Molecular Interactions of 2-Naphthol in Binary Solvent Mixtures of Water+Methanol and Water+Ethanol with DFT Study

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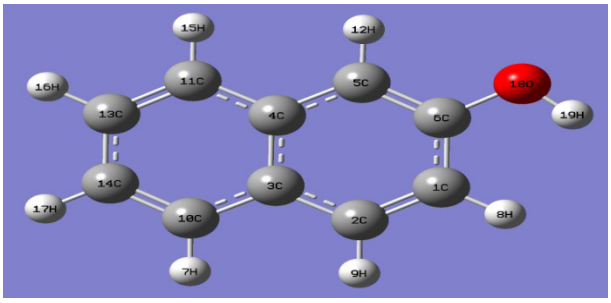
Abstract

Density of water, methanol, ethanol and water+methanol, water+ethanol binary solvent in pure form were experimentally measured. In these same series of solvents 2-naphthol was added to make saturated solutions of 2-naphthol at equilibrium. These saturated supernatant solutions were collected to measured densities and molalities of 2-naphthol at (293.15 to 313.15) K for comparative studies 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 ($\overline{V}_i^{E,\infty}$). Molecular interaction was explain by using Gaussian 09W software, DFT/B3LYP 6-31(G)d as basic set.

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

Introduction

Phenolic compounds have widespread application to produced dyes, paper, pesticides, polymeric material, pharmaceutical and petrochemical product etc. There has been an increasingly concern about industrial wastewater containing phenolic compound, which are damaging and toxic to aquatic life and human bring [1, 2]. 2-Naphthol is crystalline solid flakes. IUPAC name is Naphthalen-2-ol, with the molecular formula $C_{10}H_8O$. Molar mass is 144.17 gm/mol, melting point is about 121-123^{0}C. The Optimized molecular structure of 2-naphthol is as follows



Theoretical calculation by different methods were carried out by different people among these 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 [5, 6]. 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 simulations of unit operations [7]. Density of 2-naphthol in pure water, alcohols at certain temperatures were available but in water–alcohol mixed solvent system for 0.1 to 0.9 mole fraction of methanol and ethanol have to be

investigate. We have undertaken the measurements of densities of pure solvents, binary solvent mixtures and saturated solutions of 2-naphthol in water + methanol and water + ethanol binary solvents over the entire composition range from 0 to 1 mole fraction of methanol, ethanol.

Experimental Details

Material:-

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

Chemical Name	Supplier Name	Percentge purity	Standard
2-Naphthol	Sigma-Aldrich co.	99%	Reagent Grade
Methanol	Merck, Germany.	≥99.8%	G.R.
Ethanol	Merck, D, Germany.	≥99.8%	G.R.

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 3hr) 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 1hr. 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 $kg \cdot m^{-3}$.

Results and Discussion

The experimental values of density (ρ) of pure water, methanol, ethanol and water+methanol, water+ethanol binary solvents also the densities of the saturated solutions of 2-naphthol in water, methanol, ethanol and their binary mixtures water+methanol, water+ethanol have been experimentally measured for comparative studies 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)[8] were calculated from the measured densities of the pure components and the binary solvent mixtures as shown in Table 1,2.

Table 1-Mole fraction of methanol (x^0_C), density ρ, experimental [$V^E_{(Exp.)}$] & calculated [$V^E_{(Cal.)}$] values of excess molar volumes of water + methanol binary system and molality (m), density (ρ), apparent molar volume (V_Φ) of 2-naphthol + water + methanol 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	0.9715	-0.3044	-0.3039	0.0065	0.9719	95.8052
0.2000	0.9499	-0.6154	-0.6155	0.0486	0.9509	129.4507
0.3000	0.9283	-0.8360	-0.8432	0.2182	0.9331	128.6691
0.4000	0.9070	-0.9714	-0.9643	0.6713	0.9221	129.3843
0.5000	0.8856	-1.0009	-0.9887	2.1466	0.9225	135.2336
0.5965	0.8649	-0.9241	-0.9365	3.2316	0.9402	124.6901
0.6996	0.8448	-0.8003	-0.8082	4.8504	0.9529	123.6171
0.8000	0.8265	-0.6198	-0.6102	6.1736	0.9603	122.8186
0.8996	0.8085	-0.3369	-0.3387	7.3541	0.9654	122.0076
1.0000	0.7916	0.0000	0.0000	8.7385	0.9708	121.8129
			295.65 K			
0.0000	0.9977	0.0000	0.0000	0.0026	0.9970	417.4760
0.1000	0.9706	-0.3060	-0.3062	0.0084	0.9708	130.6704
0.2000	0.9486	-0.6158	-0.6137	0.0495	0.9496	129.3911
0.3000	0.9267	-0.8369	-0.8428	0.2227	0.9315	129.6496
0.4000	0.9051	-0.9699	-0.9689	0.7876	0.9237	127.9452
0.5000	0.8838	-1.0047	-0.9968	2.3332	0.9281	132.1657
0.5965	0.8635	-0.9468	-0.9450	3.6003	0.9442	125.1912
0.6996	0.8427	-0.8022	-0.8171	5.2006	0.9554	123.9837
0.8000	0.8247	-0.6333	-0.6238	6.7289	0.9647	123.2935
0.8996	0.8067	-0.3559	-0.3573	7.7812	0.9682	122.3401
1.0000	0.7893	0.0000	0.0000	8.9795	0.9715	121.9439
			298.15 K			
0.0000	0.9970	0.0000	0.0000	0.0027	0.9962	456.6797
0.1000	0.9698	-0.3116	-0.3117	0.0089	0.9700	133.2681
0.2000	0.9473	-0.6199	-0.6181	0.0544	0.9485	127.4734
0.3000	0.9251	-0.8404	-0.8457	0.2384	0.9303	129.6048
0.4000	0.9033	-0.9720	-0.9722	0.9326	0.9250	127.9643
0.5000	0.8819	-1.0119	-1.0023	2.5185	0.9338	129.3705
0.5965	0.8615	-0.9548	-0.9525	4.1444	0.9498	125.7560
0.6996	0.8406	-0.8069	-0.8246	5.7258	0.9605	124.1757
0.8000	0.8225	-0.6393	-0.6280	7.1510	0.9677	123.4765

