



DFT STUDY, MOLECULAR INTERACTIONS OF HYDROQUINONE IN WATER, METHANOL AND BINARY SOLVENT MIXTURES OF WATER+METHANOL AT DIFFERENT TEMPERATURES

R. R. Pawar and Chandrakant S. Aher

Department of Physical Chemistry, M.S.G. College Malegaon Camp, Pin 423105. India

ARTICLE INFO

Article History:

Received 6th August, 2017

Received in revised form 25th

September, 2017

Accepted 3rd October, 2017

Published online 28th November, 2017

Key words:

DFT, Hydroquinone, Excess Molar Volumes (V^E), Apparent Molar Volume (V_ϕ).

ABSTRACT

Density of water, methanol, and water+methanol binary solvent in pure form were experimentally measured. In these same solvents hydroquinone was added to make saturated solutions of hydroquinone at equilibrium. These saturated supernatant solutions were used to measure densities and molalities of hydroquinone 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 A_i 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.

Copyright©2017 R. R. Pawar and Chandrakant S. Aher. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

INTRODUCTION

Phenolic compounds are used for production dyes, paper, pesticides, polymeric material, pharmaceutical and petrochemical product etc. There has increase industrial wastewater containing phenolic compound, which are toxic to aquatic life and human bring [1]. Hydroquinone is crystalline white solid. IUPAC name is benzene-1,4 diol with the molecular formula $C_6H_6O_2$. Molar mass is 110.11 gm/mol, melting point is about 172°C.

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 [2, 3]. 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 [4]. Density of hydroquinone 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 have to be investigating. We have undertaken the measurements of densities of pure solvents, binary solvent mixtures and saturated solutions of hydroquinone in water + methanol binary solvents over the entire composition range from 0 to 1 mole fraction of methanol.

The experimental work was carried out at (293.15 to 313.15) K and excess molar volumes (V^E) [5] were calculated from the measured densities of the pure components and the binary mixtures as shown in Table 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 [6]. The excess molar volumes (V^E) for the binary mixtures were obtained by eq.1.

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

Where x_i , ρ_i , and M_i 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 binary solvent mixture were compared with calculated values of V^E by Redlich–Kister [7] type smoothing equation:

$$V^E = x_1 x_2 \sum_{i=0}^n A_i (x_1 - x_2)^i \quad \dots(2)$$

*Corresponding author: R. R. Pawar

Department of Physical Chemistry, M.S.G. College Malegaon Camp, Pin 423105. India

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 Hydroquinone + water + methanol ternary system at temperatures (293.15 to 313.15) K & pressure 101.32 kPa^a.

