

Thermodynamic and Theoretical solvation parameters for 2-amino-4,5-dimethylthiophene-3-carboxamide (ADTC) in Ethanol and Mixed EtOH-H₂O solvents

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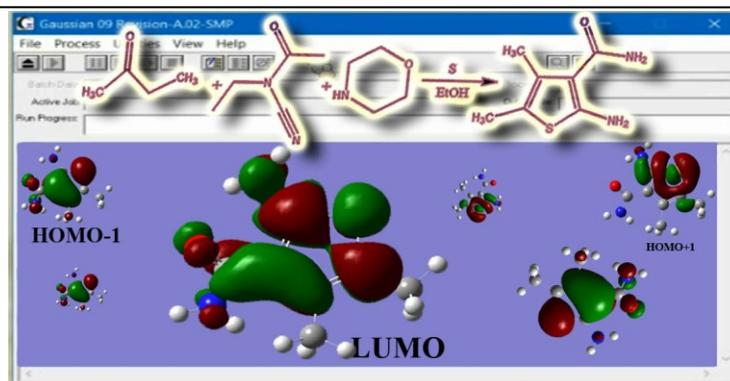
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HIGHLIGHTS

- Experimental evaluation of the thermodynamic parameters from solubility measurements.
- Theoretical calculation of the thermodynamic parameters of the used material.
- Trying to explain the experimental values theoretically.

GRAPHICAL ABSTRACT



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ABSTRACT

The molar solubility for 2-amino-4,5-dimethylthiophene-3-carboxamide (ADTC) in pure ethanol and mixed ethanol (EtOH)- water solvents were measured at five different temperatures, 293.15, 298.15, 303.15, 308.15, and 313.15 K in the used mixed solvents, the solubility were increase by increase in the mole fraction of ethanol in the mixtures and increase of temperature due to more solvation parameters. All the solvation and thermodynamic parameters for ADTC in mixed EtOH+ H₂O solvents were evaluated like solubility products, Gibbs free energies, enthalpies and entropies of solvation and discussed. Theoretical calculations for (ADTC) were done quantum mechanically by using Gaussian on set of calculations in ethanol for evaluating the different thermodynamic parameters.

1. Introduction

Co-solvents (any solvent other than the first solvent) are known to affect the solubility of solutes in solutions. Theory of effects of co-solvents is desirable in order to understand the molecular interactions for changes in

solubility and improve the properties of solutions [1]. The Kirwood – Buff theory (KBT) of solutions [2] has been used to explain the effects of co-solvents on the solubility of solutes in terms of intermolecular distributions [2, 3]. KBT is an exact theory of solution mixtures and provide information for solute understanding effects [4]. The general idea for solubility of molecules to explain the local

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microscopic experimental results. Also studying the intermediates for salvation processes are also needed. Also explaining the chemical potentials of the solute can also be expressed by statistical thermodynamic calculations [3, 4]. Studies for a quantitative description of metal ion-solvent binding are of immense importance in various fields of chemistry, physics and biology, as well as in the technological development of various practical separation processes. The subject has drawn across the board consideration [5-14].

2. Experimental

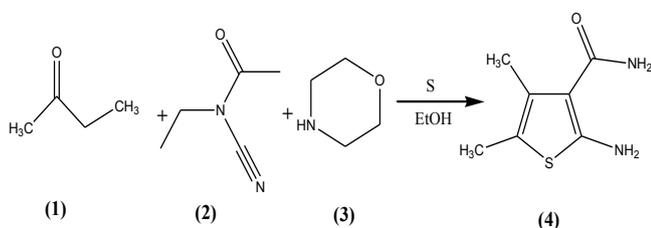
2.1. Materials

The chemicals used 2-butanone, ethyl cyanoacetamide; sulfur and morpholine are provided from Sigma Aldrich chemical company. All chemicals are used without purification to reserve them in their states. Absolute ethanol provided from El-Nasr Chemical and Pharmaceutical Company was used. High conductivity water was used.

2.2. Synthesis

The starting 2-amino-4,5-dimethylthiophene-3-carboxamide (ADTC) **4** was obtained via Gewald reaction by condensation of 2-butanone **1** with ethyl cyanoacetamide **2** in the presence of elemental sulphur and morpholine **3** (base) as in [Scheme 1](#).

