# Solvation analysis of halogenated 3-phenyl 5-amino pyrazoles

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## ARTICLE INFO

## ABSTRACT

Quantum mechanical solvation analysis accounts for electric and electro static components of solvation by microscopic surface tension. Solvation analysis is performed for two halo substituted phenyl 1H pyrazole-5 amines in different solvents. The free energy and its components such as electrostatic interaction, dispersion energy, and repulsion energy are computed. The systematic comparison of the electrostatic contribution of the free energy of solvation is carried out from the self-consistent reaction field. The effects of cavities and the dipole moments are examined. The investigated set consists of ten solvents with wide range of dielectric constant.

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## 1. Introduction

Nitrogen containing heterocyclic compounds is usually used as corrosion inhibitors for iron in acidic solution and many experiments have been carried out in this area. In general, pyridine and pyrazole compounds showed good inhibitive properties for steel. The standard state free energy of solvation is a fundamental quantity that describes the energy of interaction between a solute and solvent molecules [1–6]. This parameter can be better used to understand clearly the corrosion inhibition property of these compounds in solution. The Polarizable Continnum Solvation [PCM] is extended to nitrogen containing heterocyclic compounds such as 3–4 chlorophenyl-1 H pyrazole-5 amine and 3–4 bromophenyl-1 H pyrazole-5 amine [Fig. 1].

## 2. Method of computation

Solvation analysis is done in wide range of solvents. Computation has been performed both in the gas phase and in the solvent medium of various dielectric constants using Polarized Continuum Model (PCM) by STO–6-31 basis set to interpret the solvent effect on the behavior of the solute molecules. [7].The computer program GAMESS [8] was used for this purpose.

## 3. Results and discussion

Solvation effect is an essential component of solution chemistry and it is very useful in pharmaceutical industry for heterocyclic organic compounds. These solvation effects are frequently dominated by electrostatic interaction [9]. Thermodynamically, it is not possible to separate electrostatic contribution from the free energy of solvation. This electrostatic contribution to the free energy of solvation depends mainly on the dielectric constant of the solvent and polarizability. The various physical properties of the solvents employed as media in the present computation are listed in Table 1. The computed electrostatic interaction energy of the two halogenated pyrazole derivatives in different solvents are presented in Table 2. From the data in Table 2, it is clear that electrostatic contribution energy may well be correlated with the dielectric constant of the solvent. Generally, the electrostatic contribution energy increases with the increase in dielectric constant of the medium. The electrostatic components of the solute molecules in solvents like toluene, benzene, and carbon tetrachloride are almost the same. This observation may be due to the similar size of the cavity, dispersion and solvent structure in these solvents. By comparing the electrostatic interactions of all the solvents studied here, water provides more negative interaction energy than by other solvents. It may be pointed out that in the case of both the solute molecules the electrostatic interaction energy is the highest in water. This is due to the high dielectric constant of water which provides more macroscopic surface tension for solute–solvent interaction. The heteroatom in the solute molecule is hydrophilic due to the possibility of inter molecular hydrogen bond formation.

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3-(4-chlorophenyl)-1*H*-pyrazol-5-amine