x^0_c	Binary solvent	$V^E_{(Exp.)}$	$V^E_{(Cal.)}$	m	Ternary solution	V_ϕ
	$\rho \cdot 10^{-3} / \text{kg} \cdot \text{m}^{-3}$	$10^6 \cdot \text{m}^3 \cdot \text{mol}^{-1}$	$10^6 \cdot \text{m}^3 \cdot \text{mol}^{-1}$		$\rho \cdot 10^{-3} / \text{kg} \cdot \text{m}^{-3}$	
293.15 K						
0.0000	0.9982	0.0000	0.0000	0.5708	1.0090	90.3332
0.1001	0.9715	-0.3045	-0.3033	0.9481	0.9911	89.6852
0.2002	0.9497	-0.6108	-0.6150	1.4794	0.9805	89.9168
0.3001	0.9283	-0.8363	-0.8415	2.2706	0.9731	91.2981
0.4000	0.9070	-0.9715	-0.9606	2.9909	0.9672	90.9205
0.5000	0.8856	-1.0007	-0.9825	3.6005	0.9589	90.8385
0.6020	0.8631	-0.8936	-0.9239	4.0393	0.9507	89.3784
0.7002	0.8448	-0.8035	-0.8014	4.3587	0.9406	89.4150
0.7998	0.8265	-0.6190	-0.6097	4.5160	0.9304	88.4221
0.9000	0.8085	-0.3394	-0.3414	4.6409	0.9195	87.5862
1.0000	0.7916	0.0000	0.0000	4.7907	0.9098	86.7641
295.65 K						
0.0000	0.9977	0.0000	0.0000	0.6306	1.0097	90.1553
0.1001	0.9706	-0.3062	-0.3082	1.0437	0.9913	90.4726
0.2002	0.9483	-0.6112	-0.6014	1.6215	0.9815	90.1831
0.3001	0.9264	-0.8305	-0.8367	2.4248	0.9746	90.9978
0.4000	0.9053	-0.9748	-0.9801	3.1540	0.9680	91.0517
0.5000	0.8838	-1.0045	-1.0157	3.7431	0.9605	90.4989
0.6020	0.8631	-0.9666	-0.9468	4.2173	0.9510	90.3856
0.7002	0.8427	-0.8055	-0.8019	4.5074	0.9409	89.5634
0.7998	0.8237	-0.5895	-0.6003	4.6937	0.9308	88.5078
0.9000	0.8065	-0.3497	-0.3474	4.7759	0.9201	87.6027
1.0000	0.7893	0.0000	0.0000	4.9076	0.9103	86.6739
298.15 K						
0.0000	0.9970	0.0000	0.0000	0.6870	1.0102	90.0098
0.1001	0.9698	-0.3112	-0.3120	1.1448	0.9927	90.1537
0.2002	0.9471	-0.6156	-0.6096	1.7651	0.9831	90.0980
0.3001	0.9246	-0.8267	-0.8373	2.6420	0.9763	91.0977
0.4000	0.9034	-0.9760	-0.9727	3.3435	0.9693	91.1078
0.5000	0.8819	-1.0117	-1.0119	3.9331	0.9619	90.4799
0.6020	0.8611	-0.9747	-0.9597	4.3853	0.9521	90.3524
0.7002	0.8406	-0.8103	-0.8312	4.6925	0.9415	89.7756
0.7998	0.8225	-0.6384	-0.6291	4.8679	0.9316	88.9577
0.9000	0.8042	-0.3529	-0.3540	4.9294	0.9203	87.8168
1.0000	0.7870	0.0000	0.0000	5.0477	0.9108	86.6742
300.65 K						
0.0000	0.9964	0.0000	0.0000	0.7541	1.0108	89.9946
0.1001	0.9689	-0.3167	-0.3174	1.2946	0.9940	90.6177
0.2002	0.9459	-0.6237	-0.6193	1.9411	0.9844	90.5192
0.3001	0.9232	-0.8403	-0.8455	2.8574	0.9780	91.3352
0.4000	0.9013	-0.9744	-0.9765	3.6294	0.9708	91.5452
0.5000	0.8796	-1.0117	-1.0130	4.1612	0.9628	90.7575
0.6020	0.8588	-0.9799	-0.9617	4.6085	0.9534	90.4267
0.7002	0.8382	-0.8154	-0.8358	4.8852	0.9430	89.6272
0.7998	0.8200	-0.6420	-0.6342	5.0628	0.9324	89.0661
0.9000	0.8017	-0.3546	-0.3554	5.1035	0.9215	87.7127
1.0000	0.7844	0.0000	0.0000	5.2252	0.9115	86.7565
303.15 K						
0.0000	0.9957	0.0000	0.0000	0.8304	1.0113	90.1249
0.1001	0.9678	-0.3187	-0.3192	1.4477	0.9953	90.8834
0.2002	0.9441	-0.6201	-0.6173	2.2035	0.9869	90.7131
0.3001	0.9215	-0.8444	-0.8461	3.1009	0.9802	91.3764
0.4000	0.8994	-0.9807	-0.9835	3.8593	0.9729	91.4026
0.5000	0.8775	-1.0172	-1.0244	4.4122	0.9652	90.6107
0.6020	0.8569	-0.9977	-0.9725	4.8386	0.9545	90.6974
0.7002	0.8359	-0.8207	-0.8434	5.0766	0.9441	89.6219
0.7998	0.8176	-0.6485	-0.6409	5.2632	0.9334	89.1376
0.9000	0.7993	-0.3637	-0.3644	5.3063	0.9223	87.9584
1.0000	0.7818	0.0000	0.0000	5.3286	0.9120	86.4670
305.65 K						
0.0000	0.9949	0.0000	0.0000	0.9084	1.0119	90.2538
0.1001	0.9665	-0.3167	-0.3181	1.5931	0.9969	90.6430
0.2002	0.9430	-0.6291	-0.6213	2.3825	0.9887	90.7594
0.3001	0.9198	-0.8465	-0.8529	3.3742	0.9818	91.8121
0.4000	0.8975	-0.9847	-0.9898	4.0262	0.9742	91.2333
0.5000	0.8755	-1.0210	-1.0286	4.6403	0.9661	90.8873
0.6020	0.8549	-1.0064	-0.9761	5.0587	0.9558	90.8148

