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Investigation of Comparative Behavior of some Thermoacoustical Parameters of Binary Mixtures of Methanol, Cyclohexanol and Cyclohexane.

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Abstract: ***The Literature reveals the extensive use of ultrasonic, thermodynamic and thermoacoustical parameters to characterize physico-chemical behavior of liquid mixtures and study the molecular interactions. In the present investigation an attempt has been made to evaluate and compare thermoacoustical parameters such as volume expansivity [α],Moelwyn-Hughes parameter [c_1], Lattice Gruneisen parameter [┌/], Bayer's non linearity parameter [B/A], Internal pressure [Pi], Molecular radius [$r_{oj,}$ Gruneisen like parameter [Γ_0], Thermodynamic or Average Gruneisen parameter [┌/], Cohesive energy density [ε],Vander Waal's constant [b] etc. of binary liquid mixtures cyclohexanol in methanol and cyclohexanol in cyclohexane for entire range of mole fraction. Experimental and computed results are used to study the type and nature of inter and intra molecular interactions between mixing components. The study of molecular interactions in liquid provides valuable information about internal structure, molecular association etc.***

Keywords: Ultrasonic velocity, Methanol, Cyclohexanol, Cyclohexane, Molecular, Interaction, Molecular association

1. Introduction

Amongst the four states of matter the solid and the gaseous states have been extensively studied over a long time. It is usually said that the liquid state is intermediate in its properties between a solid and a gas. This statement should not be taken to consider that every property of liquid is intermediate in value between those of the other two states. If numerical values are compared, it is found that in great majority of cases, the values of sufficient representing a property of liquid is quite close either to that of solid or to that of gas.

All theories of liquids developed so far make approximations at some stage of their development. The pair distribution method is best for low density fluids. The solid-like theories of liquid such as the cell, free volumes or partition function methods is best applied for high density fluids i.e. for small cell.

Ultrasonic parameters are being extensively used to study molecular interaction in pure liquids and liquid mixtures[1-2] Early work on non linear behavior of ultrasonic's velocity versus concentration curves in different liquid mixtures have been reported by number of workers. [3-8] The empirical relation due to Nomoto [9] and ideal mixing relation [10-11] for ultrasonic velocity have been successively used to investigate the thermodynamic and acoustical behavior of binary liquid mixtures. Interactions in binary liquid mixtures have been studied by Rastogi[12], Jain[13], Hyderkhan[14], Hughes[15], Halzhauer[16], Delmos[17], Sheshadri[18], Naidu19, Tabhane [20-22] and others[23].

Adgaonkar24 studied the hydrogen bonded complex formation in number of binary liquid mixtures.

2. Experimental Details

The aim of the present study was to attempt to get an insight of the comparison of ultrasonic velocity, density and the thermoacoustical parameters of the binary liquid mixtures namely methanol + cyclohexanol with those of cyclohexane + cyclohexanol . The experimental data has been generated by measuring u.s. velocity at 2Mhz using interferometer and the density in these pure liquids and their binary liquid mixtures by employing ultrasonic interferometer and hydrostatic plunger method respectively in the temperature range 10- 40^0c and ultra Thermostat U – 10 min of the samples constant to 0.1^0c. The accuracy of one part in 10^4 in the velocity and one part in 10^4 in the density measurement is achieved. The variation of u and ρ in the mixtures were found to be linear with temperature and hence the method of least square was applied and the values of u and ρ at different temperatures were calculated from the equations 2 and 3 given below. The thermodynamic parameters are calculated for very small concentration 0.1, 0.2, 0.3…… 1.0 of the two pure liquid components in a given binary liquid mixture of the two components. The result and discussion of the experimental and theoretical investigation on above mentioned systems is presented in comparative manner.

3. Calculation of Ultrasonic and Thermoacoustical Parameters

1) U.S.Velocity $v = \lambda f$
The values of u and density ρ were used to obtain the coefficients of following polynomial
2) U S velocity $u = u_{o+} [du/dT]_{T=0}$
3) Density $P = \rho_0 + [d\rho/dT]_{T=0}$
4) Volume expansivity $\alpha = {}^1/\rho [d\rho/dT]$
5) Moelwyn – Hughes parameter $c_1 = [(13/3) + (\alpha T)^{-1} + (4/3) \alpha T]$

6) Lattice Gruneisen parameter $\Gamma = (5/3) + (2\alpha T)^{-1} + (2/3)\alpha T$

7) Gruneisen like parameter $\Gamma_0 = V^{1/3}(V^{-1/3} - 1)^{-1}$

8) Thermodynamic Gruneisen parameter $\bar{\varepsilon} = \frac{\Upsilon - 1}{\alpha T}$

