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Excess Molar Volume of Aqueous 1-Propanol and Apparent Molar Volume of 2-Naphthol in Water, 1-Propanol and Their Binary Mixtures at Various Temperatures with DFT Study

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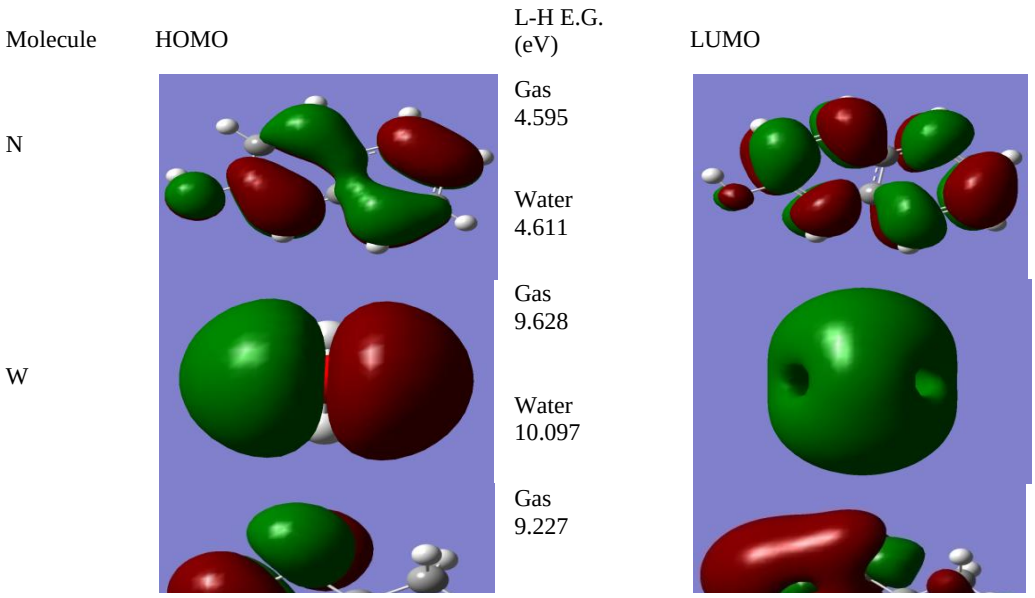
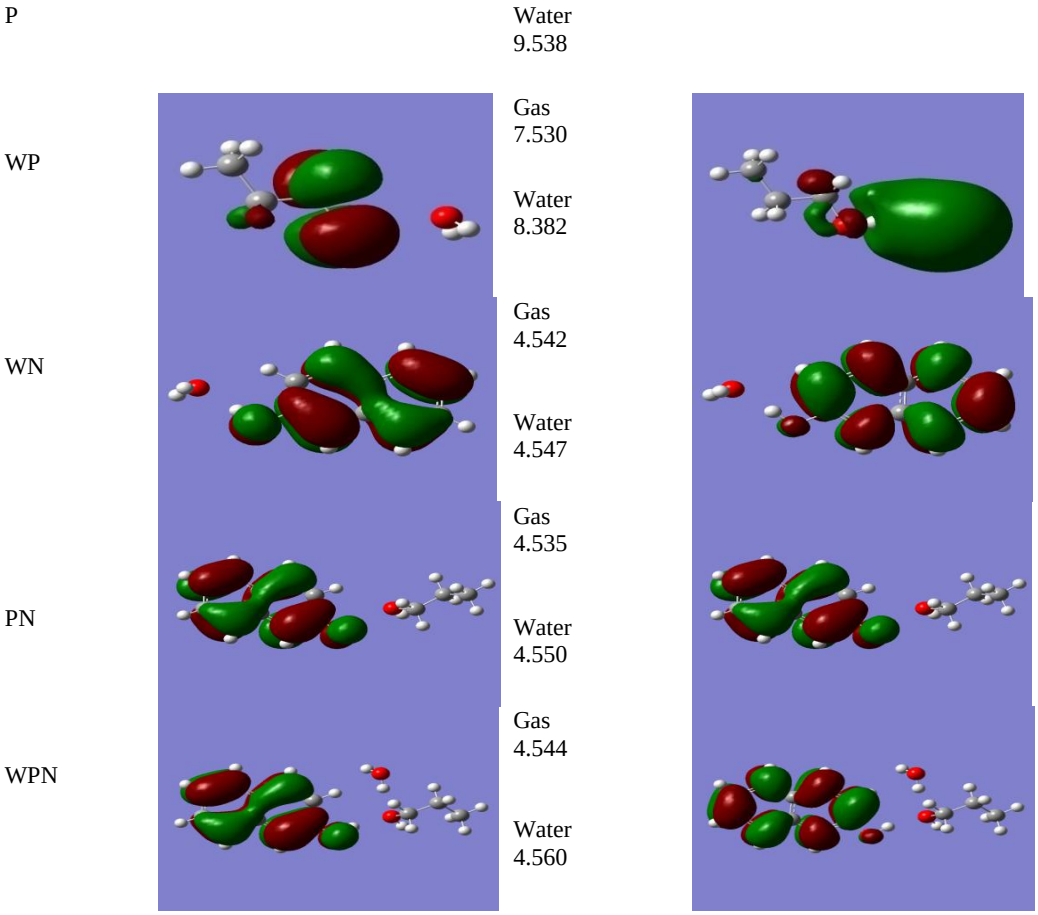
ABSTRACT

Density of water, 1-propanol and water+1-propanol binary solvent in pure form were experimentally measured. In these same solvents2-naphthol was added to make saturated solutions of 2-naphthol at equilibrium. These saturated supernatant solutions were used to measured densities and molalities of 2-naphthol at (293.15 to 313.15) K and experimental data used to calculate the excess molar volumes (V^E), apparent molar volume (V_Φ). Redlich−Kister Equation was used to calculate excess molar volumes (V^E) to correlate with the experimental excess molar volumes (V^E) of binary solvent mixture. Regressed Parameters Ai obtained from Redlich−Kister Equation were used for calculation of partial excess molar volumes at infinite dilution ($\bar{V}_i^{E,\infty}$).Molecular interaction was explained by using Gaussian 09W software, DFT method, B3LYP 6-31(G)d as basis set.