^aStandard uncertainties u are $u(T) = 0.01$ K, $u(x^0_c) = 0.0001$, $u(p) = 0.01$ MPa, $u(m) = 2 \times 10^{-3}$ mol·kg⁻¹ and the combined expanded uncertainties $U_c(\rho) = 0.00005$ 10⁻³kg·m⁻³, $U_c(V_\phi) = 0.001$ 10⁶.m³.mol⁻¹ and $U_c(V^E) = 0.001$ 10⁶.m³.mol⁻¹

0.7002	0.8338	-0.8271	-0.8492	5.3192	0.9456	89.7854
0.7998	0.8154	-0.6549	-0.6504	5.4654	0.9344	89.2837
0.9000	0.7971	-0.3744	-0.3744	5.5129	0.9230	88.2740
1.0000	0.7794	0.0000	0.0000	5.5240	0.9127	86.7167
308.15 K						
0.0000	0.9940	0.0000	0.0000	1.0176	1.0127	90.5091
0.1001	0.9652	-0.3172	-0.3181	1.7030	0.9987	89.8703
0.2002	0.9413	-0.6266	-0.6223	2.6245	0.9906	90.9821
0.3001	0.9181	-0.8492	-0.8521	3.5967	0.9835	91.8228
0.4000	0.8957	-0.9880	-0.9887	4.3145	0.9760	91.5252
0.5000	0.8735	-1.0253	-1.0324	4.8786	0.9674	91.0663
0.6020	0.8525	-0.9956	-0.9884	5.3098	0.9569	90.9479
0.7002	0.8327	-0.8727	-0.8665	5.5213	0.9466	90.1348
0.7998	0.8132	-0.6551	-0.6624	5.6537	0.9355	89.2750
0.9000	0.7949	-0.3738	-0.3725	5.6945	0.9247	88.0697
1.0000	0.7771	0.0000	0.0000	5.7520	0.9138	87.0349
310.65 K						
0.0000	0.9932	0.0000	0.0000	1.1278	1.0135	90.7187
0.1001	0.9641	-0.3213	-0.3226	1.9499	1.0005	90.7180
0.2002	0.9397	-0.6285	-0.6203	2.8276	0.9928	90.7567
0.3001	0.9158	-0.8408	-0.8501	3.9339	0.9858	92.0125
0.4000	0.8936	-0.9896	-0.9911	4.5694	0.9784	91.3183
0.5000	0.8715	-1.0301	-1.0368	5.1303	0.9689	91.1528
0.6020	0.8508	-1.0197	-0.9894	5.5472	0.9586	91.0354
0.7002	0.8294	-0.8353	-0.8626	5.7454	0.9478	89.9520
0.7998	0.8110	-0.6675	-0.6591	5.8794	0.9367	89.4067
0.9000	0.7925	-0.3762	-0.3769	5.9214	0.9257	88.2749
1.0000	0.7747	0.0000	0.0000	5.9542	0.9144	87.2989
313.15 K						
0.0000	0.9922	0.0000	0.0000	1.2823	1.0146	91.1803
0.1001	0.9632	-0.3311	-0.3317	2.2167	1.0028	91.3373
0.2002	0.9381	-0.6307	-0.6278	3.1677	0.9951	91.3917
0.3001	0.9144	-0.8537	-0.8558	4.2697	0.9877	92.4664
0.4000	0.8916	-0.9928	-0.9953	4.8789	0.9797	91.7182
0.5000	0.8692	-1.0312	-1.0382	5.4454	0.9709	91.2814
0.6020	0.8482	-1.0113	-0.9864	5.8796	0.9603	91.2687
0.7002	0.8269	-0.8339	-0.8568	6.0647	0.9493	90.2797
0.7998	0.8085	-0.6633	-0.6555	6.1528	0.9380	89.6331
0.9000	0.7900	-0.3790	-0.3797	6.1418	0.9261	88.6040
1.0000	0.7722	0.0000	0.0000	6.1862	0.9150	87.6817

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 Table 2.

