents that have been applied in CO<sub>2</sub> absorption. Most solvents are mixtures of water and base molecules. The bases can either be organic or inorganic compounds (Eirik, 2005). Most of the other common solvents are also alkanolamines, that is, molecules with both amino and hydroxyl functional groups. Different amines vary significantly in how they react with CO<sub>2</sub>. Mixture of tertiary amine with promoter is a particularly important solvent because it is the most widely used at present, and it represents the benchmark that new solvents will be compared with (Derks, 2006). Amines can be classified into different groups depending on the number of carbon atoms directly bonding to the nitrogen atom; there are primary, secondary and tertiary amines.

In addition to solvents that react chemically with CO<sub>2</sub>, there are other solvents that have a capacity to absorb CO<sub>2</sub> without reacting. These are called physical solvents. Solvents with some degree of both chemical and physical absorption might however be an interesting option. An example of a physical solvent that can be applied in such a way is sulfolane (S) (Jenab et al., 2005).

Ionic liquids (ILs) are a novel class of compounds that are emerging as potential replacements for conventional solvents and have been the focus of intensive research in recent years (Luis, 2007). They can be considered "green solvents" due to their most important characteristic as negligible vapour pressures, which makes them ideal replacements for volatile solvents. They can also be recycled and reused repeatedly. Since discovery in 1992, ILs has become a subject of growing interest among researchers as evidenced by the number of publications increasing exponentially. Researchers are interested because ILs have numerous potential industrial applications and are "greener" than traditionally used chemicals.

Predictive methods are often indispensable for chemical engineers in the design of chemical processes and plants because quite often no experimental data for certain compounds, either from databases or from experimental measurements, are available at a reasonable price for the mixture. Therefore, theoretical computational models are valuable tools for the estimation of the thermodynamic properties of solutions and mixtures, thus, reducing the time, resources, and overall cost of the screening of a large number of solvents (Eckert and Klamt, 2002). They are especially well suited for the task of solvent screening if reliable experimental data for a system is missing or not available at affordable cost. These are methods that are independent of experimental thermodynamic data of the given solutions or mixtures. Estimates are obtained from molecular structure information only.

Conductor-like screening model for real solvents (COSMO-RS) is a novel prediction method for thermodynamic equilibria of fluids and liquid mixtures,

and it was proposed by Klamt (1995). It combines the electrostatic advantages and the computational efficiency of the quantum chemical dielectric continuum solvation model, COSMO, with a statistical thermodynamic approach for local interaction of surfaces, where the local deviations from dielectric behaviour as well as hydrogen-bonding are considered. COSMO-RS is a method based on unimolecular quantum chemical calculations of the individual species in the system and not of the mixture itself, and can be considered as an alternative to the structure-interpolating Group contribution methods (GCMs). Sumon and Henni (2011) reported the use of COSMO-RS model to predict the Henry's law constants of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in 2701 ILs of widely varying structures at different temperatures. Ranking of cations, in terms of Henry's law constants is reported for each counterpart anion and vice versa. Such information is useful for designing and screening of ILs for CO<sub>2</sub> capture. In a similar manner, Luis (2007) reported the use of COSMO-RS model in predicting the solubilities and selectivities of different gases including carbondioxide in ILs.

This work is focused on screening of large number of solvents (comprising of four group of solvents which include; amine solvents, neutral solvents, mixed solvents and ILs) using the COSMO-RS method so as to contribute to the selection of optimal solvents for CO<sub>2</sub> capture.

## METHODOLOGY

The following are the methods used in carrying out the work:

1) Generate molecular structure: The Marvin sketch software is first used in sketching the structure of each individual molecule. The structure of the solvents to be screened and the components of the gas mixture were sketched. The environment has a drawing kit including all elements in the periodic table and heterocyclic structures for easy sketch of the molecular structures. They are sketched in two dimensions and then cleaned in three dimensions to obtain full structures, remove their strain energy and minimize their energies. Marvin sketch software operates on windows. The file generated is saved in xyz format and then used as an input file for TURBOMOLE to perform the quantum chemical/COSMO calculation.

The solvents considered in this work are grouped into four which include:

- i) Over 40 amine solvents (comprising of primary, secondary, tertiary, sterically hindered, multiple amines and physical solvents),
- ii) About 100 neutral solvents,
- iii) Over 300 mixed solvents,
- iv) Over 1500 ILs.

The components of the gas mixture are methane, ethane, propane, butane, pentane, nitrogen and CO<sub>2</sub>

2) Generate COSMO files: The TURBOMOLE uses the xyz file generated from Marvin sketch to perform quantum chemical/COSMO calculation to generate their screening charge densities of the molecules. The screening charge is a microscopic property of a molecule like internal energy and the main parameter

used in the COSMO-RS model. The quantum chemical/COSMO computation is parameterized using a full TURBOMOLE BP-RI-DFT COSMO optimization of the molecular structure using the large TZVP basis set denoted as BP-TZVP. The file is saved as a COSMO file and an input file to COSMOtherm to perform the statistical thermodynamics and to determine the screening charge density profiles and chemical potentials of the individual molecules. The higher the specification of the computer machine, the faster the computation of the screening charges of the molecules. A data base is created for all the COSMO files generated using the TURBOMOLE program software.

