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Research Article

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Theoretical study of the effects of solvents on energy components of indole

K. K. Srivastava[a], Shubha Srivastava[b], Md. Tanweer Alam[a] and Rituraj[a]

[a]Department of Chemistry, Vinoba Bhave University, Hazaribagh
[b]Department of Chemistry, KBW College, Hazaribagh

ABSTRACT

Quantum mechanical calculations of different energies components of indole in ground state were carried out by DFT method, in isolated state and in various solvents to study the effects of solvents on various energy components. The solvation energy, chemical potential, hardness, electrophilicity of indole were calculated with the help of computed HOMO-LUMO gap of indole in different solvents in ground state. The plots of energy components and thermodynamic parameters against the dielectric constant of the corresponding solvents were found to be polynomial of higher order.

Keyword: DFT, Ground state, indole, energy components, HOMO, LUMO, solvation energy, dielectric constants.

INTRODUCTION

Physical and chemical property of a molecule depends on the structure and the various kinds of energies of the molecule. Chemical reaction of a molecule in solution is affected by the nature of the solvent; solvent affects not only the energies of HOMO and LUMO of the molecule, but also other kinds of energies. Energy of a molecule may be considered to have various energy components such as reaction field energy, total zero-electron terms, Nuclear-nuclear, Nuclear-solvent, total one-electron terms, Electron-nuclear, Electron-solvent, Kinetic, total two-electron terms, Electronic energy, total quantum mech. energy, Gas phase energy, Solution phase energy, total solute energy, total solvent energy, Solute cavity energy, Reorganization energy, Solvation energy total internal energy , total enthalpy, total Gibbs free energy, and zero point energy. indole is a white solid, It is used in preparation of Charge transfer complexes[1-10] of various utilities. indole, is one of the most widely distributed heterocyclic compounds in nature. The word indole comes from the word India and a deep blue pigment, indigo, was imported to England from India as early as the sixteenth century[11] .

Keeping in view the utility of indole various kinds of energies of indole in the ground state in gaseous phase and in different kinds of solvents have been theoretically calculated in this paper.

EXPERIMENTAL SECTION

Computational methods

The initial structure of indole was built with Chem-Draw ultra8.0 and the structure was optimized on Chem3D ultra 8.0. The structure was exported to Maestro 9.3 of Schrodinger 2012 version. The optimization of the structure was done on the Jaguar panel of the Maestro 9. The DFT-BPLY-3 method of theory was chosen. 6-31g $^{\#\#}$ basis set was selected and 255 basis functions were created for calculation. The molecule was assigned net zero charge and singlet multiplicity. In the solvent menu of the jaguar panel PBF solver was used for optimization of the structure in both the gaseous and solution phase. The optimization the gaseous state and in the different solutions were done in ground state of the molecule.

Geometry optimization

for perform a geometry optimization one needs to guess at the geometry and the direction in which to search, a set of co-ordinates to optimize, and some criteria for when to optimization is complete. The search direction is obtained from the gradient of the energy and the initial Hessian. An initial Hessian(second derivative matrix or force constant matrix) and the gradient are used to define search direction that should result in lowering of energy. The choice if co-ordinate systems have a substantial impact on the convergence of the optimization. The ideal set of Co-ordinate is one in which the energy change along each co-ordinate is maximized, and the coupling between co-ordinates is minimized. Jaguar chooses the coordinate system by default. It has two options Cartesian and z-matrix that produces an efficient optimization requires an understanding of the coupling between simple internal co-ordinates

For optimization to minimum energy structures , the convergence criterion for SCF calculation is chosen to assure accurate analyses gradients. For these jobs, a wave function is considered converged when the root mean square (RMS) change in density matrix element is less than the RMS density matrix element change criterion, whose default value is $5.0x10^{-6}$. The geometry is considered to have converged when the energy of successive geometries and the elements of analyze gradients of the energy and the displacement has met convergence criteria. For optimization in solution, the default criteria are multiplied by a factor of three, and a higher priority is given to the energy convergence criterion. Thus if the energy change criterion is met before the gradient and displacement criteria have been met, the geometry is considered converged. The optimized geometry may not have a local minimization energy i,e it may have reside on a saddle. To know whether it is global minimization we look for the value of vibrational frequencies. If all the vibrational frequencies are real (i,e +ve) then it represents global minimum , but if any of the vibrational frequencies is negative (i,e imaginary) then it is local minimum.