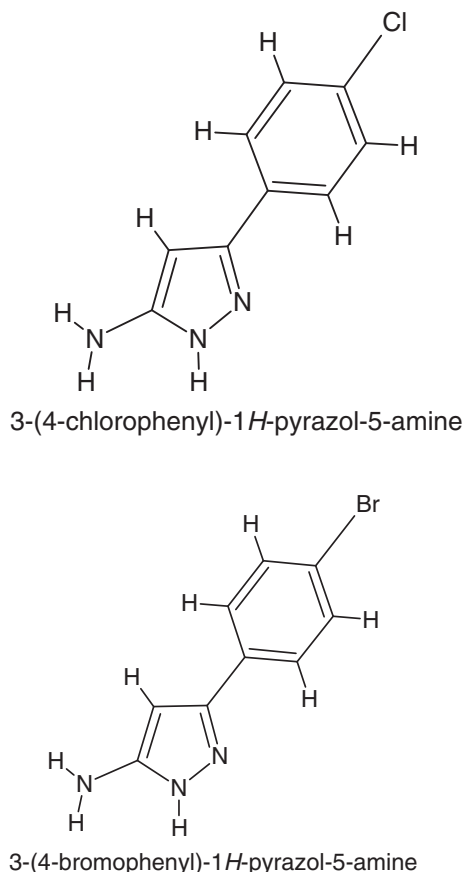3-(4-bromophenyl)-1*H*-pyrazol-5-amine

**Fig. 1.** Schematic drawing of molecular structure of Pyrazole derivatives studied here.

The electrostatic interaction energy can also be correlated with the molecular radius of the solvent. It is known that the interaction energy generally decreases with increase in the solvent molecular radius. This correlation is fairly good in protic and chlorinated solvents. Thus, the electrostatic interaction energy of the two solute molecules in water is greater in water than in methanol (Table 2).Similarly, the electrostatic interaction energy is less in $CCl_4$ than in the other two chlorinated solvents. However, this type of correlation is less satisfactory in other polar solvents. In electronic spectroscopy, the effect of quadrupolar solvent is most important [9]. It is worthwhile to describe the equilibrium and non equilibrium solvation in quadrupolar solvents [10]. The values of electrostatic interactions for quadrupolar solvents such as toluene and benzene are presented in Table 2. By comparing these two solvents the electrostatic interactions provide least negative values in Toluene than that of the other solvents studied

**Table 1**
Solvent descriptors.

| Solvent | $\varepsilon$ | n | $\gamma$ | $\alpha$ | $\beta$ | Molecular radius |
|---------|---|---|---|---|---|---|
| $H_2O$ | 78.35 | 1.33 | 71.81 | 0.82 | 0.35 | 2.77 |
| $CH_3NO_2$ | 36.56 | 1.38 | 52.58 | 0.06 | 0.31 | 4.31 |
| $CH_3OH$ | 32.63 | 1.33 | 22.12 | 0.43 | 0.47 | 3.71 |
| $C_2H_5OH$ | 24.85 | 1.36 | 31.62 | 0.37 | 0.48 | |
| Acetone | 20.49 | 1.36 | 33.77 | 0.04 | 0.49 | 4.76 |
| $CH_2Cl_2$ | 8.93 | 1.37 | 27.33 | 0.10 | 0.05 | 4.54 |
| $CHCl_3$ | 4.90 | 1.45 | 26.53 | 0.15 | 0.02 | 4.96 |
| Toluene | 2.37 | 1.50 | 40.20 | 0.00 | 0.14 | 5.64 |
| $C_6H_6$ | 2.27 | 1.50 | 40.62 | 0.00 | 0.14 | 5.26 |
| $CCl_4$ | 2.23 | 1.46 | 38.04 | 0.00 | 0.00 | 5.37 |

$\varepsilon$—dielectric constant at 298°K, n-Index of refraction at optical frequencies at 298°K.
$\gamma$-$\gamma_m/\gamma^o$; $\gamma_m$—macroscopic surface tension at a liquid-air interface. $\gamma^o = 1$ cal/mol/A$^2$.
$\alpha'$—Abraham's hydrogen bond acidity, $\beta$—Abraham's hydrogen bond basicity.
r—molecular radius in A.

**Table 2**
Electrostatic interaction energy of halogen substituted 3-phenyl 5-amino pyrazole (kJ mol$^{-1}$) in different solvents at 298 K.

| Solvents | 3-(4-bromophenyl)-5 amino pyrazole- | 3-(4-chlorophenyl)-5- amino pyrazole |
|----------|---|---|
| $H_2O$ | −65.86 | −66.11 |
| $CH_3NO_2$ | −62.63 | −63.01 |
| $CH_3OH$ | −62.67 | −63.01 |
| $C_2H_5OH$ | −61.38 | −61.75 |
| Acetone | −60.45 | −60.92 |
| $CH_2Cl_2$ | −55.64 | −55.98 |
| $CHCl_3$ | −48.48 | −48.81 |
| Toluene | −33.32 | −33.54 |
| $C_6H_6$ | −31.78 | −31.59 |
| $CCl_4$ | −31.52 | −31.69 |