0.8996	0.8043	-0.3554	-0.3571	8.2355	0.9712	122.5145
1.0000	0.7870	0.0000	0.0000	9.4245	0.9740	122.1277
			300.65 K			
0.0000	0.9964	0.0000	0.0000	0.0031	0.9957	360.8002
0.1000	0.9689	-0.3166	-0.3168	0.0097	0.9691	123.5504
0.2000	0.9459	-0.6226	-0.6201	0.0613	0.9471	128.8193
0.3000	0.9232	-0.8400	-0.8462	0.3002	0.9303	127.4904
0.4000	0.9013	-0.9746	-0.9737	1.1144	0.9267	128.2418
0.5000	0.8796	-1.0119	-1.0051	2.8105	0.9396	127.6183
0.5965	0.8593	-0.9598	-0.9557	4.5171	0.9541	125.5155
0.6996	0.8382	-0.8120	-0.8281	6.3140	0.9648	124.6500
0.8000	0.8200	-0.6429	-0.6332	7.6391	0.9711	123.6256
0.8996	0.8019	-0.3629	-0.3643	8.8293	0.9753	122.7012
1.0000	0.7844	0.0000	0.0000	9.9338	0.9781	121.9870
			303.15 K			
0.0000	0.9957	0.0000	0.0000	0.0037	0.9953	240.5303
0.1000	0.9678	-0.3197	-0.3204	0.0119	0.9678	148.3125
0.2000	0.9447	-0.6326	-0.6274	0.0759	0.9463	128.2274
0.3000	0.9215	-0.8441	-0.8537	0.3293	0.9290	128.6128
0.4000	0.8993	-0.9788	-0.9788	1.3573	0.9300	127.9875
0.5000	0.8775	-1.0174	-1.0079	3.1926	0.9451	127.0419
0.5965	0.8569	-0.9618	-0.9583	5.0993	0.9599	125.6637
0.6996	0.8359	-0.8172	-0.8328	6.7854	0.9696	124.3697
0.8000	0.8176	-0.6494	-0.6405	8.2928	0.9760	123.7944
0.8996	0.7995	-0.3701	-0.3713	9.4679	0.9790	123.0370
1.0000	0.7818	0.0000	0.0000	10.3861	0.9803	122.1260
			305.65 K			
0.0000	0.9949	0.0000	0.0000	0.0039	0.9941	357.1673
0.1000	0.9668	-0.3221	-0.3222	0.0136	0.9670	129.3863
0.2000	0.9430	-0.6281	-0.6260	0.0838	0.9447	129.5583
0.3000	0.9198	-0.8462	-0.8520	0.3875	0.9286	128.5278
0.4000	0.8974	-0.9814	-0.9805	1.6382	0.9337	127.9569
0.5000	0.8755	-1.0212	-1.0138	3.6670	0.9511	126.8145
0.5965	0.8549	-0.9701	-0.9665	5.6136	0.9647	125.7344
0.6996	0.8338	-0.8235	-0.8404	7.4896	0.9747	124.7490
0.8000	0.8154	-0.6558	-0.6454	8.8880	0.9788	124.2608
0.8996	0.7971	-0.3718	-0.3733	9.9150	0.9821	122.9819
1.0000	0.7794	0.0000	0.0000	10.9699	0.9821	122.6463
			308.15 K			
0.0000	0.9940	0.0000	0.0000	0.0041	0.9934	304.5030

0.1000	0.9657	-0.3271	-0.3270	0.0192	0.9665	107.3558
0.2000	0.9415	-0.6302	-0.6294	0.0974	0.9437	127.0039
0.3000	0.9181	-0.8489	-0.8545	0.4578	0.9288	127.8174
0.4000	0.8956	-0.9855	-0.9831	1.9823	0.9371	128.8838
0.5000	0.8735	-1.0255	-1.0165	4.1846	0.9565	127.0145
0.5965	0.8527	-0.9682	-0.9681	6.2775	0.9703	125.9393
0.6996	0.8315	-0.8232	-0.8401	8.1528	0.9790	125.0474
0.8000	0.8132	-0.6560	-0.6442	9.4125	0.9828	124.1350
0.8996	0.7949	-0.3712	-0.3731	10.5841	0.9855	123.2983
1.0000	0.7771	0.0000	0.0000	11.5805	0.9859	122.7081
			310.65 K			
0.0000	0.9932	0.0000	0.0000	0.0050	0.9923	315.4619
0.1000	0.9647	-0.3327	-0.3325	0.0245	0.9650	134.2352
0.2000	0.9400	-0.6357	-0.6350	0.1153	0.9425	128.4609
0.3000	0.9163	-0.8540	-0.8589	0.5341	0.9287	128.0101
0.4000	0.8936	-0.9898	-0.9875	2.3181	0.9412	128.7750
0.5000	0.8714	-1.0290	-1.0229	4.7697	0.9623	127.1033
0.5965	0.8508	-0.9827	-0.9776	6.9509	0.9758	126.0976
0.6996	0.8294	-0.8317	-0.8521	8.8689	0.9839	125.1800
0.8000	0.8110	-0.6684	-0.6555	10.2495	0.9874	124.5299
0.8996	0.7925	-0.3778	-0.3797	11.2889	0.9890	123.5626
1.0000	0.7747	0.0000	0.0000	12.2153	0.9892	122.8333
			313.15 K			
0.0000	0.9922	0.0000	0.0000	0.0065	0.9913	289.7311
0.1000	0.9633	-0.3331	-0.3329	0.0288	0.9639	129.1419
0.2000	0.9383	-0.6346	-0.6343	0.1331	0.9418	123.6654
0.3000	0.9144	-0.8534	-0.8584	0.7077	0.9305	128.0620
0.4000	0.8915	-0.9905	-0.9878	2.8453	0.9491	127.9780
0.5000	0.8692	-1.0313	-1.0230	5.4802	0.9688	127.2294
0.5965	0.8483	-0.9771	-0.9761	7.7717	0.9814	126.3183
0.6996	0.8269	-0.8303	-0.8485	9.7729	0.9890	125.4835
0.8000	0.8085	-0.6643	-0.6517	11.1279	0.9919	124.7873
0.8996	0.7900	-0.3763	-0.3783	12.1635	0.9930	123.9165
1.0000	0.7722	0.0000	0.0000	12.9764	0.9924	123.1339

