VOLUMETRIC STUDIES ON ETHYL-4-HYDROXY BENZOATE WITH SUBSTITUTED AMIDE LIQUID MIXTURES AT DIFFERENT TEMPERATURES

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ABSTRACT:

The Speed of sound and density have been measured for the binary mixture of Ethyl-4-hydroxy benzoate[**E-4-HB**]with Formamide and substituted amides -Dimethyl formamide[**DMF**] and N-Methyl formamide [**NMF**] from 303.15K,308.15K and 313.15K temperature at 2MHz frequency. From this experimental data have been used to deliberate various volumetric properties like available volume, free volume, apparent volume and molar volume and its excess value. The properties have been fitted to the Redlich–Kister(R-K) type polynomial condition utilizing LSM to assess the twofold blends with upshots of standard deviations.

Keywords: Binary mixture, speed of sound, density, viscosity, excess value, RK polynomial

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INTRODUCTION

Binary liquid mixtures are liquids that are composed of two different molecular components. For a particular range of temperatures and concentrations a typical binary liquid mixture will phase separate into two different liquid phases, like a mixture of oil and water. Volumetric properties of fluids are of pivotal importance in physics, physical chemistry and chemical engineering, and have thus received due attention in all modern monographs/textbooks dealing with fluids, the most profitable approach being that based on association of chemical thermodynamics with molecular theory and statistical mechanics, effectively anchoring it in the field of molecular thermodynamics.Volumetric properties determine the changes of thermodynamic functions with pressure. Volumetric properties of pure liquids and liquid mixtures and solutions are important from the theoretical point of view because they reflect the structure and the intermolecular interactions in the system. In the present study is a compilation of volumetric properties-available volume, apparent volume molar and free volume data on subcritical binary homo/ heterogeneous fluid blends. Several researchers had done many of works on these volumetric properties estimate quality of fluid blends related to food, beaver and pharmaceutical industries.[1–4]

THEORY

From the experimentally measured data of density (ρ) and speed of sound (U) are used to evaluate the volumetric properties [12] like free volume (V_f), available volume (V_a), molar volume (V_m),apparent volume(V_ϕ) at different temperatures is tabulated at table 2(1) to table 2(3)

$V_m = \frac{\text{Meff}}{\rho}$ (1)

$V_a = \frac{\text{Meff}}{\rho}\left[1 - \left(\frac{U}{U_\infty}\right)\right]$ (2)

$V_f = \left(\frac{Meff.U}{K.\eta}\right)^{3/2}$ (3)

$V_{\phi,i} = \left(V_m - \frac{V_m^E}{X_i}\right)$ (4)

Where, Meff is the effective molecular weight (Meff = Σ mi *xi* in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively and K is a temperature independent constant equal to 4.28×10^9 for all liquids. U_∞= Sheaf's limiting value taken as 1600 m/s for liquids. V_i be the volume of the individual constituents.

R-K Polynomial: Next, Redlich- Kister[9] type polynomial a nonlinear regression method is done by

$Y^E = X_1 (1-X_1) \Sigma^n_{i=1} A_i (2 X_1 - 1)^{i-1}$ (5)

Where $Y^E = V_f^E$,V_m^E are the excess values of free volume and molar volume of the liquid blends.[5]

The values of coefficients A_i were determined by least square and reported in table 3

Standard deviation (σ) written by

$(\sigma) = [\Sigma^n_{i=1}(Y^E_{exp} - Y^E_{cal})/D\text{-}N]^{1/2}$ (6)

Where D is the number of experimental data points and N is the number of parameters

MATERIAL AND METHODHS

MATERIALS The chemicals used in this study are Ethyl-4-hydroxy benzoate with formamide, DMF and NMF which are of AR grade obtained from Hi-Media Laboratories Pvt. Ltd. Mumbai, India, with purities of greater than 99%.

METHODS Ethyl-4-hydroxy benzoate be attainable within powder type and it was soluble in water with array of 885 mg/1lr at room temperature. The binary liquid mixtures were prepared just before start the experiment for different samples with the help of mass variation. The accuracy of final mole fraction was less than ±0.0001.

Table 01: Collation of measured & literature densities (ρ)and speed of sound (U) values of pure liquids.

