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Density, viscosity, DFT and FTIR study of tertiary butyl alcohol and ethanol with DMSO and DMF at room temperature

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In this work, we report a combined experimental density, viscosity, FTIR and theoretical density functional theory (DFT) method of tertiary butyl alcohol (TBA)+dimethyl sulphoxide (DMSO), ethanol (ET)+DMSO, TBA+(dimethyl formamide) DMF, ET+DMF mixtures at room temperature. Density and viscosity data over the entire composition range have been used to compute excess molar volumes and deviation in viscosity, respectively. The excess molar volume (V^E) is negative for whole composition range for both systems, DMF+ET, DMF+TBA. The negative values of V^E indicate of the important interaction between unlike molecules. The deviation in viscosity ($\Delta\eta$) is positive over whole composition range for DMF+ET and negative for the DMSO+ET, DMSO+TBA and DMF+TBA. The negative $\Delta\eta$ suggests the forces between pairs of unlike molecules are less than the forces between like molecules. The molecular geometry, harmonic vibrational frequencies, Mulliken atomic charges have been calculated by using DFT theory/B3LYP method with 6-31G(d) basis set. Energies of HOMO-LUMO predict the strength and stability of complexes.

Keywords: Excess molar volume, Deviation in viscosity, FTIR, DFT

1 Introduction

Experimental determination of excess functions for suitably chosen liquid mixtures serves as a valuable check of the predictions of different theories of solutions. The volume change on mixing at constant pressure for the binary liquid mixtures is one of the most interesting thermodynamic functions of mixing. This property remains to be of interest because the experimental procedures are relatively easy to perform with great precision.

The study of viscosities provides information on the liquids which are required in the design of processes, which involves mass transfer, fluid flow etc[1]. Thermodynamic properties of the composition are very useful tools to understand the nature and molecular aggregation due to intermolecular interaction between components[2,3]. Viscosity not only reflects the effect of molecular motion but also molecular interaction between components. The derived parameters from these measurements are important for solubility measurements.

TBA is miscible with water as well as most common organic solvents and forms azeotrope. It is used as a non-reactive solvent for chemical reactions, a non-surfactant compatibilizer for many solvent blends. ET is a versatile solvent, miscible with water and with many organic solvents. It is a powerful psychoactive drug and one of the oldest recreational drugs. Because of its ability to dissolve many kinds of compounds, DMSO plays a role in sample management and high-throughput screening operations in drug design. DMF is an excellent solvent in the production of pharmaceuticals as a reaction solvent, extracting solvent and crystallizing bath.

Aprotic solvents such as DMF or DMSO tend to have large dipole moments (separation of partial positive and partial negative charges within the same molecule) and solvate positively charged species via their negative dipole. Protic solvents like water or alkanols solvate anions (negatively charged solutes) strongly via hydrogen bonding.

It is well known that the energy of the H-bond depends on the H▪▪▪Y distance and the Y▪▪▪H─X angle, where X is a H-donor and Y is H-acceptor[4]. However, when the bond is longer than 1·6 Å, the strength of the bond depends less on the value of the Y▪▪▪H─X angle[5]. So our concentration was mainly on the length of H-bonds which are longer than 1·6 Å.

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Spectroscopy is essentially a technical procedure by which the energy differences between the allowed states of a system are mapped and recorded by determining the frequencies of the corresponding light absorbed.

In previous publications, we report synthesis, biological activities and DFT study of some heterocycles[6-9]. These heterocyclic compounds are well miscible in pure ET, TBA, DMF and DMSO and their mixtures over entire composition range. Comparison of DFT simulations of a single and two different molecules, i.e., 1:1 complex gives variation in geometrical parameters as well as modes of vibrations.

In the present paper, binary liquid mixtures of TBA+DMSO, ET+DMSO, TBA+DMF and ET+DMF have been studied with FTIR and DFT methods.

2 Experimental Details

Binary mixtures were prepared by mixing known masses of each liquid in airtight-stoppered glass bottles. The measurements were made on a digital balance (SHIMADZU, AUX 220) to an accuracy of $\pm 1\times10^{-4}$ mg. The more volatile component (ET) was filled directly into the bottle and the closed bottle was weighed. The other component was injected into the bottle through the stopper by means of a syringe. This method allowed negligible vapour loss and contamination. The possible error in mole fraction is calculated to be less then $\pm 1\times10^{-4}$. The preferential evaporation of solvents from the mixture was kept to a minimum as evidenced by reproducible measurements of the physical properties of these liquid mixtures over a time interval of 1 or 2 days.

