



Corrosion inhibition studies and Solvation Analysis of Pyridine N-oxides by Polarizable Continuum Model method

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ABSTRACT

Solvation analysis and corrosion inhibition studies has been carried out for pyridine N oxide, 3-carboxypyridine N-oxide and 2-methylpyridine N- oxide in polar and nonpolar solvents having a wide range of dielectric constants. The test set consists of water, methanol, ethanol, acetone, dichloromethane, chlorobenzene, chloroform, toluene, benzene and carbon tetrachloride. The physical properties of the systems such as free energies of solution, electrostatic interaction, dispersive energies, repulsive energies and dipole moments are discussed. Quantum mechanical self consistent fields explain the properties of the compounds satisfactorily.

Indexing terms/Keywords

Solvation analysis, corrosion inhibitors, dipole moment

Academic Discipline And Sub-Disciplines

Applied Physics

SUBJECT CLASSIFICATION

Physics Subject Classification; Spectroscopy

TYPE (METHOD/APPROACH)

Quantum Chemical Studies- DFT calculations

INTRODUCTION

The chemistry and application of N-oxides have recently received much attention due to their usefulness as synthetic intermediates and their biological importance [1]. The nitrogen containing heterocyclic aromatic ring systems such as pyridines and pyrimidine derivatives are of biological importance as they are constituents of DNA and RNA and they play key role in the structure and properties of nucleic acids [2]. Pyridine ring system is present in several natural products, pharmaceutical and agrochemical compounds [3]. In the past four decades, several organic substances have been used as corrosion inhibitors in steel industry. The significant criteria involved in the selection of inhibitors are hydrophobicity, molecular structure and electron density of the donor atoms, solubility and ability to disperse in solution [4, 5]. Pyridine derivatives were found to be effective and efficient corrosion inhibitors for steel [6]. Many pyridines of commercial interest find application in market areas where bioactivity is important, as in medicinal drugs and in agricultural products such as herbicides, insecticides, fungicides plant growth regulators and cancer drug. The main aim of the present investigation is to study the solvation analysis of the three selected pyridine N-oxide molecules. An attempt has been made to establish the theoretical property that contributes significantly for solvation in different solvents. Implicit solvation models are widely used to predict a variety of solvent effects including: Gibbs energy of solution, solubility and vapour pressure. In industrial, environmental and pharmacological applications, these properties are required over a range of temperatures. However, almost all implicit solvation models have been designed or tested only for predicting these quantities at room temperature [7-10].

METHODS OF COMPUTATION

Theoretical calculations have been carried out at the ab-initio level [11-13] on the pyridine-N oxides. In the present study solvation analysis is done using a wide range of solvents, which has been performed in media of different dielectric constants using Polarizable Continuum Model (PCM) by Gaussian DFT method to interpret the solvent effect of the molecules. The modeling of water, methanol, ethanol, acetone, dichloromethane, chlorobenzene, chloroform, toluene, benzene and carbon tetrachloride are considered as solvents in this study. All calculations were carried out with the Gaussian 03 package [14] computer program GAMESS Schmidt 10 was used for this purpose [15]. The optimized structures of the three pyridine N-oxides molecules are shown in Figure 1.