**Table 3**
Dispersion energy of halogen substituted 3-phenyl 5-amino pyrazole.(kJ mol$^{-1}$) in different solvents at 298 K.

| Solvents | 3–4 bromophenyl-1H pyrazole-5 amine | 3–4 chlorophenyl-1H pyrazole-5 amine |
|----------|---|---|
| $H_2O$ | −176.01 | −175.60 |
| $CH_3NO_2$ | −192.63 | −174.38 |
| $CH_3OH$ | −175.80 | −175.18 |
| $C_2H_5OH$ | −185.85 | −185.14 |
| Acetone | −185.81 | −185.01 |
| $CH_2Cl_2$ | −190.75 | −190.03 |
| $CHCl_3$ | −214.66 | −213.82 |
| Toluene | −224.01 | −223.07 |
| $C_6H_6$ | −223.74 | −222.86 |
| $CCl_4$ | −217.55 | −216.71 |

here. This may be due to the quadrupolar effects of these solvents. Among the two aromatic solvents, the electrostatic interaction is more negative in toluene than in benzene. This may be due to negative quadrupole moment of benzene and positive quadrupole moment of Toluene.

Dispersion energy also plays an important role in solvation. These values are calculated for the two pyrazole derivatives in various solvents and they are presented in Table 3. Dispersion energy depends upon the polarizability of the solvent molecule, its size, ionization potential and dipole moment. Thus the dispersion energy is higher for a given solute in more polar solvent like water and is less in less polar solvent like Toluene. Plots of dispersion energy against dielectric constant and ionization potential are given in Figs. 2 and 3. In a given solvent, the dispersion energy is less for bromo pyrazole derivative
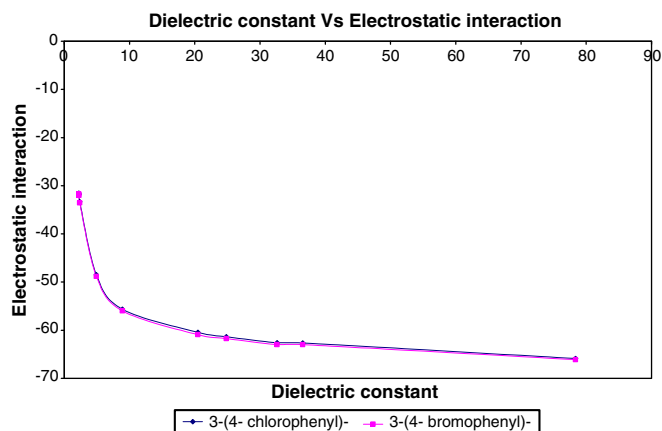


**Fig. 2.** Schematic drawing of Dielectric constants various solvents studied here Vs corresponding Electrostatic interactions of Pyrazole derivatives.
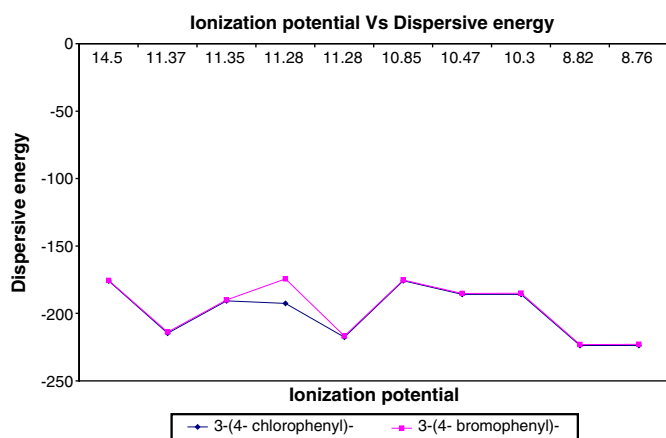
**Ionization potential Vs Dispersive energy**

Fig. 3. Schematic drawing of Ionization Potential of various solvents studied here vs corresponding Dispersive energies of Pyrazole derivatives.