Graphical Abstract:





HOMO, LUMO structures with LUMO-HOMO Energy Gap

Keywords: 2-Naphthol, Excess Molar Volumes (V^E), Apparent Molar Volume (V_Φ), DFT.

INTRODUCTION

Class of phenolic compounds has widespread application to produce dyes, paper, pesticides, polymeric material, pharmaceutical and petrochemical products etc. There has been an increasingly concern about industrial wastewater containing phenolic compound, which are damaging and toxic to aquatic life and human beings [1]. 2-naphthol commonly used as dye possesses a very good antimicrobial property [2, 3]. 2-naphthol is crystalline solid flakes. IUPAC name is Naphthalen-2-ol.

DFT was very popular in the field of chemistry for interpretation of structure and reactivity of various organic molecules. Theoretical data obtained by Gaussian 09W software was very good agreement with the instrumental analysis of organic molecules [4, 5]. Here we used DFT to explaining interaction between solvent-solvent and solute-solvent molecules. Solvent-solvent and solvent-solute interactions of electrolytes are extremely important for the synthesis, design of processes and stimulations of unit operations [6]. Density of 2-naphthol in pure water, alcohols at certain temperatures were available but in water+1-propanol binary solvent system for 0.1 to 0.9 mole fraction of 1-propanol have to be investigating. We have undertaken the measurements of densities of pure water, 1-propanol, water+1-propanol binary solvent and saturated solutions of 2-naphthol in water + 1-propanol binary solvents over the entire composition range from 0 to 1 mole fraction of 1-propanol. The experimental work was carried out at

(293.15 to 313.15) K and excess molar volumes (V^E) [7] were calculated from the measured densities of the pure components and the binary mixtures as shown in table 1.

Table 1. Mole fraction of 1-propanol (x^0_C), density ρ, experimental [$V^E_{(Exp.)}$] & calculated [$V^E_{(Cal.)}$] values of excess molar volumes of water + 1-propanol binary system and molality (m), density (ρ), apparent molar volume (V_Φ) of 2-Naphthol + water + 1-propanol ternary system at temperatures (293.15 to 313.15) K & pressure 101.32 kPa^a.

x^0_C	**Binary solvent** $\rho.10^{-3}$ /kg.m^{-3}	$V^E_{(Exp.)}$ 10^6.m^3.mol^{-1}	$V^E_{(Cal.)}$ 10^6.m^3.mol^{-1}	m mol.Kg^{-1}	**Ternary solution** $\rho.10^{-3}$/ kg.m^{-3}	V_Φ m^3.mol^{-1}
293.15 K						
0.0000	0.9982	0.0000	0.0000	0.0023	0.9976	393.8230
0.1000	0.9562	-0.4827	-0.4765	-	-	-
0.2005	0.9183	-0.6241	-0.6592	-	-	-
0.3000	0.8913	-0.7010	-0.6705	-	-	-
0.4000	0.8691	-0.6589	-0.6098	3.6486	0.9507	124.5577
0.4946	0.8506	-0.4775	-0.5481	4.2880	0.9539	121.4553
0.6000	0.8388	-0.5340	-0.5115	4.9236	0.9535	122.0968
0.7002	0.8285	-0.4923	-0.5059	5.0630	0.9487	121.7672
0.7986	0.8209	-0.4998	-0.4857	5.1835	0.9441	122.0261
0.8999	0.8125	-0.3585	-0.3614	5.2055	0.9403	121.2094
1.0000	0.8032	0.0000	0.0000	5.0592	0.9332	120.2235
295.65 K						
0.0000	0.9977	0.0000	0.0000	0.0026	0.9970	417.4760
0.1000	0.9545	-0.4707	-0.4655	-	-	-
0.2005	0.9160	-0.6018	-0.6299	-	-	-
0.3000	0.8890	-0.6825	-0.6610	-	-	-
0.4000	0.8677	-0.6823	-0.6502	3.8816	0.9532	124.6206
0.4946	0.8510	-0.6063	-0.6351	4.5426	0.9553	122.6820
0.6000	0.8381	-0.6143	-0.6162	5.1806	0.9553	122.6498
0.7002	0.8275	-0.5624	-0.5789	5.3500	0.9505	122.4470
0.7986	0.8190	-0.5155	-0.4950	5.4691	0.9459	122.4494
0.8999	0.8099	-0.3152	-0.3192	5.4847	0.9422	121.4052
1.0000	0.8011	0.0000	0.0000	5.3928	0.9357	120.7787
298.15 K						
0.0000	0.9970	0.0000	0.0000	0.0027	0.9963	404.6808
0.1000	0.9529	-0.4603	-0.4563	-	-	-
0.2005	0.9143	-0.5943	-0.6207	-	-	-
0.3000	0.8873	-0.6774	-0.6475	-	-	-
0.4000	0.8657	-0.6697	-0.6290	4.2537	0.9561	125.0839
0.4946	0.8476	-0.5206	-0.6080	4.8591	0.9584	122.3642