Performing a solvation calculation

It involves several iterations in which the wave functions for the molecule in the gas phase are calculated. The program ch performs electrostatic potential fitting, which represents the wave function as a set of point charges on the atomic centers. The interactions between the molecule and the solvent are evaluated by Jaguar's Poisson-Boltzmann solver [12-13], which fits the field produced by the solvent dielectric continuum to another set of point charges. These charges are passed back to scf, which performs a new calculation of the wave function for the molecule in the field produced by the solvent point charges. Electrostatic potential fitting is performed on the new wave function, the solvent-molecule interactions are reevaluated by the Poisson-Boltzmann solver, and so on, until the solvation free energy for the molecule converges.

For solvation calculations on neutral systems in water the program pre evaluates the Lewis dot structure for the molecule or system and assigns atomic van der Waals radii accordingly. These van der Waals radii are used to form the boundary between the solvent dielectric continuum and the solute molecule. The Lewis dot structure and van der Waals radii information both appear in the output from the program pre. The radii are listed under the heading "vdw2" in the table of atomic information below the listing of non-default options. After the pre output, the usual output appears for the first, gas-phase calculation, except that the energy breakdown for the scf output also describes the electron-nuclear and kinetic contributions to the total one-electron terms in the energy, as well as the virial ratio –V/T, where V is the potential energy and T is the kinetic energy. This ratio should be –2 if the calculation satisfies the virial theorem. After the first scf output, the output from the first run of the program ch appears. Since performing a solvation calculation enables electrostatic potential fitting to atomic centers, the usual output for that option is included every time output from the program ch appears in the output file. The post program writes out the necessary input files for the Poisson-Boltzmann solver; this step is noted in the output file. The next output section comes from the Poisson-Boltzmann solver. The output includes information on the area (in Å2) of the molecular surface formed from the intersection of spheres with the van der Waals radii centered on the various atoms; the reaction field energy in kT (where T = 298 K), which is the energy of the interaction of the atom-centered charges with the solvent; the solvent-accessible surface area (in Å2), which reflects the surface formed from the points whose closest distance from the molecular surface is equal to the probe radius of the solvent; and the cavity energy in kT, which is computed to be the solvation energy of a nonpolar solute whose size and shape are the same as those of the actual solute molecule. The output from the program solv follows the Poisson-Boltzmann solver results, giving the number of point charges provided by the solver to model the solvent, the sum of the surface charges, the nuclear repulsion energy already calculated by Jaguar, the nuclear-point charge energy representing the energy of interaction between the molecule's nuclei and the solvent point charges, and the point-charge repulsion energy, which is calculated but not used because it is irrelevant to the desired solvation results. After this output, the output for the second solvation iteration begins. The output from scf comes first, giving the results for the molecule-and-solvent-point-charges system. Total quantum mech. energy corresponds to the final energy from the scf energy table for that iteration, and includes the entire energies for the molecule-solvent interactions. The output next includes the gas phase and the solution phase energies for the molecule, since these terms are, of course, necessary for solvation energy calculations. The first solution phase energy component is the total solute energy, which includes the nuclear-nuclear, electron nuclear, kinetic, and two-electron terms, but no terms involving the solvent directly. The second component of the solution phase energy is the total solvent energy, which is computed as half of the total of the nuclear-solvent and electron-solvent terms, since some of its effect has already changed the solute energy. Third, a solute cavity term, which computes the solvation energy of a nonpolar solute of identical size and shape to the actual solute molecule, as described in reference [12], is included. This is only done for water as solvent. The last solution phase energy component (shown only if it is nonzero) is term (T), the first shell correction factor, which depends on the functional groups in the molecule, with atoms near the surface contributing most heavily. Finally, the list ends with the reorganization energy and the solvation energy. The reorganization energy is the difference between the total solute energy and the gas phase energy, and does not explicitly contain solvent terms. The final solvation energy is calculated as the solution phase energy described above minus the gas phase energy. The solvation energy is listed in Hartrees and in kcal/mol,