3) Statistical thermodynamic calculations: The COSMOtherm is the software that solves the COSMO-RS model based on self consistency field algorithm (SCF) to statistically determine the screening charge density profiles and the chemical potentials of the molecules. The COSMOtherm performs statistical thermodynamic calculations. The COSMOtherm was parameterized using BP\_TZVP\_C21\_0107.ctd. The chemical potentials are determined using COSMOtherm software.

4) Determination of Henry law coefficients  $H^{(i)}$ : The chemical potentials  $\mu_j^{(p)}$  of all pure compounds j and the chemical potentials  $\mu_j^{(i)}$  at infinite dilution in compound i are calculated. Then the Henry's law coefficients  $H_j^{(i)}$  for all compounds j are calculated from the activity coefficients and the vapour pressures of the compounds. It is also possible to calculate the Henry's law coefficients at a given finite concentration that is, in a mixture of solvents.

The activity coefficient is determined from the chemical potential as thus:

$$\ln \gamma_j = \frac{(\mu_j^{(i)} - \mu_j^{(p)})}{RT} \quad (1)$$

The Henry's law coefficient depends on the pure compound vapour pressure.

The solubility of a gas in a liquid, is frequently described in terms of Henry's law constants, which is defined as,

$$H_1(T, p) \equiv \lim_{x_1 \rightarrow 0} \frac{f_1^L}{x_1} \approx \frac{p_1}{x_1} \quad (2)$$

Where  $H_1(T, P)$  is the Henry's constant,  $x_1$  is the mole fraction of gas dissolved in the liquid phase,  $f_1^L$  is the fugacity of vapour in

the liquid phase and  $p_1$  is the pressure of the gas. Equation 2 implies that, in the Henry's law region, the solubility is linearly related to the pressure.

5) Determination of solubility of the solvents in water: The solubility of the solvents in water was determined from COSMOtherm using the equation as follows;

$$\log_{10}(x_j^{SOL}) = \frac{[\mu_j^{(p)} - \mu_j^{(i)} - \max(0, \Delta G_{fus})]}{RT \ln(10)} \quad (3)$$

Where  $\Delta G_{fus}$  is the heat of fusion per mole, T is temperature in Kelvin, R is molar gas constant in KJ/mol/Kelvin,  $\mu_j^{(i)}$  is chemical potential of solute j in solvent i in energy/mole,  $\mu_j^{(p)}$  is chemical potential of pure compound j in energy/mole, and  $x_j$  is mole fraction of the solubility of solutes in water. If the compound is solid, the energy change of a compound from the super cooled liquid state to the ordered solid state has to be taken into account, that is, the solutes Gibbs free energy of fusion  $\Delta G_{fus}$  (or equivalently its Gibbs free energy of crystallization  $\Delta G_{cryst} = -\Delta G_{fus}$ ) has to be

either given and computed from experimental data or estimated by COSMOtherm. For a liquid, it is automatically specified but for solids it has to be determined using QSPR and then specified manually.

6) Determination of octanol-water partition coefficients from COSMOtherm using the equation as follows:

$$\log_{10}(P^{2,1}) = \log_{10} \left[ \exp \left( \frac{(\mu_j^{(1)} - \mu_j^{(2)})}{RT} \right) * V_1 / V_2 \right] \quad (4)$$

Where  $V_1$  and  $V_2$  are volume quotients of Phases 1 and 2,  $\mu_j^{(1)}$  is the chemical potential of solvent in phase 1 in energy/mole,  $\mu_j^{(2)}$  is the chemical potentials of solvent in Phase 2 in energy/mole, and P is partition coefficient.

### Post processing

From the Henry's law coefficient determined for all the solvents considered across the component of the gas mixture, the capacity of the solvent in absorbing CO<sub>2</sub> from the gas mixture and the selectivity of the solvent for CO<sub>2</sub> with respect to the other component of the gas mixture was determined.

### Capacity and selectivity of solvent

Capacity is the amount of gas (CO<sub>2</sub>) which can be absorbed by a certain amount of solvent. From Equation 2, it can be seen that the capacity is inversely proportional to the Henry's law constant. Therefore, for the purpose of screening, the inverse of the Henry's constant will be used to compare the capacity of the various solvents.