0.6000	0.8364	-0.6277	-0.5883	5.4658	0.9573	122.9963
0.7002	0.8255	-0.5618	-0.5555	5.6288	0.9526	122.6483
0.7986	0.8164	-0.4701	-0.4775	5.8539	0.9484	122.8790
0.8999	0.8078	-0.3078	-0.3070	5.7794	0.9453	121.3454
1.0000	0.7991	0.0000	0.0000	5.6860	0.9385	120.9275
300.65 K						
0.0000	0.9964	0.0000	0.0000	0.0031	0.9957	360.8002
0.1000	0.9511	-0.4487	-0.4474	-	-	-
0.2005	0.9122	-0.5805	-0.5926	-	-	-
0.3000	0.8851	-0.6644	-0.6392	-	-	-
0.4000	0.8633	-0.6520	-0.6555	4.5446	0.9591	124.8686
0.4946	0.8473	-0.6164	-0.6480	5.2568	0.9605	123.6300
0.6000	0.8342	-0.6259	-0.6065	5.8219	0.9599	123.2351
0.7002	0.8231	-0.5489	-0.5377	6.0535	0.9559	122.9393
0.7986	0.8137	-0.4364	-0.4479	6.1619	0.9508	122.8713
0.8999	0.8056	-0.3089	-0.3070	6.0939	0.9468	121.8844
1.0000	0.7968	0.0000	0.0000	5.9583	0.9407	121.0522
303.15 K						
0.0000	0.9957	0.0000	0.0000	0.00368	0.9949	350.8991
0.1000	0.9495	-0.4416	-0.4403	-	-	-
0.2005	0.9102	-0.5698	-0.582	-	-	-
0.3000	0.8829	-0.6541	-0.6285	-	-	-
0.4000	0.8611	-0.6416	-0.6441	4.83086	0.9624	124.5143
0.4946	0.8449	-0.5949	-0.6327	5.66253	0.9636	123.8615
0.6000	0.8319	-0.6149	-0.5848	6.23599	0.9631	123.4331
0.7002	0.8205	-0.5153	-0.5126	6.43983	0.9582	123.2545
0.7986	0.8113	-0.4189	-0.4275	6.51013	0.9531	123.0951
0.8999	0.8032	-0.3013	-0.2997	6.44127	0.9487	122.3423
1.0000	0.7946	0.0000	0.0000	6.29126	0.9440	121.0437
305.65 K						
0.0000	0.9949	0.0000	0.0000	0.0039	0.9941	357.1673
0.1000	0.9479	-0.4337	-0.4315	-	-	-
0.2005	0.9085	-0.5641	-0.5792	-	-	-
0.3000	0.8810	-0.6458	-0.6220	-	-	-
0.4000	0.8590	-0.6296	-0.6320	5.1757	0.9660	124.3400
0.4946	0.8432	-0.6072	-0.6253	6.0452	0.9667	124.0488
0.6000	0.8299	-0.6102	-0.5959	6.6795	0.9659	123.8476
0.7002	0.8187	-0.5336	-0.5417	6.7987	0.9610	123.4316

0.7986	0.8098	-0.4600	-0.4558	6.8543	0.9561	123.2086
0.8999	0.8012	-0.3033	-0.3040	6.8305	0.9524	122.3709
1.0000	0.7925	0.0000	0.0000	6.6599	0.9466	121.4583
308.15 K						
0.0000	0.9940	0.0000	0.0000	0.0041	0.9934	304.5030
0.1000	0.9463	-0.4273	-0.4251	-	-	-
0.2005	0.9065	-0.5510	-0.5657	-	-	-
0.3000	0.8789	-0.6307	-0.6091	-	-	-
0.4000	0.8571	-0.6223	-0.6203	5.5724	0.9694	124.4678
0.4946	0.8409	-0.5831	-0.6090	6.4584	0.9698	124.1736
0.6000	0.8278	-0.5960	-0.5687	7.0165	0.9681	123.9584
0.7002	0.8162	-0.4867	-0.5074	7.1648	0.9635	123.4953
0.7986	0.8076	-0.4388	-0.4293	7.2116	0.9583	123.4503
0.8999	0.7992	-0.2987	-0.3001	7.2037	0.9543	122.8390
1.0000	0.7905	0.0000	0.0000	6.9980	0.9486	121.8694
310.65 K						
0.0000	0.9932	0.0000	0.0000	0.0050	0.9923	315.4619
0.1000	0.9446	-0.4195	-0.4179	-	-	-
0.2005	0.9046	-0.5431	-0.5551	-	-	-
0.3000	0.8769	-0.6247	-0.6028	-	-	-
0.4000	0.8550	-0.6149	-0.6214	6.0976	0.9726	125.0538
0.4946	0.8392	-0.5991	-0.6145	7.0088	0.9740	124.5029
0.6000	0.8256	-0.5881	-0.5734	7.5846	0.9720	124.2726
0.7002	0.8143	-0.5033	-0.5084	7.6209	0.9660	123.9450
0.7986	0.8054	-0.4296	-0.4287	7.6782	0.9613	123.7514
0.8999		-0.3021	-0.3022	7.5609	0.9566	123.0603
1.0000	0.7884	0.0000	0.0000	7.3721	0.9508	122.2632
313.15 K						
0.0000	0.9922	0.0000	0.0000	0.0065	0.9913	289.7311
0.1000	0.9428	-0.4125	-0.4119	-	-	-
0.2005	0.9024	-0.5276	-0.5362	-	-	-
0.3000	0.8748	-0.6156	-0.5884	-	-	-
0.4000	0.8526	-0.6001	-0.6230	6.7141	0.9759	125.6551
0.4946	0.8374	-0.6132	-0.6294	7.5414	0.9770	124.9428
0.6000	0.8240	-0.6231	-0.5923	8.0644	0.9747	124.6601
0.7002	0.8123	-0.5144	-0.5228	8.1085	0.9691	124.1992
0.7986	0.8033	-0.4365	-0.4400	8.1125	0.9636	124.0911
0.8999	0.7951	-0.3169	-0.3159	7.9762	0.9591	123.3458