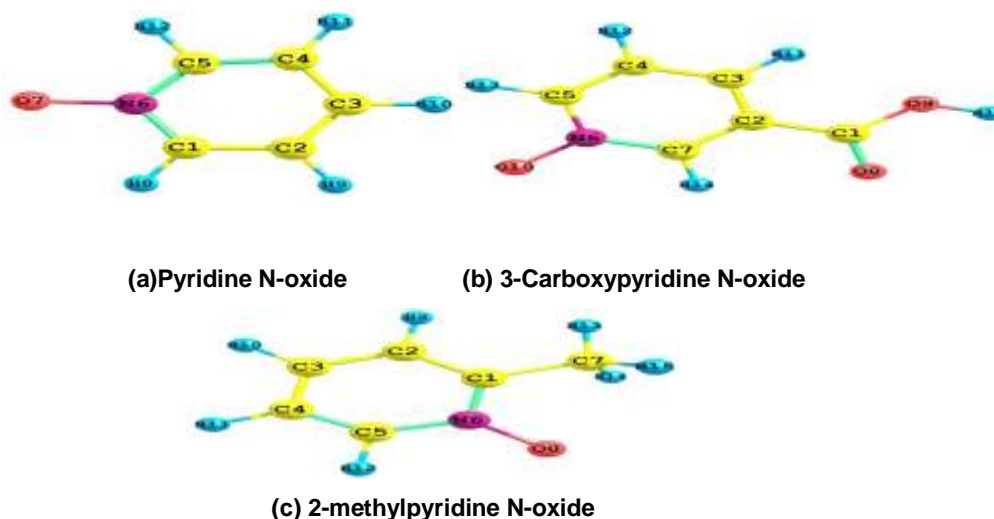


Figure 1 Optimized structures of (a) Pyridine N-oxide (b) 3-Carboxypyridine N-oxide (c) 2-methylpyridine N-oxide

RESULTS AND DISCUSSION

Electrostatic Contributions in Free Energy

Gibbs free energy of solvation is an important parameter among solution parameters. It gives an idea about the solute-solvent interaction and it can be related to the work which necessarily builds up a solute in the solvent environment. Table 1 contains the list of solvent descriptors. Free energy of solution is computed by PCM method for the pyridine N-oxides in different solvents. The computed free energies of solvation and its components of the three compounds are listed in Table 2 to Table 4. The data show how the different characteristics of each solvent affect the free energy of solvation of the three selected molecules. The free energy of solvation is the algebraic sum of the electrostatic interaction, gravitational energy, dispersion energy and repulsion energy. The electrostatic contribution to the free energies of solution depends partly on the dielectric constant of the solvent. The electrostatic contribution to the free energy of the solution increases with increase in the dielectric constant of the medium [16, 17]. By comparing the electrostatic contribution values in different media, it is found that the electrostatic contribution is the least in CCl_4 which has a dielectric constant value of 2.23 while it is highest in water which has a dielectric constant of 78.35. The plot of electrostatic interaction energy against dielectric constant is shown in Figure 2. The curve in this plot indicates that the electrostatic interaction energy is influenced by the dielectric constant. It may be pointed out here that the electrostatic contribution to the solution free energy in a given medium is higher for 3-carboxypyridine N-oxide compared to other two compounds. This may be due to greater polarizability of methyl group than carboxyl group. Increase in polarizability increases covalent character in the molecule.

Among the nonpolar solvents, the free energy of solution for the investigated molecules is higher in dichloromethane and this is due to smaller surface tension of this solvent. Since the free energy of solution in this solvent is more compared to other nonpolar solvents, the metallic iron can be easily corroded in dichloromethane than in other nonpolar solvents. It can be pointed out that the free energy of solution of three of the pyridine N-oxides which act as corrosion inhibitors for iron, the feasibility of corrosion is easier in dichloromethane. On the other hand, among the polar solvents the free energy of solution of the three molecules in water is more and hence these inhibitor molecules can act as effective inhibitors for the corrosion of iron in water.

Table 1 Solvent descriptors at 298 K

Solvent	dielectric constant(ϵ)	Refractive index(n)	Surface tension(γ)	Hydrogen bond acidity factor(α)	Hydrogen bond acidity factor(β)
POLAR					
H ₂ O	78.54	1.33	71.99	0.82	0.35
CH ₃ OH	32.63	1.33	22.12	0.43	0.47
C ₂ H ₅ OH	24.85	1.36	31.62	0.37	0.48
CH ₃ COCH ₃	20.49	1.36	33.77	0.04	0.49
NON POLAR					
CH ₂ Cl ₂	8.93	1.37	27.33	0.1	0.05
C ₆ H ₅ Cl	5.62	1.52	32.69	0	0.17
CHCl ₃	4.9	1.45	26.53	0.15	0.02