By definition, selectivity of a solvent for CO<sub>2</sub> with respect to another component j is given as:

$$S_{CO_2, j}^{Solvent} = \frac{C_{CO_2}^{Solvent}}{C_j^{Solvent}} \quad (5)$$

Since the capacity is inversely proportional to Henry's constant, then

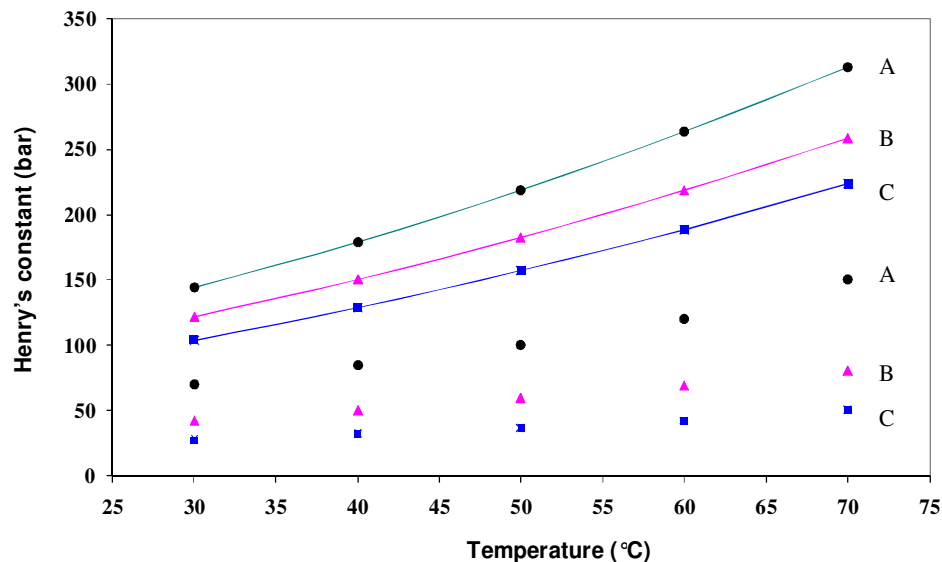
$$S_{CO_2, j}^{Solvent} = \frac{H_j^{Solvent}}{H_{CO_2}^{Solvent}} = \frac{\text{Henry's Constant of Component j in the Solvent}}{\text{Henry's Constant of CO}_2 \text{ in the Solvent}} \quad (6)$$

The screening criteria of the solvents are as follows:

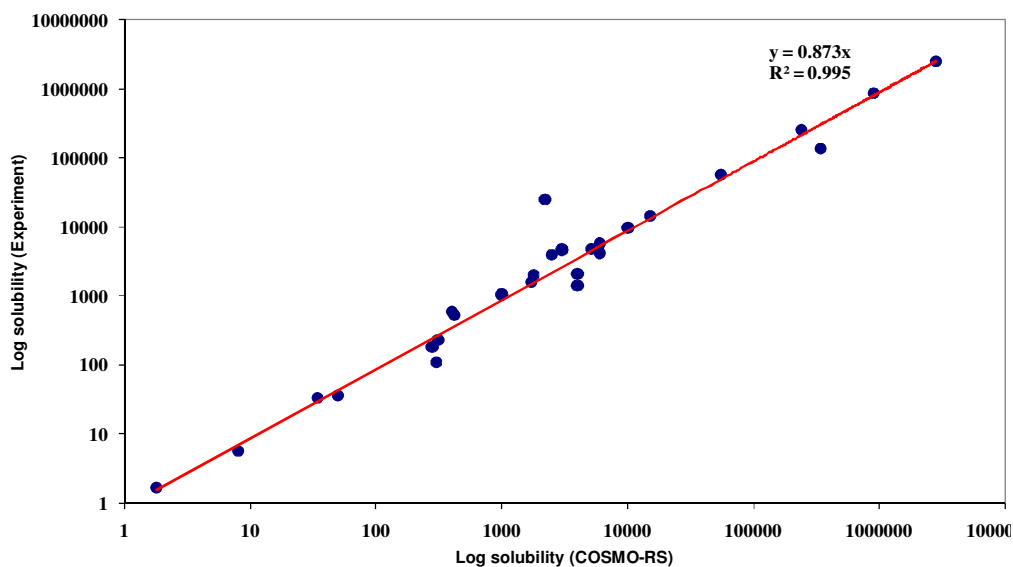
Using a benchmark solvent (BS) of (MDEA + Piperazine), which is a widely used solvent in the industry; the solvents are screened as follows:

- 1) The capacity of the solvent must be greater than the capacity of the BS,
- 2) The selectivity of the solvent for CO<sub>2</sub> with respect to the other component of the gas component must be greater than that of the BS.

Based on the above criteria, solvents with the highest capacity and selectivity were recommended. From the four group of solvents considered in this work, the best two solvents from each group were recommended. Apart from the capacity and selectivity criteria, other criteria for ranking of the best solvents are volatility of the solvents, the environmental impact, vapour pressure and octanol-water partition coefficient of the selected solvents.



**Figure 1.** Comparison of plot of Henry's Constant versus temperature of CO<sub>2</sub> in three IL: A([C<sub>4</sub>mim][BF<sub>4</sub>]), B([C<sub>2</sub>mim][TF<sub>2</sub>N]), C([C<sub>4</sub>mim][TF<sub>2</sub>N]), Lines are COSMO-prediction and the points are experimental data. The experimental data were obtained from Luis (2007).