9) Bayer's non linearity parameter $\frac{B}{A} = J_0 + J(x)$ where $J_0 = \frac{\Upsilon - 1}{\alpha T}$ and $J(x) = \frac{2y}{\sqrt{y} - 1}$

$$Y = 1 + \frac{\Gamma 0}{3\alpha T}$$

and $x = 1 + \frac{1}{(2 + \sqrt{3}y)}$

10) Reduced Volume $\bar{v} = \left[\frac{1 + 4\alpha T/3}{1 + \alpha T}\right]^3$

11) Molecular radius $r_0 = \left(\frac{3M}{16\pi\rho N}\right)^{1/3}\left[1 - \left(\frac{\Upsilon RT}{M\,c2}\right)\left\{\left(\frac{Mc2}{3\Upsilon RT} + 1\right)^{1/2}\right) - 1\right\}\right]$

12) vander waals' constant $b = \frac{16}{3}\pi N r_0^3$

13) Internal pressure $P_i = \frac{\rho u 2}{(\frac{B}{A} + 1)}$

Table 1: The values of experimentally measured u.s. velocity [Uexpt.] and density [ρ expt], [du/dt] ,[dρ/dt] of systems Methonol + Cyclohexanol and Cyclohaxane+Cyclohexanol at temperature 303.15^{0}K. [u x cm-sec^{-1}, ρ x gm cc^{-1}]

Methonol + Cyclohexanol					Cyclohaxane+Cyclohexanol			
Cm	**u**	**du/dt**	**ρ**	**dρ/dt**	**u**	**du/dt**	**ρ**	**dρ/dt**
0	1101.15	-	0.780893	-0.8723	1248.3	-4.68	0.765683	-0.8367
0.1	1169.7	-	0.817368	-0.7653	1251.1	-4.4	0.784603	-0.8959
0.2	1222.83	-	0.848275	-0.757	1263.55	-4.526	0.798808	-0.8557
0.3	1269.88	-	0.868193	-0.6443	1281.85	-4.458	0.81931	-0.8596
0.4	1304.88	-	0.881323	-0.6431	1300.65	-4.198	0.835345	-0.7582
0.5	1347.73	-	0.899548	-0.5861	1230.35	-4.102	0.854888	-0.7565
0.6	1368.27	-	0.891408	-0.6197	1300.65	-4.198	0.835345	-0.7582
0.7	1395.57	-	0.9167	-0.64	1281.85	-4.458	0.81931	-0.7596
0.8	1418.4	-	0.924848	-0.6781	1263.55	-4.526	0.798888	-0.8557
0.9	1433.28	-	0.930468	-0.6333	1251.1	-4.4	0.784603	-0.8959
1	1483.83	-	0.937075	-0.661	1483.83	-6.459	0.937075	-0.661

Table 2: Some physical parameters (Input data) for pure liquid at 303.15 k.

Liquids	Molecular Weight	Density ρ kg/m^3	U.S. velocity m/s	βε	σ A^0
Methanol	32.04	0.7765	1086.07	28.471	3.832
Cyclohexanol	101.16	0.9338	1451.6	48.68	5.794
Cyclohexane	84.14	0.7615	1225.1	43.08	5.680

Table 3 some Thermo acoustical parameters

Cm	**α**	**C_1**	**Γ**	**Γ_0**	**$\bar{\Gamma}$**	**B/A**	**$\bar{v}$**	**r_0 X10^{-8}**	**b**	**P_{iX10^9}**
0.0	0.001117	7.7812	3.3986	13.0122	5.1899	10.7517	1.2711	1.2681	20.566	0.8857
0.1	0.000936	8.2894	3.6447	14.7528	5.6171	11.7823	1.2344	1.3328	23..878	0.8749
0.2	0.000892	8.4482	3.7241	15.2810	5.7769	12.1684	1.2251	1.3899	27.084	0.9638
0.3	0.000742	9.1508	4.8758	17.5654	6.4775	13.5289	1.1923	1.4452	30.445	0.9636
0.4	0.000738	9.2228	4.1118	17.7963	6.5495	13.7195	1.1895	1.4981	33.914	1.019
0.5	0.000652	9.7426	4.3713	19.4510	7.0781	14.7512	1.1716	1.5432	37.078	1.037
0.6	0.000695	9.4366	4.2183	18.4810	6.7641	14.2189	1.1816	1.5997	41.288	1.097
0.7	0.000698	9.4173	4.2886	18.4196	6.7448	14.2284	1.1823	1.6330	43.920	1.172
0.8	0.000733	9.2814	4.1007	17.7383	6.5289	13.8759	1.1982	1.6735	47.272	1.251
0.9	0.000681	9.5341	4.2678	18.7910	6.8616	14.5125	1.1783	1.7130	50.782	1.232
1.0	0.000785	9.3789	4.1854	18.2718	6.6984	14.2871	1.1839	1.7497	54.033	1.350