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

$$rmsd(\sigma) = \sqrt{\frac{1}{N} \sum_i^N (V_{cal(i)}^E - V_{exp(i)}^E)^2} \quad \dots (5)$$

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

TK	A_0	A_1	A_2	A_3	A_4	R^2	σ
	$10^6 \cdot m^3 \cdot mol^{-1}$	$10^6 \cdot m^3 \cdot mol^{-1}$	$10^6 \cdot m^3 \cdot mol^{-1}$	$10^6 \cdot m^3 \cdot mol^{-1}$	$10^6 \cdot m^3 \cdot mol^{-1}$		
Methanol + Water							
293.15	-3.93012	0.40483	-0.031047	-1.049606	0.901018	0.909	0.013
295.65	-4.06296	0.36466	1.124118	-0.998518	-0.728486	0.943	0.010
298.15	-4.04747	0.14349	0.437946	-0.682919	0.166331	0.925	0.010
300.65	-4.05199	0.162883	0.240192	-0.669760	0.392415	0.920	0.010
303.15	-4.09762	0.123362	0.465973	-0.685635	0.005239	0.904	0.012
305.65	-4.11451	0.157459	0.372446	-0.859905	0.071319	0.902	0.013
308.15	-4.12973	0.009860	0.159382	-0.608700	0.466942	0.982	0.005
310.65	-4.14727	0.024608	0.438229	-0.630470	-0.045857	0.878	0.015
313.15	-4.15275	0.100786	0.518541	-0.681939	-0.319414	0.887	0.012

The values of the partial excess volume of solvent₁ and solvent₂ at infinite dilution $\bar{V}_1^{E,\infty}$ can be calculated as in Table 3 from the adjustable parameters of Redlich–Kister smoothing equation as

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

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

Where $V_{cal(i)}^E$ and $V_{exp(i)}^E$ 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) [8,9] of solution of hydroquinone in pure solvents and binary solvent mixture was calculated by using eq.6

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

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.

Table 3- Calculated Partial Excess Molar Volumes at Infinite Dilution at $T = (293.15 \text{ to } 313.15) \text{ K}$ from Redlich–Kister Parameters A_i

T(K)	Methanol(1) + Water(2)	
	$\bar{V}_1^{E,\infty}$	$\bar{V}_2^{E,\infty}$
	$10^6 \cdot \text{m}^3 \cdot \text{mol}^{-1}$	$10^6 \cdot \text{m}^3 \cdot \text{mol}^{-1}$
293.15	-2.415377	-3.704928
295.65	-3.033476	-4.301187
298.15	-2.903766	-3.982624
300.65	-2.912510	-3.926265
303.15	-3.064131	-4.188677
305.65	-2.968298	-4.373191
308.15	-2.904569	-4.102248
310.65	-3.149032	-4.360755
313.15	-3.372470	-4.534777

Experimental Sections

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

Chemical Name	Supplier Name	Percentage purity	Standard
Hydroquinone	Sigma-Aldrich co.	99%	Reagent Grade
Methanol	Merck, Germany.	$\geq 99.8\%$	G.R.
Ethanol	Merck, D, Germany.	$\geq 99.8\%$	G.R.

Apparatus and Procedure:- The apparatus and procedures used for density measurement have been described earlier in detail [10, 11]. Briefly in this work; an excess amount of hydroquinone was added to the binary solvents mixtures prepared by weight (Shimadzu, Auxzzo) with an uncertainty of $\pm 0.1 \text{ mg}$, 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 hydroquinone 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 [12, 13]. For calibration of pycnometer triply distilled and degassed water with a density of $0.99705 \text{ g} \cdot \text{cm}^{-3}$ 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 ($\pm 0.1 \text{ K}$) 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 $10 \text{ kg} \cdot \text{m}^{-3}$.

RESULTS AND DISCUSSION

The experimental values of density (ρ) of pure water, methanol and water+methanol binary solvents also the densities of the saturated solutions of hydroquinone in water, methanol and

their binary mixtures water+methanol 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 ($\bar{V}_i^{E,\infty}$) at $T = (293.15 \text{ to } 313.15) \text{ K}$ from Redlich–Kister Parameters A_i shown in Table 3 . V^E negative contribution, might arise from following effects

- Strong interactions between water and alcohol methanol, which enhance the solvent structure in the mixtures.
- Breaking of inter-molecular hydrogen-bonded structure of water by the addition of methanol 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 methanol fill up the all interstitial space between water molecules from 0.1 to 0.5 mole fraction methanol further addition of methanol from 0.6 to 0.9 mole fractions start to increase the V^E values. As shown in fig.1.