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

Table 2- Mole fraction of ethanol (x^0_C), density ρ, experimental [$V^E_{(Exp.)}$] & calculated [$V^E_{(Cal.)}$] values of excess molar volumes of water + ethanol binary system and molality (m), density (ρ), apparent molar volume (V_Φ) of 2-naphthol + water + ethanol 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
0.1005	0.9659	-0.5204	-0.5241	0.0282	0.9658	150.7578
0.2000	0.9374	-0.8912	-0.8741	0.5521	0.9462	134.5699
0.3000	0.9094	-1.0518	-1.0564	2.0130	0.9468	130.6992
0.4000	0.8844	-1.0815	-1.1080	3.0330	0.9486	126.7222
0.5000	0.8639	-1.0738	-1.0735	4.1520	0.9547	124.5126
0.5958	0.8469	-1.0073	-0.9882	5.0294	0.9577	123.3727
0.6996	0.8304	-0.8619	-0.8453	6.2611	0.9645	122.7322
0.7994	0.8156	-0.6225	-0.6452	6.8948	0.9645	122.0186
0.8996	0.8029	-0.3670	-0.3626	6.8555	0.9574	121.2703
1.0000	0.7905	0.0000	0.0000	7.1851	0.9556	120.4570
			295.65 K			
0.0000	0.9977	0.0000	0.0000	0.0026	0.9970	417.4760
0.1005	0.9646	-0.5181	-0.5215	0.0341	0.9650	138.2032
0.2000	0.9355	-0.8813	-0.8658	0.5817	0.9466	130.7088
0.3000	0.9073	-1.0417	-1.0456	2.0857	0.9480	129.3941
0.4000	0.8823	-1.0757	-1.0986	3.2730	0.9537	125.2549
0.5000	0.8616	-1.0642	-1.0683	4.4894	0.9576	124.6354
0.5958	0.8447	-1.0088	-0.9872	5.4094	0.9611	123.5075
0.6996	0.8281	-0.8612	-0.8471	6.5500	0.9657	123.0282
0.7994	0.8134	-0.6262	-0.6472	7.1524	0.9657	122.1959
0.8996	0.8006	-0.3674	-0.3633	7.2137	0.9587	121.8274
1.0000	0.7882	0.0000	0.0000	7.6849	0.9581	121.2153
			298.15 K			
0.0000	0.9970	0.0000	0.0000	0.0027	0.9962	456.6797
0.1005	0.9634	-0.5163	-0.5191	0.0392	0.9636	144.7293
0.2000	0.9337	-0.8729	-0.8600	0.6718	0.9470	129.7873
0.3000	0.9053	-1.0334	-1.0369	2.1788	0.9494	128.3275
0.4000	0.8803	-1.0697	-1.0890	3.5371	0.9557	125.5027
0.5000	0.8595	-1.0579	-1.0600	4.9288	0.9620	124.7036
0.5958	0.8425	-0.9998	-0.9817	5.9135	0.9652	123.8618
0.6996	0.8259	-0.8541	-0.8444	6.7594	0.9661	123.2419
0.7994	0.8114	-0.6294	-0.6455	7.3687	0.9660	122.4568
0.8996	0.7984	-0.3642	-0.3611	7.5757	0.9630	121.4484
1.0000	0.7861	0.0000	0.0000	8.3197	0.9614	122.0798
			300.65 K			
0.0000	0.9964	0.0000	0.0000	0.0031	0.9957	360.8002

0.1005	0.9619	-0.5125	-0.5157	0.0415	0.9626	131.2456
0.2000	0.9317	-0.8621	-0.8476	0.8147	0.9477	129.8431
0.3000	0.9030	-1.0189	-1.0224	2.3613	0.9510	127.8830
0.4000	0.8778	-1.0565	-1.0779	3.7955	0.9573	125.7036
0.5000	0.8571	-1.0480	-1.0522	5.2734	0.9645	124.8330
0.5958	0.8402	-0.9945	-0.9740	6.3725	0.9686	124.0720
0.6996	0.8235	-0.8483	-0.8350	7.1454	0.9678	123.6405
0.7994	0.8088	-0.6178	-0.6376	7.9382	0.9667	123.7115
0.8996	0.7961	-0.3638	-0.3599	7.9793	0.9647	121.9194
1.0000	0.7837	0.0000	0.0000	8.4831	0.9622	121.9375
			303.15 K			
0.0000	0.9957	0.0000	0.0000	0.0037	0.9953	240.5303
0.1005	0.9605	-0.5109	-0.5135	0.0447	0.9614	129.2416
0.2000	0.9297	-0.8539	-0.8423	0.9535	0.9480	130.2528
0.3000	0.9009	-1.0134	-1.0148	2.6227	0.9541	127.4777
0.4000	0.8756	-1.0506	-1.0703	4.3238	0.9630	125.7439
0.5000	0.8548	-1.0438	-1.0471	5.6811	0.9671	125.1600
0.5958	0.8378	-0.9910	-0.9722	6.7567	0.9700	124.5544
0.6996	0.8211	-0.8445	-0.8352	7.6833	0.9713	123.9172
0.7994	0.8065	-0.6204	-0.6362	8.2956	0.9702	123.3773
0.8996	0.7936	-0.3583	-0.3552	8.3635	0.9672	122.0084
1.0000	0.7813	0.0000	0.0000	8.6687	0.9630	121.8730
			305.65 K			
0.0000	0.9949	0.0000	0.0000	0.0039	0.9941	357.1673
0.1005	0.9592	-0.5083	-0.5108	0.0483	0.9603	125.3418
0.2000	0.9278	-0.8440	-0.8329	1.1160	0.9493	129.9160
0.3000	0.8988	-1.0028	-1.0036	2.9117	0.9566	127.6374
0.4000	0.8735	-1.0411	-1.0608	4.6727	0.9653	126.0432
0.5000	0.8526	-1.0344	-1.0388	6.1945	0.9713	125.2900
0.5958	0.8357	-0.9835	-0.9632	7.1589	0.9729	124.6194
0.6996	0.8189	-0.8339	-0.8258	8.1029	0.9749	123.7639
0.7994	0.8043	-0.6153	-0.6306	8.5435	0.9718	123.2670
0.8996	0.7915	-0.3603	-0.3573	8.8507	0.9704	122.2607
1.0000	0.7792	0.0000	0.0000	8.9210	0.9642	121.9126
			308.15 K			
0.0000	0.9940	0.0000	0.0000	0.0041	0.9934	304.5030
0.1005	0.9578	-0.5080	-0.5105	0.0531	0.9592	122.2869
0.2000	0.9259	-0.8379	-0.8268	1.3255	0.9518	129.3053
0.3000	0.8967	-0.9949	-0.9962	3.2600	0.9599	127.6775
0.4000	0.8714	-1.0375	-1.0556	5.1828	0.9697	126.2176
0.5000	0.8505	-1.0318	-1.0357	6.7290	0.9752	125.4934
0.5958	0.8334	-0.9761	-0.9600	7.7423	0.9770	124.8015
0.6996	0.8168	-0.8344	-0.8218	8.5336	0.9769	124.0531
0.7994	0.8021	-0.6114	-0.6284	9.0628	0.9751	123.4617

