

Computational study of pKa and Carbamate stability constant values, for amines important in Post Combustion CO₂ Capture Process

Mayuri Gupta^{a)}, Eirik Falck Da Silva^{b)}, Hallvard F. Svendsen^{a)}

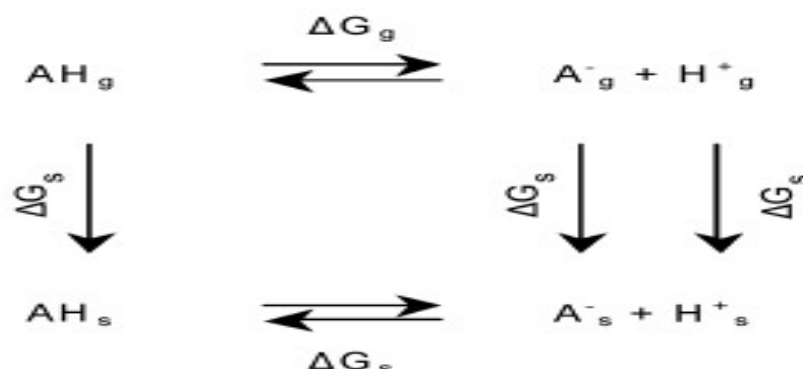
a) Department of Chemical Engineering, Norwegian University of Science and Technology, Trondheim, Norway b) Process Technology, SINTEF Materials and Chemistry, Trondheim, Norway

Temperature dependency of piperazine and related amines in the temperature range 298-393 K is studied using density functional theoretical calculations. B3LYP functional and 6-311++G (d, p) basis set was used in all the calculations.

The gas-phase acidity (ΔG) is defined as the Gibbs free energy change of the following equilibrium:

$$\Delta G = G(A_{g^-}) + G(H_{g^+}) - G(AH_g) \quad (1)$$

The value of Gibbs free energy of the proton in the gas phase is set to -6.29 kcal/mol using translational entropy calculated according to the well-known Sackur-Tetrode equation. The solution phase free energy for proton is -263.977 kcal/mol in this work. Absolute pKa calculations are based on the following thermodynamic cycle:



The following relations were applied to calculate the pKa:

$$pK_a = (1 / 2.303 RT) \Delta G_{ps} \quad (2)$$

$$\Delta G_{ps} = G(A_{g^-}) + G(H_{g^+}) - G(AH_g) + RT \ln(24.46) + \Delta G_s(A^-) + \Delta G_s(H^+) - \Delta G_s(AH) \quad (3)$$

From the pKa and carbamate formation reaction energy values it can be seen that the structural changes of amines have a critical effect on their behavior and that it varies significantly with temperature. Equilibrium temperature sensitivity of key reactions like pKa and carbamate formation plays an important role in determining which solvents are suitable for CO₂ capture. The higher the pKa value of amine, the higher its sensitivity towards temperature changes. The stronger the changes in pKa value and carbamate stability constant with temperature, the more it would be regarded as a promising solvent for acid gas capture. The PCM model for solvation energies provides a good basis for calculating the effect of solvation of amines and we propose that the differences in temperature dependency observed can be attributed to the small variations in their structures.