A single capillary pycnometer (specific gravity bottle) was chosen for the present work[10,11]. The pycnometer was washed thoroughly with fresh chromic acid to remove impurities. Subsequently the pycnometer was washed with distilled water and then with acetone and dried with a stream of warm air from hot blower. It was then kept in an oven at about 60 °C for half an hour. The weights of empty pycnometer and pycnometer filled with experimental liquids were taken on SHIMADZU (AUX 220) balance having a sensitivity of 0.01 mg. The pycnometer was calibrated with freshly prepared triply distilled water.

The density measurements using mass/volume relationship for each experimental liquid were repeated at least three to four times and the results averaged. This procedure enabled us to get an uncertainty of ± 0.0005 g cm^{-3} in density measurements.

In the present study, the capillary flow method was employed to determine the viscosity of fluid at room temperature. The usual form of this simple, yet accurate, apparatus, an Ostwald viscometer was used for calculating viscosities of different liquids.

The viscosity values were determined using the relation:

$$\eta = \rho(at - b/t) \quad \dots (1)$$

where η is the viscosity, ρ is density of the liquid, t is flow time, a and b are the constants for a given viscometer.

The viscometer was calibrated with triply distilled water. The constants a and b were obtained by measuring the flow times of triply distilled water at experimental temperatures.

3 Theory

The excess molar volume (V^E) can be computed from experimental density data using the relationship:

$$V^E = x_1M_1[1/\rho_m - 1/\rho_1] + x_2M_2[1/\rho_m - 1/\rho_2] \quad \dots (2)$$

where x_i, M_i and ρ_i designate the mole fraction, the molecular weight and the density of the component i. ρ_m is the density of mixture.

Deviations in viscosities ($\Delta\eta$) were obtained as follows:

$$\Delta\eta = \eta_{mix} - (x_1\eta_1 + x_2\eta_2) \quad \dots (3)$$

where η_1 and η_2 are the viscosities of pure components 1 and 2, respectively, and η_{mix} is the viscosity of the liquid mixture.

FTIR spectra were recorded on a FTIR spectrometer (SIMADZU 8400S PC) in the region 400 -4000 cm^{-1} with 4 .0 cm^{-1} resolution.

3.1 Computational method

The quantum chemical calculations have been performed using Gaussian 03 package[28] and visualized by Gauss-View program which makes it use easier. Geometry optimization of single and 1:1 comlexes was performed without physical constraint forcing to any point group symmetry. DFT with Becky's three parameter (B3) exchange functional along with the Lee-Yang-Parr (LYP) nonlocal correlation functional (B3LYP) has been accepted by

the *ab-initio* quantum chemists as a cost of effective approach for the computation of molecular structure, molecular interactions, vibrational frequencies and energies[25-27].

Localization of the frontier orbital were investigated by a single point energy calculation using 6-3lG(d) basis set for DFT levels of theory. The spatial distribution of HOMO and LUMO explain the charge transfers within the molecule or from one molecule to another molecule. The structures of 1:1 complexes of DMF and DMSO with ME, ET and TBA complexes were fully optimized by DFT/B3LYP using the 6-3lG(d) basis set.

The calculations of atomic charges play an essential role in quantum chemical calculations due to the effect of these charges to dipole moment, polarizability and electronic parameters[29].

4 Results and Discussion

Experimental densities (ρ) and viscosity (η) values of pure liquids are given in Table 1. The densities and viscosities for the binary mixtures of TBA+DMSO, ET+DMSO, TBA+DMF and ET+DMF at different compositions and at atmospheric pressure are listed in Table 2. From these experimental data, V^E and Δη have been calculated. Polynomial equation results for the V^E and Δη of binary mixtures with correlation coefficient (R^2) are listed in the Table 3. FTIR frequencies of hydroxyl functional group are given in the Table 4.

4.1 Alkanols + DMSO systems

Figure 1 shows the variation of V^E for TBA+DMSO and ET+DMSO over the entire composition range, respectively. V^E are positive up to x_1 = 0.4128 for TBA+DMSO and for ET+DMSO, up to x_1 = 0.5 and then become negative with an increase in x_1 for both systems. The positive contribution to V^E may be due to the breaking up of DMSO/DMF or alkanol molecules and weakening of the interaction between the molecules (mutual dissociation of the component molecule) because of the small difference in the molar volume of the component. The positive V^E also suggests that the dispersion force prevails between alkanols and DMSO.

It is also seen that the V^E values are positive and then become negative evidence that the self association of TBA and ET molecules first breaks and then the interaction between unlike components takes place. The positive values may be due to repulsive forces caused by electronic charges on the component liquids[30].