0.8996	0.7894	-0.3632	-0.3599	9.2315	0.9717	122.6302
1.0000	0.7771	0.0000	0.0000	9.4801	0.9673	122.3490
			310.65 K			
0.0000	0.9932	0.0000	0.0000	0.0050	0.9923	315.4619
0.1005	0.9563	-0.5058	-0.5079	0.0575	0.9580	119.1694
0.2000	0.9240	-0.8331	-0.8238	1.5466	0.9540	129.1073
0.3000	0.8946	-0.9878	-0.9914	3.6663	0.9639	127.6616
0.4000	0.8696	-1.0416	-1.0482	5.6503	0.9734	126.3890
0.5000	0.8481	-1.0126	-1.0265	7.3442	0.9791	125.7504
0.5958	0.8311	-0.9663	-0.9503	8.2378	0.9795	125.0529
0.6996	0.8145	-0.8269	-0.8122	8.9551	0.9783	124.4116
0.7994	0.7998	-0.6016	-0.6187	9.5143	0.9778	123.5362
0.8996	0.7871	-0.3542	-0.3511	9.7897	0.9746	122.9800
1.0000	0.7749	0.0000	0.0000	9.7968	0.9694	122.3072
			313.15 K			
0.0000	0.9922	0.0000	0.0000	0.0065	0.9913	289.7311
0.1005	0.9548	-0.5019	-0.5043	0.0642	0.9572	108.1025
0.2000	0.9218	-0.8186	-0.8073	1.8581	0.9559	129.9564
0.3000	0.8923	-0.9725	-0.9787	4.1069	0.9678	127.6580
0.4000	0.8675	-1.0405	-1.0504	6.1964	0.9769	126.7555
0.5000	0.8464	-1.0312	-1.0398	8.0512	0.9838	126.0380
0.5958	0.8294	-0.9853	-0.9626	8.8235	0.9826	125.4037
0.6996	0.8121	-0.8143	-0.8136	9.5310	0.9810	124.7103
0.7994	0.7976	-0.6021	-0.6120	10.0012	0.9795	123.9078
0.8996	0.7849	-0.3506	-0.3484	10.2617	0.9766	123.2374
1.0000	0.7727	0.0000	0.0000	10.3576	0.9730	122.4504

[a]Standard uncertainties u are u(T) = 0.01 K, u(x^0_C) = 0.0001, $u(p)$ = 0.01 MPa, $u(m) = 2\times10^{-5}$ mol·kg^{-1} and the combined expanded uncertainties $U_c(\rho) = 0.00005\ 10^{-3}$kg·m^{-3}, $U_c(V_\Phi) = 0.001\ 10^6$.m^3·mol^{-1} and $U_c(V^E) = 0.001\ 10^6$.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 [9]. The excess molar volumes (V^E) for the binary mixtures were obtained by eq.1.

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

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+methanol and water+ethanol binary solvent mixture were compared with calculated values of V^E by Redlich−Kister [10] type smoothing equation:

$$V^E = x_1 x_2 \Sigma^n_{i=0} A_i (x_1 - x_2)^i \quad .....(2)$$

Where x_1 was the molar fraction of alcohols used in study, x_2 was mole fraction of water, A_i was the adjustable parameter, and n was 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 Tables 3. The values of the partial excess volume of solvent$_1$ and solvent$_2$ at infinite dilution $\bar{V}_1^{E,\infty}$ can be calculated as in Table 4 from the adjustable parameters of Redlich−Kister smoothing equation as

$$\bar{V}_1^{E,\infty}=A_0-A_1+A_2-A_3+A_4 \quad \ldots (3)$$
$$\bar{V}_2^{E,\infty}=A_0+A_1+A_2+A_3+A_4 \quad \ldots. (4)$$

Table 3- Regressed Parameters Ai and correlation coefficient R^2 of the Redlich−Kister Equation and the Root-Mean-Square Deviation (σ)

TK	A_0 $10^6.m^3\cdot mol^{-1}$	A_1 $10^6.m^3\cdot mol^{-1}$	A_2 $10^6.m^3\cdot mol^{-1}$	A_3 $10^6.m^3\cdot mol^{-1}$	A_4 $10^6.m^3\cdot mol^{-1}$	R^2	σ
Methanol + Water							
293.15	-3.95499	0.36018	0.00205	-0.92575	0.95754	0.960	0.008
295.65	-3.98732	0.32446	0.14359	-1.04834	0.53195	0.964	0.007
298.15	-4.00916	0.27501	0.12457	-0.90879	0.54269	0.944	0.008
300.65	-4.02051	0.25585	0.16834	-0.90129	0.33629	0.948	0.007
303.15	-4.03175	0.28512	0.04554	-0.98373	0.41189	0.941	0.008
305.65	-4.05535	0.21262	0.12297	-0.87269	0.29594	0.943	0.007
308.15	-4.06594	0.22256	0.17639	-0.83403	0.17752	0.924	0.008
310.65	-4.09148	0.16497	0.08636	-0.75583	0.21504	0.902	0.009
313.15	-4.09188	0.18547	0.16657	-0.76831	0.10575	0.907	0.008
Ethanol + Water							
293.15	-4.29391	1.30911	-1.62128	-0.30413	1.03823	0.984	0.016
295.65	-4.27328	1.21639	-1.60730	-0.19546	0.99151	0.985	0.015
298.15	-4.24013	1.16882	-1.65368	-0.12270	1.04656	0.990	0.012
300.65	-4.20895	1.13412	-1.43674	-0.09199	0.69097	0.986	0.014
303.15	-4.18842	1.06594	-1.46994	0.04193	0.78764	0.990	0.012
305.65	-4.15522	1.06237	-1.32230	-0.00416	0.48235	0.990	0.012
308.15	-4.14265	1.04265	-1.18873	-0.00573	0.21121	0.990	0.012
310.65	-4.10578	1.06630	-1.22266	0.02441	0.32887	0.991	0.011
313.15	-4.15913	0.95729	-0.59894	0.18611	-0.43081	0.992	0.010