C ₆ H ₅ CH ₃	2.37	1.5	40.2	0	0.14
C ₆ H ₆	2.27	1.5	40.62	0	0.14
CCl ₄	2.23	1.46	38.04	0	0

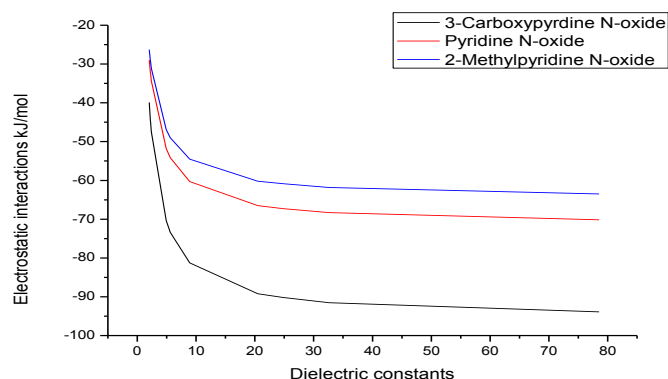


Figure 2 Plots of dielectric constant versus electrostatic interaction energy

Dispersion energy

The dispersion energies are mainly due to polarization of the solvent molecules by the solute molecules [18]. This polarization, in turn may depend on the refractive index and dipole moment of the solvent molecule. From the data in Table 2 to Table 4, it can be seen that the dispersion energy of the solute molecules varies with the refractive index of the solvent molecules. This is supported by the higher values of the dispersion energies of the 3-carboxypyridine N-oxide in all the solvents compared to the other pyridine N-oxides. Thus, the dispersion energy of the molecules in different solvents may be correlated with the refractive index of the solvent. Plots of the refractive index versus dispersion energy for the three investigated compounds are shown in Figure 3. The refractive index of water is the least among all the solvents used for investigation and the dispersion energy is the having the highest value. On the other hand, chlorobenzene among nonpolar solvents has high refractive index and dispersion energies for the investigated solutes in this solvent are also high.

Table 2 Free energy of solution and its components of Pyridine N- oxide at 298 K

Solvent of solution	Electrostatic Interaction kJ/mole	Dispersive energy kJ/mole	Repulsive energy kJ/mole	Free energy kJ/mole
POLAR				
H ₂ O	-70.16	-49.83	4.43	-115.56
CH ₃ OH	-68.32	-42.96	3.68	-107.6
C ₂ H ₅ OH	-67.27	-43.93	3.68	-107.52
CH ₃ COCH ₃	-66.52	-40.12	3.30	-103.34
NON POLAR				
CH ₂ Cl ₂	-60.29	-42.00	3.34	-98.95
C ₆ H ₅ Cl	-54.14	-47.99	5.85	-96.28
CHCl ₃	-51.79	-37.94	2.84	-86.89
C ₆ H ₅ CH ₃	-34.30	-48.49	6.19	-76.6
C ₆ H ₆	-32.50	-47.57	6.15	-73.92
CCl ₄	-32.21	-38.45	2.88	-67.78