Chemical potential (μ)*[14]* HOMO as ionization energy(IE) and LUMO as electron affinity (EA) have been used for calculating the electronic chemical potential (m) which is half of the energy of HOMO and LUMO

$\mu= (E_{HOMO}+E_{LUMO})/2$

Hardness (η)[15]

The hardness (h) as half of the gap energy of HOMO and LUMO has been calculated using the following equation

$Gap= E_{HOMO}-E_{LUMO}$

$\eta = Gap/2$

Electrophilicity (ω)[16]

The electrophilicity (ω) has been calculated using equation

$\omega= \mu^2/2\ \eta$

Reaction field energy (in KT)

This gives us the energy of the interactions of atom centered charges with the solvent; Solvent accessible surface area (SASA in $A^{0\,2}$) reflects the surface formed form the points whose closest distance from the molecular surface is equal to the probe radius of the solvent.

Cavity energy (in KT)

This is solvation energy of a non-polar solute whose size and shape are the same as those of actual solute molecule.

Quantum mechanical energy

This term corresponds to the entire energies for the molecule solvent interaction and is equal to the sum of total zero electron terms and electronic energy.

Reorganisation energy

This is the difference between the total solute energy and the gas phase energy, and does not explicitly contain solvent terms.

RESULTS AND DISCUSSION

Solvent parameters:
Table-1 summarizes the solvent parameters such as dielectric constants, molecular weight, density and polarity of the solvents used for the present theoretical study by Poisson-Boltzmann solver. In table-3 the energy components calculated by DFT method on Jaguar panel of the Maestro 9.3 with 6-31g$^{\#\#}$ basis set utilizing 255 basis functions for indole in the ground state have been incorporated. The pictures of HOMO and LUMO of indole in gaseous state and in various solvents have been shown in fig.1

An electron acceptor represents the ability to obtain an electron in the LUMO and HOMO represents the ability to donate electron.

The ***(E_{HOMO}-E_{LUMO}) gap*** is an important scale of stability [17] and compounds with large (E_{HOMO}-E_{LUMO}) gap value tend to have higher stability. The perusal of the table-2 indicates the stability of indole increases in the solvents in the ground state in the order;

Acetonitrile>water>methanol>dmf>dichloromethane>THF>chloroform>benzene>carbontetrachloride>cyclohexane

Therefore, if it is desired to stabilize indole in the ground state then out of ten solvents studied acetonitrile is the best.

The plot of the energy gap between HOMO and LUMO versus dielectric constant of solvents in ground state have been shown in the fig 2. The dependence of the energy gap (y) on dielectric constant (x) in ground state follows the equation $y = 4E\text{-}09x^5 - 6E\text{-}07x^4 + 4E\text{-}05x^3 - 0.0009x^2 + 0.0093x - 5.3254$,($R^2 = 0.9936$)

The chemical potentials(μ) of indole in the ground state increases in the order;

Cyclohexane>carbontetrachloride>benzene>chloroform>THF>dichloromethane>water>dmf>methanol>acetonitrile.

Therefore, if it is desired to have highest chemical potential, indole in the ground state, then out of ten solvents studied cylohexane is the best.