The structures were confirmed by various spectroscopic techniques, including IR, ¹H NMR and mass spectroscopy. The IR spectra of compound showed characteristic absorption bands in the region within $\nu = 3411-3163 \text{ cm}^{-1}$ due to the stretching vibrations of 2 NH₂ groups. The bands in the region within $\nu = 1670 \text{ cm}^{-1}$ are due to the stretching vibrations of carbonyl group. The absorption bands in the region within $\nu = 1265-1280 \text{ cm}^{-1}$ are assigned to the stretching vibrations of 2 CH₃ groups.



Scheme 1. 2-amino-4,5-dimethylthiophene-3-carboxamide (**4**) was obtained via Gewald reaction by condensation of 2-butanone (**1**) with ethyl cyanoacetamide (**2**) in the presence of elemental sulfur and morpholine (**3**).

Beside the expected signals in the ¹H NMR spectrum of compound, it displayed a characteristic broad signal at δ 12.97 and 13.15 ppm assigned to 2NH₂ groups and a broad signal δ 2.30 due to the methyl group protons. The mass spectrum of the compound showed the molecular ion peaks at m/z 172 (M++2), 171 (M++1), 170 (M+) which is in agreement with molecular formula of the compound C₇H₁₀N₂OS.

2.3. Preparation of saturated solutions.

The saturated solutions of 2-amino-4,5-dimethylthiophene-3-carboxamide (ADTC) in mixed EtOH-H₂O solvents were prepared by dissolving solid material (ADTC) in closed test tubes containing different mole fractions of ethanol-water solvents. The tubes were put in water thermostat of type assistant for a period of one day at temperatures 293.15, 298.15, 303.15, 308.15, and 313.15 K till equilibrium reached.

The solubility of (ADTC) was measured by taking 1ml of each saturated solution putting in a small weighed beaker (10ml) and evaporate under I.R. Lamp till dryness and then weights [15-17].

3. Results and discussion

3.1. Calculation of thermodynamic parameters of solvation

3.1.1. Molal solubility

The molal solubility of compound ADTC in mixed ethanol - water solvent was evaporated till dryness in small beaker.

$$\text{Molal solubility (S)} = (W \times 1000) / (M.wt)(d) \quad (1)$$

W is the weight of the residue in the beaker. M.wt is the molecular weight of the compound. d is the density of solvent.

3.1.2. Solubility product

The solubility product of compound (ADTC) was calculated by using (eq. 2)

$$\text{pK}_{sp} = -\text{Log } S \quad (2)$$

Where $\text{P}_{k_{sp}}$ is the solubility product and S is the molal solubility and all the data at different temperatures were calculated in [tables 1-5](#).

Table 1: Molal solubility (S), Log S, log activity coefficient ($\log \gamma$), solubility product (pK_{sp}), Gibbs free energy (ΔG), transfer Gibbs free energy (ΔG_t) for ADTC at different mole fraction (X_s) and different concentrations of EtOH in EtOH – H₂O mixtures at 293.15 K.

EtOH vol. %	X_s	S	Log S	$\log \gamma_{\pm}$	pK_{sp}	ΔG_s in (kJ mol ⁻¹)	ΔG_t in (kJ mol ⁻¹)
0	0	0.0163	-1.788	-0.0507	3.6782	20.646	0.000
20	0.0717	0.0263	-1.579	-0.06299	3.2846	18.436	-2.209
40	0.1708	0.0371	-1.43	-0.07493	3.0103	16.897	-3.749
60	0.3166	0.0707	-1.151	-0.10013	2.502	14.043	-6.602
80	0.5527	0.6334	-0.198	-0.21273	0.8221	4.6144	-16.031
100	1	1.9717	0.2948	-0.63966	0.6897	3.871	-16.775

Table 2: Solubility S, Log Solubility, log activity coefficient ($\log \gamma$), solubility product (pK_{sp}), Gibbs free energy (ΔG), transfer Gibbs free energy (ΔG_t) for ADTC at different mole fraction (X_s) and different concentrations of EtOH in EtOH – H₂O mixtures at 298.15 K.

EtOH vol. %	X_s	S	Log S	$\log \gamma_{\pm}$	pK_{sp}	ΔG_s in (kJ mol ⁻¹)	ΔG_t in (kJ mol ⁻¹)
0	0	0.0189	-1.724	-0.05397	3.5566	20.304	0.000
20	0.0717	0.032	-1.495	-0.06815	3.1265	17.848	-2.456
40	0.1708	0.0425	-1.372	-0.07903	2.9014	16.563	-3.740
60	0.3166	0.11	-0.959	-0.11511	2.1475	12.259	-8.044
80	0.5527	0.6974	-0.157	-0.21781	0.7487	4.2739	-16.030
100	1	2.0133	0.3039	-0.65124	0.6947	3.9657	-16.338

Table (3): Solubility S, Log Solubility, log activity coefficient ($\log \gamma$), solubility product (pK_{sp}), Gibbs free energy (ΔG), transfer Gibbs free energy (ΔG_t) for ADTC at different mole fraction (X_s) and different concentrations of EtOH in EtOH – H₂O mixtures at 303.15 K.