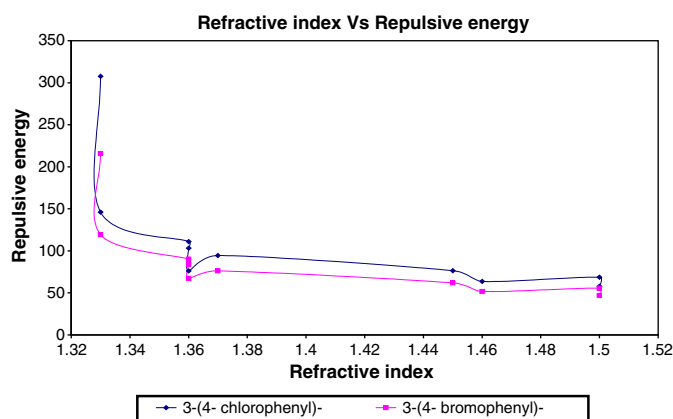**Refractive index Vs Repulsive energy**

Fig. 4. Schematic drawing of Refractive index constants of various solvents studied here vs corresponding Repulsive energies of Pyrazole derivatives.

than the chloro compound. This may be due to larger polarizability of the bromo derivative because of the larger size of bromine atom.

Repulsion energy between solute and solvent molecules is yet another parameter to be considered in solvation analysis. Table 4 contains the computed values of repulsion energies for the two halogenated pyrazoles in different media. Plots of repulsion energy against dielectric constant and refractive index are depicted in Figs. 4 and 5. The repulsion energies are positive in all the solvents as expected and it is reflected for the two solute molecules. It must be noted that the repulsion energy depends upon several properties of solvent such as dielectric constant, refractive index, polarizability and molecular radius. From the data in Table 4, we observed that the repulsive energy of water is more for both solute molecules studied here. This may be due to the least refractive index and molecular radius of the solvent. By comparing the repulsive energies of the chlorinated solvents, the repulsive energies decrease with the refractive index of the corresponding solvent molecules. The combined effect is that the repulsion energy values are varied for the two solute molecules in different solvents. Plots in Fig. 5 also suggest that the refractive of the solvent affects the repulsion energy considerably. The data in Table 5 suggest how different characteristics of solvent affect the free energy of solvation for the two solute molecules. For example, with similar range of refractive index to those of solvent such as ccl4 and a small dielectric constant, it provide more favourable free energy for the two solute molecules. This may be due to the hydrogen bond acidity and basicity of the solvent molecules. Between the two protic solvents, water and methanol, the free energy of solvation is more favorable in methanol. This is due to large value of repulsion energy in water than in methanol. For the solvent acetone, the refractive index is smaller than those of benzene and toluene. In addition, the hydrogen bond basicity parameter for acetone is larger

than those of both benzene and toluene. These two factors result in free energies of solvation of solute molecule and it provides less favorable than those of corresponding free energies of solvation in benzene and toluene. Further, the free energy of solvation is more negative in toluene than in benzene. This may be due to positive quadrupole moment of toluene and negative quadrupole moment of benzene. Thus it may be pointed out that the quadrupole moment also plays role in solvation, especially in the case of less polar solvents.

Solvation effects are essential components of liquid state chemistry. These solvation effects are frequently dominated by electrostatic interaction [11]. Thermodynamically, there is no way to separate electrostatic contribution to the free energy of the solvation. These electrostatic contributions to the free energy of solvation depend on the dielectric constant of the solvent. By comparing the electrostatic contribution listed in Table 2 with dielectric constant of the respective solvent, it is observed that, the electrostatic interaction increases with the increase of dielectric constant. By comparing the electrostatic contribution of the solute molecules, with solvents such as toluene, $C_6H_6$, $CCl_4$, we observed that, there is no much deviation in their values. This may be due to the approximately equal size of the cavity, dispersion and solvent structure. By comparing the electrostatic interactions of all the solvents studied here, water provides more negative than that of the other solvents. This is due to the highest dielectric constant and providing more macroscopic surface tension for the solvent–solute interactions.