The plot of the chemical potential versus dielectric constant of solvents in ground state have been shown in the fig3. The dependence of the chemical potential (y) on dielectric constant(x) follows the equation $y = -2E\text{-}08x^5 + 3E\text{-}06x^4 - 0.0002x^3 + 0.0042x^2 - 0.0443x - 2.7547$,($R^2 = 0.9987$)

The hardness(η) of indole increases in the ground state in the following order;

Cyclohexane>carbontetrachloride=benzene>chloroform> THF=dichloromethane>dmf=methanol>water=acetonitrile

The indole molecule has been found to be hardest in cyclohexane in the ground state. Therefore, if it is desired to increased hardness of indole to largest extent in the ground state then out of ten solvents studied cyclohexane is the best

The plot of hardness versus dielectric constant of solvents in the ground state have been shown in the fig4. The dependence of hardness (y) on dielectric constant(x) follows $y = -2E\text{-}09x^5 + 3E\text{-}07x^4 - 2E\text{-}05x^3 + 0.0004x^2 - 0.0047x + 2.6627$,($R^2 = 0.9936$)

The electrophilicity $(\omega)$of indole molecule has been found to possess high electrophilicity in the ground in dmf, methanol and acetonitrile.

Therefore, if it is desired to increase electrophilicity of indole to larger extent in the ground state, then out of ten solvents dmf , methanol and acetonitrile are the best.

The plot of electrophilicity (y) versus dielectric constant(x) of solvents in ground state have been shown in the fig5. The dependence of the electrophilicity on dielectric constant follows the $y = -1E\text{-}11x^6 + 3E\text{-}09x^5 - 2E\text{-}07x^4 + 5E\text{-}06x^3 - 7E\text{-}05x^2 + 0.0006x + 0.0135$($R^2 = 0.9997$) in the ground.

The Solvation energy of indole in the ground state are in the following order;

Acetonitrile=methanol>dmf>dicloromethane>THF>chloroform> water>benzene >carbontetrchloride> cyclohexane.

Thus, it was found that indole is most highly solvated in the ground state in acetonitrile and methanol than other studied solvents.

The plot of the solvation energy versus dielectric constant of solvents in ground state have been shown in the fig.6. The dependence of the solvation energy(y) on dielectric constant(x) follows

$y = -8E\text{-}07x^5 + 0.0001x^4 - 0.008x^3 + 0.1924x^2 - 1.9299x + 0.0378$
$R^2 = 0.9992$

Table1. Physical parameters of various solvents

Solvents	M.W g/mol	Density g/ml	Dielectric constant	Probe radius A^O
1.Acetonitrile	37.5	0.777	37.5	2.19
2.Benzene	78.12	0.87865	2.284	2.6
3.Carbontetrachloride	153.82	1.594	2.238	2.67
4.Chloroform	119.38	1.4832	4.806	2.52
5.Cyclohexane	84.16	0.77855	2.023	2.78
6.Dichloromethane	84.93	1.3266	8.93	2.33
7.DMF	73.09	0.944	36.7	2.49
8.methanol	32.04	0.7914	33.62	2
9.THF	72.11	0.8892	7.6	2.52
10.Water	18.02	0.99823	80.37	1.4

Table 2. Values of HOMO-LUMO energy, μ, η, ω of indolecalculated by DFT -B3LYP/6-31G- level

Solvents HOMO, LUMO energy in eV	HOMO	LUMO	Gap	μ=Ehomo+Elumo/2	η=(Lumo-Homo)/2	Electrophilicity $\omega=\mu^2/2\eta$
acetonitrile	-5.595	-0.312	-5.283	-2.953	2.642	0.016
benzene	-5.491	-0.183	-5.308	-2.837	2.654	0.014
carbontetrachloride	-5.490	-0.181	-5.309	-2.835	2.654	0.014
chloroform	-5.539	-0.241	-5.297	-2.890	2.649	0.015
cyclohexane	-5.481	-0.171	-5.310	-2.826	2.655	0.014
dichlormethane	-5.568	-0.276	-5.291	-2.922	2.646	0.015
dmf	-5.593	-0.307	-5.287	-2.950	2.643	0.016
methanol	-5.594	-0.309	-5.286	-2.951	2.643	0.016
THF	-5.559	-0.266	-5.292	-2.913	2.646	0.015
Water	-5.571	-0.287	-5.284	-2.929	2.642	0.015