Table 4- Calculated Partial Excess Molar Volumes at Infinite Dilution at T = (293.15 to 313.15) K from Redlich−Kister Parameters Ai

	Methanol(1) + Water(2)		Ethanol(1) + Water(2)	
	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$
T(K)	$10^6.m^3\cdot mol^{-1}$	$10^6.m^3\cdot mol^{-1}$	$10^6.m^3\cdot mol^{-1}$	$10^6.m^3\cdot mol^{-1}$
293.15	-2.42983	-3.56097	-5.88193	-3.87199
295.65	-2.58791	-4.03565	-5.91000	-3.86814
298.15	-2.70812	-3.97567	-5.89337	-3.80114
300.65	-2.87045	-4.16132	-5.99686	-3.91260
303.15	-2.87570	-4.27292	-5.97859	-3.76285
305.65	-2.97636	-4.29652	-6.05338	-3.93697
308.15	-3.10056	-4.32350	-6.15709	-4.08324
310.65	-3.19923	-4.38094	-6.09028	-3.90886
313.15	-3.23672	-4.40240	-6.33228	-4.04549

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

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

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 3 indicates good agreement between the calculated and experimental values.

From Figure 1,2 it was cleared that molality of 2-naphthol was increase with increase in mole fractions of alcohol and it was more in methanol mole fractions than in ethanol mole fraction. From Figure 1, molality of 2-naphthol was negligible in 0.1 and 0.2 mole fraction of methanol, suggested that intermolecular interactions more in water+methanol(solvent-solvent) than 2-naphthol+methanol(solute-solvent). After 0.2 mole fraction of methanol molality slightly increase and from 0.3, its increase was considerably, suggested that intermolecular interactions increases in 2-naphthol+methanol than water+methanol. From Figure 2, in case of ethanol system as soon as mole fraction of ethanol increase molality start to increases from 0.1 to 0.7 mole fraction of ethanol but for 0.8 and 0.9 mole fraction of ethanol molarity nearly remains constant, that is there is no effect of further addition of ethanol. Trends of decreasing molality of 2-naphthol in binary solvents: 2-naphthol+methanol(0.8 & 0.9) > 2-naphthol+ethanol(0.8 & 0.9) > 2-naphthol+ethanol(0.1 to 0.7) > 2-naphthol+methanol(0.1 to 0.7). Trend of decreasing molality of 2-naphthol in pure solvents: methanol > ethanol > water, this was according to rule 'like dissolve like'.

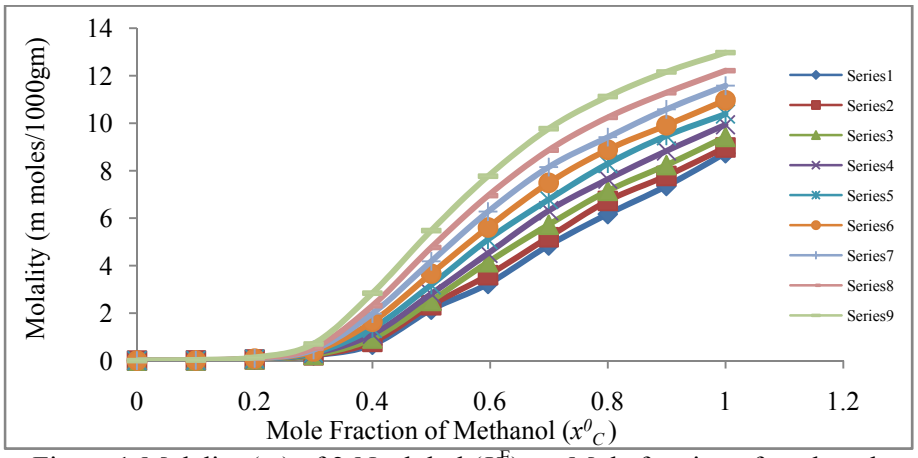


Figure 1-Molality (m) of 2-Naphthol (V^E) vs. Mole fraction of methanol.

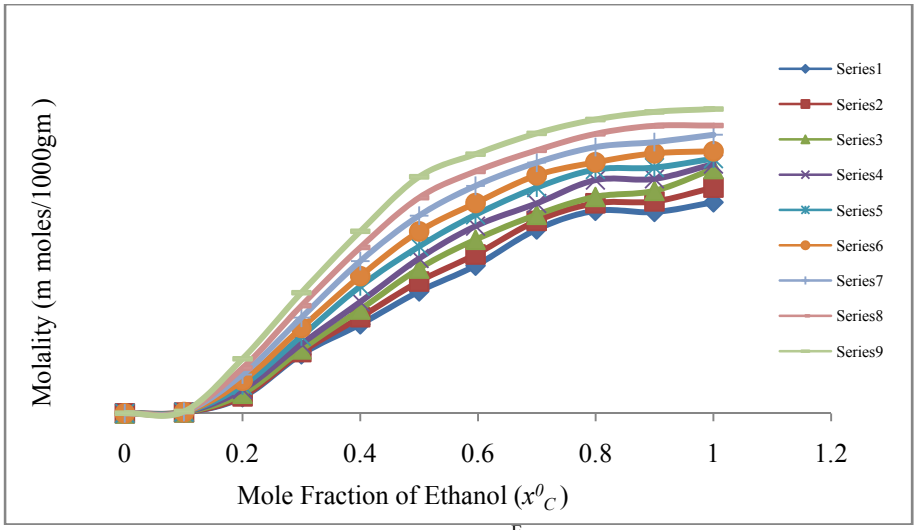


Figure 2-Molality (m) of 2-Naphthol (V^E) vs. Mole fraction of ethanol.