EtOH vol. %	X_s	S	Log S	$\log \gamma_{\pm}$	pK_{sp}	ΔG_s in (kJ mol ⁻¹)	ΔG_t in (kJ mol ⁻¹)
0	0	0.0195	-1.709	-0.05534	3.5291	20.484	0.000
20	0.0717	0.0386	-1.413	-0.07351	2.9728	17.256	-3.229
40	0.1708	0.045	-1.347	-0.08084	2.856	16.577	-3.907
60	0.3166	0.1141	-0.943	-0.1176	2.121	12.311	-8.173
80	0.5527	0.7717	-0.113	-0.22356	0.6723	3.9022	-16.582
100	1	2.2286	0.348	-0.66681	0.6376	3.7007	-16.784

Table 4: Solubility S, Log Solubility, log activity coefficient ($\log \gamma$), solubility product (pK_{sp}), Gibbs free energy (ΔG), transfer Gibbs free energy (ΔG_t) for ADTC at different mole fraction (X_s) and different concentrations of EtOH in EtOH – H₂O mixtures at 308.15 K

EtOH vol. %	X_s	S	Log S	$\log \gamma_{\pm}$	pK_{sp}	ΔG_s in (kJ mol ⁻¹)	ΔG_t in (kJ mol ⁻¹)
0	0	0.0215	-1.669	-0.0581177	3.4533	20.375	0.000
20	0.0717	0.0389	-1.41	-0.07705477	2.9747	17.551	-2.824
40	0.1708	0.0467	-1.331	-0.08757112	2.8373	16.74	-3.635
60	0.3166	0.119	-0.925	-0.13776618	2.1246	12.536	-7.839
80	0.5527	0.906	-0.043	-0.28244954	0.6506	3.8388	-16.536
100	1	2.4116	0.3823	-0.6889448	0.6133	3.6186	-16.756

Table 5: Solubility S, Log Solubility, log activity coefficient ($\log \gamma$), solubility product (pK_{sp}), Gibbs free energy (ΔG), transfer Gibbs free energy (ΔG_t) for ADTC at different mole fraction (X_s) and different concentrations of EtOH in EtOH – H₂O mixtures at 313.15 K

EtOH vol. %	X_s	S	Log S	$\log \gamma_{\pm}$	pK_{sp}	ΔG_s in (kJ mol ⁻¹)	ΔG_t in (kJ mol ⁻¹)
0	0	0.0234	-1.631	-0.0607354	3.3829	20.284	0.000
20	0.0717	0.043	-1.367	-0.0818743	2.8971	17.371	-2.913
40	0.1708	0.0499	-1.302	-0.093041	2.7904	16.731	-3.552
60	0.3166	0.1236	-0.908	-0.1519647	2.1198	12.71	-7.574
80	0.5527	0.933	-0.03	-0.2996969	0.6597	3.9553	-16.328
100	1	2.6349	0.4208	-0.727544	0.6136	3.6788	-16.605

Table 6: Enthalpy change (ΔH) and entropy change (ΔS) of solvation for ADTC in (EtOH–H₂O) mixed solvents at different temperatures in (kJ mol⁻¹).

EtOH vol. %	X_s	ΔH (kJ mol ⁻¹)	ΔS 293.15K	ΔS 298.15K	ΔS 303.15K	ΔS 308.15K	ΔS 313.15K
0	0	24.423	0.0129	0.0138	0.0130	0.0131	0.0132
20	0.0717	32.757	0.0489	0.0500	0.0511	0.0493	0.0491
40	0.1708	17.797	0.0031	0.0041	0.0040	0.0034	0.0034
60	0.3166	28.094	0.0479	0.0531	0.0521	0.0505	0.0491
80	0.5527	14.991	0.0354	0.0359	0.0366	0.0362	0.0352
100	1	8.222	0.0148	0.0143	0.0149	0.0149	0.0145

3.1.3. Activity coefficient

The activity coefficients were calculated using Debye – Hückel equation (3) [18] and their values and the solubilities are given in [tables 1 & 2](#).

$$\log \gamma_{\pm} = - 0.5062 \times (S)^{0.5} \quad (3)$$

3.1.4. Free energy of solvation

From the solubility products the Gibbs free energies of solvation and the transfer Gibbs free energies from water to mixed solvents were calculated by using equations 4 & 5.

$$\Delta G_s = RT \ln pK_{sp} \quad (4)$$

$$\Delta G_t = \Delta G_s - \Delta G_w \quad (5)$$

All the data are tabulated in [tables 1-5](#) at different temperatures and shown in [figures 3 & 4](#).