The chemical or specific interactions between constituent molecules of the mixture result in a volume decrease[31]. In the present work, specific interaction between alkanols and DMSO molecules takes place through hydrogen bond formation. The structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volumes and free volumes between components, lead to negative contribution to V^E. With higher alkanols, the geometrical contribution is negligible and clustering decreases with an increase in chain length and branching of the alkanols. Therefore, the mixture containing TBA gives less negative V^E values as compared to mixture containing ET. Negative values of V^E indicate that volume contraction occurs upon mixing of DMSO with alkanols. More negatives exhibit on the system containing TBA, which may result from the sterically hindered effect.

Table 1 — Experimental densities (ρ) and viscosities (η) of pure liquids at 298.15, 303.15 and 308.15 K.

Liquids	Temperature	$\rho \times 10^{-3}$ (kg m^{-3})		$\eta \times 10^3$ (kg m^{-1}s^{-1})	
		Experimental	Literature	Experimental	Literature
ET	298·15	0·78522	0·785 22[a]	1·109	1·109[l]
	303·15	0·78054	0 ·78050[b]	0·986	0·986[k]
	308.15	0.76387	0.76391[c]	0.768	0.767[c]
TBA	298·15	0·78123	0·78120[d]	4.3839	4.372[d]
	303·15	0·77541	0·77540[e]	3·3787	3·378[g]
	308.15	0.7702	0.77022[f]	-	-
DMSO	298·15	1·0955	1·0955[g]	1·9971	1·997[m]
	303·15	1·0901	1·0896[h]	1·8303	1·830[l]
	308.15	1.0856	1.08560[i]	1.6138	1.614[e]
DMF	298·15	0·9438	0·9438[j]	0·8125	0·812[j]
	303·15	0·9412	0·94120[d]	0·7545	0·756[d]
	308.15	0.9358	0.93581[k]	0.712	0.711[k]

a:Ref[12], b:Ref.[13], c:Ref.[14], d:Ref.[15], e:Ref.[16], f:Ref.[17], g:Ref.[18], h:Ref.[19], i:Ref.[20], j:Ref.[21], k:Ref.[22], l:Ref.[23], m:Ref.[24]

Table 2 — Densities (ρ), viscosities (η), excess volumes (V^E) and viscosity deviations (Δη) of binary liquid mixtures at temperature 303.15 K.

x_1	$\rho \times 10^{-3}$ (kg m^{-3})	$\eta \times 10^3$ (kg m^{-1} s^{-1})	$V^E \times 10^6$ (m^3 mol^{-1})	$\Delta\eta \times 10^3$ (kg m^{-1} s^{-1})
TBA + DMSO				
0.1049	0.8049	2.805	22.34	0.81
0.2086	0.8310	2.472	16.33	0.32
0.3116	0.8558	2.081	10.75	-0.23
0.4128	0.8831	2.012	5.07	-0.45
0.5131	0.9132	1.900	-0.61	-0.71
0.6124	0.9448	1.792	-6.22	-0.97
0.7109	0.9789	1.732	-11.77	-1.19
0.8082	1.0168	1.667	-17.33	-1.40
0.9044	1.0549	1.594	-22.71	-1.62
ET + DMSO				
0.1582	0.8130	1.145	20.48	-0.71
0.2978	0.8401	1.089	13.98	-0.64
0.4209	0.8679	1.087	8.41	-0.54
0.5307	0.8950	1.115	3.56	-0.41
0.6293	0.9221	1.158	-0.63	-0.28
0.7179	0.9550	1.239	-4.67	-0.12
0.7983	0.9859	1.314	-8.11	0.03
0.8715	1.0190	1.446	-11.24	0.22
0.9385	1.0548	1.631	-14.12	0.47
TBA + DMF				
0.0976	0.9959	3.008	-5.85	2.00
0.1956	1.0100	2.263	-8.56	1.00
0.2946	1.0241	1.776	-11.19	0.25
0.3935	1.0400	1.534	-13.96	-0.25
0.4931	1.0568	1.357	-16.84	-0.68
0.5932	1.0731	1.205	-19.55	-1.10
0.6942	1.0879	1.084	-22.21	-1.48
0.7954	1.1051	1.032	-24.99	-1.80
0.8972	1.1240	0.937	-27.90	-2.16
ET + DMF				
0.1497	1.1300	0.952	-13.74	-0.01
0.2836	1.1121	0.945	-13.53	-0.05
0.4044	1.0959	0.941	-13.39	-0.08
0.5137	1.0800	0.966	-13.23	-0.09
0.6134	1.0641	1.001	-13.10	-0.09
0.7043	1.0489	1.041	-12.98	-0.08
0.7872	1.0341	1.078	-12.84	-0.06
0.8638	1.0200	1.121	-12.75	-0.04
0.9343	1.0068	1.170	-12.67	0.00

Thus, more positive V^E values are observed in the mixture of the TBA with DMSO. The maximum values of V^E for them follow the order TBA + DMSO > ET + DMSO.