1.0000	0.7862	0.0000	0.0000	7.8247	0.9536	122.6375

[a]Standard uncertainties u are u(T) = 0.01 K, u(x^0_C) = 0.0001, $u(p)$ = 0.01 MPa, $u(m)$ = 2×10^{-5} mol·kg^{-1} and the combined expanded uncertainties $U_c(\rho) = 0.00005\times10^{-3}$kg·m^{-3}, $U_c(V_\Phi) = 0.001\times10^{6}$.m^3·mol^{-1} and $U_c(V^E) = 0.001\times10^{6}$.m^3·mol^{-1}

Excess molar volume of binary mixture can be defined as the difference in molar volume of the mixture and the sum of the molar volume each component at given conditions [8]. The excess molar volumes (V^E) for the binary mixtures were obtained by eq.1.

$$V^E=[x_1 M_1 + x_2 M_2]/\rho_{12} - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 .....(1)$$

Where xi,ρi, and Mi represent the mole fraction, the density and the molecular weight of the pure component respectively, while ρ_{12} represents the density of the binary solvent mixtures. The values of experimental $V^E$for water+1-propanol binary solvent for 0.1 to 0.9 mole fractions of 1-propanol were compared with calculated values of V^E by Redlich−Kister [9] type smoothing equation:

$$V^E = x_1 x_2 \sum_{i=o}^{n} Ai(x_1 - x_2)^i \ .....(2)$$

Where x_1 is the mole fraction of 1-propanol used in study, x_2 is mole fraction of water, Ai is the adjustable parameter, and n is the number of the fitted parameters. The parameters for the Redlich−Kister equation was obtained by the least-squares fit method and the results were listed in table2.

Table 2. Regressed Parameters Ai and correlation coefficient R^2 of the Redlich−Kister Equation and the Root-Mean-Square Deviation (σ).

	A_0	A_1	A_2	A_3	A_4		
TK	10^6.m^3·mol^{-1}	10^6.m^3·mol^{-1}	10^6.m^3·mol^{-1}	10^6.m^3·mol^{-1}	10^6.m^3·mol^{-1}	R^2	σ
1-Propanol + Water							
293.15	-2.18096	1.03840	-3.87773	-0.36882	0.01937	0.977	0.034
295.65	-2.53708	0.31075	-2.51139	1.10627	-0.52302	0.983	0.021
298.15	-2.42791	0.38236	-2.69421	1.02727	-0.21404	0.962	0.037
300.65	-2.58701	0.47885	-0.96105	0.77765	-2.41372	0.990	0.016
303.15	-2.52483	0.59258	-0.77824	0.60241	-2.65654	0.988	0.019
305.65	-2.49750	0.34124	-1.45230	0.85370	-1.60767	0.993	0.013
308.15	-2.43081	0.51549	-1.06604	0.55480	-2.23485	0.988	0.017
310.65	-2.45303	0.47981	-0.80358	0.50912	-2.52152	0.994	0.011
313.15	-2.51457	0.29638	-0.30044	0.58189	-3.26202	0.987	0.017

The values of the partial excess volume of solvent$_1$ and solvent$_2$ at infinite dilution $\overline{V}_1^{E,\infty}$ can be calculated as in Table 3 from the adjustable parameters of Redlich−Kister smoothing equation as

$$\overline{V}_1^{E,\infty} = A_0 - A_1 + A_2 - A_3 + A_4 \quad \ldots (3)$$

$$\overline{V}_2^{E,\infty} = A_0 + A_1 + A_2 + A_3 + A_4 \quad \ldots. (4)$$

Table 3. Calculated Partial Excess Molar Volumes at Infinite Dilution at$T$ = (293.15 to 313.15) K from Redlich−Kister Parameters Ai

	1-propanol(1) + Water(2)	
	$\overline{V}_1^{E,\infty}$	$\overline{V}_2^{E,\infty}$
***T*(K)**	**10^6.m^3·mol^{-1}**	**10^6.m^3·mol^{-1}**
293.15	-6.70890	-5.36974
295.65	-6.98851	-4.15447

298.15	-6.74580	-3.92653
300.65	-7.21828	-4.70528
303.15	-7.15460	-4.76462
305.65	-6.75241	-4.36254
308.15	-6.80200	-4.66141
310.65	-6.76706	-4.78920
313.15	-6.95530	-5.19876

The following equation was used to calculate the root-mean-square deviation (rmsd) values:

$$rmsd(\sigma) = \sqrt{\frac{1}{N}\sum_i^N (V^E_{cal\,(i)} - V^E_{exp\,(i)})^2} \ldots. (5)$$

Where $V^E_{cal(i)}$ and $V^E_{exp(i)}$ are the calculated and experimental values of the excess molar volume respectively and N is the number of data points for each data set. Values of rmsd listed in Table 2 indicates good agreement between the calculated and experimental values.

Apparent molar volume (V_Φ) [10-12] of solution of 2-naphthol in pure water, 1-propanol and water+1-propanol binary solvent for 0.1to 0.9 mole fraction of 1-propanol were calculated by using eq.6

$$V_\Phi = 1000(d^0\text{-}d)/dd^0m + M/d \ldots (6)$$

Where d is density of ternary solution, d^0 is density of binary solvent, m is molality of solution (moles/1000gm of solvent) and M is molecular weight of solute.