3.1.5. Enthalpies and entropies of solvation

Enthalpies can be calculated by drawing a relation between $\log K_{sp}$ for ADTC against $1/T$, the slope= $-\Delta H/2.303R$. So, the entropy (ΔS) of solvation for ADTC concentration solutions can be calculated using Gibbs-Helmholtz equation [19-25].

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

All the data are tabulated in [table 6](#). The solvation experimental thermodynamic parameters ΔG and ΔS for ADTC in mixed EtOH-H₂O solvents are increased with increase in the percentage (mole fraction) of ethanol in the mixed solvents favoring more solute-solvent interactions.

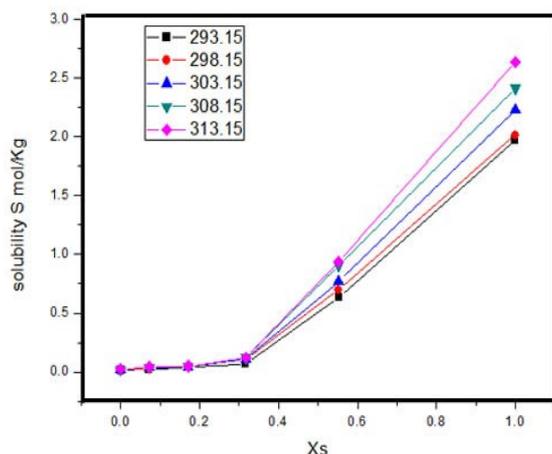


Fig. 1. : Relation between the solubility (S) of ADTC and the mole fraction (X_s) of EtOH in (EtOH-H₂O) mixed solvents at different temperatures

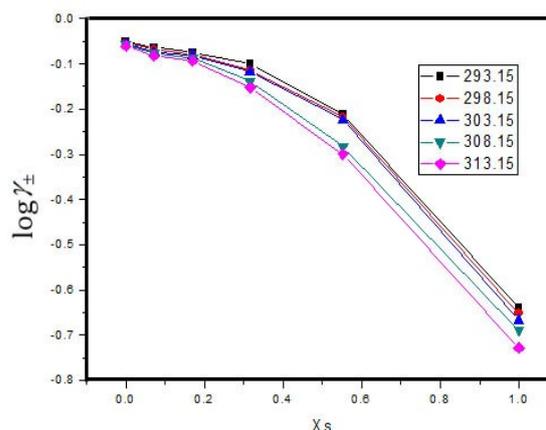


Fig. 2. Relation between the activity coefficient ($\log \gamma_{\pm}$) of ADTC and the mole fraction (X_s) of EtOH in (EtOH-H₂O) mixed solvents at different temperatures.

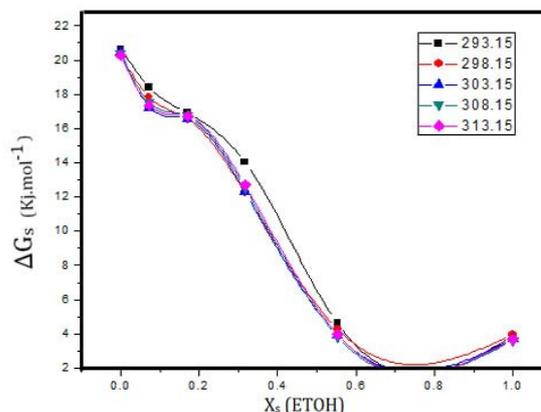


Fig. 3. : Relation between the Gibbs free energies change of solvation (ΔG_s) for ADTC and the mole fraction (X_s) of EtOH in (EtOH-H₂O) mixed solvents at different temperatures.

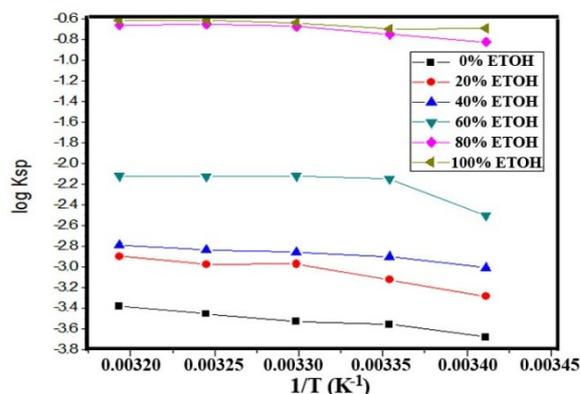


Fig. 4. : Plot of $\log K_{sp}$ for ADTC versus $1/T$ at different vol. % of EtOH.