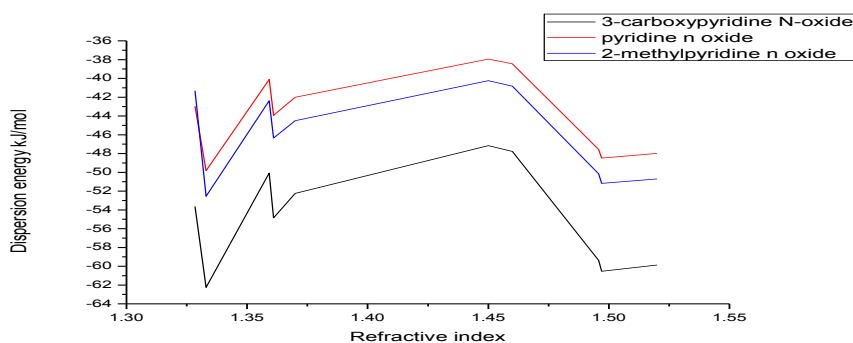


Figure 3 Plots of refractive index versus dispersion energy

Repulsion energy

The repulsion energy of a solute molecule in a solution depends upon not only on the dielectric constant of the solvent but also on the hydrogen bond acidity (α) and basicity (β) values. This is because the solute may be acidic, basic or amphoteric. The solute molecules used in the present investigation are almost neutral and hence the repulsive energy may depend upon both these properties of solvents. The repulsion energies of pyridine N-oxides in different solvents are given in Table 2 to Table 4. These values indicate that the dielectric constants as well as the molecular size of the solvent molecules determine the repulsion energies. This is supported by the higher values of the repulsion energies of the 3-carboxypyridine N-oxide in all the solvents compared to the other pyridine N-oxides. It can be seen that the repulsion energies of the three pyridine N-oxides are higher in benzene and toluene which also has higher refractive index and lesser in chloroform compared to other solvents. This may be due to slight attraction between methyl groups and pyridine N-oxides. The trend in the repulsive energies also suggests that the repulsion energy depends upon α and β values of the solvents. It can also be seen that α and β values of halogenated solvents are zero and hence the repulsive energies are minimum for the solutes in these solvents. Plot of refractive index versus repulsion energy are shown in Figure 4.

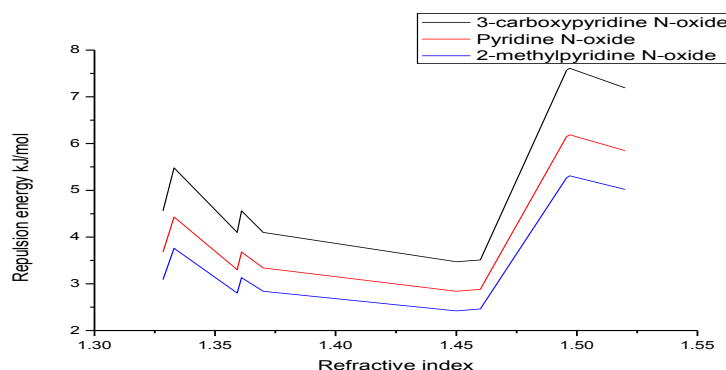


Figure 4 Plots of Refractive index versus repulsion energy

Table 3 Free energy of solution and its components of 3-carboxypyridine N- oxide at 298 K

Solvent of solution	Electrostatic Interaction kJ/mole	Dispersive energy kJ/mole	Repulsive energy kJ/mole	Free energy kJ/mole
POLAR				
H ₂ O	-93.88	-62.25	5.48	-150.65
CH ₃ OH	-91.54	-53.63	4.56	-140.61
C ₂ H ₅ OH	-90.21	-54.85	4.56	-140.5
CH ₃ COCH ₃	-89.24	-50.08	4.10	-135.22
NON POLAR				
CH ₂ Cl ₂	-81.25	-52.25	4.10	-129.4
C ₆ H ₅ Cl	-73.38	-59.87	7.19	-126.06
CHCl ₃	-70.33	-47.15	3.47	-114.01
C ₆ H ₅ CH ₃	-47.40	-60.54	7.61	-100.33
C ₆ H ₆	-44.97	-59.37	7.57	-96.77
CCl ₄	-44.64	-47.78	3.51	-88.91



Table 4 Free energy of solution and its components of 2-methylpyridine N-oxide at 298 K