MATERIALS AND METHODS

Materials: Triple distilled water was used in all experiments. Other chemicals were supplied by

Chemical Name	Supplier Name	Percentage purity	Standard
2-Naphthol	Sigma-Aldrich co.	99%	Reagent Grade
1-Propanol	Spectrochem Pvt.Ltd, Mumbai, India.	≥99.8%	HPLC

Apparatus and Procedure: The apparatus and procedures used for density measurement have been described earlier in detail [13, 14]. Briefly in this work; an excess amount of 2-naphthol was added to the binary solvents mixtures prepared by weight (Shimadzu, Auxzzo) with an uncertainty of ± 0.1 mg, in a specially designed 100 mL jacketed flask. Water was circulated at constant temperature between the outer and inner walls of the flask. The temperature of the circulating water was controlled by thermostat to within (± 0.1) K. The solution was continuously stirred using a magnetic stirrer for sufficient time (about 3h) so that equilibrium is assured, no further solute dissolved, and the temperature of solution is same as that of circulating water, the stirrer was switched off and the solution was allowed to stand for 1h. Then 5 mL of the supernatant liquid was withdrawn from the flask in a weighing bottle with the help of pipette which is hotter than the solution. Solutions were dried gravimetrically till constant weight of weighing bottle was reached. Molality of 2-naphthol was calculated by constant weights of solute. This flask solution was used to fill bicapillary pycnometer.

Densities were determined using a 15 cm^3 bicapillary pycnometer as described earlier [15,16]. For calibration of pycnometer triply distilled and degassed water with a density of 0.99705 $g{\cdot}cm^{-3}$ at 298.15 K was used. The filled pycnometer (without air bubble) with experimental liquids was kept in a transparent walled thermostat maintained at constant temperature (±0.1 K) for 10 to 15 min to attain thermal equilibrium. The heights of the liquid levels in the two arms were measured with the help of a travelling

microscope, which could read to 0.01 mm. The estimated standard uncertainty of the density measurements of the solvent and binary mixtures was 10 kg·m^{-3}.

RESULTS AND DISCUSSION

The experimental values of density (ρ) of pure water, 1-propanol and water+1-propanol binary solvents and the densities of the saturated solutions of 2-naphthol in water, 1-propanol and water+1-propanol binary mixtures have been experimentally measured at temperatures (293.15, 295.65, 298.15, 300.65, 303.15, 305.65, 308.15, 310.65, 313.15)K. Excess molar volumes (V^E) data were correlated to values obtained from Redlich-Kister, apparent molar volume (V_Φ) are given in table-1. Calculated partial excess molar volumes at infinite dilution ($\overline{V}_i^{E,\infty}$)at T = (293.15 to 313.15) K from Redlich-Kister Parameters *Ai* shown in Table 3. ($\overline{V}_i^{E,\infty}$) values are more negative for 1-propanol than water. In case of V^E negative contribution, might arise from following effects

- Strong interactions between water and 1-propanol, which enhance the solvent structure in the mixtures.
- Inter-molecular hydrogen-bonded structure of water was breaks by the addition of 1-propanol to form new intermolecular hydrogen-bond which gives a more compact structure as well as geometrical effects such as interstitial accommodation, making V^E negative.
- As added 1-propanol fill up the all interstitial space between water molecules from 0.1 to 0.3 mole fraction 1-propanol further addition of 1-propanolat 0.4 to 0.9 mole fractions gradually start to increase the V^E values as shown in fig.1.This suggests lower the intermolecular interactions among solvents molecules.

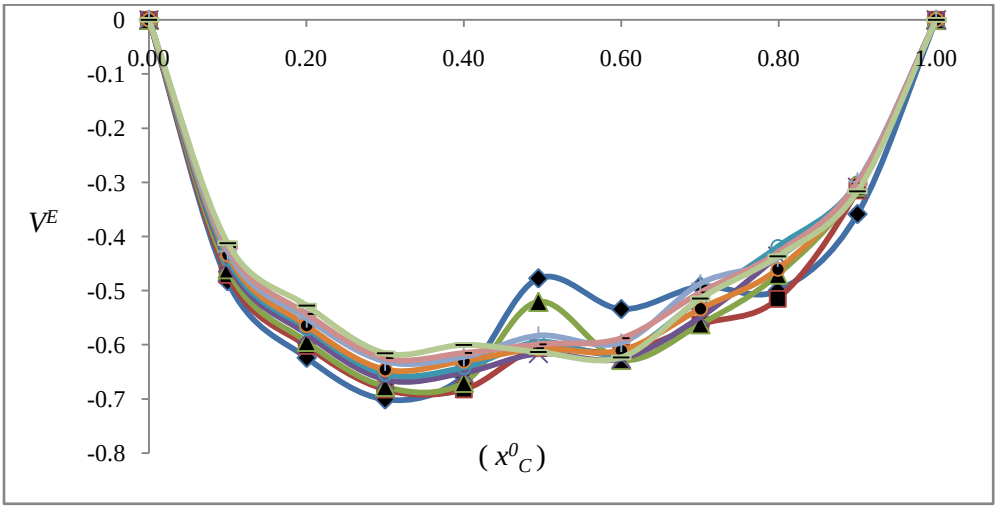


Fig 1. Excess molar volumes (V^E) vs. Mole fraction of 1-Propanol (x_c^0) at Temperatures
(◆T=293.15 K, ■T=295.15 K; ▲T=298.15K; ×T=300.15 K; ○T=303.15 K;
●T=305.15 K; +T=308.15 K; -T=310.15 K & ▬ T=313.15 K).