The enthalpy changes are decrease with increase of the ethanol percentage favoring more endothermic solvation process. Little effect of temperature is noticed experimentally for solvation of ADCT in mixed EtOH-H₂O solvents due to small entropies of solvation and the endothermic reaction happened.

3.2. Theoretical Thermochemistry of the new Schiff base, ADTC

The equation used entropy, energy and heat capacity resulting from the calculation frequencies using Gaussian 09 package are given below [26-30]:

$$S = N K_B + N K_B \ln \left(\frac{Q(V, T)}{N} \right) + N K_B T \left(\frac{\partial \ln Q}{\partial T} \right)_v \quad (7)$$

Where $N = n N_A$, $K_B = R$, N_A is Avogadro's number, R is gas constant and Q is the partition function changing into logarithm we obtain:

$$S = R \ln(Q_t \cdot Q_e \cdot Q_r \cdot Q_v \cdot e) + T_v \quad (8)$$

Where Q is the partition function (total), the Q_t , Q_e , Q_r , Q_v , denote, the translational, electronic, rotational and vibrational partition function. The thermal energy can be obtained from the partition function:

$$E = N K_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v \quad (9)$$

The heat capacity can be obtained by using equation 10 :

$$CV = \left(\frac{\partial E}{\partial T} \right)_{N, v} \quad (10)$$

Where CV is the heat capacity at constant volume, ∂E is the difference in internal energy, ∂E is the difference in temperatures used, N is the number of particles, v is the vibrational quantum number

The above equations will be used for estimation the available thermodynamic for the organic compounds used from the evaluated partition functions. The calculations were done from the contributions for the translation, rotational motion and electronic contributions from vibrational mode of contribution.

The data were obtained from frequency analysis by the need or partition function. For vibrational motion,

choosing the first vibrational energy K , level to be zero level, the corresponding partition function is expressed as [31, 32].

$$Q_{r.k} = \frac{1}{1 - e^{-h\nu_k/k_B T}} \quad (11)$$

Where K_B is Boltzmann constant ($K_B = 1.38066 \times 10^{-23}$ J/K), h is Planck's constant ($h = 6.626 \times 10^{-23}$ J.S) and $h\nu_k / K_B T = \theta_{v,k}$, k is defined as vibrational frequency of mode k .

The zero of energy is defined as the fully dissociated limit (free electrons and bare nuclei), at absolute zero temperature, which is the small motion of molecules and is called "the zero-point vibrational energy" (ZPVE or ZPE).

The ZPVE must be added to obtain energy at absolute zero temperature ($T=0$ K). For all the $3N-6$ ($3N-5$ for linear molecules) vibrational modes, the total ZPVE [28-30] is:

$$ZPVE = \frac{1}{2} \sum_{k=1}^{3N-6} \frac{h\nu_k}{k_B T} = \frac{1}{2} \sum_{K=1}^{3N-6} \theta_{v,E} \quad (12)$$

The ZPVE is calculated for compounds using the data are given in table (7, 8 and 9) for the different solutions [33, 34].

3.2.1. Different contributions of Motions

The different types of motions were theoretically studied for the Schiff bases and summarized in the next text.

3.2.1.1. Contributions from translation

The translational partition function is used to calculate the translational entropy (which donate the factor e which comes from Stirling's approximation [30-36]):

$$St = R \ln(Q_t e) + T \left(\frac{3}{2T} \right) = R \left(\ln Q_t + 1 + \frac{3}{2} \right) \quad (13)$$

The contribution to internal energy is:

$$E_t = N_A K_B T^2 v = RT^2 \quad (14)$$

Finally, the heat capacity at constant volume is given by

$$C_t = \left(\frac{\partial E_t}{\partial T} \right) \quad (15)$$

3.2.1.2. Contributions from electronic motion

The contributions can be calculated from electronic partition function

$$Q_e = W_0 e^{-\epsilon_0/KBT} + W_1 e^{-\epsilon_1/KBT} + W_2 e^{-\epsilon_2/KBT} \quad (16)$$

Where w is the degeneracy of energy level, E_n is the energy in n -th level.