Table 2. . Values of energy components of indole in gaseous state and various solvents in ground state calculated by DFT -B3LYP/6-31G- level

Ground state Energy components , in eV	Gas-phase	Acetonitrile	Benzene	Carbon tetrachloride	Chloroform	Cyclohexane	Dichloro methane	dmf	methanol	THF	Water
(A)Total zero electon terms		10881.84	10888.27	10884.28	10883.65	10883.82	10882.67	10882.86	10882.89	10882.96	10883.52
(B)Nuclear-nuclear	0.00	10863.83	10880.69	10876.89	10871.27	10877.27	10867.48	10865.11	10864.99	10868.55	10867.72
(C)Nuclear-solvent		18.01	7.58	7.40	12.37	6.56	15.19	17.75	17.90	14.41	15.80
(E)Total one electron terms	-34916.26	-34904.46	-34925.07	-34912.32	-34909.75	-34911.61	-34906.89	-34906.57	-34906.60	-34907.82	-34908.57
(F)Electron-nuclear		-44687.58	-44723.77	-44707.62	-44699.37	-44707.83	-44693.30	-44690.10	-44689.96	-44695.09	-44694.31
(G)Electron-solvent		-18.84	-7.90	-7.72	-12.93	-6.84	-15.88	-18.57	-18.73	-15.07	-16.57
(H)Kinetic		9801.96	9803.01	9803.02	9802.56	9803.06	9802.29	9802.10	9802.10	9802.34	9802.31
(I)Total two electron terms	14130.81	14121.70	14127.48	14127.56	14125.40	14127.34	14123.41	14122.79	14122.78	14124.08	14124.18
(L)Electronic energy (E+I)	-20785.44	-20782.76	-20784.76	-20784.76	-20784.34	-20784.27	-20783.48	-20783.79	-20783.82	-20783.74	-20784.40
(N)Total quantum mechanical energy(A+L)	-9900.17	-9900.93	-9900.49	-9900.48	-9900.70	-9900.45	-9900.81	-9900.92	-9900.93	-9900.78	-9900.88
(O)Gas phase energy		-9900.17	-9900.17	-9900.17	-9900.17	-9900.17	-9900.17	-9900.17	-9900.17	-9900.17	-9900.17
(P)Solution phase energy(Q+R+S)		-9900.51	-9900.32	-9900.32	-9900.42	-9900.30	-9900.46	-9900.51	-9900.51	-9900.45	-9900.38
(Q)Total solute energy(N-C-G)		-9900.10	-9900.16	-9900.16	-9900.13	-9900.16	-9900.12	-9900.10	-9900.10	-9900.12	-9900.10
(R)Total solvent energyC/2+G/2)		-0.41	-0.17	-0.16	-0.28	-0.14	-0.35	-0.41	-0.41	-0.33	-0.39
(S)Solute cavity energy	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.11
(U)Reorganization energy(Q-O)		0.07	0.01	0.01	0.04	0.01	0.05	0.07	0.07	0.05	0.07
(V)solvation energy(P-O) (kj/mol		-7.90	-3.51	-3.43	-5.64	-3.06	-6.76	-7.86	-7.90	-6.51	-4.83

Figure1.Picture of HOMO-LUMO of indolin the ground state in gaseous and ten various solvents