The Δη of DMSO-alkanols mixtures are essentially due to two factors[32]; (i) the depolarization of the associated entities like DMSO and alkanols to monomeric moieties on mixing, which leads to a negative contribution to Δη; and (ii) replacement of like contacts in pure alkanols and DMSO by unlike contacts, which responsible for positive values.

The Δη values are positive initially and then become negative from the composition x_1 = 0.3 for TBA + DMSO. For the ET + DMSO system, the deviations are negative initially and then changed to positive after the composition x_1 = 0.7. Δη values are decreased with increase in moles of TBA while Δη values are increased with increase in moles of ET for TBA + DMSO and ET + DMSO systems, respectively.

4.2 Alkanols + DMF systems

It has been observed that V^E values for both binary mixtures are negative and decrease (increase negative V^E) with increase in moles of alkanols.

Negative V^E reveals the existence of a specific interaction between unlike molecules[33,34]. The maximum negative values of V^E follow the order TBA + DMF > ET + DMF.

Figure 2 shows the variation of Δη verses x_1 for alkanols + DMF systems. The deviations were curved in nature for the ET + DMF system, while linear for TBA + DMF system. Δη curve is negative for the mixture ET + DMF over the entire composition range and initially positive then become negative for TBA + DMF system from x_1 = 0.4 to 0.9. Negative Δη values occur where dispersion or weak dipole-dipole forces are primarily responsible for the interaction between component molecules[35,36]. The observed negative Δη data for ET + DMF are decreased up to x_1 = 0.5, indicating dispersion or weak dipole-dipole forces between ET and DMF molecules. However, negative Δη values are increased form x_1 = 0.6 with increase in moles of ET, indicating strong interactions through H-bonding between hydrogen of OH in ET and oxygen atom of C=O in DMF.

For TBA + DMF system, Δη values are positive up to x_1 = 0.3 and then become negative and linearly decreases with increase in moles of TBA, suggesting dispersion or weak dipole-dipole forces between TBA and DMF molecules. This may be due to steric effect of bulky methyl groups in TBA and DMF.

4.3 FTIR study

In IR spectroscopy, the main preoccupation of an organic chemist is the region 4000-650 cm^{-1}. Absorption of an IR light can occur only if the dipole moment of the molecule is different in the two vibration levels. The stretching frequency of chemical bond depends upon bond strength and reduced masses of the atoms forming bond. Any factor which will

Table 3 — Polynomial equation results for the V^E and Δη of binary mixtures with correlation coefficient (R^2).

S. No.	System	Polynomial equation		R^2	
		V^E	Δη	V^E	Δη
1	(x_1)ET + $(1-x_1)$ DMSO	$y = -398.7x^6 + 1366.x^5 - 1850.x^4 + 1250.x^3 - 435.3x^2 + 26.76x + 23.21$	$y = 33.29x^6 - 102.0x^5 + 127.0x^4 - 81.41x^3 + 29.17x^2 - 4.832x - 0.425$	0.99	0.99
2	(x_1)TBA + $(1-x_1)$ DMSO	$y = 415.3x^6 - 1322.x^5 + 1668.x^4 - 1053.x^3 + 343.9x^2 - 109.3x + 31.05$	$y = 45.11x^6 - 135.3x^5 + 157.0x^4 - 90.44x^3 + 29.73x^2 - 9.330x + 1.552$	0.99	0.99
3	(x_1)ET + $(1-x_1)$ DMF	$y = -7.459x^6 + 26.79x^5 - 38.61x^4 + 28.26x^3 - 10.88x^2 + 1.514x - 0.341$	$y = 3.873x^6 - 9.472x^5 + 7.610x^4 - 1.477x^3 - 0.347x^2 - 0.165x + 0.025$	0.99	0.99
4	(x_1)TBA + $(1-x_1)$ DMF	$y = 574.2x^6 - 1814.x^5 + 2220.x^4 - 1321.x^3 + 393.7x^2 - 87.15x + 18.86$	$y = -130.1x^6 + 375.9x^5 - 411.7x^4 + 206.1x^3 - 39.58x^2 - 6.125x + 2.259$	0.99	0.99

Table 4 — υOH (cm^{-1}) for % alkanols + DMSO and + DMF systems.