**Figure 2.** Comparison of experimental solubility values against COSMO-RS values (Laurie, 2004).

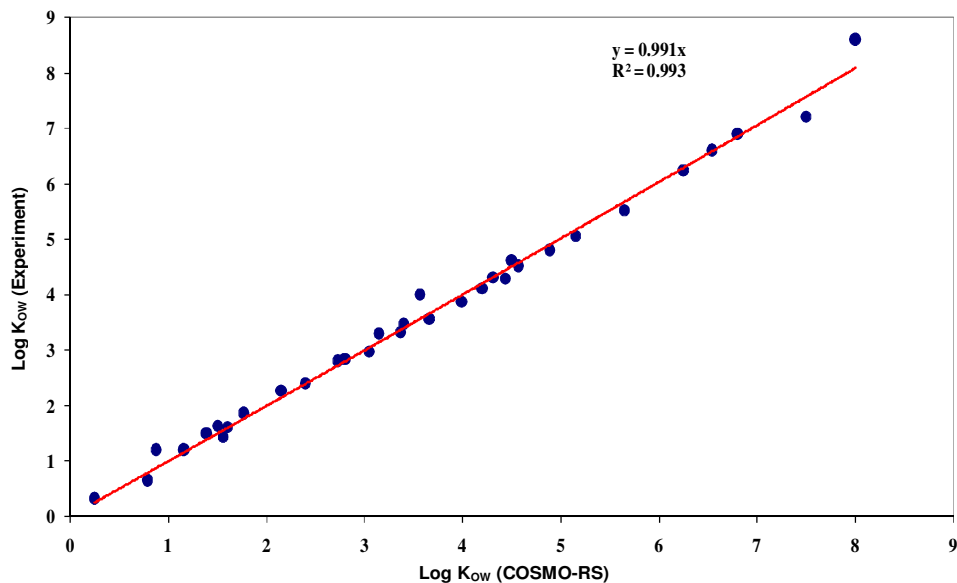
## RESULTS AND DISCUSSION

### Validation of results

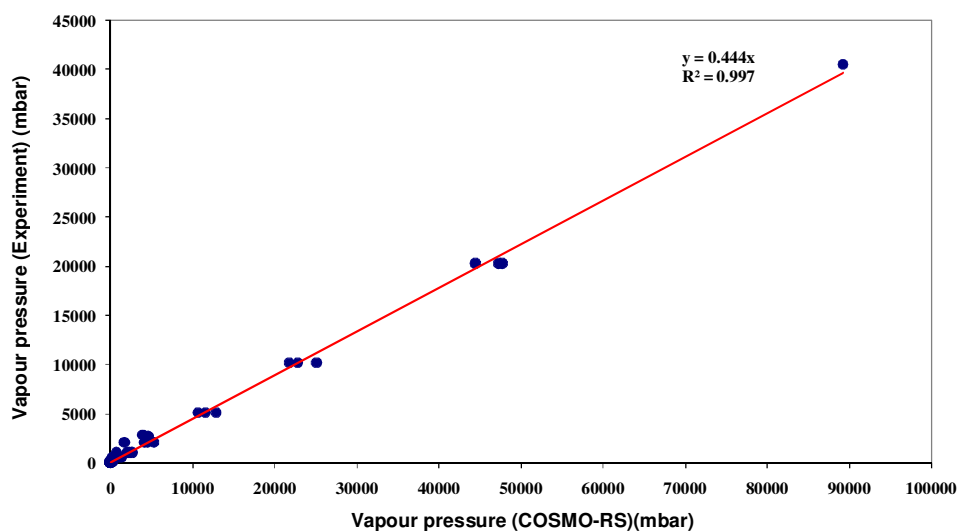
Validation of results is very essential in computational work to confirm the accuracy and reliability of the results obtained by comparing the results obtained from the COSMO-RS model with that of experimental values obtained from literature. Figure 1, 2, 3 and 4 are different

thermodynamic properties used to validate the reliability and accuracy of the COSMO-RS model.

Figure 1 shows that CO<sub>2</sub> is experimentally more soluble in solvent C than in solvents B and A. Also, that trend is correctly described and well captured by the model predictions. The temperature dependency is also fairly well described in the three solvents. Although, the COSMO-RS model values are not exact compare to the experimental values, but we can rely on the trend which



**Figure 3.** Comparison of octanol-water partition coefficient values against COSMO-RS values (Laurie, 2004).



**Figure 4.** Comparison of experimental vapor pressure values against COSMO-RS values (<http://murov.info/orgsolvents.htm>).

is well represented by the model predictions in screening large number of solvents.

Comparison of experimental solubility values against the COSMO-RS values of different solvents is presented in Figure 2. The experimental results were obtained from Laurie (2004).

It can be seen that the results from the COSMO-RS model is comparable with that of experimental results. This shows the accuracy of the method in determining the solubility of the solvents in water with a very high

correlation coefficient factor of 0.995.

Another important property considered in this work is the octanol-water partition coefficient. This is one of the most widely used parameter for assessing the environmental impact of chemical specie (Sonia, 2011). It is useful in the ecosystem risk analysis. Figure 3 shows the comparison of octanol-water partition coefficient values against COSMO-RS values.