The highest negative V^E values for water+1-propanolwere noticeably observed at 0.3 and nearly same at 0.4 mole fraction of 1-propanol. The positive value of V_Φ indicates weak solute-solvent interactions only in terms of Vander Waals force of attraction, H-bonding and not any strong electrostatic force of attractions. V_Φ values of 2-naphthol in water are very higher than in 1-propanol, indicates 2-naphthol interaction is stronger in1-propanol than water. Hence 2-naphthol is more soluble in 1-propanol than in water which is confirmed from *m* values in table-1 and fig. 2, *m* values of 2-naphthol is nearly zero indicates insoluble in water. These *m* values are increasing for 0.4, 0.5 and 0.6 mole fraction of 1-propanol and remain constant from 0.6 to 1 mole fraction of 1-propanol. Interesting situation of *m* values for 0.1, 0.2 and 0.3 mole fractions of 1-propanol is the system undergoes phase separation. At unsaturated level solution was clear

or transparent. As soon as excess amount of 2-naphthol is added solution became saturated or supersaturated at this concentration level due to various molecular interaction change the phase of solution. The solution became heterogeneous and we observed the phase separation. Thus, these *m* and V_Φ for 0.1, 0.2, 0.3 mole fractions of 1-propanol at all experimental temperatures are not given in the Table 1.

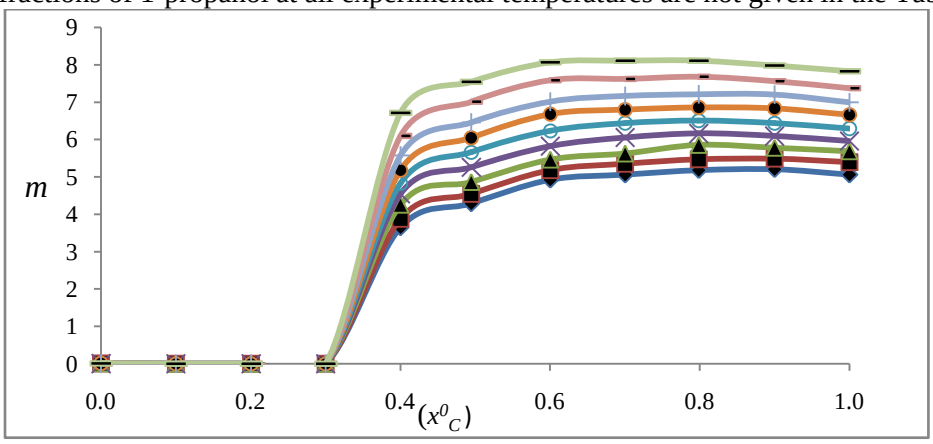


Fig 2. Plot of Molality (*m*) Vs. Mole Fraction of 1-Propanol(x^0_C) for 2-Naphthol+ Water + 1-Propanol System. (◆T=293.15; ■ T =295.65; ▲ T =298.15; × T =300.65; ○ T =303.15; ● T =305.65;+ T =308.15; - T =310.65; ▬ T =313.15).

Molalities of 2-naphthol are very much higher in 1-propanol than in water and which is very slowly increase with increase in temperature. For ternary system it was observed that V_Φ values are very higher in water. Lower V_Φ values was observed in all mole fraction of 1-propanol and nearly constant for all mole fraction of 1-propanol at all experimental temperatures (Fig.3).

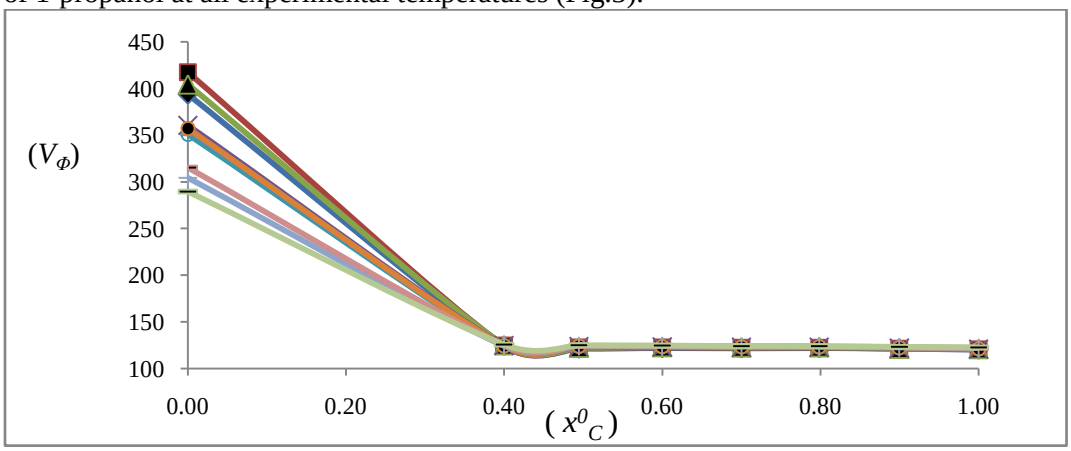
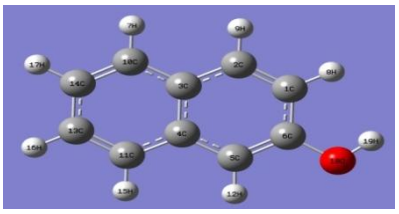
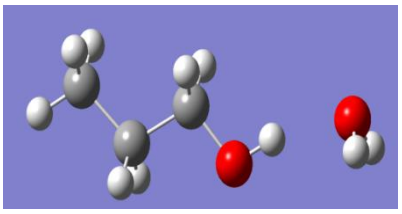


Fig 3. Apparent molar volume (V_Φ) of 2-Naphthol vs. Mole fraction 1-Propanol (x^0_C) at Temperatures (◆T=293.15 K, ■T=295.65 K; ▲T=298.15K; ×T=300.65 K; ○T=303.15 K; ●T=305.65 K; +T=308.15 K; -T=310.65 K & ▬T=313.15 K).