%	TBA+DMSO	TBA+DMF	ET+DMSO	ET+DMF
0	3369.65	3369.65	3327.32	3327.32
10	3383·26 (vs), 3358·18 (s)	3379·40 (s)	3346·61 (s)	3448·84 (vw)
20	3389·69 (s)	3394·83 (s)	3360·11 (vs)	3443·05 (w)
30	3402·54 (m), 3389·04 (m)	3416·05 (m)	3329·25 (s), 3381·33 (s)	3439·19 (vw)
40	3396·76 (m)	3429·55 (w)	3381·33 (s)	3427·62 (w)
50	3404·47 (m)	3429·55 (w)	3398·69 (m)	3417·98 (w), 3410·26(m)
60	3400·62 (m)	3439·19 (vw)	3387·11 (w)	3398·69 (m), 3390·97(m)
70	3414·12 (w)	3450·77 (vw), 3435·34(vw)	3394·83 (w)	3350·46 (m)
80	3416·05 (w)	3452·70 (vw), 3437·26 (vw)	3394·83 (w)	3350·46 (s)
90	3410·26 (vw), 3396·76(vw)	-	3425·69 (vs)	3348·54 (s), 3335·03 (s)
100	3369·75 (vs)	3369·75 (vs)	3346.61 (vs)	3346·61 (vs)

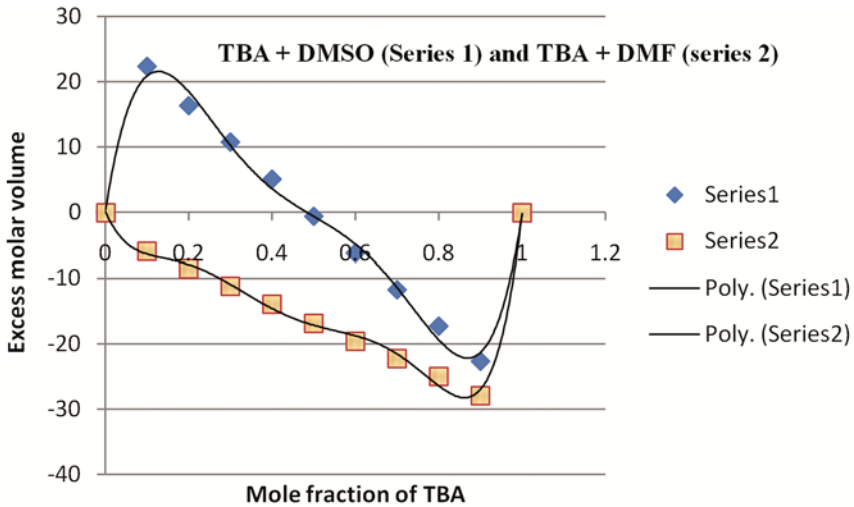

Fig. 1 — Variation of excess molar volumes (V^E) with mole fraction of alkanols (x_1) in binary mixture of (×) TBA + DMSO, (▲) TBA + DMF, (■) ET + DMSO, (♦) ET + DMF at room temperature.

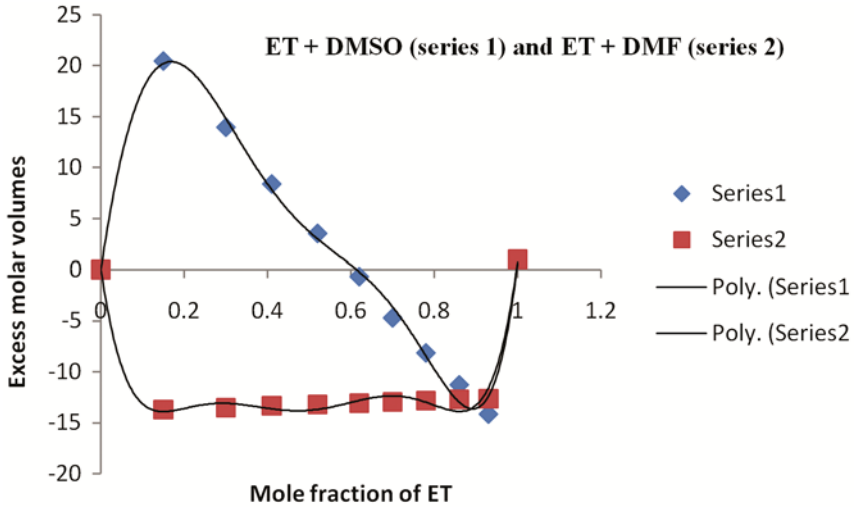

Fig. 2 — Variation of viscosity deviation (Δη) with mole fraction (x_1) of alkanols in binary mixture of (×) TBA + DMSO, (▲) TBA + DMF, (■) ET + DMSO, (♦) ET + DMF at room temperature.

increase bond strength will increase stretching frequency of the bond, and if the mass of atoms forming the chemical bond is increased, the reduced mass will increase and stretching frequency will decrease. FTIR of alcohols have characteristic absorptions associated with both the νO-H and the νC-O vibrations. These appears in the regions 3500-3200 cm^{-1} (a very intense, broad band) and 1260-1050 cm^{-1}, respectively.

