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Computational Analysis of pKa Values of Alkanolamines

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Abstract: Removal of CO_2 and its storage called Carbon dioxide Capture and Storage (CCS) is a noble area of research; many works are done in this area to screen a suitable solvent for CCS. The pKa values of different (primary, secondary and tertiary) alkanolamines, an industrially important molecule and a suitable candidate for CCS, were calculated by computational analysis employing a DFT-B3LYP level of theory with 6-31+G (d, p) as basis set. The linear relationship of the pKa value with the free energy of protonation is verified. The gas phase basicity and proton affinity values of different alkanolamines were computed. The gas phase basicity and proton affinity are found to vary with the structure of alkanolamine molecules. The study can be further extended to the temperature dependence of pKa values, as the post combustion of CCS has temperature dependence and to screen suitable candidates for CO_2 removal.

Introduction

Carbon dioxide, a major greenhouse gas, partakes about 60% of global warming. This makes the removal of CO_2 from gas streams and thereby reducing the atmospheric CO_2 concentration, an interesting and noble area in research. In this scenario the study of solvents for CO_2 capture and storage (CCS) is highly significant (Becke, 1993).

Alkanolamines are versatile, polyfunctional molecules that combine the characteristics of amines and alcohols. They are capable of undergoing reactions typical of both alcohols and amines, but the amine group usually exhibits the greater activity. One of the important applications of these compounds is that their aqueous solution can be used in Carbon dioxide Capture and Storage (CCS). Since most of the reactions starts with the protoation/deprotonation reactions, the study of acid dissociation constant i.e., the pKa value is significant (Charif *et al*., 2007) thepKa values play a major role in CO_2 capturing mechanism. The pKa value is known to affect the kinetics and possibly the mechanism of CO_2 capture (Clayden *et al*., 2001). In the present work, the pKa values of six different alkanolamines namely Monoethanolmine (MEA), Diethanolamine (DEA), Triethanolamine (TEA), Diisopropanolamine (DIPA), Methyldiethanolamine (MDEA) and 2-amino-2-methylpropanol (AMP) were computed. The pKa values often depend on structural factors. The aim of the work is to study the theoretical methods to compute the pKa values and to find out its structure and temperature dependence.

The proposed work also includes the evaluation of the gas phase basicity (GB) and gas base proton affinity (PA) of alkanolamines by computational method. The PA and GB values (which are structure dependent) determine the proton accepting tendency of a molecule and are important in atmospheric chemistry and biochemistry (Cramer, 2004). The experimental measurements are difficult when the molecules are too large, volatile, thermally decomposable, etc., and leading to inaccurate results. In this scenario use of a computational model is of particular relevance. The computational models are

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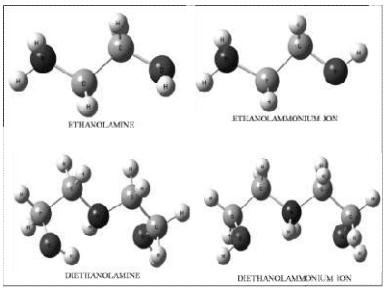
simple, less time consuming and can give accurate results.

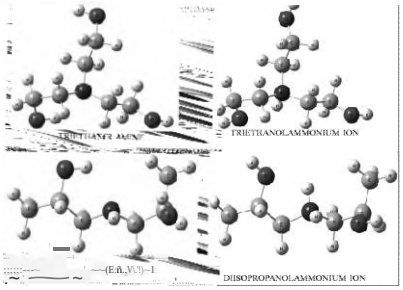
Computational methodology

Computational Chemistry is the study of problems on a computer based on quantum mechanical calculations and it simulates the chemical structures and reactions numerically based on fundamental laws of physics. Density Functional Theory (DFT) is an important computational technique for calculating geometries and energies of molecules. Unlike the other computational techniques, DFT is not based on wave function, but rather on electron probability density function or simply the electron density function (Folger, 2014). The level of theory adopted was B3LYP, which consists of Becke's exchange functional (Gupta *et al*., 2012) in conjunction with Lee-Yang–Parr correlation functional (Hajmalek *et al*., 2013) and the basis set used is 6-31+G (d, p). All the computational works are carried out through Gaussian 09 software package.

Many methods are available for the calculation of pKa values. Most of the works reported in the literature explaining the computational models to predict the pKa values are based on the free energy calculations (Lee *et al*., 1988). The present work is based on the free energy values. Structures of all the alkanolamines and their protonated ions are optimized both in gas phase and in solution (solvent = water) phase. Their thermodynamic properties can be directly obtained from the Gaussian output file. All the parameters are computed except the Gibb's free energy and enthalpy of proton in gas and solution phase which are taken from the literature. The optimized structures of neutral and protonated alkanolamines are given in Figs. 1 (a), (b) and (c).