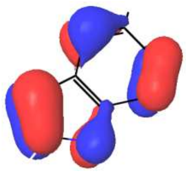
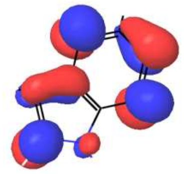
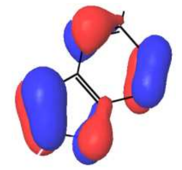
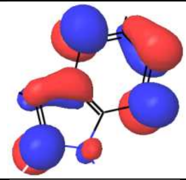
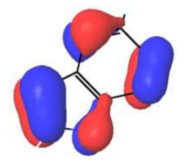
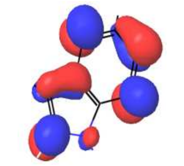
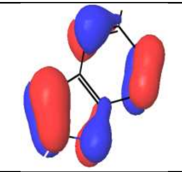
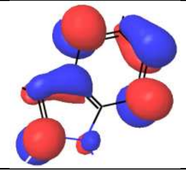
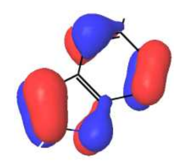
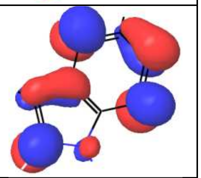
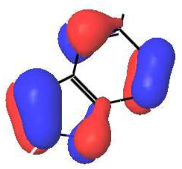
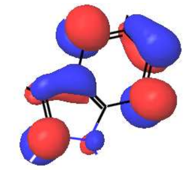
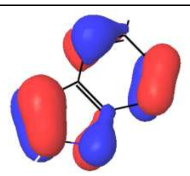
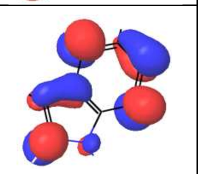
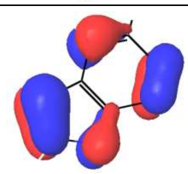
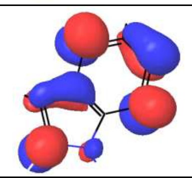
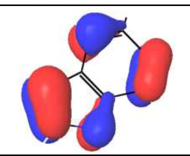
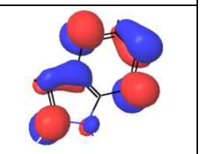
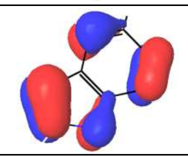
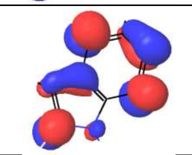
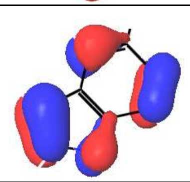
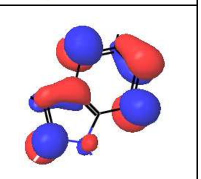
State	HOMO	LUMO	State	HOMO	LUMO
Gaseous state			dichloromethane		
cyclohexane			methanol		
carbontetrchloride			DMF		
Benzene			acetonitrile		
chloroform			water		
THF					

Figure 2. Effect of dielectric constant on the HOMO-LUMO gap of indole in the GS

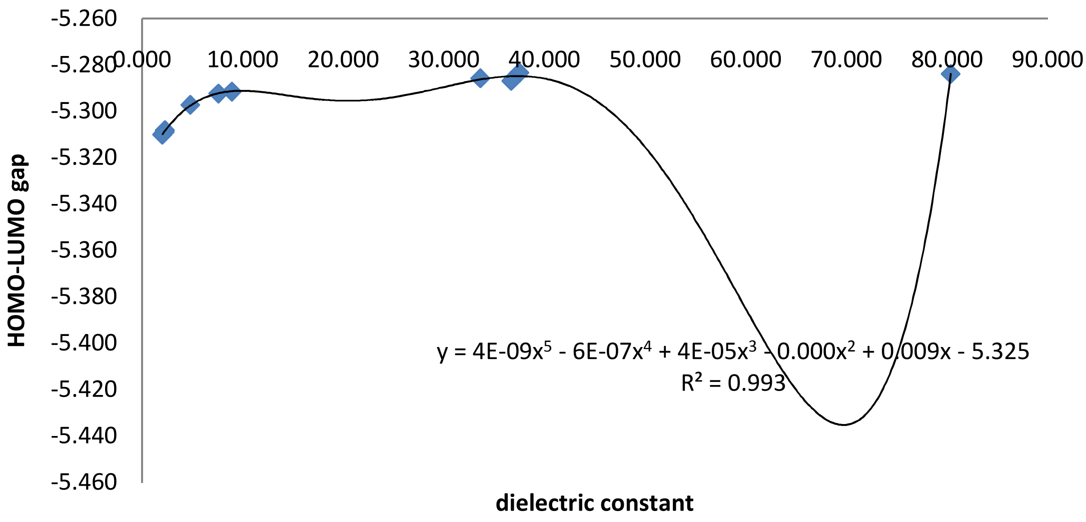


Figure 3.Effect of dielectric constant on the chemical potential of indole in the GS