Apparent molar volume (V_Φ)[11,12] of solution of 2-naphthol in pure solvents and binary solvent mixture was calculated by using eq.6

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

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

Excess molar volumes (V^E) data were correlated to values obtained from Redlich−Kister , apparent molar volume(V_Φ) are given in Table 1,2. Calculated partial excess molar volumes at infinite dilution ($\bar{V}_i^{E,\infty}$) at T = (293.15 to 313.15) K from Redlich−Kister Parameters Ai shown in Table 4. V^E negative contribution, might arise from following effects

i. Strong interactions between water and alcohol, which enhance the solvent structure in the mixtures.
ii. Breaking of inter-molecular hydrogen-bonded structure of one solvent by the addition of other solvent 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.
iii. As solute 2-naphthol and solvents alcohols, water, their mixtures are polar shows dipole-dipole interactions.

The trend of V^E values was more negative in water+ethanol system than water+methanol for all measured temperatures over the entire composition of binary solvent mixture. The highest negative V^E values for water+ethanol and water+methanol were noticeably observed at 0.4 and 0.5 mole fraction of respective binary solvent systems as shown in Figure 3, 4. The positive value of V_Φ indicates weak solute-solvent interactions only in terms of H-bonding and not any strong electrostatic force of attractions. V_Φ values of 2-naphthol decrease very slowly with increasing mole fraction of the system. In water V_Φ values are very higher than in pure alcohols because very low solubility of 2-naphthol in water as indicates lower m values in Table 1, 2. Also noted that positive value of V_Φ for 2-naphthol are more in water+methanol than water+ethanol ternary system as shown in Figure 5, 6.

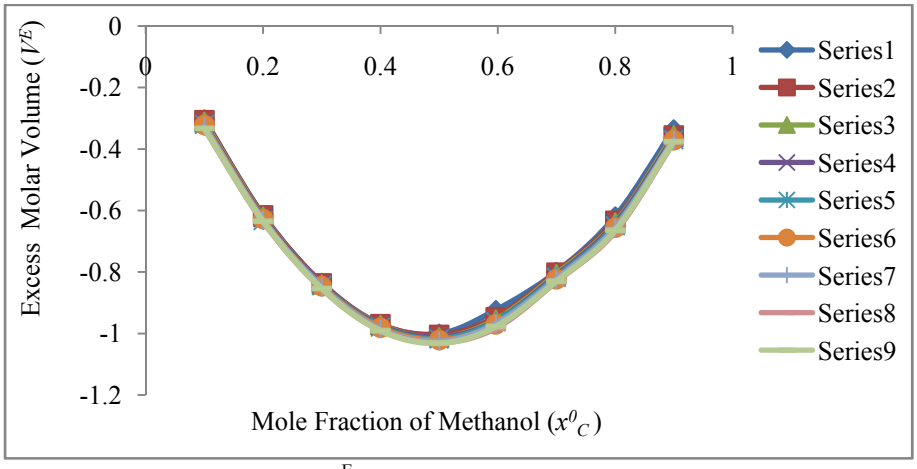


Figure 3-Excess molar volumes (V^E) vs. Mole fraction of water+methanol binary system

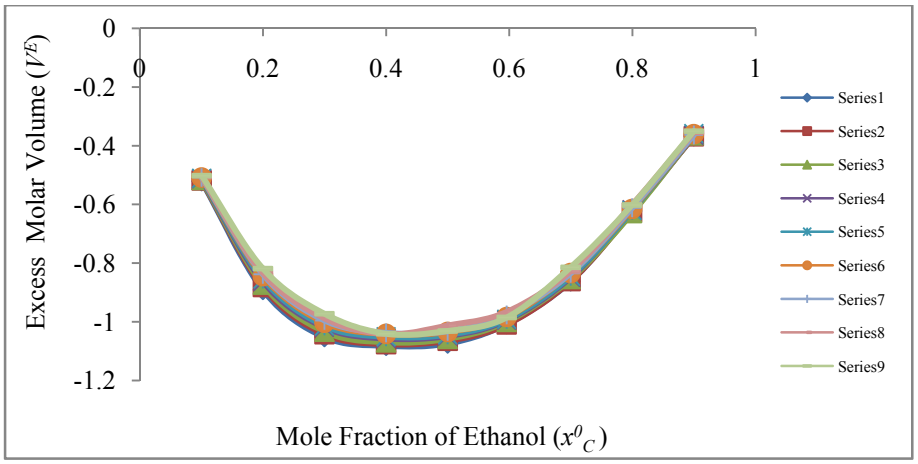


Figure 4-Excess molar volumes (V^E) vs. Mole fraction of water+ethanol binary system.

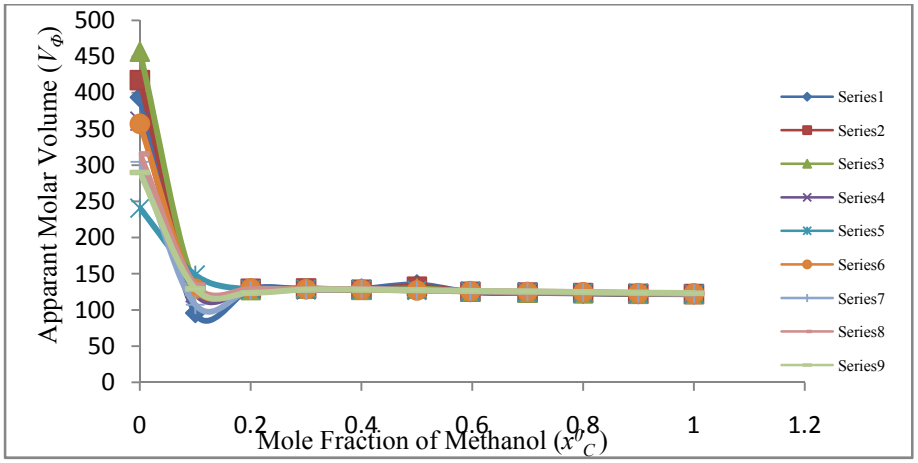


Figure 5-Apparent molar volume (V_Φ) of 2-naphthol vs. Mole fraction methanol.