(a)



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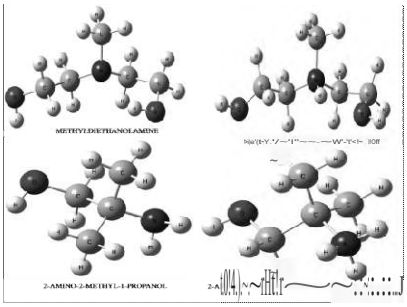

(c)

Fig. 1. Optimized structures of neutral and protonated **(a)** MEA and DEA **(b)** TEA and DIPA**(c)** MDEA and AMP

Most of the pKa value calculation studies are carried out by using DFT method and the computations were performed both in gas phase as well as in solution phase. The solution phase reactions are usually carried out by using the continuum models. In the Polarization Continuum Models (PCM) the solvent is described by a dielectric medium and a cavity is defined inside this dielectric medium (Lewars, 2004). This cavity is formulated to insert the molecule in the solvent phase. These models are basically parameterized to calculate the free energy of solvation as given by Eq. (1):

$$\Delta G_{solv}=\Delta G_{es}+\Delta G_{vdw}+\Delta G_{cav} \quad (1)$$

whereΔG_{es} is the electrostatic, ΔG_{vdw} is the van der Waals and ΔG_{cav} is the activation energy contributions to free energy of solvation which are obtained from the output of the Gaussian file. There are different PCM models available which are designed to improve the computational performance of the method. The present work employs IEFPCM solvation model (Valadbeigi *et al*., 2014).

All the alknolamines, in the neutral and in protonated state, are optimized both in gas phase and in solution phase with 6-31+G (d, p) as basis set. Most of the studies in literature are found to use 6-31+G (d, p) as basis set, but here the lower basis set is enough for getting accurate results. The pKa values show a linear relationship with the free energy of protonation. So from the free energy measurements, pKa values can be computed. The computed results are then compared with the available experimental data and are in good agreement.

By using the thermodynamic cycle (Fig. 2) showing protonation reactions, the pKa values were computed (Lewars, 2004). The gas phase basicity and gas phase proton affinity have also been computed by using the thermodynamic cycle.

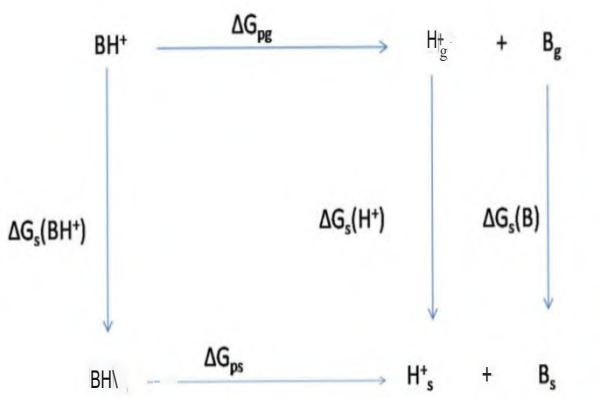

Fig. 2. Thermodynamic cycle employed for the calculation of pKa values.

The necessary equations are:

$pKa=\Delta G_{ps}/(2.303RT)$ (2)

$\Delta G_{ps} = \Delta G_{pg} + \Delta G_s$ (3)

$\Delta G_{pg}= G_g(B) + G_g(H^+) - G_g(BH^+)$ (4)

$\Delta G_s = \Delta G_s(B) - \Delta G_s(BH^+)$ (5)

where, $\Delta G_{ps}$is the change in free energy of protonation. Here the quantities such as free energy of proton in gas phase (-6.29 kcal/mol) and that in solution (-263.977 kcal/mol) were taken from the literature (Lewars, 2004) and all others are computed using Gaussian 09 software. The gas phase basicity can be calculated from Eq. (4). The gas phase proton affinity is the change in enthalpy of protonation in gas phase and is calculated by Eq. (6).

$\Delta H_{pg}=H_g(B)+H_g(H^+)-H_g(BH^+)$ (6)

where the gas phase enthalpy of proton affinity value (1.48 kcal/mol) is taken from the literature.

Results and discussion

Calculation of pKa values of Alkanolamines

The pKa value is necessary in physical, organic and biological chemistry. The properties of amino groups are greatly correlated with their pKa values. Greater the pKa value of an amine or alkanolamine stronger will be the basic character. Study of pKa value of the CO_2 capturing solvents is of particular relevance because this basic nature is useful to explain their capturing capacity. Six different alkanolamines including primary, secondary and tertiary were studied and their pKa values computed are tabulated in Table 1. From Table 1 it is clear that the computed results are in correlation with the experimental results.

