

Acoustical Studies in Ternary Liquid Mixtures of 4-Methyl Anisole with 1-Propanol in N-Hexane as Solvent at Various Temperatures

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ABSTRACT: Density, Viscosity, Ultrasonic Velocity has been measured for ternary liquid mixtures containing 4-methyl anisole+1-Propanol+n-hexane at 303K, 308K and 313K. The adiabatic compressibility, free length, free volume, internal pressure, formation constant values have been calculated from the experimental data. These parameters are used to discuss the molecular interactions in the mixtures.

KEYWORDS: Ultrasonic Velocity, Internal pressure, Formation constant.

I. INTRODUCTION

Ultrasonic studies of liquid mixtures have found wide applications due to their ability to characterize physico-chemical behavior of solution. The studies on ultrasonic and viscometric properties of liquid mixtures and their dependence on composition and temperature are important in many fields of applied research and find applications in many important chemical, industrial and biological processes¹⁻⁶. The propagation of an acoustic wave in a liquid is a pure thermodynamic phenomenon. The study of the velocity of ultrasonic waves through a liquid when combined with the density of the liquid helps to compute various thermodynamic parameters like Adiabatic compressibility, Free length, Free volume, Internal pressure, Absorption Coefficient, etc. Thus the propagation of ultrasonic waves provides a useful tool for the study of various thermodynamic parameter of a liquid⁷.

Variations in Ultrasonic velocity and related parameters yield information regarding structural changes associated with the liquid mixtures having weakly as well as strongly interacting components⁸. The study of molecular associations in ternary mixtures having alcohol as one of the component is of particular interest since alcohols are strongly self-associated liquids with the 3-D network of hydrogen bonds and can be associated with any other group having some degree of polar attractions^{9&10}. The ultrasonic velocity measurements are highly sensitive to molecular interactions which provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures. Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interactions in pure liquids.

Therefore in order to have clear understanding of the molecular interactions between the component molecules, a thorough study on the liquid mixtures (4-methyl anisole + 1-propanol + n-hexane) using ultrasonic velocity data has been performed at 303K, 308K and 313K.

II. THEORY AND CALCULATIONS

The AR grade chemicals were purified and used to prepare 4-methyl anisole + 1-propanol + n-hexane liquid mixtures of various concentrations. The densities, viscosities and ultrasonic velocities of these chemicals were determined at various temperatures 303K, 308K, 313K.

i. ULTRASONIC VELOCITY (U): The relation used to determine the ultrasonic velocity is given by, $U = f\lambda$ ms⁻¹ -----
-----1 Where f - Frequency of ultrasonic waves; λ - Wave length

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ii. DENSITIES OF THE MIXTURE: $(\rho_2 = (w_2/w_1) \rho_1)$ -----2

Where w_1 = weight of distilled water; w_2 = weight of experimental liquid; ρ_1 = Density of water; ρ_2 = Density of experimental liquid.

iii. ADIABATIC COMPRESSIBILITY: $(k)\kappa = (1/U^2\rho)$ $\text{kg}^{-1} \text{ms}^{-2}$ -----3

Where U - Ultrasonic velocity; ρ - Density of the solution..

iv. ABSORPTION COEFFICIENT : $(\alpha/l^2)\alpha/l^2 = 8\pi^2\eta/3\rho U^3$ -----4

Where U - Ultrasonic velocity; ρ - Density of the solution; η - Viscosity.

v. FREE LENGTH (L_f): Jacobson¹¹ suggested the following relation to calculate the intermolecular free length in liquids.

$L_f = (K/U \rho^{1/2}) \text{ m}$ -----5

Where U - Ultrasonic velocity of liquid; ρ - Density of liquid; K - Jacobson temperature $K = (93.875 + 0.345T) \times 10^8$.
Decrease in free length shows significant molecular interactions between the molecules of a liquid or liquid mixture and vice versa.

vi. FREE VOLUME (V_f): A formula for free volume in terms of the ultrasonic velocity (U) and the viscosity of the liquid (η) is given as

$V_f = (M_{\text{eff}} U / K \eta)^{3/2} \text{ m}^3$ -----6

Where, M_{eff} is the effective molecular weight, which is expressed as $M_{\text{eff}} = (X_1 M_1 + X_2 M_2 + X_3 M_3)$, X and M are mole fraction and molecular weight of the individual component in the mixture respectively. 'K' is the temperature independent constant and its value is 4.28×10^9 .

vii. INTERNAL PRESSURE (π_i): On the basis of Suryanarayana¹² statistical thermodynamics, derived an expression for the determination of internal pressure.