Solvent of solution	Electrostatic Interaction kJ/mole	Dispersive energy kJ/mole	Repulsive energy kJ/mole	Free energy kJ/mole
POLAR				
H ₂ O	-63.51	-52.55	3.76	-112.3
CH ₃ OH	-61.83	-41.31	3.09	-100.05
C ₂ H ₅ OH	-60.87	-46.35	3.13	-104.09
CH ₃ COCH ₃	-60.20	-42.38	2.80	-99.78
NON POLAR				
CH ₂ Cl ₂	-54.51	-44.51	2.84	-96.18
C ₆ H ₅ Cl	-48.99	-50.71	5.02	-94.68
CHCl ₃	-46.86	-40.25	2.42	-84.69
C ₆ H ₅ CH ₃	-31.08	-51.17	5.31	-76.94
C ₆ H ₆	-29.45	-50.16	5.27	-74.34
CCl ₄	-29.20	-40.83	2.46	-67.57

Prediction of dipole moment

The dipole moments are more sensitive to details of the model, because the non-electrostatic effects are not treated self consistently [19]. The dipole moments are calculated based on the wave function. The changes in the dipole moments are based on the dielectric behaviour of the solvent. The dipole moment of the solute is also an important parameter to determine the solubility [20, 21]. The dipole moment of pure solute in the presence of solvents is computed by *ab-initio* method and the values are given in Table 5. The induced dipole moment is proportional to polarizability which increases with increase of molar volume. The high value of dipole moment probably increases the corrosion inhibition ability of inhibitors. It can be seen that the dipole moment is high for all the three molecules. It can be seen that the dipole moment of 2-methylpyridine N-oxide is slightly less than the other two molecules. The value of the dipole moments increases with increase in dielectric constant of the molecules. Further the dipole moment values are higher for all the solutes in water. This may probably be due to higher dielectric constant value of water.

Table 5 Dipole moment of the solute molecules in different solvents at 298 K

Solvent	3-carboxypyridine N-oxide	pyridine N-oxide	2-methylpyridine N-oxide
	μ/D	μ/D	μ/D
POLAR			
H ₂ O	7.629	6.152	5.772
CH ₃ OH	7.548	6.086	5.697
C ₂ H ₅ OH	7.502	6.05	5.657
CH ₃ COCH ₃	7.467	6.024	5.629
NON POLAR			
CH ₂ Cl ₂	7.232	5.831	5.431
C ₆ H ₅ Cl	7.001	6.082	5.241
CHCl ₃	6.923	5.58	5.176
C ₆ H ₅ CH ₃	6.339	5.1	4.706
C ₆ H ₆	6.238	5.054	4.663
CCl ₄	6.274	5.047	4.656



CONCLUSION

Quantum mechanical solvation analysis is carried out for different pyridine derivatives namely 3-carboxy pyridine N-oxide, 2-methylpyridine N-oxide and pyridine N-oxide. The PCM model for pyridine N-oxides in different solvents lends itself to specific parameterization for more complicated condensed phases. The electrostatic interaction energy correlates well with the dielectric constant of the solvent. However, dispersion energy correlation is satisfactory with refractive index of the solvent. The repulsion energy of the solute molecule depends upon more than one physical property of the solvent. Free energy of solution values also reported for the solutes in ten different solvents. The free energy of solution is the least negative in aqueous solution for three of the different molecules and hence they may be effective coating for iron and inhibit corrosion of iron in aqueous medium. Further it is still less negative for 2-methylpyridine N-oxide and hence it may be more corrosion inhibitor than other pyridine N-oxides. Due to methyl group being an electron donating group its electron density is more on nitrogen atom and its inhibition efficiency is high compared to other molecules. The dipole moments values caused by the solvent-solute interaction lead to a systematic increase in all molecules studied here. The interaction between the three pyridine N-oxides and various solvents are investigated to explain the condensed phase simulation, which will be useful for the study of solvation of the compounds. It is concluded that these features will be useful to develop the three pyridine N-oxides as effective corrosion inhibitors.

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