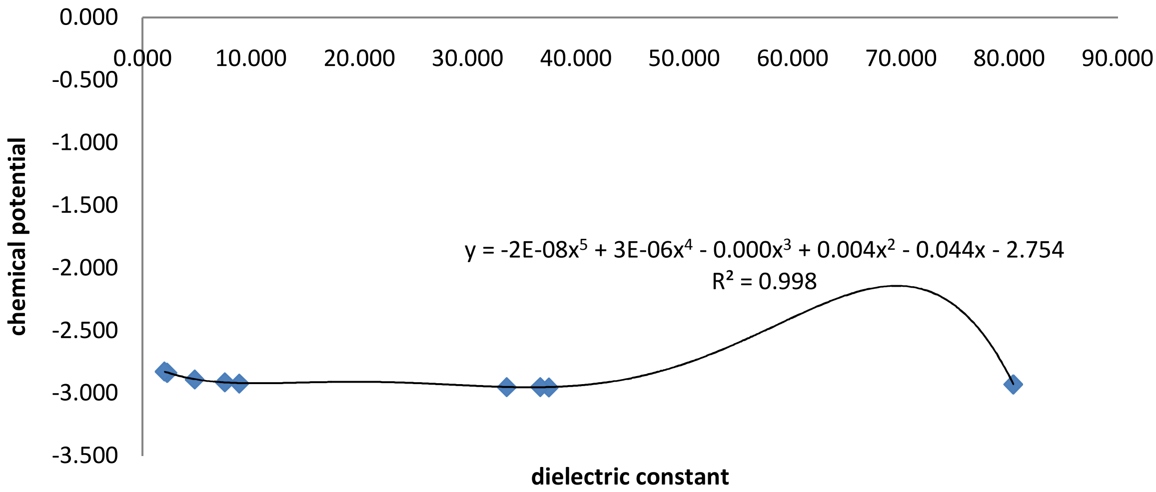


Figure 4.Effect of dielectric constant on the hardness of indole in the GS

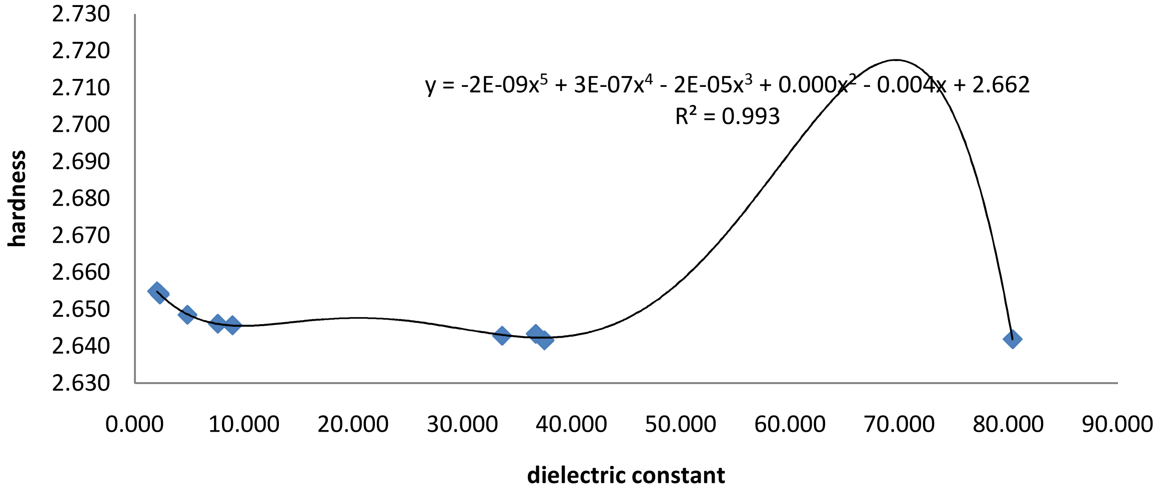


Figure 5.Effect of dielectric constant on the electrophilicity of indole in the GS