As shown in Figure 3, the COSMO-RS prediction of octanol-water partition coefficient shows a very good

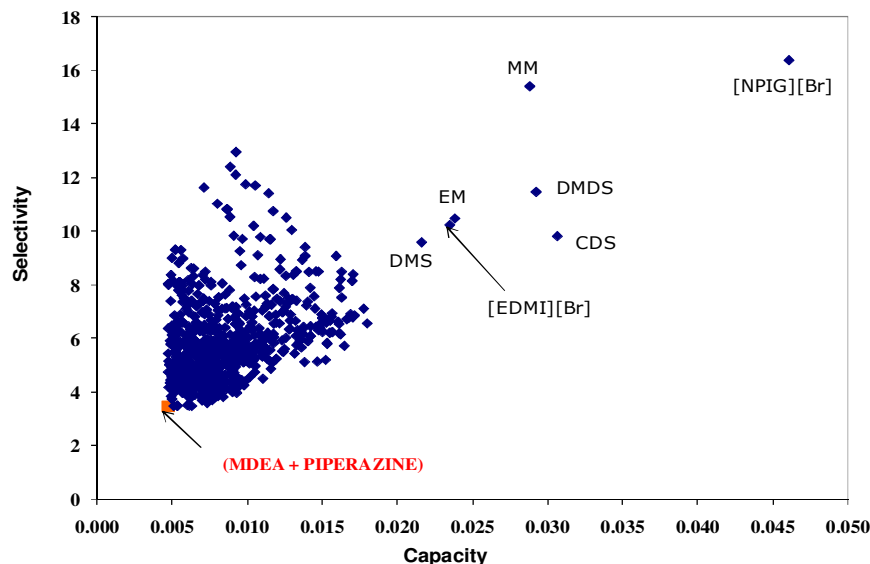


Figure 5. Plot of selectivity versus capacity of solvents screened.

comparison with the experimental data with a high correlation coefficient factor of  $R^2 = 0.993$ .

Figure 4 shows the comparison of experimental vapour pressure values with COSMO-RS values. Similarly, Figure 4 shows a very good correlation between the COSMO-RS model prediction and the experimental data. Based on the comparison of the results obtained from the model with experimental data, the COSMO-RS model predictions of thermodynamic properties can be relied on in screening large number of solvents.

### Screened solvents

Based on the criteria of high capacity and high selectivity, the solvents were screened out of some solvents by comparing the capacity and selectivity values of the solvent with a BS. The BS is the combination of tertiary amine and promoter (MDEA + Piperazine) which is widely used in the industry. Figure 5 presents a plot of selectivity against capacity showing the solvents that have higher capacity and selectivity than the BS.

The plot clearly shows that each of the screened solvent has capacity and selectivity greater than that of the BS. For further analysis of the screened solvents to be able to rank the solvent, the best two solvents from each group of solvents as defined in this work were selected. From the plot, it can be seen that the best two ionic solvent are ([NPIG][Br]) and ([EDMI][Br]). Also, the best two neutral solvents are Methylmercaptan (MM) and Dimethyldisulfide (DMS). Similarly, the best amine solvents are S and Pyridine (P). Finally, the best mixed solvents are (NMP + S) and (NMP + P).

Figure 6 examines the effect of temperature on Henry's

constant of the selected solvents. From Figure 6, for each of the selected solvent, the solubility of  $\text{CO}_2$  decreases with increase in temperature which is typical for a gas dissolving in liquid. This is in agreement with the work of Sumon and Henni (2011) which reported that both the solubility of  $\text{CO}_2$  and selectivity decrease as temperature is increased. Also, Luis (2007) reported the same conclusion relating solubility of  $\text{CO}_2$  to temperature. The reason for this gas solubility relationship with temperature is very similar to the reason that vapour pressure increases with temperature. Increased temperature causes an increase in kinetic energy. The higher kinetic energy causes more motion in molecules which break intermolecular bonds and escape from solution.

A model equation relating Henry's constant to temperature on each of the selected solvent is presented as shown in Table 1.

The Model equation is thus:

$$H = AT^2 + BT + C \quad (7)$$

Where, H = Henry's Constant (bar), T = Temperature ( $^{\circ}\text{C}$ ), A, B and C are constants for each solvents

### Environmental impact of the selected solvents

The octanol-water partition coefficient ( $K_{OW}$ ) of the solvents was determined and the result is presented in Figure 7.

It can be seen from the figure that some of the selected solvents show better octanol-water partition coefficient values than that of the BS. P, Methylmercaptan, (NMP +