System- A: Methanol + Cyclohexanol

System B: Cyclohexane + Cyclohexanol

Cm	**α***	**C1***	**Γ***	**Γ_0***	**$\bar{\Gamma}$***	**B/A***	**$\bar{v}$***	**r_0*X10^{-8}**	**b***	**Pi*X10^9**
0.0	0.001093	7.8384	3.4192	13.2126	5.1669	11.2745	1.2663	1.7604	55.023	0.9720
0.1	0.001142	7.7251	3.3629	12.8165	5.0546	11.1089	1.2768	1.7578	54.78300	1.015
0.2	0.001071	7.1986	3.4458	13.3978	5.2199	11.3927	1.2628	1.7588	54.783	1.029
0.3	0.000927	8.3212	3.6686	14.8585	5.6489	12.1500	1.2325	1.7551	54.536	1.024
0.4	0.000988	8.3911	3.6956	15.0914	5.7188	12.2998	1.2284	1.7548	54.507	1.063
0.5	0.000885	8.4771	3.7385	15.3764	5.8047	12.4789	1.2235	1.7521	54.256	1.106
0.6	0.000908	8.3911	3.6956	15.0914	5.7188	12.3062	1.2284	1.7765	56.546	1.062
0.7	0.000927	8.3212	3.6686	14.8585	5.6489	12.1627	1.2325	1.7987	58.694	1.023
0.8	0.001071	7.8916	3.4458	13.3978	5.2199	11.4140	1.2620	1.8246	61.269	1.027
0.9	0.001142	7.7259	3.3629	12.8165	5.0546	11.1386	1.2760	1.8461	63.466	1.012
1.0	0.000785	9.3789	4.1854	18.2718	6.6984	14.2871	1.1839	1.7497	54.033	1.350

4. Discussion of Results

In the system methanol + cyclohexanol it is found that the ultrasonic **u**, density **ρ** increases with increase in mole fraction **x.** Molwyn – Hughes parameter $\mathbf{c_1}$ shows overall increase in mole fraction **x**. It shows the peaks at the molar ratio of 5:5 and a dip at 2:8. The trend of variation of reduced volume $\bar{v}$ is opposite to that of Γ (= K) and c_1 , Grunesein like parameter Γ_0, Bayer's non linearity parameter (B/A), Thermodynamic Grunesein parameter $\bar{\Gamma}$, show overall increase in mole fraction **x**. Peaks are obtained at molar ratios 8:2, 6:4 , and 2: 8. This variation is similar to the variation of internal pressure P_i.

In the system cyclohexane + cyclohexanol the parameters **u** ,ρ, **Γ (= K)** and $\mathbf{c_1}$ are highest at the molar ratio of 5:5 and deceases steeply on either side of this concentration. The trend of variation of α and $\bar{v}$ is opposite to that of velocity **u** and density **ρ**. The variation of $\bar{v}$ and Γ (= K) with mole fraction x is identical but opposite to the trend of variation of c_1. Grunesein parameter $\bar{\Gamma}$ falls sharply from 9:1 to 7:3 of molar ratio and remains fairly constant from 7:3 to 3:7 molar ratio of composition. These parameters steeply increase from the ratio 3:7. The internal pressure P_i rises to highest at 5:5 molar ratio where as it remains constant in the range 9:1 to 8:2 and 2:8 to 1:9 .