Table 4 includes νOH for two binaries. The OH stretching vibrations of TBA and ET occur around 3369 and 3327 cm^{-1}, respectively. There is an increase in the normal νOH from 3383 to 3404 cm^{-1} up to 50% of TBA in TBA + DMSO and from 3379 to 3452 cm^{-1} up to 90% of TBA in TBA + DMF systems. Therefore, strong hydrogen bonding is seen in TBA + DMSO system. There is decrease in the normal νOH from 3448 to 3348 cm^{-1} up to 90% ET in ET + DMF, but it increases from 3346 to 3425 cm^{-1} in ET + DMSO system with increase in percentage of ET, indicating strong hydrogen bonding in ET + DMF as compared to ET + DMSO system. Selected νOH of pure and binary mixtures are shown in Fig. 3. This IR study supports to the negative V^E over the entire composition range in ET + DMF.

4.4 DFT study

To understand the electronic nature of the protic-aprotic binary mixtures, we turned our attention on their optimized geometries using DFT/B3LYP/

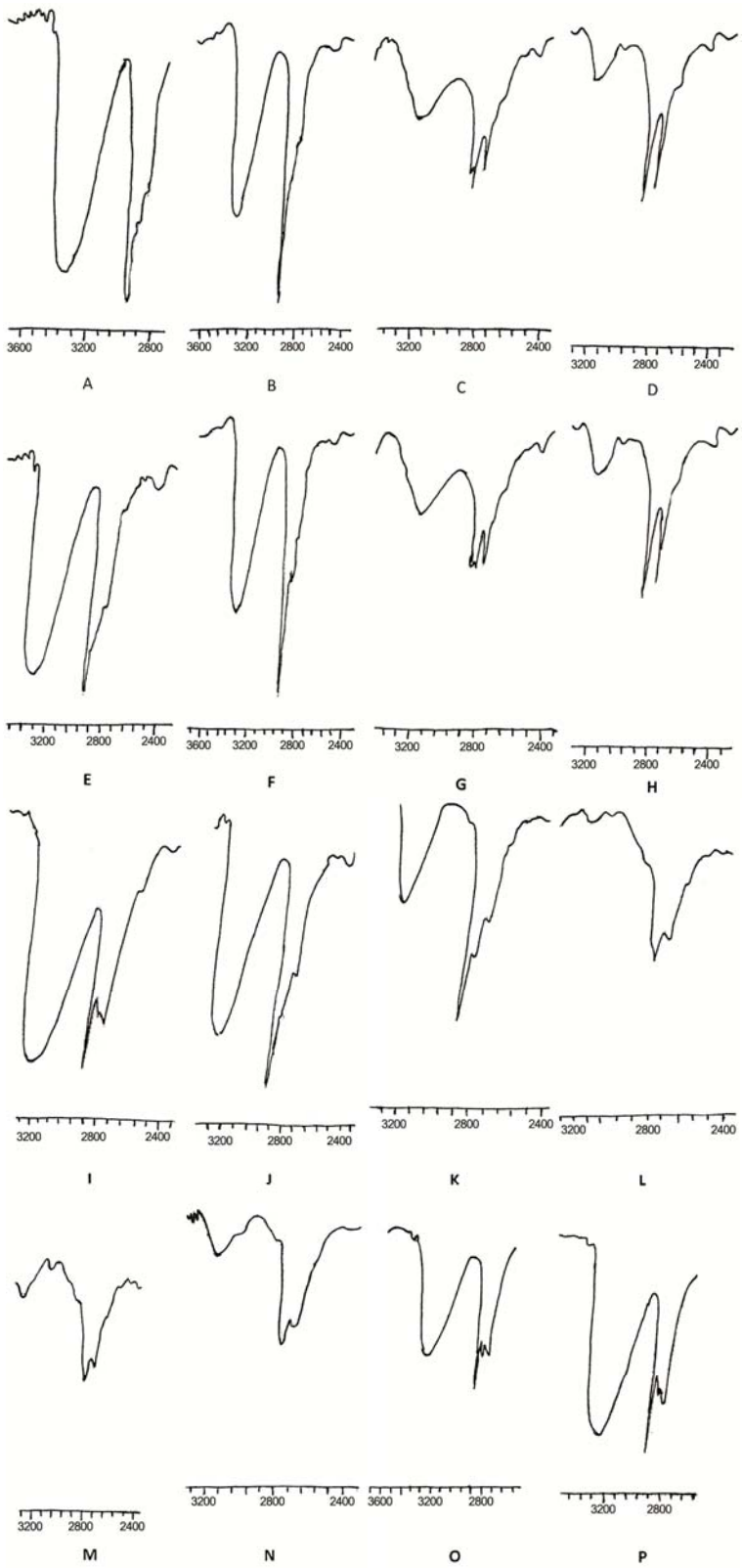

Fig. 3 — Experimental FTIR stretching frequency of OH (cm^{-1}) in : A) 10% TBA+DMSO ; B) 50% TBA+DMSO ; C) 90% TBA+DMSO; D) 100% DMSO; E) 100% TBA; F) 10% ET+DMSO; G) 50% ET+DMSO ; H) 90% ET+DMSO ; I) 100% ET ; J)10% TBA+DMF ; K) 50% TBA+DMF ; L) 90% TBA+DMF ; M) 100% DMSO; N) 10% ET+DMF; O) 50% ET+DMF ; P) 90% ET+DMF

6-31G(d) levels of theory. For optimized DMF and DMSO with alkanols complexes, the most interesting changes are found in the elongation of -OH bond length of the alkanols by 0·00031 Å and 0·00041 Å, respectively. The reason may be due to increase of electron density at -O-H