The entropy due to electronic motion is:

$$S_e = R(\ln Q_e + T) \left(\frac{\partial \ln Q_e}{\partial T} \right)_v \quad (17)$$

$$S_e = R(\ln Q_e + 0) \quad (18)$$

Since there are no temperature dependent terms in partition functions, the electronic capacity and internal energy due to electronic motion are both zero.

3.2.1.3. Contribution from rotational motion:

For linear molecules, the rotational partition function is:

$$Q_r = \frac{1}{\delta_r} \left(\frac{t}{\theta_r} \right) \quad (19)$$

Where $\theta_r = h^2 / 8 \pi^2 I k_B$, I is the moment of inertia. δ_r is the rotational diameter. The rotational contribution to the entropy is:

$$S_r = R (\ln Q_r + T) \left(\frac{\partial \ln Q_r}{\partial T} \right)_v \quad (20)$$

The contribution to rotation for internal energy is:

$$E_r = RT^2 \left(\frac{\partial \ln Q_r}{\partial T} \right)_v \quad (21)$$

And the contribution to the heat capacity is:

$$C_v = \left(\frac{\partial \ln E_r}{\partial T} \right)_v \quad (22)$$

For our general case which is nonlinear, the rotational energy and heat capacity are:

$$E_r = RT^2 \left(\frac{3}{2T} \right) \quad (23)$$

$$C_v = \frac{3}{2} R \quad (24)$$

3.2.1.4. Contributions from vibrational motion

The contributions follow equation (19):

$$Q_{v,k} = \frac{e^{-\theta_{v,k}/2T}}{1 - e^{-\theta_{v,k}/T}} \quad (25)$$

The total entropy, energy and C_v from the vibrational partition function are:

$$S_v = R (\ln(Q_v) + T) \left(\frac{\partial \ln Q}{\partial T} \right) \quad (26)$$

$$E_v = R \sum_{u,k} \theta_{u,k} \left(\frac{1}{2} + \frac{1}{e^{\theta_{v,k}/T} - 1} \right) \quad (27)$$

$$C_v = R \sum_k e^{\theta_{v,k}/T} \theta \left(\frac{\theta_{v,k}/T}{e^{\theta_{v,k}/T} - 1} \right) \quad (28)$$

3.2.1. Thermochemistry studies of 2-amino-4,5-dimethylthiophene-3-carboxamide (ADTC)

Different partition functions (Q) values for compound ADTC in ethanol were studied by three different methods i.e. Hartree-fock 6-311g(d,p), PM3 and AM1 and tabulated in [table 7](#). As concluded, the vibration partition function (Q) values for all ADTC are greater than translational and rotational values. In [table 8](#), Different quantum chemical results for compound ADTC in ethanol were calculated by three different methods (Hartree-Fock 6-311g(d,p), PM3 and AM1). The dipole moment, HOMO and LUMO energy levels are also calculated for ADTC in the table. As shown in the [table 9](#), the Sum of electronic and zero point energies, Sum of electronic and thermal energies, Sum of electronic and thermal enthalpies and Sum of electronic and thermal free energies for ADTC in ethanol by three different methods were tabulated.

The basis set used for calculations is 6-311g for Hartree-Fock method. Electronic, translational and rotational partition functions are calculated for ADTC in pure ethanol solvent. Most of the data obtained theoretically are approximately similar other than parameters like the total energy of ADTC, HOMO, LUMO energies.

Kinetic energy, rotational constant, polarizability, zero point vibrational energy are calculated by applying the three methods and found that they are greater on using Hartree-fock method than others.

Table 7. Different partition functions (Q) values for compound ADTC in ethanol by using three different methods (Hartree-fock 6-311g(d,p), PM3 and AM1).

	Hartree-fock 6-311g		PM3		AM1	
	Q	Ln (Q)	Q	Ln (Q)	Q	Ln (Q)
TotalBot	0.307740D-64	-148.543946	0.213198D-57	-132.792885	0.358527D-60	-139.180856
Total V=0	0.121789D+18	39.341070	0.238734D+19	42.316710	0.185038D+18	39.759339
Vib (Bot)	0.331913D-78	-180.704520	0.225949D-71	-164.970988	0.390508D-74	-171.331603
Electronic	0.100000D+01	0.000000	0.100000D+01	0.000000	0.100000D+01	0.000000
Translational	0.871617D+08	18.283275	0.871617D+08	18.283275	0.871617D+08	18.283275
Rotational	0.106374D+07	13.877299	0.108255D+07	13.894828	0.105334D+07	13.867472

Table 8. Different quantum chemical results for compound ADTC in ethanol by three different methods (Hartree-fock 6-311g(d,p), PM3 and AM1).