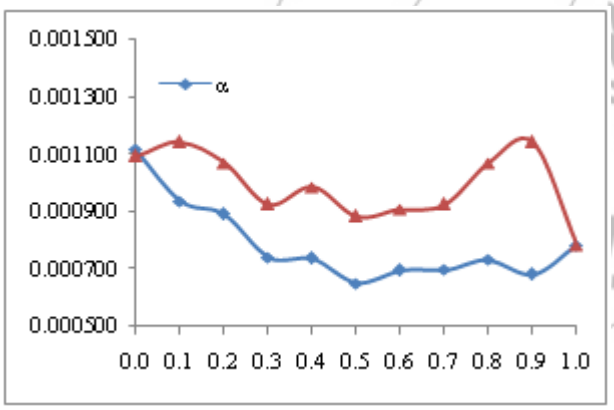

Figure 1: Variation of **α** and **α*** versus Cm of system A and B

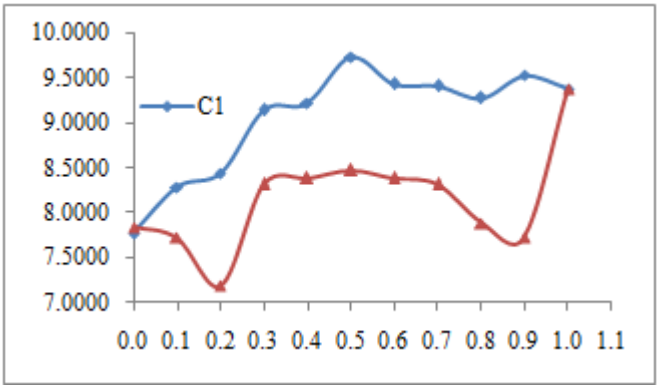

Figure 2: variation of $\mathbf{C_1}$ and **C1*** versus Cm of system A and B

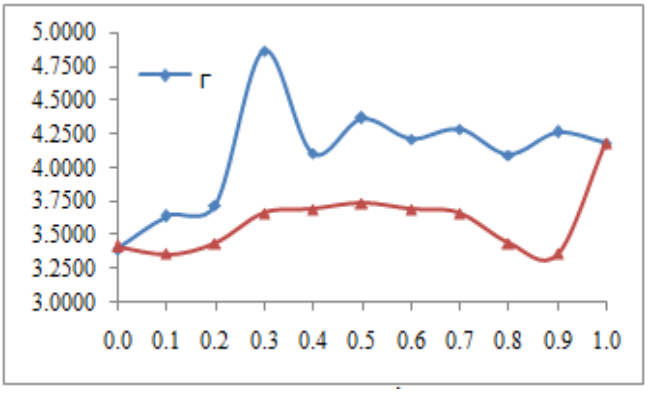

Figure 3: variation of Γ and Γ* versus Cm of system A and B

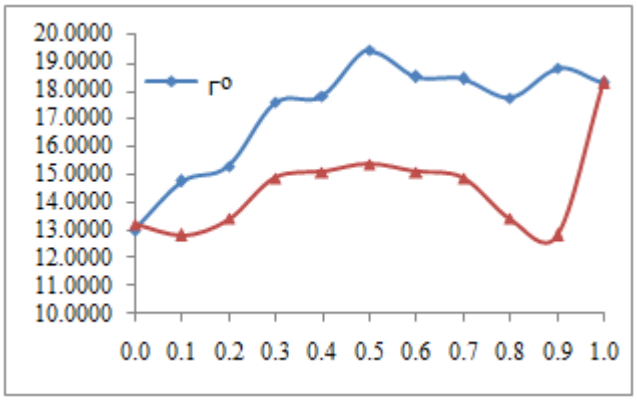

Figure 4: variation of Γ_0 and Γ_0* versus Cm of system A and B

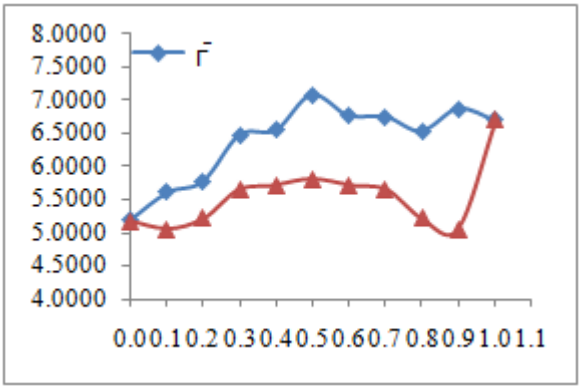

Figure 5: variation of $\bar{\Gamma}$ and $\bar{\Gamma}$* versus Cm of system A and B