$\pi_i = bRT (k\eta/U)^{1/2} (\rho^{2/3}/M_{\text{eff}})^{7/6}$ -----7

Where T - Absolute temperature; ρ - Density, R is the gas constant; M_{eff} - effective molecular weight.

viii. AVAILABLE VOLUME (V_a): $V_a = V_m(1 - U/U_a) \text{ m}^3$ -----8

Where V_m is the molar volume and $U_a = 1600 \text{ ms}^{-1}$

ix. LENARD JONES POTENTIAL : LJP = $6V_m/V_a$ -----9

Where V_m - the molar volume and V_a - the available volume

x. VISCOUS RELAXATION TIME (τ): $\tau = 4\eta/3\rho U^2$ -----10

xi. COHESIVE ENERGYCE = $\pi_i V_m \text{ kJ mol}^{-1}$ -----11

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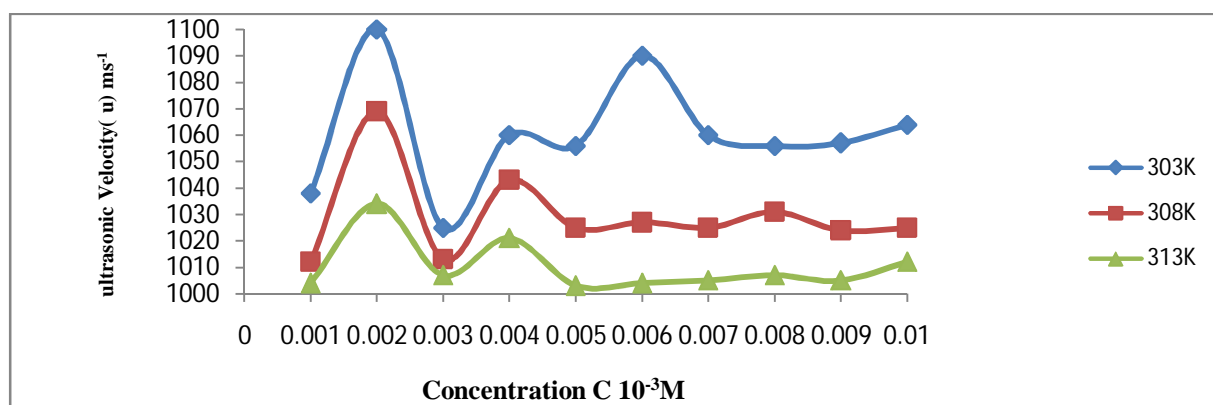
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II. RESULT AND DISCUSSION

Table 1: Values of Ultrasonic velocity, Density and Viscosity of the system: : 4 methyl anisole +1propanol + n-hexane.

CONC (M)	Ultrasonic Velocity (U) ms ⁻¹			Density ρ kg/m ³			Viscosity η ×10 ⁻⁴ Nsm ⁻²		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	1038	1012	1004	640	639	638	3.509	3.369	3.229
0.002	1100	1069	1034	643	642	641	3.526	3.385	3.38
0.003	1025	1013	1007	638	636	635	3.364	3.219	3.214
0.004	1060	1043	1021	641	640	639	3.38	3.375	3.369
0.005	1056	1025	1003	637	635	631	3.493	3.348	3.194
0.006	1090	1027	1004	639	638	637	3.504	3.364	3.359
0.007	1060	1025	1005	639	638	637	3.369	3.229	3.224
0.008	1056	1031	1007	636	634	633	3.353	3.343	3.204
0.009	1057	1024	1005	630	629	628	3.455	3.317	3.311
0.01	1064	1025	1012	640	639	637	3.509	3.369	3.359

Fig 1: Variation of Ultrasonic Velocity Vs Concentration for system :4 methyl anisole +1-propanol + n-hexane at different temperatures.



On the basis of a model for propagation proposed by Kincaid and Eyring (1938). Ultrasonic Velocity should increase if the intermolecular free length decreases as a result of mixing the components and vice versa. Hexane is a nonpolar chain molecule, only Van der Waalstype interactions are present in n- hexane, while alcohols are polar and associate strongly through hydrogen bonding. In alcohols + n- hexane mixtures, the alcohol molecules associate in inert hexane medium and form clusters. The increase in free length with increase of temperature is due to the loose packing of molecular inside the shield, which may be brought about by weakening of molecular interactions. A decrease in free volume and a increase in internal pressure to the increase in magnitude of interaction.