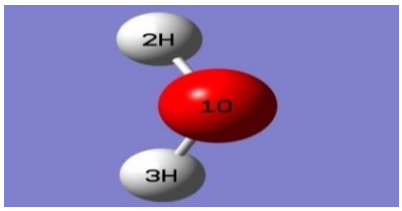
Computational study using Gaussian 09W software, DFT method, B3LYP 6-31(G)d as basis set was performed to understand the fundamental interactions between solvent-solvent and solute-solvent molecules. First, the structures of the solvent were optimized and stable conformers were obtained. The optimized structure of 1-propanol then interacted with water molecule and 2-naphthol molecule as shown in Fig.4.



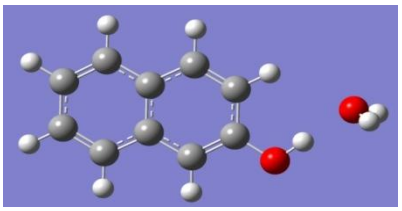
Optimized structure of **N**



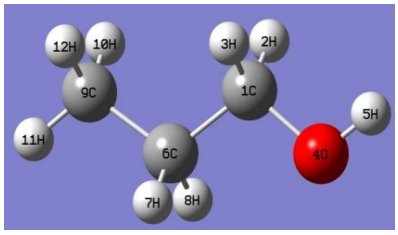
Optimized structure of **WP**



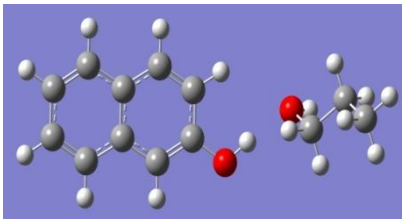
Optimized structure of **W**



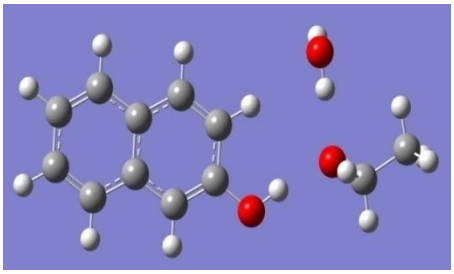
Optimized structure of **WN**



Optimized structure of **P**



Optimized structure of **PN**



Optimized structure of **WPN**

Fig 4. Optimized structures of solute, solvents combinations by DFT method at B3LYP level using 6-31G(d) basis set [Abbreviations:W: Water, P: 1-Propanol, N: 2-Naphthol]

Dipole moment, total energy, molecular symmetry, I.R. frequency of alcoholic-OH group, alcoholic-OH bond distance in angstroms unit and distance of intermolecular hydrogen bonding present between alcohol with water and 2-naphthol was given in Table 4.

Table 4. Calculated –OH str.freq. along with palarizability, dipole moment, -OH bond distance, intermolecular H-bond distance for pure substance, binary solvents & ternary solutions by DFT/B3LYP method at 6-31G (d) basis set

System	Phase/ Media	Dipole Moment (Debye)	(α) $Bohr^3$	Alcoholic υ-OH cm^{-1}	Alcoholic (-OH) Bond Dist. (^0A)	Intermolecular H-Bond Dist.(^0A)
N	Gas	1.594	105.19	3610.83	-	-
	Water	2.145	144.55	3600.25	-	-
W	Gas	2.0952	5.22	3584.18(sy.str.) 3701.29(Uns.str.)	-	-
	Water	2.3139	5.52	3584.78(sy.str.) 3684.62(Uns.str.)	-	-
P	Gas	1.488	36.84	3608.16	0.9689	-
	Water	1.845	44.69	3602.54	0.9699	-
WP	Gas	2.296	43.49	3473.21	0.9772	1.9034
	Water	3.388	52.02	3381.89	0.9823	1.8343
WN	Gas	4.714	113.60	3395.49	-	1.8271
	Water	5.428	153.64	3232.27	-	1.7516
PN	Gas	4.990	142.32	3597.03	0.9705	1.8088
	Water	5.758	193.97	3591.29	0.9717	1.7499
WPN	Gas	4.436	154.30	3602.31	0.9707	1.9177
	Water	6.350	201.41	3593.4	0.9721	1.8044

[Abbreviations:-W: Water, P: 1-Propanol, N: 2-Naphthol]

HOMO-LUMO with energy gap between them is shown in Fig.5. Energies of all optimized structure of HOMO, LUMO and their energy gap were shown in Table.5

Table 5. HOMO, LUMO energies and Energy Gap between LUMO-HOMO Calculated by DFT method at B3LYP level using 6-31G (d) basis set.

System	Phase/Media	HOMO (eV)	LUMO (eV)	LUMO-HOMO Energy gap (eV)
N	Gas	-5.517	-0.922	4.595
	Water	-5.665	-1.054	4.611
W	Gas	-7.924	1.704	9.628
	Water	-8.035	2.062	10.097
P	Gas	-7.114	2.113	9.227
	Water	-7.210	2.328	9.538
WP	Gas	-6.502	1.028	7.530
	Water	-6.794	1.588	8.382
WN	Gas	-5.103	-0.561	4.542
	Water	-5.486	-0.939	4.547
PN	Gas	-5.080	-0.546	4.535
	Water	-5.491	-0.941	4.550
WPN	Gas	-5.135	-0.591	4.544
	Water	-5.509	-0.949	4.560

