TEMPERATURE DEPENDENT POLYAMINE STUDY FOR CO_2 CAPTURE

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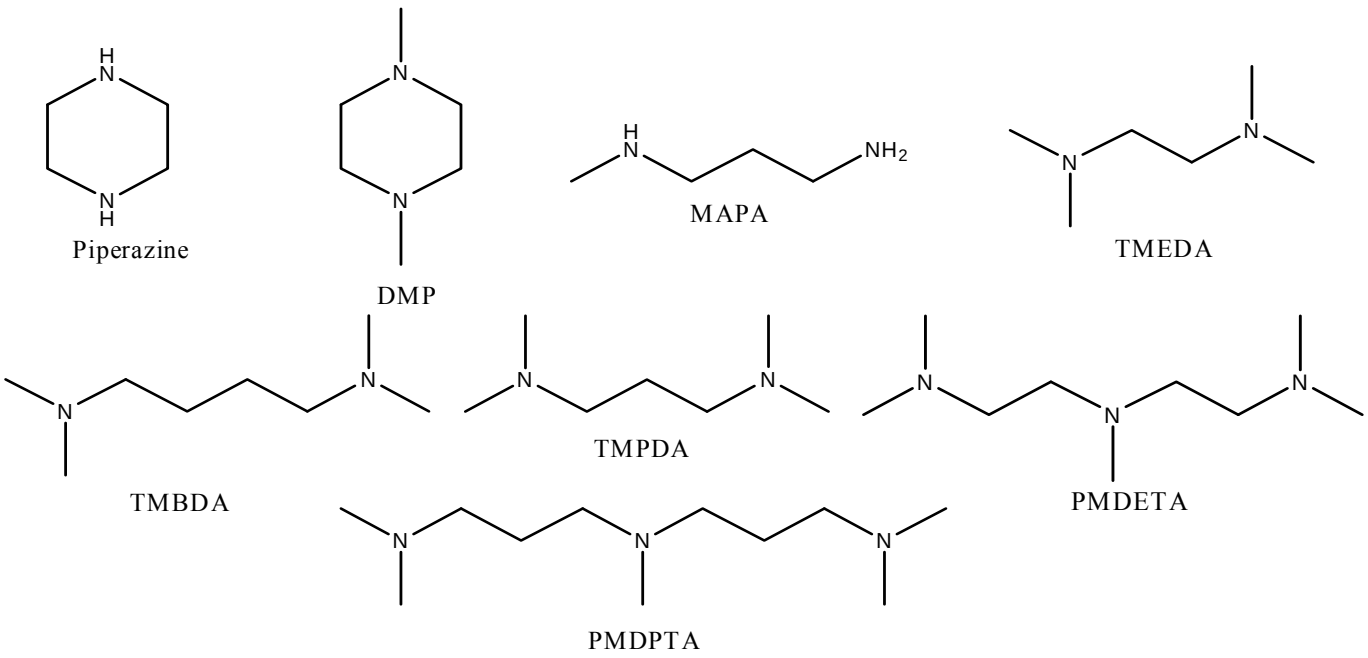
Carbon capture and storage (CCS) is very important to control human CO_2 emissions. Post combustion CO_2 capture is a widely accepted technology for CO_2 capture. Solvent development in post combustion CO_2 capture is very important in order to identify CO_2 absorbent systems that have close to ideal properties with regard to energy use and stability. Polyamine solutions can act as very promising solvents for CO_2 absorption. Computational chemistry studies are done on polyamine systems to estimate and determine needed properties for new solvent components and systematically evaluate the relationship between molecular structural properties and solvent performance parameters. Of special interest is the identification of solvent constituents fulfilling certain requirements with regard to pKa values and carbamate stability constants, and their temperature dependencies. The pKa values of the conjugate acids of amines are important variables to understand their CO_2 reaction rate and absorption capacity. The reliable prediction of these properties would be of great interest when screening for new promising solvents for CO_2 capture. It could be helpful to establish an ideal solvent which has the ability to capture the sour gases in the various practical industrial applications. The following relations were applied to calculate the pKa:

$$pK_a = (1 / 2.303\ RT)\ \Delta G_{ps} \quad (1)$$

$$\Delta G_{ps} = G(A_g^-) + G(H_g^+) - G(AH_g) + RT\ \ln(24.46) + \Delta G_s(A^-) + \Delta G_s(H^+) - \Delta G_s(AH) \quad (2)$$

Main systems studied are piperazine-water-carbondioxide solutions for the effect of various temperatures and pressures. Other polyamines studied were dimethylpiperazine (DMP), 3-amino-1-methylaminopropane (MAPA), N,N,N′,N′-tetramethylethylenediamine (TMEDA), N,N,N′,N′-tetramethylpropylenediamine (TMPDA), N,N,N′,N′-tetramethylbutylenediamine (TMBDA), N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDETA), and N,N,N′,N′,N″-pentamethyldipropylenetriamine (PMDPTA).



The procedures for the calculations using Spartan 08 and Gaussian 03 are outlined as follows:

(a) The first step is to obtain the equilibrium geometry of the molecule in the ideal gas phase from molecular energy minimization using Density Functional Theory (DFT) with B3LYP functional at 6-311++G (d, p) basis set level with Spartan 08.

(b) The second step is to carry out the PCM calculations and gaseous phase frequency calculations in Gaussian 03 for the temperature range of 298-393 K, using the optimized structure obtained in the previous step. All calculations were done using Density Functional Theory (DFT) with B3LYP functional at 6-311++G (d, p) basis set level. PCM calculations were done using the default settings in Gaussian 03 in aqueous phase.

(c) The third step is to carry out SM8 calculations using Spartan for the temperature range of 273.15-373 K. All calculations were done on the optimized geometries using Density Functional Theory (DFT) with B3LYP functional at 6-311++G (d, p) basis set level

Hence the effect of solvation of these polyamines and temperature effects at operating temperatures of post combustion CO_2 capture plant were investigated with PCM and SM8 solvation models. With increasing temperature, the pKa values decreases. This decrease is steeper in the amines with higher pKa values. By comparing the results for various polyamines with the other conventional amines which are being used for CO_2 capture, polyamine solutions may come out to be the future solvents in gas treating plants.