Table 1. pKa values of Alkanolamines

Alknolamine	pKa value (computed)	pKa value (experimental)
Ethanolamine	9.43	9.52
Diethanolamine	8.94	8.95
Triethanolamine	8.05	7.78
Diisopropanolamine	9.18	9.10
Methyldiethanilamine	8.62	8.63
2-Amino-2-methyl-1-propanol	9.81	9.70

The alcoholic groups in alkanolamines destabilize the protonated form of amine because of the electron withdrawing nature of the alcoholic group. The alcoholic group forms

hydrogen bond with the amine group and thus the pKa value of most of the alkanolamines are less than that of corresponding methylamines. In TEA the three bulky ethyl groups surrounds the amine nitrogen together with strong electron withdrawing effect. But in the protonated form, however, there is only one proton that these groups can bond with, limiting the stabilizing effect. The sterric effect in TEA also plays a role that the electron pairs at nitrogen cannot easily donate and results in low pKa value In AMP the amino group and the alcoholic group are farther away (see Fig 1), results in a weak hydrogen bond and thus have high pKa value. So in the case of alkanolamines, apart from the sterric effect, the hydrogen bonding is also a factor to reduce the pKa value i.e., as moving from primary to tertiary alkanolamines the sterric and hydrogen bonding effect increases resulting in the reduction of pKavlue. For example the pKa values of MEA (1°), DEA (2°) and TEA (3°) are 9.13, 8.99 and 7.45 respectively. The graphical representation of the computed and experimental pKa values was shown in Fig 3.

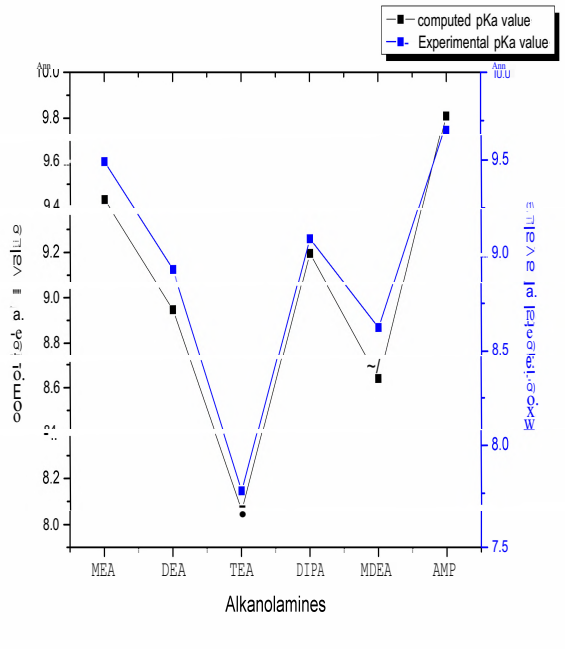

Fig 3. Computed pKa value versus experimental pKa value

3.1 Calculation of gas phase proton affinity (PA) and gas phase bsicity (GB)

Table 2. Gas phase proton affinity of Alkanolamines

Alknolamine	GB value (kcal/mol)	PA value (kcal/mol)
Ethanolamine	208.1218	215.3616
Diethanolamine	224.9333	232.6983
Triethanolamine	225.7282	233.2296
Diisopropanolamine	229.0623	236.7758
Methyldiethanilamine	223.6496	231.3115
2-Amino-2-methyl-1-propanol	214.7809	222.0916

From the Table 2, it is clear that the GB and PA values increase as going from primary to tertiary. This is due to the electron releasing capacity of alkyl groups. The GB and PA values also increase with the number of carbon atoms.

Conclusion

A computational DFT-B3LYP analysis has been performed to compute the pKa value of 6 different alkanolamines with basis set 6-31+ G (d, p). The computed pKa values are in good correlation with the experimental results. Greater the pKa value of an amine or alkanolamine stronger will be the basic character. The alcoholic groups in alkanolamines destabilize the protonated form of amine because of the electron withdrawing nature of the alcoholic group. In the case of alkanolamines, apart from the sterric effect, the hydrogen bonding is also a factor to reduce the pKa value i.e., as moving from primary to tertiary alkanolamines the sterric and hydrogen bonding effect increases resulting in the reduction of pKavlue. 2-Amino-2-methyl-1-propanol has the highest and Triethanolamine has the lowest pKa values. The work also computed the GB and PA values and is increases with increase in the number of carbon atom.

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