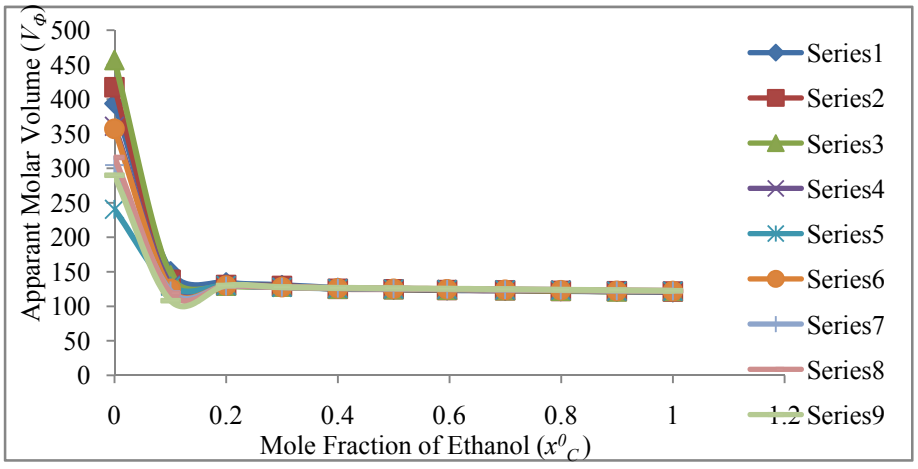


Figure 6-Apparent molar volume (V_Φ) of 2-naphthol vs. Mole fraction of ethanol.

This was explain by DFT, as dipole moment of 2-naphthol+ethanol is more than the dipole moment of 2-naphthol+methanol in both gas and water phase that means more association of 2-naphthol+ethanol in water than 2-naphthol+methanol in water. Hence the trend for apparent molar volume of 2-naphthol in water+methanol was higher than in the water+ethanol.

Computational study using Gaussian 09W software, DFT method, B3LYP 6-31(G)d as basic 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 alcohols then interacted with water molecule as shown in Figure 7,8, also with 2-naphthol molecule as shown in Figure 9,10. 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 5. From this υ-OH(stretching frequency) for methanol+2-naphthol were higher than the ethanol+2-naphthol system, suggested that interaction between ethanol+2-naphthol higher than methanol+2-naphthol.

Table 5- Theoretical data obtained by Gaussian 09 by DFT, B3LYP , 6-31(G)d method.

Molecule	Phase	Dipole Moment (Debye)	Total Energy(a.u.)	Symmetry Point group	Alcoholic (-OH) Freq.cm^{-1}	Alcoholic (-OH) Bond Distance(^{0}A)	H-Bonding Distance(^{0}A) in Alcohol & Water
Methanol	Gas	1.6942	-115.71441	C2V	3609.22	0.968744	-
	Water	1.9739	-115.71943	C2V	3606.66	0.969642	-
Ethanol	Gas	1.5613	-115.03380	CS	3607.31	0.969031	-
	Water	1.9063	-115.03856	CS	3601.80	0.970082	-
Methanol+H_2O	Gas	2.2338	-192.13567	C1	3391.18	0.976877	1.903509
	Water	3.4643	-192.14679	C1	3477.48	0.982090	1.832844
Ethanol+H_2O	Gas	2.2392	-231.45914	C1	3469.99	0.977556	1.905407
	Water	3.4239	-231.46581	C1	3381.81	0.982355	1.835451
Methanol+ 2-naphthol	Gas	4.7450	-576.83842	C1	3612.07	0.969533	1.811346
	Water	5.4784	-576.84996	C1	3604.27	0.970836	1.745909
Ethanol+ 2-naphthol	Gas	4.9778	-616.15844	C1	3595.58	0.970679	1.813720
	Water	5.6422	-616.16976	C1	3588.35	0.971841	1.747904

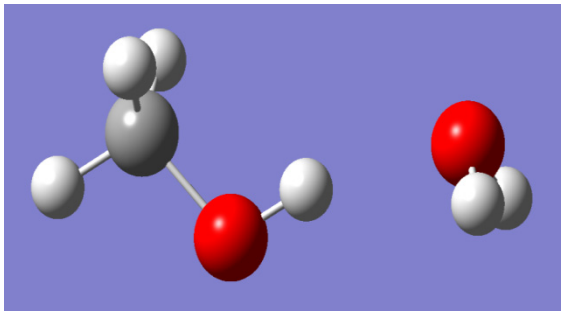


Figure 7-Optimized structure of Methanol+ Water

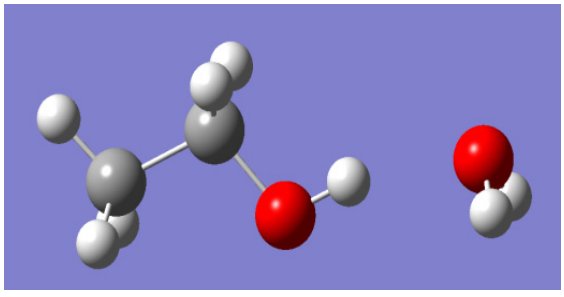


Figure 8-Optimized structure of Ethanol+ Water

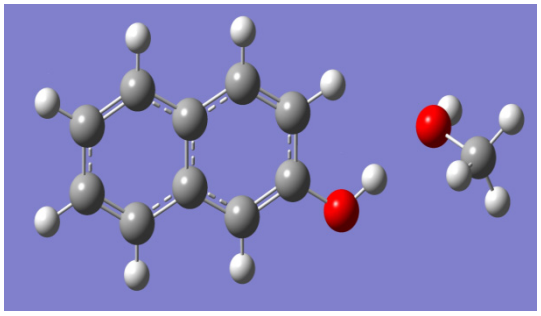


Figure 9-Optimized structure of 2-Naphthol+Methanol

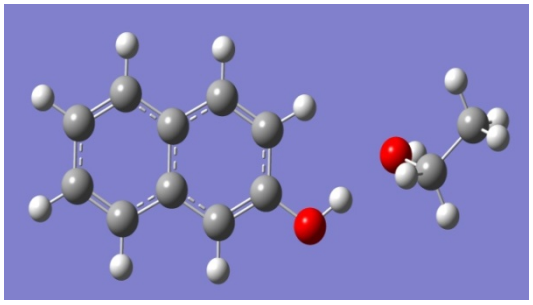
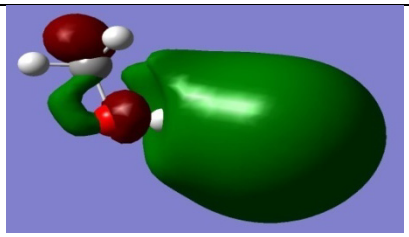


Figure 10-Optimized structure of 2-Naphthol+Ethanol

HOMO-LUMO structure of water+alcohol, 2-naphthol+alcohol and energy gap between them are shown in Figure 11, 12. Energies of all optimized structure of HOMO, LUMO and their energy gap were shown in Table 6 Here we observed that methanol containing systems show more energy gap than ethanol containing systems that means methanol containing systems are more stable than ethanol systems. Exception for 2-naphthol+methanol was showing nearly same/less energy gap as that of 2-naphthol+ethanol in water medium.