In the present investigation, the solute–solvent interaction is mainly of dipole–dipole type of attraction. In order to assess the

**Table 4**
Repulsion energy of 3-4-halo substituted phenyl 1H pyrazole-5 amine in kJ/mol at 298 K.

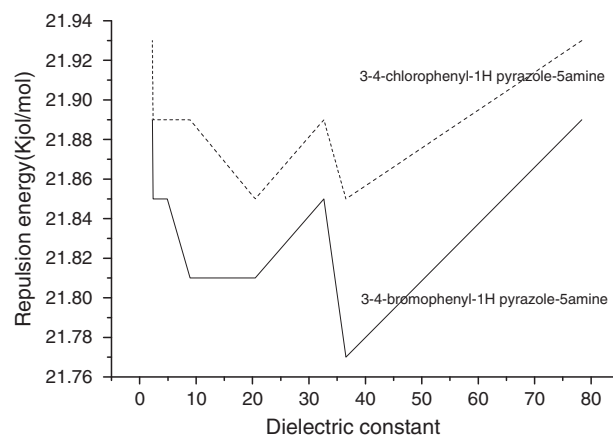| Solvents | 3–4 bromophenyl-1H pyrazole-5 amine | 3–4 chlorophenyl-1H pyrazole-5 amine |
|---|---|---|
| $H_2O$ | 307.56 | 215.60 |
| $CH_3NO_2$ | 110.87 | 90.14 |
| $CH_3OH$ | 146.08 | 119.32 |
| $C_2H_5OH$ | 103.12 | 83.86 |
| Acetone | 76.07 | 67.11 |
| $CH_2Cl_2$ | 94.37 | 76.20 |
| $CHCl_3$ | 76.33 | 61.88 |
| Toluene | 57.90 | 46.89 |
| $C_6H_6$ | 68.75 | 55.72 |
| $CCl_4$ | 63.76 | 51.66 |

Fig. 5. Schematic drawing of Dielectric constants of various solvents studied here vs corresponding Repulsive energies of Pyrazole derivatives.

**Table 5**

| Solvents | 3–4 bromophenyl-H pyrazole-5 amine | 3–4 chlorophenyl-1H pyrazole-5 amine |
|---|---|---|
| a. Free energy of 3-4-halo substituted phenyl 1H pyrazole-5 Amine in kJ/mol at 298 K [includes ES + DISP + REP which are in the Self-Consistent Wave function]. | | |
| $H_2O$ | −65.69 | −13.86 |
| $CH_3NO_2$ | −144.36 | −148.09 |
| $CH_3OH$ | −92.40 | −118.86 |
| $C_2H_5OH$ | −144.07 | −163.03 |
| Acetone | −170.19 | −178.86 |
| $CH_2Cl_2$ | −152.06 | −169.31 |
| $CHCl_3$ | −186.86 | −200.67 |
| Toluene | −199.42 | −209.72 |
| $C_6H_6$ | −186.81 | −199.08 |
| $CCl_4$ | −185.31 | −196.74 |
| b. Free energy of 3-4-halo substituted phenyl 1H pyrazole-5 amine in kJ/mol at 298 K [includes ES + DISP + REP + CAV, cavitation is not in SCF energy]. | | |
| $H_2O$ | 179.75 | 124.77 |
| $CH_3NO_2$ | −45.22 | −50.16 |
| $CH_3OH$ | −8.83 | −37.05 |
| $C_2H_5OH$ | −58.32 | −79.00 |
| Acetone | −87.34 | −97.64 |
| $CH_2Cl_2$ | −65.82 | −84.82 |
| $CHCl_3$ | −102.70 | −118.23 |
| Toluene | −105.88 | −118.02 |
| $C_6H_6$ | −92.03 | −106.22 |
| $CCl_4$ | −97.80 | −110.95 |

solute–solvent interaction, the dipole moment and induced dipole moment values are calculated and presented in Tables 6 and 7. The induced dipole moment of 3–4 halo substituted phenyl, 1H pyrazole 5-amine in $H_2O$ are higher than those of other solvents. These values indicate a strong solute–solvent interaction mainly in mixtures of 3–4 halo substituted phenyl, 1 H pyrozole 5-amine and $H_2O$. This is also supported by higher electrostatic interaction in this medium. The geometry and charge in the presence of solvent by polarizability, and hence solvation alters the electrostatic properties of the solute by changing the geometry and by polarizing its charged distribution. The polarization effect by the solvent is reflected by the charge in