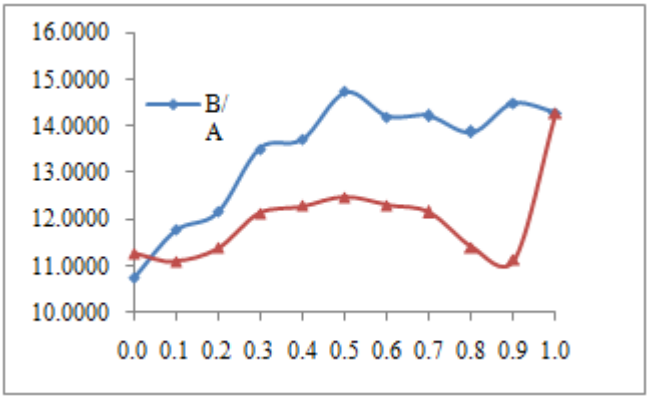

Figure 6: variation of **B/A** and **B/A*** versus Cm of system A and B

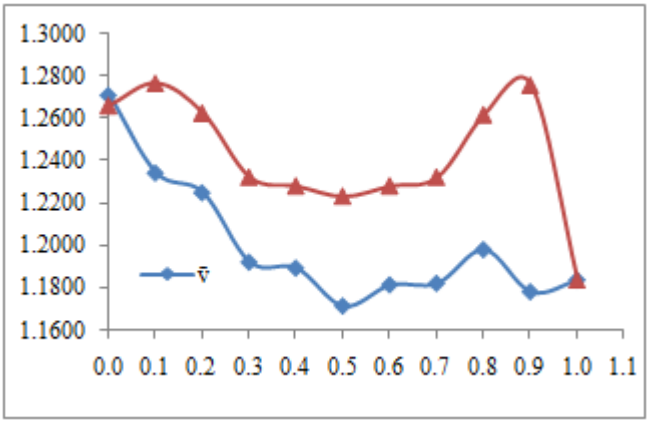

Figure 7: variation of $\bar{v}$ and $\bar{v}$* versus Cm of system A and B

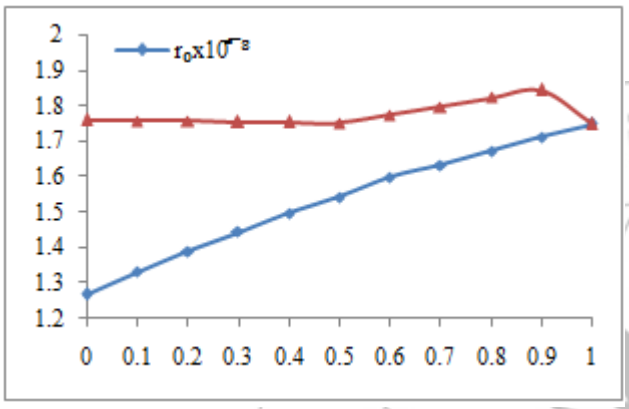

Figure 8: variation of r_o and r_o* versus Cm of system A and B

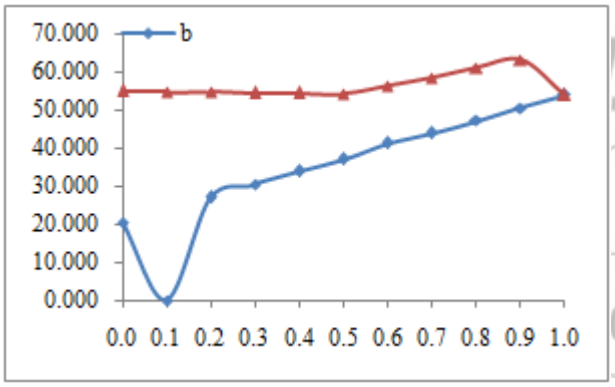

Figure 9: variation of **b** and **b*** versus Cm of system A and B

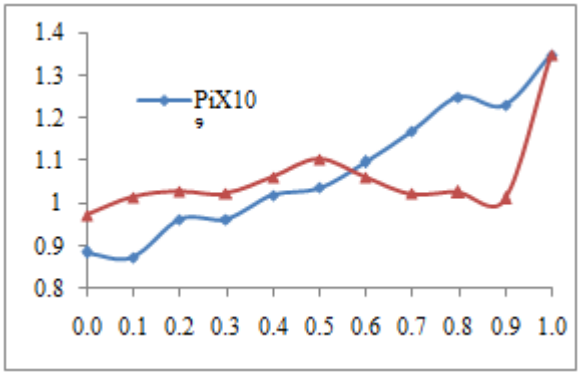

Figure 10: variation of P_i and **Pi*** versus Cm of system A and B

5. Conclusion

In methanol + cyclohexanol an appreciable AB interaction is strong associative nature. The AB interaction of methanol with cyclohexanol results in breaking up the cyclohexanol cluster. The peaking of variation towards the higher concentration of cyclohexanol indicates AB interaction to be stronger than the strength of BB and AA interaction. In cyclohexane + cyclohexanol , cyclohexane is the non associative liquid while cyclohexanaol is the associative liquid due the presence of OH^- goup in the later. The associative nature of the liquid may manifest in the form of demarization process due to the possibility of H- bond between H of cyclohexane and OH of cyclohexanol.

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