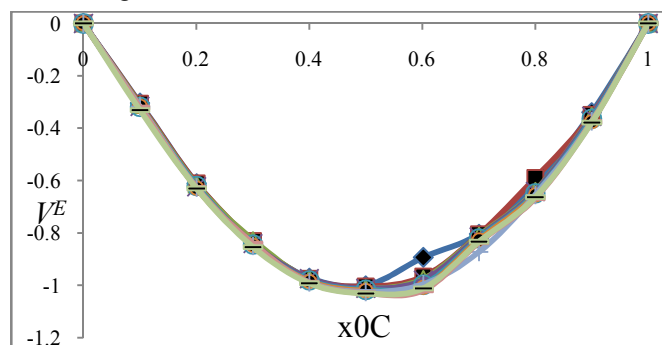


Fig 1 Excess molar volumes (V^E) vs. Mole fraction of Methanol (x_C^0) at Temperatures (\blacklozenge T=293.15 K, \blacksquare T=295.15 K; \blacktriangle T=298.15K; \times T=300.15 K; \circ T=303.15 K; \bullet T=305.15 K; $+$ T=308.15 K; $-$ T=310.15 K & — T=313.15 K).

The highest negative V^E values for water+methanol were noticeably observed at 0.5 mole fraction of methanol. 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 hydroquinone in water are more than in methanol, indicates hydroquinone interaction is stronger in methanol than water. Hence hydroquinone is more soluble in methanol than in water which is confirmed from m values in Table-1 and Fig.2.

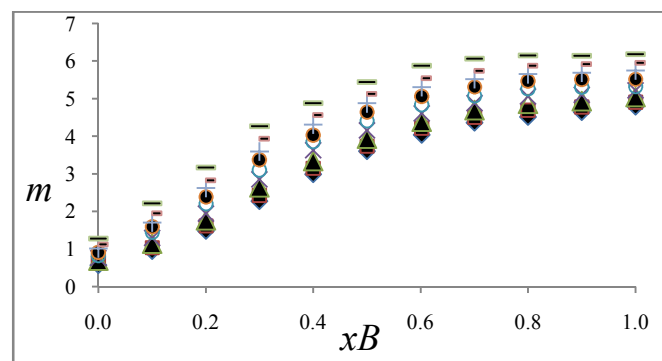


Fig 2 Plot of Molality(m) Vs. Mole Fraction of Methanol(x_C) for Hydroquinone+ Water + Methanol System. (\blacklozenge T=293.15; \blacksquare T =295.65; \blacktriangle T =298.15; \times T =300.65; \circ T =303.15; \bullet T =305.65; $+$ T =308.15; $-$ T =310.65; — T =313.15).

Molalities of hydroquinone are very much higher in methanol than in water and which is continuously increased with increase in temperature. For ternary system it was observed that V_ϕ values increase from 0.1 to 0.3/0.4 mole fraction of methanol and decrease from 0.4/0.5 to 0.9 mole fraction of methanol (Fig.3).

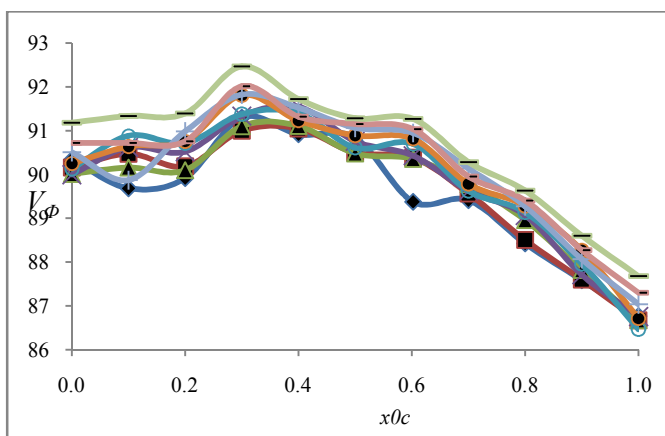


Fig 3 Apparent molar volume (V_ϕ) of Hydroquinone vs. Mole fraction methanol (x^0_c) at Temperatures (\blacklozenge T=293.15 K; \blacksquare T=295.65 K; \blacktriangle T=298.15K; \times T=300.65 K; \circ T=303.15 K; \bullet T=305.65 K; $+$ T=308.15 K; $-$ T=310.65 K & — T=313.15 K).