**Table 6**
Dipole moments of 3-4-halo substituted phenyl 1H pyrazole-5 amine in Debyes.

| Methods | 3–4 bromophenyl-1H pyrazole-5 amine | 3–4 chlorophenyl-1H pyrazole-5 amine |
|---|---|---|
| AM1 | 5.06 | 4.93 |
| PM3 | 4.95 | 4.85 |
| MNDO | 5.05 | 5.16 |
| Ab initio | 6.12 | 6.28 |

**Table 7**
Induced dipole moments of 3-4-halo substituted phenyl 1H pyrazole-5 amine in Debyes.

| Solvents | 3–4 bromophenyl-1H pyrazole-5 amine | 3–4 chlorophenyl-1H pyrazole-5 amine |
|---|---|---|
| $H_2O$ | 7.02 | 7.34 |
| $CH_3NO_2$ | 7.22 | 7.40 |
| $CH_3OH$ | 7.18 | 7.38 |
| $C_2H_5OH$ | 7.21 | 7.38 |
| Acetone | 7.23 | 7.37 |
| $CH_2Cl_2$ | 7.12 | 7.28 |
| $CHCl_3$ | 7.02 | 7.16 |
| Toluene | 6.77 | 6.89 |
| $C_6H_6$ | 6.73 | 6.86 |
| $CCl_4$ | 6.73 | 6.85 |

**Table 8**
Enthalpy, entropy and Gibb's Free energy of 3-4-halo substituted phenyl 1H pyrazole-5 Amine in kJ/mol at 298 K. (Pierotti Method).

| Solvents | | 3–4 bromophenyl-1H pyrazole-5 amine | 3–4 chlorophenyl-1H pyrazole-5 amine |
|---|---|---|---|
| $H_2O$ | $\Delta H$ | 14.36 | 13.98 |
| | $\Delta G$ | 84.91 | 82.69 |
| | $\Delta S$ | 0.237 | 0.230 |
| $CH_3NO_2$ | $\Delta H$ | 66.65 | 64.85 |
| | $\Delta G$ | 68.62 | 66.86 |
| | $\Delta S$ | 0.006 | 0.007 |
| $CH_3OH$ | $\Delta H$ | 47.02 | 45.76 |
| | $\Delta G$ | 58.10 | 56.60 |
| | $\Delta S$ | 0.037 | 0.036 |
| $C_2H_5OH$ | $\Delta H$ | 49.02 | 47.69 |
| | $\Delta G$ | 58.15 | 56.64 |
| | $\Delta S$ | 0.031 | 0.030 |
| Acetone | $\Delta H$ | 62.00 | 60.37 |
| | $\Delta G$ | 58.15 | 56.64 |
| | $\Delta S$ | 0.031 | 0.030 |
| $CH_2Cl_2$ | $\Delta H$ | 62.00 | 60.37 |
| | $\Delta G$ | 58.11 | 56.65 |
| | $\Delta S$ | −0.023 | −0.013 |
| $CHCl_3$ | $\Delta H$ | 57.23 | 55.68 |
| | $\Delta G$ | 55.64 | 54.26 |
| | $\Delta S$ | −0.005 | −0.004 |
| Toluene | $\Delta H$ | 62.50 | 60.83 |
| | $\Delta G$ | 61.50 | 59.91 |
| | $\Delta S$ | −0.003 | −0.003 |
| $C_6H_6$ | $\Delta H$ | 78.96 | 76.83 |
| | $\Delta G$ | 63.18 | 61.54 |
| | $\Delta S$ | −0.053 | −0.051 |
| $CCl_4$ | $\Delta H$ | 64.10 | 62.38 |
| | $\Delta G$ | 57.40 | 55.97 |
| | $\Delta S$ | −0.022 | −0.021 |