Liquid	*Temp* (K)	*Density*(ρ) (Kg m^{-3})		*Speed of sound*(U) (m s^{-1})	
		Lit	**Expt**	**Lit**	**Expt**
	303.15	1.1035[a]	1.1032	1523.0[a]	1523.4
E-4-HB	308.15	1.0313[a]	1.0310	1541.4[a]	1541.2
	313.15	0.9973[a]	0.9975	1572.6[a]	1570.6
	303.15	1.1257[b]	1.1251	1588.0[b]	1584.6
FORMAMIDE	308.15	1.1198[b]	1.1185	1577.2[b]	1579.4
	313.15	1.1183[b]	1.1178	1568.0[b]	1574.2
	303.15	0.9476[c]	0.9478	1459.6[c]	1456.2
DMF	308.15	0.9421[c]	0.9426	1434.7[c]	1434.8
	313.15	0.9351[c]	0.9349	1420.8[c]	1421.6
	303.15	0.9946[d]	0.9943	1408.5[d]	1408.2
NMF	308.15	0.9903[d]	0.9901	1400.6[d]	1401.6
	313.15	0.9861[d]	0.9858	1382.2[d]	1381.2

[a] Reference[7] [b,c,d] Reference [8]

The speed of sound was measured at 303.15K to 313.15K using ultrasonic interferometer (M-81S, M/s Mittal Enterprises, New Delhi,India) operating at the frequency of 2 MHz with an accuracy of ±0.1m.s^{-1} for the binary systems of E-4-HB with amides.

The densities of the pure components and their multi components were measured with 10 ml specific gravity bottle in high accurate digital electronic balance (Baijnath Premnath SF 400A, Kanpur, U.P) with an accuracy of ±0.00002 g. The precision of experimentally measured values of density and speed of sound data was compared with their literature values and uncertainties are shown in table 01.

RESULTS & DISCUSSIONS

From the experimental data of Speed of sound, density and viscosity we found the volumetric properties. It is seen that, free volume increases with rise in concentration for all the mixtures. Thermal energy facilitates increase in molecular collation and thus leads to increase in molar volume. Frequency change however does not affect the molar volume. Molar volume and free volume changes with molecular weight which is also evident in our observation. Molar volume in all cases increases with increase of concentration of all mixtures. However, the rate of decline is maximum in case of benzoate and minimum in case of formamide. This leads to the conclusion that interaction with E-4-HB is maximum leading to formation of strong bonds. The interaction gradually increases from formamide to substituted amide.[9]

In other case, available and apparent volumes decrease with increase in concentration. Temperature remaining constant, there is slow increase in available volume with the increase in frequency. This may be due to the increase in vibration of the molecules. Available volume also decreases in the same way as molar volume. That means, V_ϕ is maximum for formamide and then varies gradually from formamide to substituted amides.[10]

Table-2(1): Free volume (V_f), available volume (V_a), molar volume(V_m),apparent volume(V_ϕ) values of Ethyl -4-hydroxy benzoate + Formamide at different temperatures

Mole fraction	Molar volume (V_m) $m^3\ mol^{-1}$	Free volume (V_f) $m^3\ mol^{-1}$	Apparent volume(V_ϕ) $m^3\ mol^{-1}$	Available volume (V_a) $m^3\ mol^{-1}$
303.15K				
0.0000	0.4003	0.1462	8.1664	0.9106
0.2448	0.7148	0.3922	5.7347	0.7440
0.4619	0.9937	0.7078	4.1085	0.5457
0.6736	1.2690	1.2130	2.2483	0.2428
0.8560	1.5042	2.2075	1.2688	0.1309
1.0000	1.7058	3.7659	0.3903	0.0842
308.15K				
0.0000	0.4027	0.1717	6.6849	0.8030
0.2448	0.7199	0.4734	5.0683	0.7491
0.4619	1.0044	0.8678	3.3226	0.6350
0.6736	1.2903	1.6574	2.2222	0.4215
0.8560	1.5655	2.7078	1.2778	0.1696
1.0000	1.8252	4.2536	0.5738	0.0945
313.15K				
0.0000	0.4029	0.1986	3.4665	0.8033
0.2448	0.7223	0.5092	2.9772	0.6515
0.4619	1.0251	0.9909	2.2973	0.4143