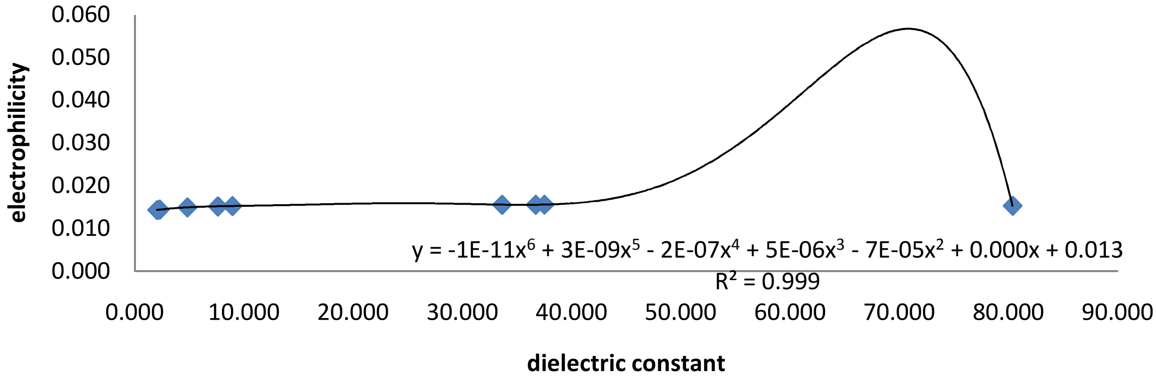
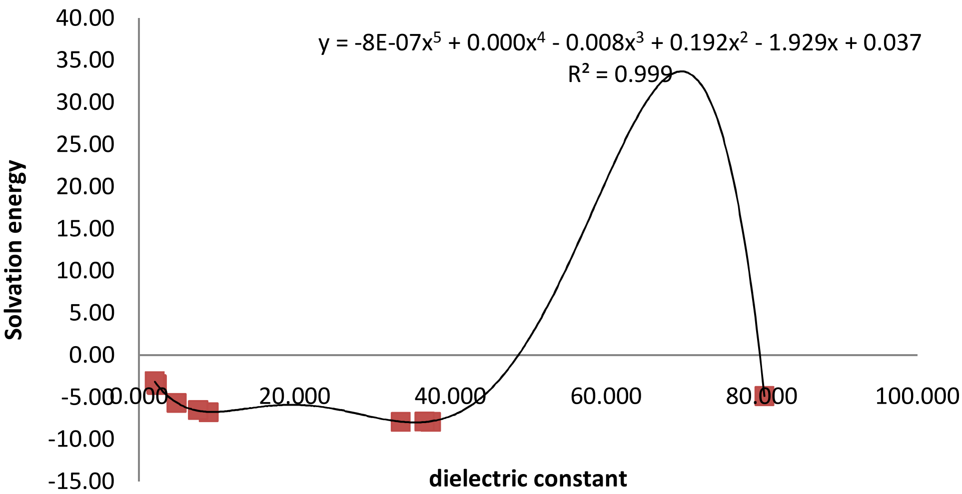


Figure 6.Effect of dielectric constant on the solvation energy of indole in the GS



CONCLUSION

The present study on solvent effect on the energy components of indole in ground state by ten different solvents has lead us to conclude it is highly solvated in acetonitrile and methanol while lowest in cyclohexane. It has been found that indole is most hard, in cyclohexane and least hard in water and acetonitrile. The chemical potential of indole is found to be highest in cyclohexane and lowest in acetonitrile.

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