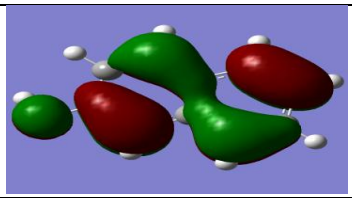
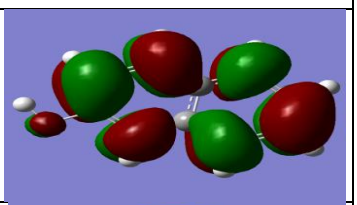
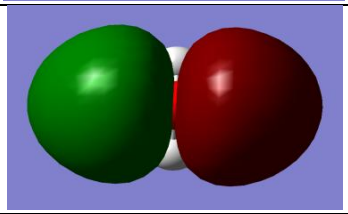
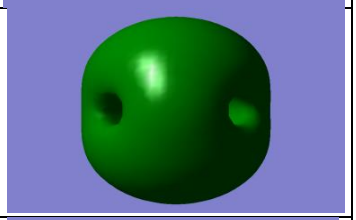
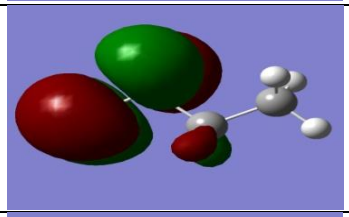
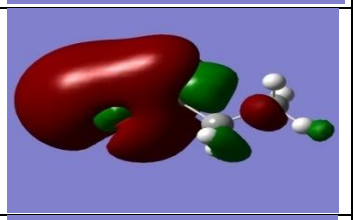
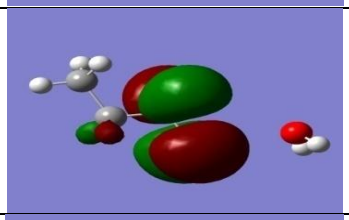
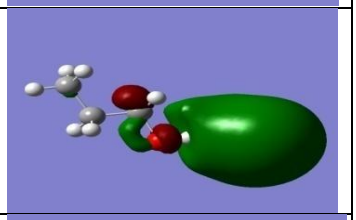
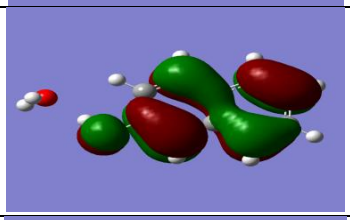
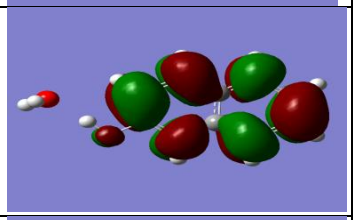
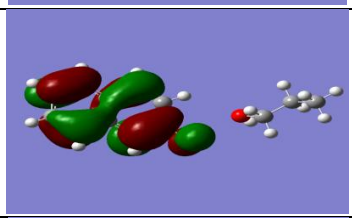
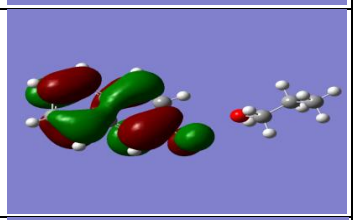
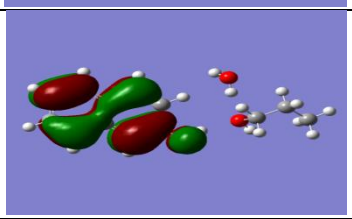
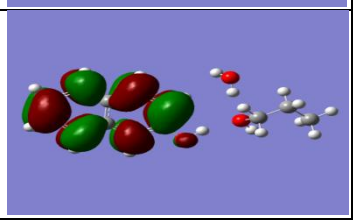
Molecule	HOMO	L-H E.G. (eV)	LUMO
N		Gas 4.595 Water 4.611	
W		Gas 9.628 Water 10.097	
P		Gas 9.227 Water 9.538	
WP		Gas 7.530 Water 8.382	
WN		Gas 4.542 Water 4.547	
PN		Gas 4.535 Water 4.550	
WPN		Gas 4.544 Water 4.560	

Fig 5. HOMO, LUMO structures with LUMO-HOMO Energy Gap

Here we observed that solvents (W, P, WP) shows more energy gap than 2-naphthol solutions (solvent-solvent interactions) stronger and stable than solute-solvent interactions. The trend of dipole moment (given in Table 4) for solvent was water+1-propanol> water >1-propanol. This indicates that stronger

interactions in binary system were there than in the pure solvents. Which was confirmed form negative V^E values.

APPLICATIONS

Excess molar volume of aqueous 1-propanol, solubility in terms of molality, apparent molar volume, density data of 2-naphthol in water, 1-propanol and various mole fractions of 1-propanol are more useful n field of physical chemistry and chemical engineering calculations involving fluid flow, heat and mass transfer, pharmaceutical industry, agriculture, biology, medicine. Solubility data is required for selection of proper solvent and design an optimized crystallization process.

CONCLUSIONS

Densities of binary system decrease with mole fraction of 2-Naphthol and temperatures. But in case ternary solution densities decreases with mole fraction of 2-Naphthol at same temperature but increases with temperatures this is due to increase of molality (*m*) of 2-naphthol as given in Table 1. The trend of *m* in is shown as water+1-propanol >1-propanol >> water at same temperature. At 0.8 mole fraction of 1-propanol *m* values are highest. These values of *m* increase with increase in temperature due to solubility increase with temperature. Which explains solubility rule 'like dissolved like', because 2-napthtol is polar aromatic compound so it is molar soluble in polar organic solvents. Thus 2-naphthol is nearly insoluble in water due to its aromatic nature. As V^E are more negative up to 0.6 mole fraction of 1-propanol, *m* values increase up to 0.6 mole fraction of 1-propanol and V^E started become less negative from 0.6 to 0.9 mole fraction of 1-propanol shown in fig.1. Similarly, *m* values remain constant for 0.6 to 0.9mole fraction of 1-propanol. From these results we say that solubility increase with mole fraction of 1-propanol but after 0.6 mole fraction addition of 1-propanol is less significant for solubility of hydroquinone.

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