0.6736	1.3513	1.8393	1.7299	0.1604
0.8560	1.6540	2.9835	1.1918	0.0819
1.0000	1.8865	4.4986	0.6497	0.0408

Table-2(2): Free volume (V_f), available volume (V_a), molar volume(V_m), apparent volume(V_ϕ) values of Ethyl -4-hydroxy benzoate + DMF at different temperatures

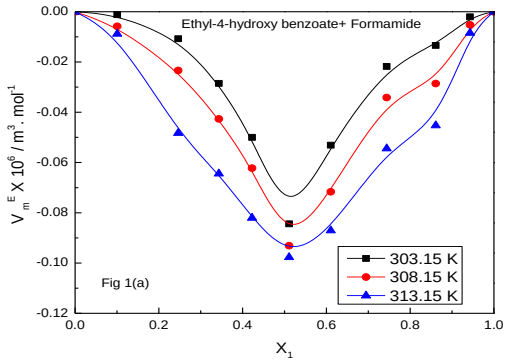
Mole fraction	**Molar volume (V_m) m^3 mol^{-1}**	**Free volume (V_f) m^3 mol^{-1}**	**Apparent volume(V_ϕ) m^3 mol^{-1}**	**Available volume (V_a) m^3 mol^{-1}**
303.15K				
0.0000	0.7712	1.8374	9.3491	1.7066
0.2468	1.0589	2.2467	9.1337	1.5423
0.4527	1.2856	2.8576	8.4446	1.3451
0.6682	1.5079	3.2164	8.3242	1.1278
0.8749	1.7233	4.0691	8.1664	1.1021
1.0000	1.7058	3.7659	6.9307	0.8940
308.15K				
0.0000	0.7754	1.9431	9.2623	1.7147
0.2468	1.0670	2.3864	8.7095	1.6205
0.4527	1.2732	2.9702	8.4131	1.5466
0.6682	1.5023	3.8202	8.0061	1.3406
0.8749	1.7261	4.0795	7.5948	0.7195
1.0000	1.8252	4.2536	6.6849	0.0997
313.15K				
0.0000	0.7818	2.1225	9.6447	1.7529
0.2468	1.0526	2.5611	9.5351	1.5003
0.4527	1.2823	3.2897	8.9280	1.2088
0.6682	1.5287	3.8768	8.7170	1.1058
0.8749	1.7563	4.4510	7.1568	0.9608
1.0000	1.8865	4.4986	3.4665	0.7808

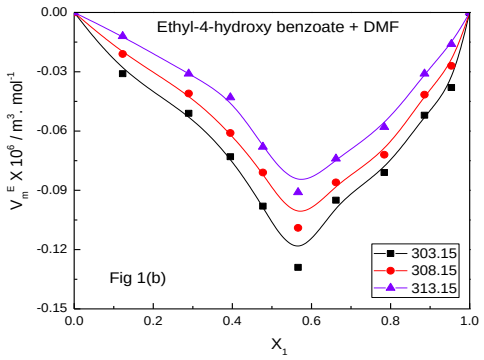
Table-2(3): Free volume (V_f), available volume (V_a), molar volume (V_m),apparent volume(V_ϕ) valuesofEthyl -4-hydroxy benzoate + NMF at different temperatures

Mole fraction	Molar volume (V_m) $m^3\ mol^{-1}$	Free volume (V_f) $m^3\ mol^{-1}$	Apparent volume(V_ϕ) $m^3\ mol^{-1}$	Available volume(V_a) $m^3\ mol^{-1}$
303.15 K				
0.0000	0.5940	0.4297	9.6609	1.2880
0.2243	0.8747	0.8701	8.9275	1.1231
0.4781	1.1657	1.4716	8.5735	0.1084
0.6492	1.3318	2.0674	8.0672	0.0830
0.8256	1.5134	2.7919	7.1204	0.0668
1.0000	1.7058	3.7659	7.0664	0.0100
308.15 K				
0.0000	0.5965	0.4769	9.8286	1.3601
0.2243	0.8816	0.9552	9.4253	1.1449
0.4781	1.2023	1.6460	8.9044	1.1005
0.6492	1.4094	2.3112	8.6870	0.9065
0.8256	1.6124	3.2157	7.3967	0.7421
1.0000	1.8252	4.2536	6.6849	0.4246
313.15 K				
0.0000	0.5991	0.5266	12.2169	1.1931
0.2243	0.8898	1.0278	11.3346	1.1808
0.4781	1.2186	1.7647	10.9894	1.1613
0.6492	1.4370	2.4834	8.1928	1.0383
0.8256	1.6629	3.5045	6.3607	0.0826
1.0000	1.8865	4.4986	3.4665	0.0522