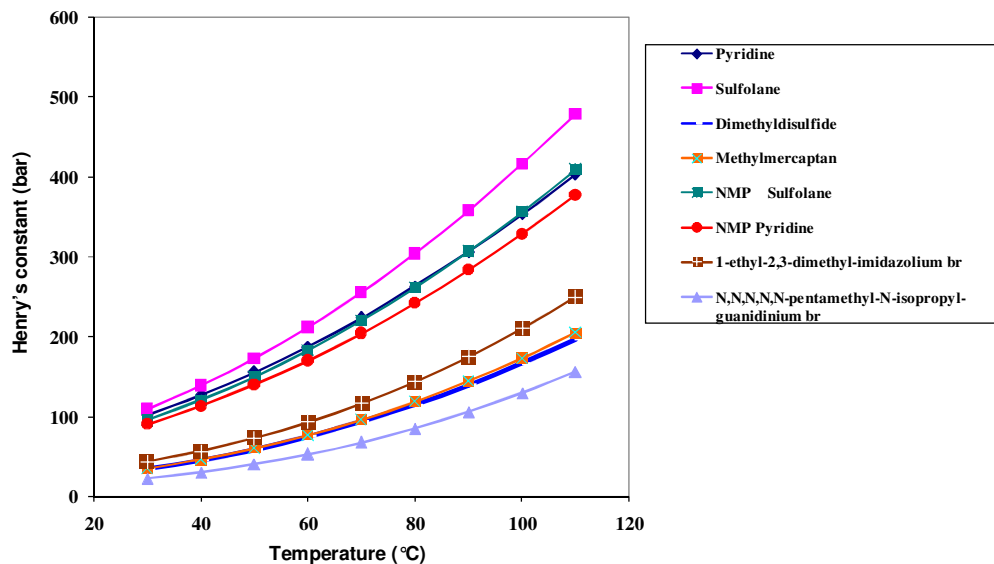


Figure 6. Plot of Henry's constant versus temperature on the selected solvents.

Table 1. Constant values of the model equation for each of the selected solvent.

| Solvent           | A     | B      | C      | R <sup>2</sup> |
|-------------------|-------|--------|--------|----------------|
| Sulfolane         | 0.024 | 1.244  | 50.110 | 1.000          |
| Pyridine          | 0.018 | 1.209  | 48.960 | 1.000          |
| NMP + Sulfolane   | 0.020 | 1.050  | 45.270 | 1.000          |
| NMP + Pyridine    | 0.018 | 0.996  | 43.340 | 1.000          |
| Methylmercaptan   | 0.015 | 0.018  | 21.100 | 1.000          |
| Dimethyldisulfide | 0.014 | 0.064  | 20.050 | 1.000          |
| [NPIG][Br]        | 0.013 | -0.246 | 17.390 | 0.999          |
| [EDMI][Br]        | 0.018 | -0.023 | 27.250 | 1.000          |

EDMI, 1-ethyl-2,3-dimethyl-imidazolium; NPIG, N,N,N,N-Pentamethyl-N-IsopropylGuanidinium.

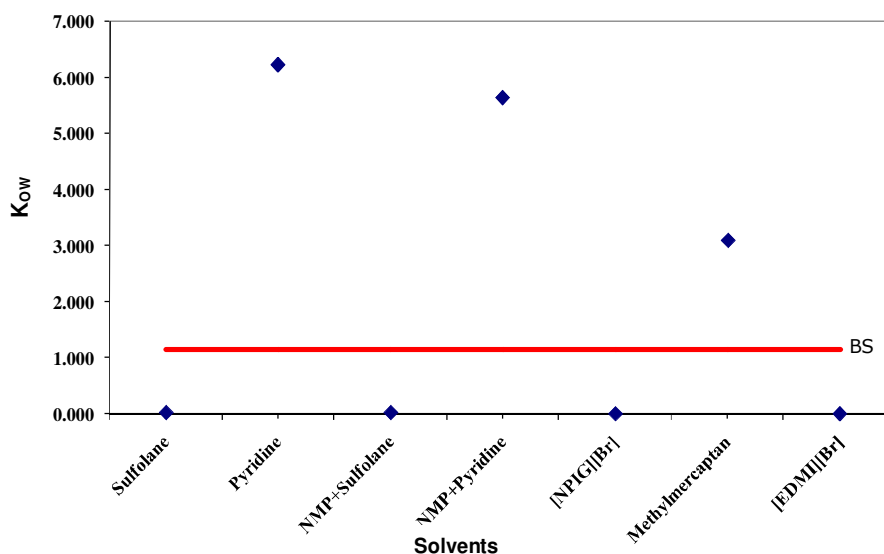


Figure 7. Octanol-water partition coefficient of the selected solvents.