bond. In these complexes, H-bond lengths are increased from ET to TBA complexes, i.e., DMF and DMSO with ET H-bonds are significantly shorter than the other bonds, indicating these complexes are geometrically more stable. This can be due to the increasing branching from ET to TBA.

In DMF and DMSO with alkanols (1:1) complexes, dihedral angles of DMF/DMSO with TBA complexes are found to be less (35.429° and 0°, respectively), indicating that these are less stable than other complexes. The C─O─H bond angle is increased from ET to TBA complexes, this may be due to branching of alkyl groups which is increased from ET to TBA complexes.

Since HOMO is the outermost orbital containing electrons, it could act as an electron donor. Similarly, LUMO is the innermost unoccupied orbital, that could act as an electron acceptor. Values of HOMO and LUMO energy levels for the DMF and DMSO with alkanol complexes obtained by DFT/B3LYP/6-31G(d) calculations are given in Table 5. When the HOMO and LUMO are close together, the energy gap between the two is very low, indicating molecules are more reactive to form covalent bonds or complexes. When the energy gap between HOMO and LUMO is large, molecules are less reactive (Fig. 4).

Table 5 — Comparison of three HOMO and LUMO energy levels (eV) for the DMF and DMSO with alkanols complexes obtained by DFT/B3LYP/6-31G(d) calculations.

	HOMO	LUMO
TBA	-0.25930	0.06601
ET	-0.26018	0.07270
DMSO	-0.22244	0.04255
DMF	-0.24218	0.03221
TBA:DMSO	-0.23638	0.03415
TBA:DMF	-0.23486	0.01684
ET:DMSO	-0.23669	0.03487
ET:DMF	-0.23609	0.01702