Fig 1 reveals the results of V_f^E, Free volume decreases when actual available volume decreases or when molecular mobility decreases. Hence free volume should be low for amides and should increase for hydroxy group. However, free volume appears to be lowest for substituted amides. This may be due to the presence of impurity or moisture content. Free volume also decreases with increase in frequency of the incoming sound wave. This may be due to the increase in vibration of the molecules about their mean position. Temperature and frequency remain constant, free volume decreases with increase in concentration. In this case the molecules arrange themselves in such a way that the void space is less available showing in between the molecules. This ordered structural arrangement decreases the entropy.[6,11]

Fig 2 reveals the results of V_m^E when temperature increases excitation energy of E-4-HB increases and hence molar volume decreases. Negative V_m^E indicates increase in molecular attraction in the mixture and hence decreases force of cohesion in –OH fragments in alcohols. Whereas thermal energy of fragments increases with temperature hence molar volume should be more. It is observed that at a fixed temperature with sore in captivation of amides velocity increases which may be due to the structural changes occurring in the mixture resulting from rise of intermolecular forces.[12-14]





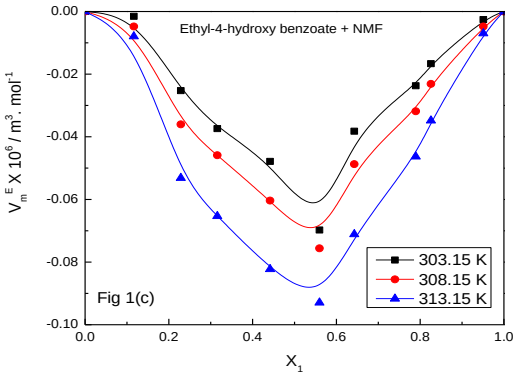
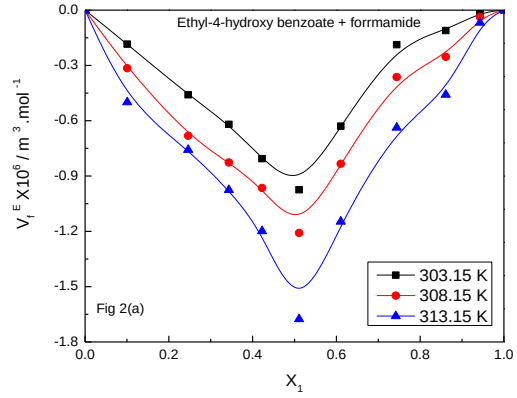
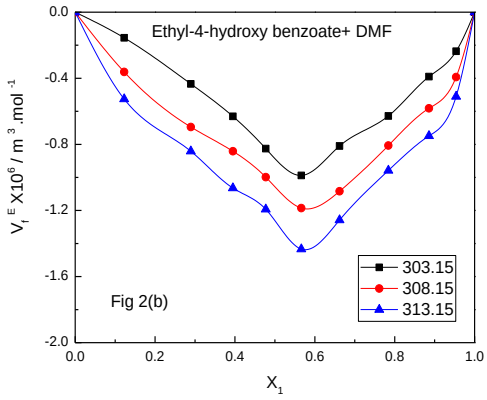


Fig 1(a-c). Variation of excess molar volume of Ethyl-4-hydroxy benzoate with Formamide/ DMF/ NMF at different temperatures