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 methanol then interacted with water molecule and hydroquinone molecule as shown in Fig.4.

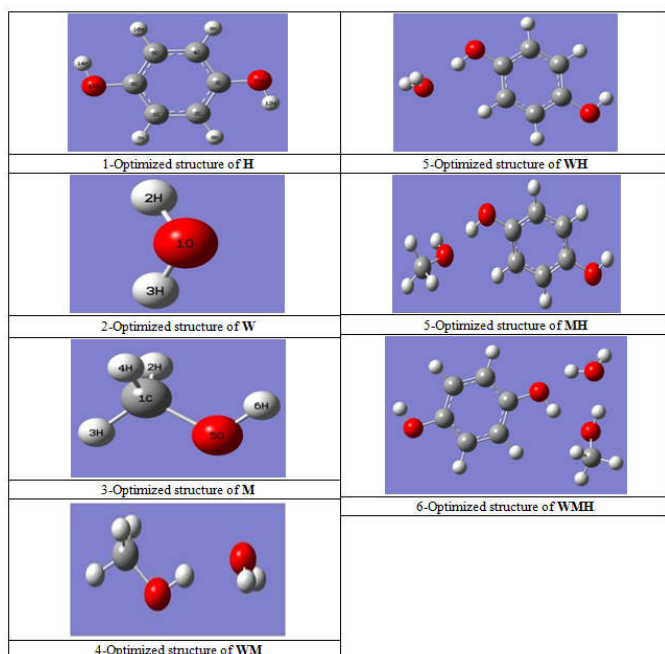


Fig 4 Optimized structures of solute, solvents combinations by DFT method at B3LYP level using 6-31G(d) basis set

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 hydroquinone was given in Table 4.

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

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

Molecule	HOMO	L-H E.G. (eV)	LUMO
H		Gas 5.350	
		Water 5.361	
W		Gas 9.628	
		Water 10.097	
M		Gas 9.246	
		Water 9.564	
WM		Gas 7.561	
		Water 8.427	
WH		Gas 5.290	
		Water 5.280	
MH		Gas 5.283	
		Water 5.282	
WMH		Gas 5.359	
		Water 5.361	

Here we observed that solvent shows more energy gap than hydroquinone solutions those solvent-solvent interactions stronger and stable than solute-solvent interactions. The trend of dipole moment (given in Table-4) for solvent is water+methanol > water > methanol, which indicates that stronger interactions in binary system than pure solvents that confirmed form highest negative V^E values.

CONCLUSION

The data of densities increases as function of concentration. The molality (m) of hydroquinone in pure and binary solvent system was given in Table 1. The trend of m in are shown as methanol > water+methanol >> water at same temperature, which explained solubility rule 'like dissolved like'. Also these values of m increase with increase in temperature. As V^E are more negative at 0.5 mole fraction of methanol, m values increase rapidly up to 0.5 mole fraction of

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

System	Phase/Media	Dipole Moment (Debye)	(α) Bohr ³	Alcoholic ν -OH cm ⁻¹	Alcoholic(-OH) Bond Dist. (°A)	Intermolecular H-Bond Dist.(°A)
H	Gas	0.0007	64.14	3612.75(sym.str.) 3611.67(uns.str.)	-	-
	Water	0.0003	83.35	3598.54(sym.str.) 3597.4(uns.str.)	-	-
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.)	-	-
M	Gas	1.6942	15.70	3609.22	0.96874	-
	Water	1.9739	17.99	3606.66	0.96964	-
WM	Gas	2.2338	22.17	3391.18	0.97688	1.9035
	Water	3.4643	25.17	3477.48	0.98209	1.8328
WH	Gas	3.5292	71.58	3408.1	-	1.8354
	Water	3.7993	91.46	3258.78	-	1.7647
MH	Gas	3.4376	82.46	3398.06	0.98147	1.8210
	Water	3.6816	104.31	3263.29	0.98864	1.7612
WMH	Gas	1.3354	90.13	3322.99	0.98703	1.7874
	Water	1.6954	112.99	3296.57	0.98805	1.7778