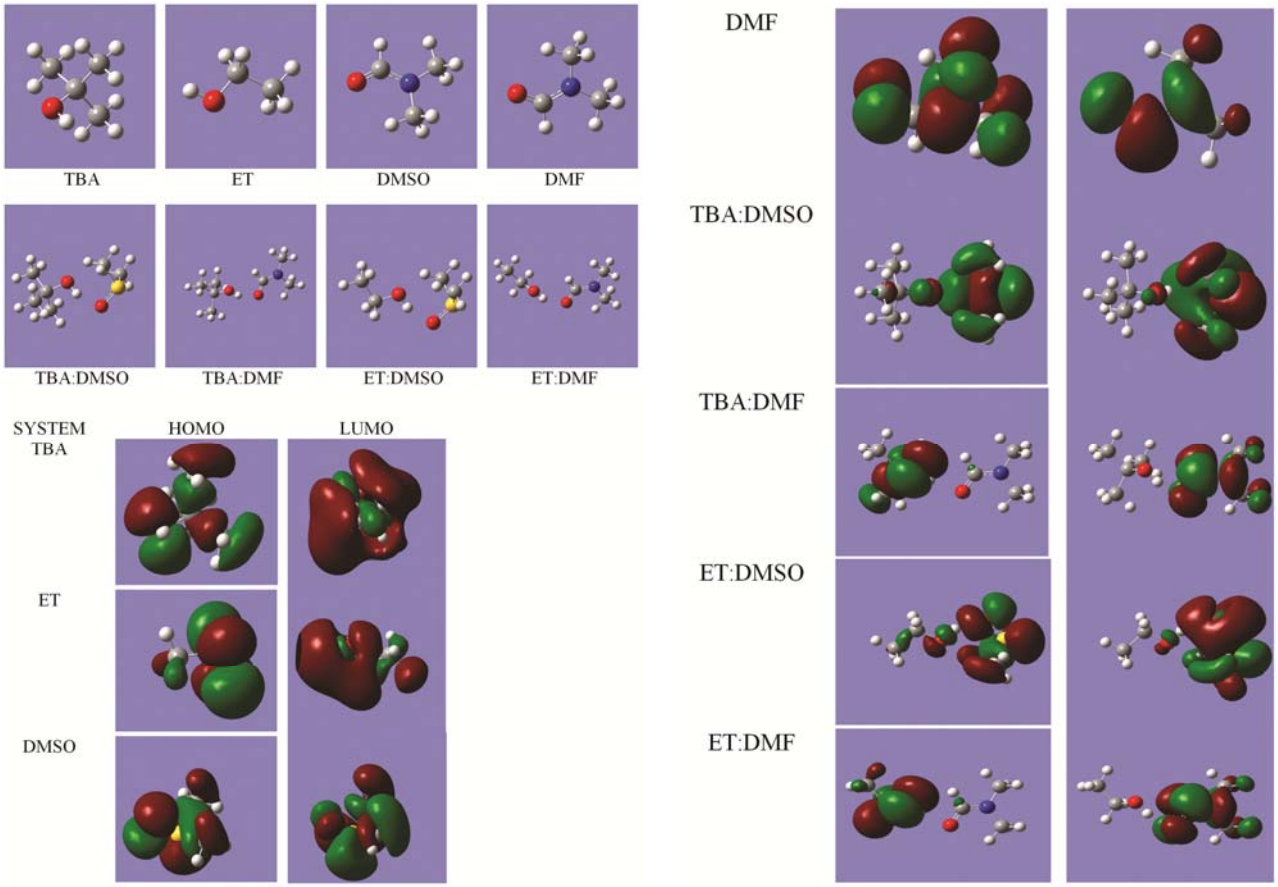

Fig. 4 — The optimized geometries and 3D orbital pictures of HOMO and LUMO calculated at the B3LYP/6-31G(d) level.

Table 6 — Bond lengths, bond angles and charge distribution of DMF and DMSO with alkanols complexes obtained by DFT/B3LYP/6-3lG(d) calculations.

Parameters	DMSO + ET	DMSO + TBA	DMF + ET	DMF + TBA
	Bond length (Å)			
S═O	1·52904	1·52933	-	-
O─H	0·98588	0·98631	0·97811	0·97842
S═O▪▪▪H─O (H-bond)	1·82623	1·83736	-	-
C═O	-	-	1·22709	1·22761
N─C═O▪▪▪H─O (H-bond)	-	-	1·86608	1·88825
	Bond angle (Degree)			
C─O─H	109·660	108·781	107·629	107·767
C─S─O	106·657	106·64	-	-
S═O▪▪▪H─O (Dihedral)	001·557	00·000	-	-
N─C═O	-	-	126·989	126·922
N─C═O▪▪▪H─O (Dihedral)	-	-	37·856	35·429
	Mulliken atomic charges			
S	0·774	0·773	-	-
$O_{S=O}$	-0·660	-0·660	-	-
O_{OH}	-0·670	-0·690	-0·653	-0·680
H_{OH}	0·420	0·420	0·435	0·433
$O_{C=O}$	-	-	-0·484	-0·483
$C_{C=O}$	-	-	0·355	0·355

The charge distribution on various atoms which forms the H-bonds of DMF and DMSO with alkanols complexes are listed in Table 6. In DMF/DMSO alkanols complexes, the electron density at O_{OH} increased from ET to TBA. The electron density at H-atom is lower than oxygen atom in all complexes, indicating that all bonds are favorable for H-bonding. Among these H-bonding, the H-bonding in DMSO complexes is most favorable (H_{OH} = 0·420 e).

HOMO is irregular trend in electron density which is observed for DMF/DMSO; alkanols complexes. All complexes show negative values. However DMF with alkanols show less negative values as compared to DMSO with alkanols complexes.

LUMO is decreased from ET to TBA in DMF and DMSO with alkanols complexes. All complexes are negative.

The DMF/DMSO: TBA complexes are found to be more reactive than DMF/DMSO: ET complexes. The oxygen of DMF and DMSO acts as electron donor while carbon and sulphur act as electron acceptor respectively.

5 Conclusions

Finally, it has been concluded that volumetric and viscometric investigations indicate that the presence of dispersion forces, dipole-induced dipole and dipole-dipole interactions between the components of the system. Presence of hydrogen bonding between OH of ET/TBA with oxygen of S=O group of DMSO, C=O of DMF are confirmed by FTIR study.

The DFT results suggested that the HOMO and LUMO states of these binary mixtures are localized on the DMF and DMSO moieties. The energy difference of localized LUMO levels strongly depend on the functional groups of the DMF and DMSO and the structure of the binary mixtures. DMSO: TBA complex is found to be the most energetic among all these complexes.

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