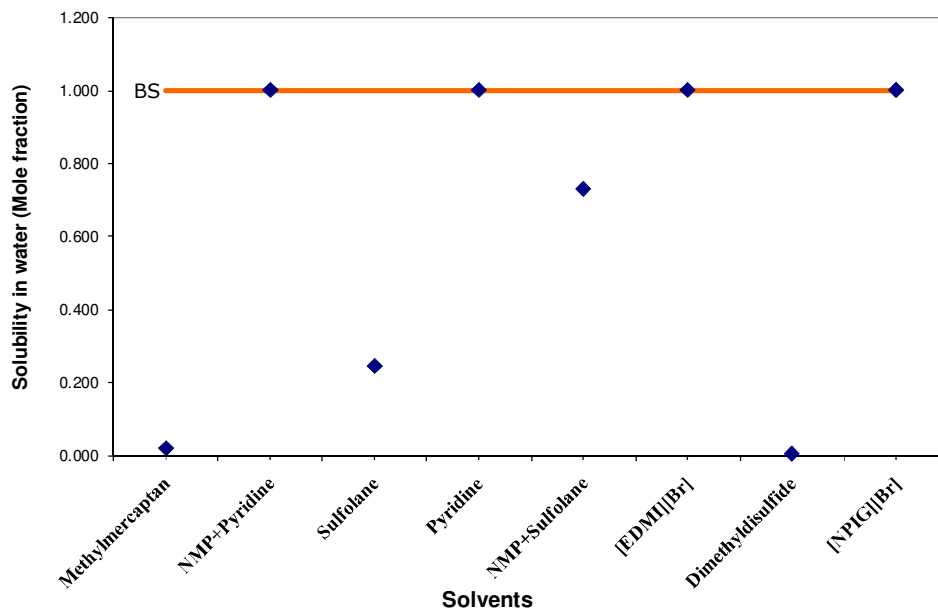


Figure 8. Solubility in water (mole fraction) of the selected solvents.

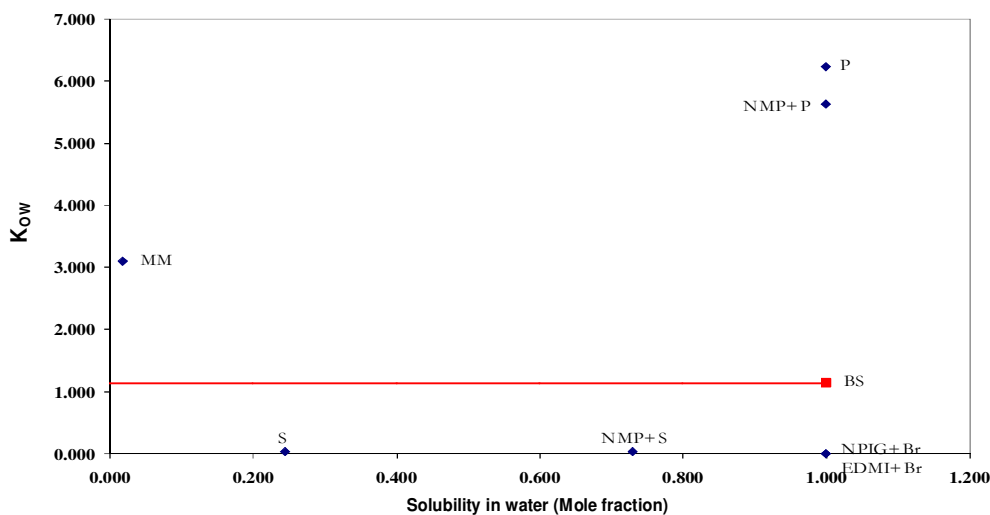


Figure 9. Plot of octanol-water partition coefficient versus solubility.

P), and Dimethyldisulfide solvents are not better than the BS in terms of the  $K_{OW}$ . Although, all the selected solvents have very low  $K_{OW}$  far less than the hazard limit of 10,000 (EPA, 1996). A solvent with  $K_{OW}$  of greater than 10,000 is considered environmentally unfriendly. S, (NMP + S), ([NPIG][Br]), ([EDMI][Br]) show better  $K_{OW}$  values than the BS.

Another property examined is the solubility of a solvent in water which shows the affinity of a solvent for water. The hydrophobicity of a solvent can give an indication of how easily a compound might be taken up in

groundwater to pollute waterways, and its toxicity to animals and aquatic life. It is also a measure of ease of regeneration of a solvent. Figure 8 shows the result of the solubility of the selected solvents in water.

It clearly shows that some of the solvents and the BS are completely miscible in water. The result shows that Methylmercaptan and Dimethyldisulphide have the least solubility in water although their octanol-water partition coefficient values were not better than the BS.

Therefore, there is a need to compare the relationship of  $K_{OW}$  and solubility which is presented in Figure 9. From