[Abbreviations:-W: Water, M: Methanol, E: Ethanol, P: 1-Propanol, H: Hydroquinone]

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)
H	Gas	-5.412	-0.062	5.350
	Water	-5.536	-0.174	5.361
W	Gas	-7.924	1.704	9.628
	Water	-8.035	2.062	10.097
M	Gas	-7.198	2.047	9.246
	Water	-7.281	2.283	9.564
WM	Gas	-6.536	1.025	7.561
	Water	-6.846	1.581	8.427
WH	Gas	-4.926	0.365	5.290
	Water	-5.316	-0.036	5.280
MH	Gas	-4.914	0.370	5.283
	Water	-5.321	-0.039	5.282
WMH	Gas	-5.375	-0.016	5.359
	Water	-5.524	-0.164	5.361

methanol and V^z started become less negative from 0.6 to 0.9 mole fraction of methanol, m values increases very slowly. From these result we say that solubility increase with mole fraction of methanol but after 0.5 mole fraction addition of methanol is less significant for solubility of hydroquinone.

Acknowledgments

The authors express their sincere thanks to the general secretary M. G. Vidyamandir and Principal M.S.G. College, Malegaon Camp, and for providing laboratory facility and encouragement.

References

- Francisco J., Enguita, Leitão A. L. 2013. Review Article: Hydroquinone: Environmental Pollution, Toxicity, and Microbial Answers. Hindawi Publishing Corporation, BioMed Research International Vol. 2013, Article ID 542168, <http://dx.doi.org/10.1155/2013/542168>.
- R. S. Mahdi, 2009. Computational Methods for Study of Hydrogen Bonding Between Phenol Derivatives with Ethanol. *Asian Journal of Chemistry* Vol. 21, No. 2, 879-884
- Zhang F. 2017. Comparative theoretical study of three C56 fullerenes, their chlorinated derivatives, and chlorofullerene oxides. *Computational and Theoretical Chemistry*, 1117, 81-86.
- Mydlarz, J., Jones, A. G. 1991. Solubility and Density Isotherms for Magnesium Sulfate Heptahydrate-Water-Propan-1-ol. *J. Chem. Eng. Data*, 36, 119-121.
- Jose V. Herr'aez · R. Belda, *J Solution Chem* (2006) 35:1315-1328
- Girma G., Mohamad A.B., Nawshad M., Sami U. 2015. Density and excessmolar volume of binary mixture of thiocyanate-based ionic liquids and methanol at temperatures 293.15-323.15 K *Journal of Molecular Liquids* 211, 734-741
- Redlich O., Kister A. T. 1948. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.*, 40, 345-348.
- Ajita D., Sharma P.K., Awadhya P. February-2013. *International Journal of Scientific & Engineering Research* Volume 4, Issue 2,
- I.M. Abdulagatov Lala A. Akhmedova-Azizova N.D., *Fluid Phase Equilibria* (2014), [http:// dx.doi.org/10.1016/j.fluid.2014.05.032](http://dx.doi.org/10.1016/j.fluid.2014.05.032)
- Pawar R. R.; Nahire S. B.; Hasan M. 2009. Solubility and density of potassium iodide in binary water-ethanol solvent mixtures at (298.15, 303.15, 308.15, and 313.15) K. *J. Chem. Eng. Data*, 54, 1935-37.
- Pawar R. R., Golait S. M., Hasan M., Sawant A. B. 2010. Solubility and density of potassium iodide in binary water-propan-1-ol solvent mixtures at (298.15, 303.15, 308.15 and 313.15) K. *J. Chem. Eng. Data*. 55, 1314-16.
- Kadam U. B., Hiray A. P., Sawant A. B., Hasan M. 2006. Density, Viscosities, and Ultrasonic Velocity Studies of Binary Mixtures of Chloroform with Propan-1-ol and Butan-1-ol at (303.15 and 313.15) K. *J. Chem. Eng. Data*. 51, 60-63.
- Hasan, M., Shirude D. F., Hiray A. P., Kadam U. B., Sawant A. B. 2006., Densities, Viscosities and Speed of Sound Studies of Binary Mixtures of Methylbenzene with Heptan-1-ol, Octan-1-ol and Decan-1-ol at (303.15 and 313.15) K. *J. Chem. Eng. Data.*, 51, 1922-26.