	Hartree-fock 6-311g	PM3	AM1
Eps	24.852000	20.493000	24.852000
SCF Done (A.U.)	E(RHF)= -852.330476048	E(RPM3) = -0.479586987603E-01	E(RAM1) = -0.604958234463E-01
Dipole moment (Debye)	4.6889	2.9204	3.4629
HOMO	-0.29205	-0.32233	-0.31447
LUMO	0.12374	-0.01781	-0.00573
KE	8.492668572995D+02	-3.860527198823D+01	-3.795418230410D+01
Rotational temperatures	0.06745 K	0.06596 K	0.06767 K
Rotational constants (GHZ)	1.40541	1.37434	1.40991
Exact polarizability	159.455	144.205	163.291
Zero-point vibrational energy	111.31918	103.74992	106.01950

Stoichiometry C7H10N2OS, Deg. of freedom 57, Full point group C1

Table 9. Theoretical thermodynamic parameters for compound ADTC in ethanol by three different methods (Hartree-fock 6-311g(d,p), PM3 and AM1)

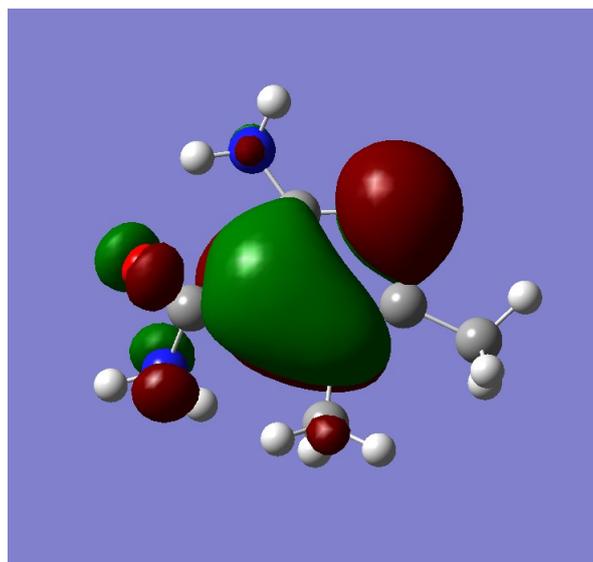
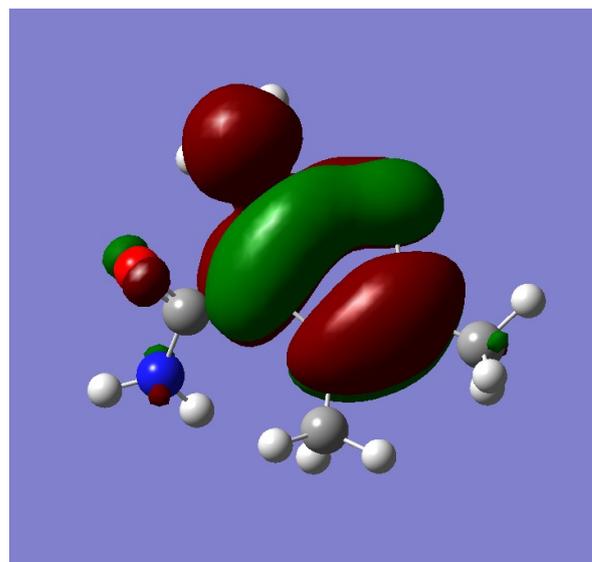
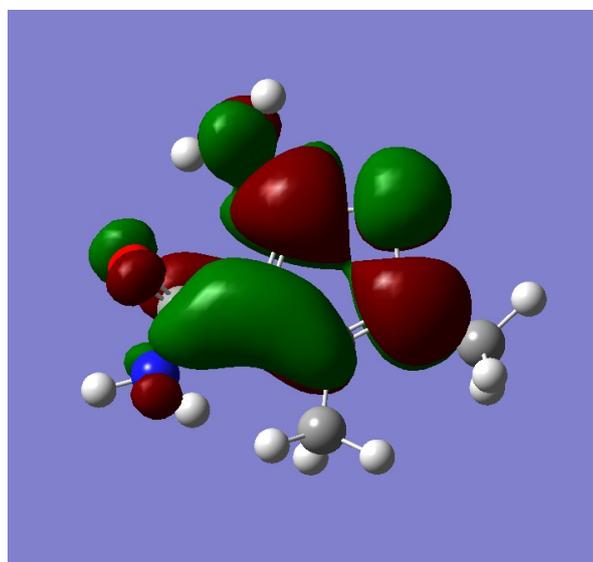
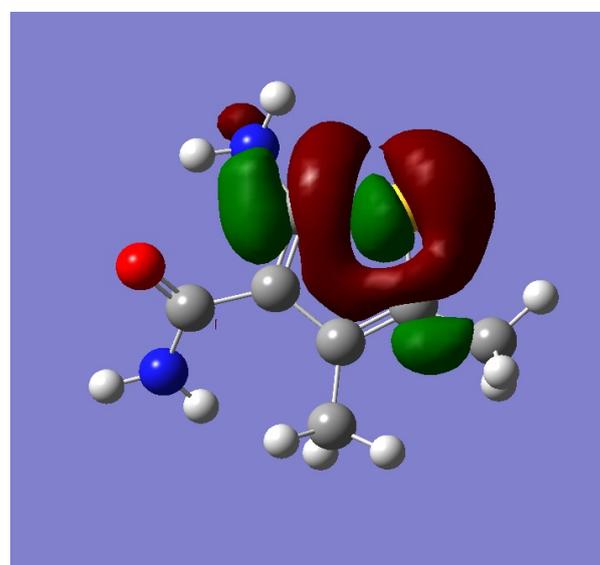
	Hartree-fock 6-311g	PM3	AM1
Sum of electronic and zero-point Energies	-852.153078	0.117377	0.108457
Sum of electronic and thermal Energies	-852.141726	0.130063	0.120356
Sum of electronic and thermal Enthalpies	-852.140782	0.131007	0.121300
Sum of electronic and thermal Free Energies	-852.190223	0.077422	0.070917