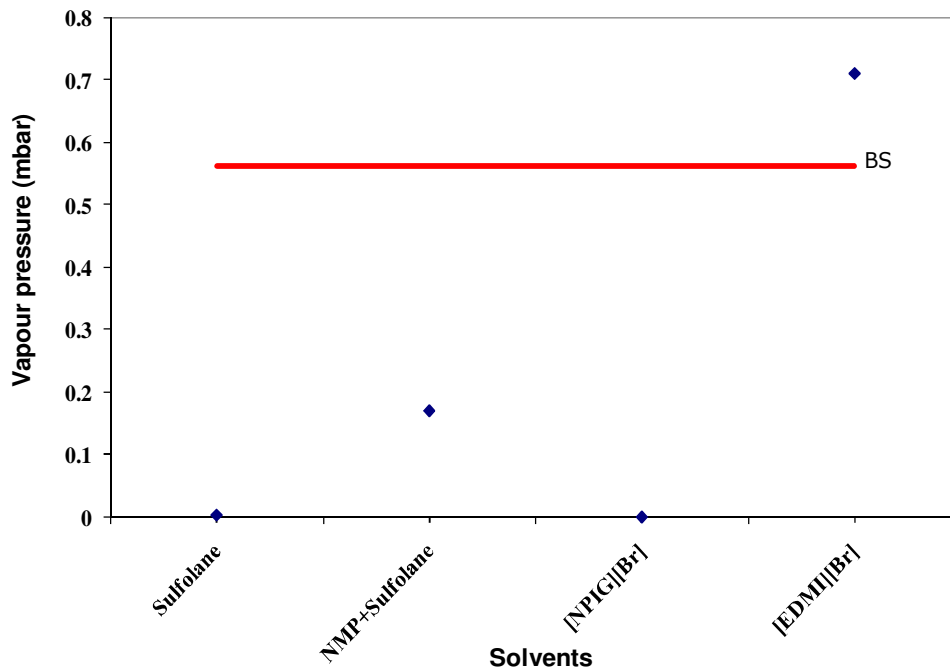


Figure 10. Vapor pressure (mbar) of the selected solvents.

the plot of octanol-water partition coefficient against solubility in water, S, (NMP + S), ([NPIG][Br]) and ([EDMI][Br]) shows properties better than the BS.

It is important to examine the volatility of these solvents. Solvents with low vapour pressure could reduce air pollution and worker exposure to harmful airborne chemicals. The vapour pressures of the solvents are presented in Figure 10.

So far from the results of the properties determined, four of the selected solvents show results better than the BS. But from Figure 10, one of the solvent ([EDMI][Br]) has a vapour pressure value higher than the BS. Basically, this work is aimed at finding solvents with better properties than the BS. Therefore, S, (NMP + S) and ([NPIG][Br]) have been found to have all properties examined better than the BS thus recommended.

S is generally a very stable chemical, and therefore can be reused multiple times in many of the various processes in which it is utilized. Due to its stable nature, it is generally considered safe if it is stored appropriately, and it is not explosive. It can, however, be hazardous if stored incorrectly. It is a poisonous substance to humans, and should not be ingested or inhaled. Because S operates at a relatively low solvent-to-feed ratio, it is relatively cost effective compared to similar-purpose solvents. It has the advantages of high acid gas loading and ease of solvent regeneration.

The IL recommended contain bromide ion. It is established by Danckwerts (2001) that the presence of small amounts of chlorine or bromine greatly accelerates

the rate of absorption of CO<sub>2</sub> in aqueous buffer solutions. This is because the halogens are hydrolyzed to OCl<sup>-</sup> or OBr<sup>-</sup>, which are powerful catalysts for the reaction between CO<sub>2</sub> and water. Edward (2008) revealed that the interactions between the anions and CO<sub>2</sub> play a major role through weak Lewis acid-base or electrostatic interactions, while the cations play a secondary role. This may be the possible reason while the IL shows a very good solubility in CO<sub>2</sub>. Bromide ion when exposed to ozone forms bromate anion which is undesirable because it is a suspected human carcinogen. Due to IL's stable nature, it is generally considered safe if it is stored appropriately. It can, however, be hazardous if stored incorrectly. More so, as a result of its most distinctive characteristic, low vapour pressure (nearly zero mbar), will help in reducing air pollution and worker exposure to harmful airborne chemicals.

## Conclusion

Out of more than 2000 solvents considered for screening in this work, the best 2 solvents from each of the four groups of solvents were selected based on the criteria of high capacity and high selectivity of the solvent in comparison to (MDEA + Piperazine).

All the 8 selected solvents were found to be environmental friendly having very low octanol-water partition coefficient  $K_{OW}$  far less than the hazard limit of 10,000. Out of the 8 selected solvents, 3 solvents were

recommended having all properties examined better than the BS. The 3 recommended solvents are S, (NMP + S), and ([N,N,N,N,N-Pentamethyl-N-IsopropylGuanidinium][Br]).

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## ABBREVIATIONS

**ILs**, Ionic liquids; **COSMO-RS**, conductor-like screening model for real solvents; **GCMs**, group contribution methods; **MDEA**, methyl-diethanolamine; **MEA**, monoethanolamine; **DEA**, diethanolamine; **DIPA**, diisopropanolamine; **AMP**, 2-amino-2-methylpropanol; **ESIS**, European chemical substance information system; **CSM**, continuum solvation model; **QM**, Quantum methods; **MM**, methylmercaptan; **EM**, ethylmercaptan; **DMS**, dimethylsulfide; **DMDS**, dimethyldisulfide; **CDS**, carbondisulfide; **NMP**, N-methylpyrrolidone; **CO<sub>2</sub>**, Carbon dioxide; **CH<sub>4</sub>**, methane; **C<sub>2</sub>H<sub>6</sub>**, Ethane; **N<sub>2</sub>**, Nitrogen; **H<sub>2</sub>S**, hydrogen sulfide; **S**, sulfolane; **BS**, benchmark solvent; **P**, pyridine; **C<sub>2</sub>mim**, 1-ethyl-3-methyl-imidazolium; **C<sub>4</sub>mim**, 1-butyl-3-methyl-imidazolium; **BF<sub>4</sub>**, tetrafluoroborate; **TF<sub>2</sub>N**, bis(trifluoromethylsulfonyl)imide.

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