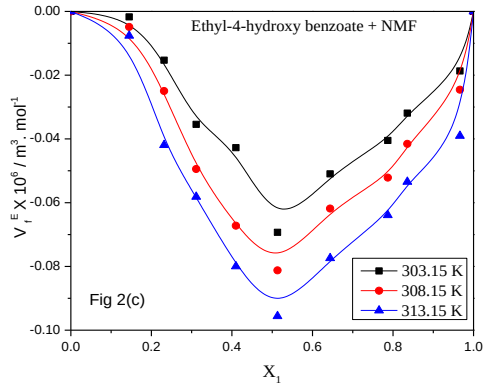


Fig 2 (a-c). Variation of excess free volume of Ethyl-4-hydroxy benzoate with Formamide/ DMF/ NMF at different temperatures

R-K Polynomial: The excess values of were correlated with the mole fraction of E-4HB using R-K equation at the three different temperatures 303.15K, 308.15K and 313.15 K. Table 3 divulge the goodness of fit is debated by acquiring a number of parameters and standard deviation for Redlich and Kister ($Y^E = V_m^E$ and V_f^E) upshots for the mix of Ethyl-4-hydroxy benzoate + amides. The pouncing of up comes not only flaunts the viability of blends but also anticipate the rising of digression/ atomic segregation. Also stipulates the leverage of cohesive forces arising from the breakage of hydrogen bonds in the motes.[15–17]

Table 03 R-K polynomial parameters (A_k) and Standard deviation(σ) Ethyl-4-hydroxy benzoate + amides at T= 303.15 K, 308.15K and 313.15K

Parameter	Temperature(K)	A_1	A_2	A_3	σ
	Ethyl-4-hydroxy benzoate**+** Formamide				
	303.15	-1.9451	-0.3607	0.0436	0.0401
$10^6V_f^E$ /($m^3.mol^{-1}$)	308.15	-2.6040	-0.7542	-0.6344	0.0570
	313.15	-3.0143	-1.0587	-1.6354	0.0714
	303.15	-3.5128	-1.6843	-1.8864	0.3047
$10^6V_m^E$ /($m^3.mol^{-1}$)	308.15	-4.7918	-2.8064	-1.7240	0.4507
	313.15	-5.1746	3.0360	-1.5472	0.5138
	Ethyl-4-hydroxy benzoate **+** DMF				
	303.15	-1.7844	-0.4097	1.4724	0.0280
$10^6V_f^E$ /($m^3.mol^{-1}$)	308.15	-2.2146	-0.8073	1.1031	0.0538
	313.15	-3.1013	-1.3080	0.7002	0.0854
	303.15	-3.0813	-0.8484	-1.4336	0.0682
$10^6V_m^E$ /($m^3.mol^{-1}$)	308.15	-4.1368	-1.3576	-1.0146	0.0833
	313.15	-5.4012	-1.6087	-0.8035	0.0949
	Ethyl-4-hydroxy benzoate + NMF				
	303.15	-1.3024	-0.6400	0.4173	0.0140
$10^6V_f^E$ /($m^3.mol^{-1}$)	308.15	-3.3436	-0.8176	0.7637	0.0262
	313.15	-4.7819	-1.6779	-0.5634	0.0384
	303.15	-3.1800	0.7831	-0.3522	0.1036
$10^6V_m^E$ /($m^3.mol^{-1}$)	308.15	-4.3683	0.9272	0.7151	0.4507
	313.15	-5.7567	-1.3814	-0.9687	0.7702

CONCLUSIONS

It is obvious that, there exist a molecular interaction between the components of the mixture. In specific weak molecular interaction (like dipole-dipole, dipole-induced dipole and dispersive forces) are found to exist between components of the individual mixtures. The parameters studied in this work are discussed in the light of molecular interactions in the mixtures. However, the interaction between molecules appears to be weaker in hydroxy compounds which may be attributed to steric hindrance. Higher value of available volume predicts breaking of liquid order (dissociation) on mixing. Hence it leads to expansion. This may be also due to dispersion forces, steric hindrance in component molecules, unfavorable geometric fitting and electrostatic repulsion. Low values of apparent and free volume lead to reduction in volume. This may be due to the formation of new

bonds. Molar volume is less in case of NMF and DMF whereas for formamide it comes out to be high. This high molar volume in aniline as we have pointed out before may be due to the presence of moisture which leads to hydrogen bonding. Variation with temperature in each case indicates that the interaction becomes weaker as temperature increases.

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CONFLICT OF INTREST: Authors have no conflict of Interest

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