Table 6-Energies of HOMO, LUMO, HOMO-LUMO Energy gap

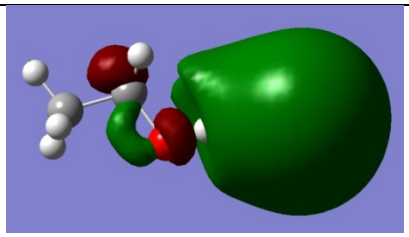
Molecules	Phase	HOMO Energy (a.u.)	LUMO Energy (a.u.)	HOMO-LUMO Energy Gap (a.u.)
Methanol+Water	Gas	-0.24019	0.03766	0.27785
	Water	-0.25157	0.05811	0.30968
Ethanol+Water	Gas	-0.23889	0.03820	0.27709
	Water	-0.24951	0.05836	0.30787
2-Naphthol+Methanol	Gas	-0.18723	-0.02050	0.16673
	Water	-0.20174	-0.03457	0.16717
2-Naphthol+Ethanol	Gas	-0.18660	-0.01995	0.16665
	Water	-0.20173	-0.03455	0.16718



LUMO of Methanol+Water ↑

Energy gap=0.27785 a.u.(Gas phase)
Energy gap=0.30968 a.u.(Water phase)

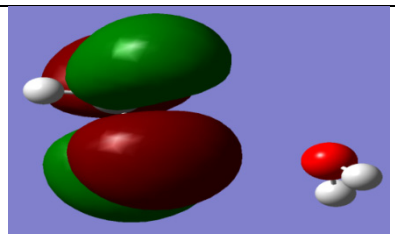
↓



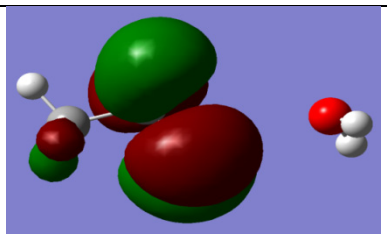
LUMO of Ethanol+Water ↑

Energy gap=0.27709 a.u.(Gas phase)
Energy gap=0.30787 a.u.(Water phase)

↓

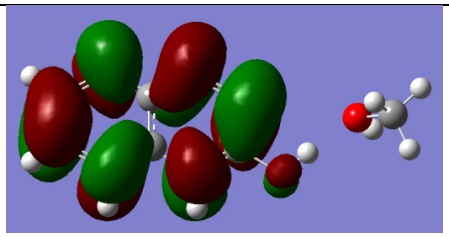


HOMO of Methanol+Water



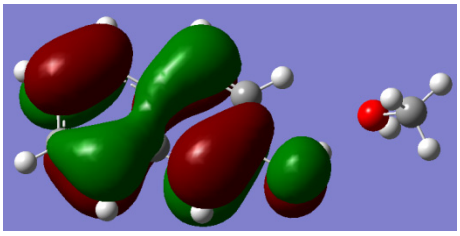
HOMO of Ethanol+Water

Figure 11-HOMO, LUMO structure with energy gap for water+ alcohol.

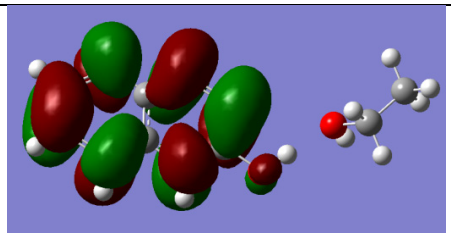


LUMO of 2-Naphthol+Methanol

Energy gap=0.16673 a.u.(Gas phase)
Energy gap=0.16717 a.u.(Water phase)

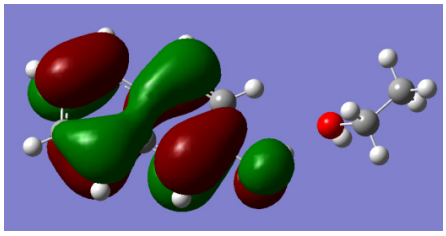


HOMO of 2-Naphthol+Methanol



LUMO of 2-Naphthol+Ethanol

Energy gap=0.16665 a.u.(Gas phase)
Energy gap=0.16718 a.u.(Water phase)



HOMO of 2-Naphthol+Ethano

Figure12- HOMO, LUMO structure with energy gap for 2-naphthol+ alcohol.

Conclusion

The data of densities increases as function of concentration. The molality (m) of 2-naphthol in pure and binary solvent system were given in Table 1, 2. The trend of m in pure solvents are shown as methanol > ethanol >> water at same temperature, which explained solubility rule 'like dissolved like'. Also these values of m increase with increase in temperature. In general m values in binary solvent mixture were shown as water+ethanol > water+methanol. But it should be notice that higher mole fraction of water+methanol molality values was observed to be higher than water+ethanol system which was exactly reverse than that of general trend. From Table 1, 2 we have the results in details as

i. At low temperature range (293.15 to 303.15) K, water+ ethanol 0.1 to 0.8 mole fractions shows more m values but for water+ methanol 0.9 mole fraction shows more m values.

ii. At temperature range (305.15 to 310.65) K, water+ ethanol 0.1 to 0.7 mole fractions shows more m values but for water+ methanol 0.8 to 0.9 mole fractions shows more m values.

iii. At high temperature 313.15 K, water+ ethanol 0.1 to 0.8 mole fractions shows more m values but for water+ methanol 0.7 to 0.9 mole fraction shows more m values.

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