**Table 9**
Enthalpy, entropy and Gibb's free energy of 3-4-halo substituted phenyl 1H pyrazole-5 amine in kJ/mol at 298 K. (Sinanoglu Method).

| Solvent | | 3–4 bromophenyl-1H pyrazole-5 amine | 3–4 chlorophenyl-1H pyrazole-5 amine |
|---|---|---|---|
| $H_2O$ | $\Delta H$ | 147.80 | 143.65 |
| | $\Delta G$ | 92.44 | 89.84 |
| | $\Delta S$ | 0.1867 | −0.180 |
| $CH_3NO_2$ | $\Delta H$ | 91.90 | 89.84 |
| | $\Delta G$ | 42.99 | 41.70 |
| | $\Delta S$ | 0.1641 | 0.1590 |
| $CH_3OH$ | $\Delta H$ | 61.50 | 59.99 |
| | $\Delta G$ | 32.02 | 31.23 |
| | $\Delta S$ | −0.099 | −0.096 |
| $C_2H_5OH$ | $\Delta H$ | 60.83 | 59.32 |
| | $\Delta G$ | 31.57 | 30.77 |
| | $\Delta S$ | −0.098 | −0.095 |
| Acetone | $\Delta H$ | 13.31 | 12.73 |
| | $\Delta G$ | 18.55 | 17.71 |
| | $\Delta S$ | 0.017 | 0.016 |
| $CH_2Cl_2$ | $\Delta H$ | 17.04 | 16.33 |
| | $\Delta G$ | 23.40 | 22.44 |
| | $\Delta S$ | 0.021 | 0.020 |
| $CHCl_3$ | $\Delta H$ | 15.57 | 14.82 |
| | $\Delta G$ | 20.72 | 19.76 |
| | $\Delta S$ | 0.017 | 0.016 |
| Toluene | $\Delta H$ | 64.02 | 61.83 |
| | $\Delta G$ | 29.43 | 28.39 |
| | $\Delta S$ | −0.116 | −0.112 |
| $C_6H_6$ | $\Delta H$ | 65.10 | 62.88 |
| | $\Delta G$ | 29.68 | 28.64 |
| | $\Delta S$ | −0.119 | −0.114 |
| $CCl_4$ | $\Delta H$ | 59.66 | 57.57 |
| | $\Delta G$ | 27.30 | 26.37 |
| | $\Delta S$ | −0.108 | −0.104 |

molecule dipole moment in the solvent–solute interaction [12,13]. The change in dipole moment that is induced dipole moment can be reasonably estimated using STO-6-31G in ab-initio calculations. The solvation effect leads to a systematic increase in dipole moment. In general, there is a good agreement with the dipole moments calculated by AMI, PM3, MNDO and ab-initio calculation.

The cavitational free energy is an important contribution to the solvation free energy. It is of basic importance in the usual partition that is based on the different nature of solute–solvent interactions. The cavitational energies in Tables 8 and 9 were obtained in the present calculation. They have reasonable accuracy from the formulas given by the Sinanoglu and Pierotti method. The values calculated using these formulas are different [14,15]. The cavitation free energy is positive. The cavitation enthalpies are also positive, but the cavitation entropies are positive or negative depending on the system. These observations show that there is a strong interaction between solvents and solutes and is directly related to the polarity of the medium.

## 4. Conclusion

Quantum mechanical solvation analysis is carried out for two industrially important pyrazole amines. The PCSM model for pyrazole derivatives in different solvents lends itself to specific parametrization for more complicated condensed phases. The electrostatic interaction energy correlates well with the dielectric constant of the solvent.

However, dispersion energy correlation is satisfactory only in certain sets of solvents. The repulsion energy of solute molecule depends upon more than one physical property of the solvent. Free energy of solvation values is also reported. The cavitation enthalpies and entropies are computed for the two systems. It is anticipated that these features will make useful tools in developing the two pyrazole amines as effective corrosion inhibitors.

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