Table 10. Different thermodynamic parameters such as thermal, heat capacity at constant volume CV, entropies for the electronic, translational, rotational and vibrational movement for ADTC in ethanol by applying three different methods

	Hartree-fock 6-311g			PM3			AM1		
	E (Thermal) KCal/mol	CV Cal/mol- Kelvin	S Cal/mol- Kelvin	E (Thermal) KCal/mol	CV Cal/mol- Kelvin	S Cal/mol- Kelvin	E (Thermal) KCal/mol	CV Cal/mol- Kelvin	S Cal/mol- Kelvin
Total	118.442	42.304	104.058	111.710	44.762	112.778	113.486	43.623	106.041
Electronic	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Translational	0.889	2.981	41.301	0.889	2.981	41.301	0.889	2.981	41.301
Rotational	0.889	2.981	30.558	0.889	2.981	30.593	0.889	2.981	30.538
Vibrational	116.665	36.343	32.199	109.933	38.801	40.885	111.709	37.661	34.202

Sum of electronic+ zero point energies, sum of electronic + thermal energies and sum of electronic+ thermal enthalpies was calculated by using the above mentioned methods and found to be greater using Hartree-fock method than others. The different thermodynamic parameters such as thermal, heat capacity at constant volume CV, entropies for the electronic, translational, rotational and vibrational movement for ADTC in ethanol were also calculated by applying the three different methods theoretical and found to give the greatest values

on using PM3 method supporting the activity of ADTC in ethanol medium (table 10). The electronic gap energy E(LUMO)-E(HOMO) gave bigger result 0.4157 eV (electron Volt) in case of Hartree-fock method than other methods indicating the applicability of this compound ADTC as semiconductor. As shown in Fig. 5, the shape of HOMO and HOMO-1 indicate that HOMO orbitals are full occupied than that of HOMO-1. Also LUMO orbitals are clear to have more orbital free to be occupied than that of LUMO+1 orbitals.

**HOMO-1****HOMO****LUMO****LUMO +1****Fig. 6.** The HOMO-1, HOMO, LUMO, LUMO+1 for ADTC in ethanol.

4. Conclusions

The solvation experimental thermodynamic parameters ΔG and ΔS for ADTC in mixed EtOH-H₂O solvents are increased with increase in the percentage (mole fraction) of ethanol in the mixed solvents favoring more solute-solvent interactions. The enthalpy changes are decreased with increase of the ethanol percentage favoring more endothermic solvation process. Different methods of calculation were proceeded like, Hartree-Fock 6-311g (d,p), PM₃ and AM1 fore estimating the different thermodynamic parameters in ethanol. The different thermodynamic parameters like thermal, heat capacity at

constant volume CV, entropies for the electronic, translational, rotational and vibrational movement and other theoretical parameters for ADTC in ethanol were also calculated by applying the three different methods theoretical and found to give the grate values supporting the activity of ADTC in ethanol medium. This indicates that the solubility of ADCT is increased by increase in ethanol mole fraction in the mixed solvents.

5. References

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