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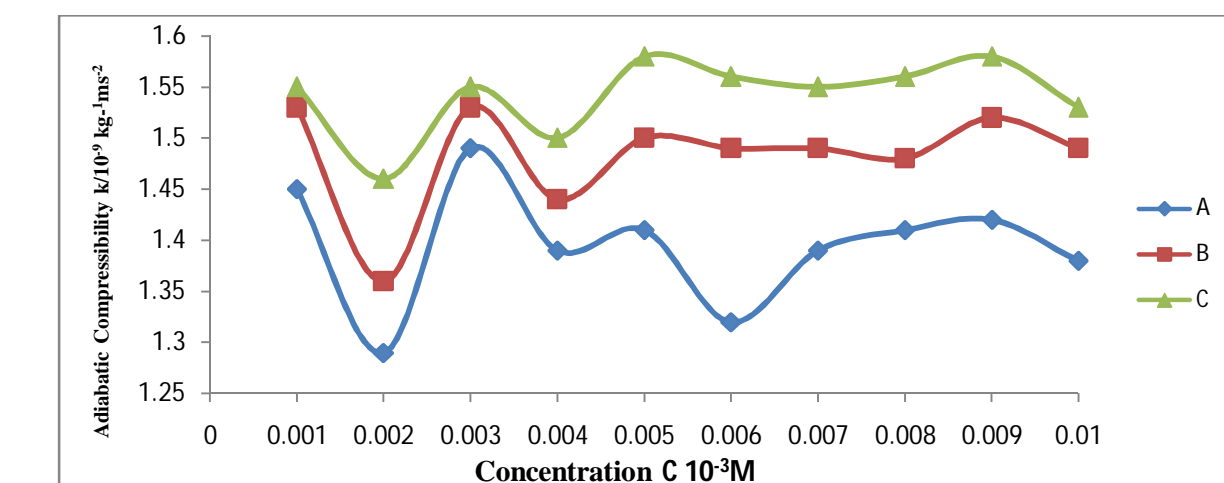
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Table 2 : Values of **Adiabatic Compressibility (k)**, **Free Length (L_f)**, **Free Volume (V_f)** & **Internal pressure(π_i)** of the system: 4 methyl anisole + 1-propanol + n-hexane at different temperatures.

CONC (M)	Adiabatic Compressibility ×10 ⁻⁹ kg ⁻¹ ms ⁻²			Free Length (L _f) pm			Free Volume (V _f)×10 ⁻⁷ m ³			Internal Pressure π _i atm		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	1.45	1.53	1.55	75.6	77.6	76.3	5.910	6.048	6.598	2.051	2.033	1.977
0.002	1.29	1.36	1.46	70.5	72.6	70.5	4.805	4.893	5.12	2.504	2.486	2.452
0.003	1.49	1.53	1.55	76.0	77.0	76.0	4.638	4.867	4.965	2.521	2.475	2.464
0.004	1.39	1.44	1.5	73.3	74.6	73.3	4.843	4.738	4.866	2.492	2.508	2.488
0.005	1.41	1.5	1.58	73.8	76.2	73.8	4.583	4.67	5.242	2.528	2.507	2.417
0.006	1.32	1.49	1.56	71.4	75.8	71.4	4.784	4.651	5.097	2.497	2.518	2.445
0.007	1.39	1.49	1.55	73.4	76.0	73.4	4.866	4.93	5.197	2.483	2.47	2.429
0.008	1.41	1.48	1.56	73.9	75.8	73.9	4.872	4.723	5.217	2.474	2.495	2.419
0.009	1.42	1.52	1.58	74.1	76.6	74.1	4.666	4.73	4.973	2.494	2.48	2.442
0.01	1.38	1.49	1.53	73.1	75.9	73.1	4.603	4.626	4.916	2.532	2.525	2.477

Fig 2: Variation of **Adiabatic compressibility Vs Concentration** for the system: 4 methyl anisole + 1-propanol + n-hexane at different temperatures.



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Fig 3: Variation of **Internal pressure Vs Concentration** for the system: 4 methyl anisole + 1-propanol + n-hexane at different temperatures.

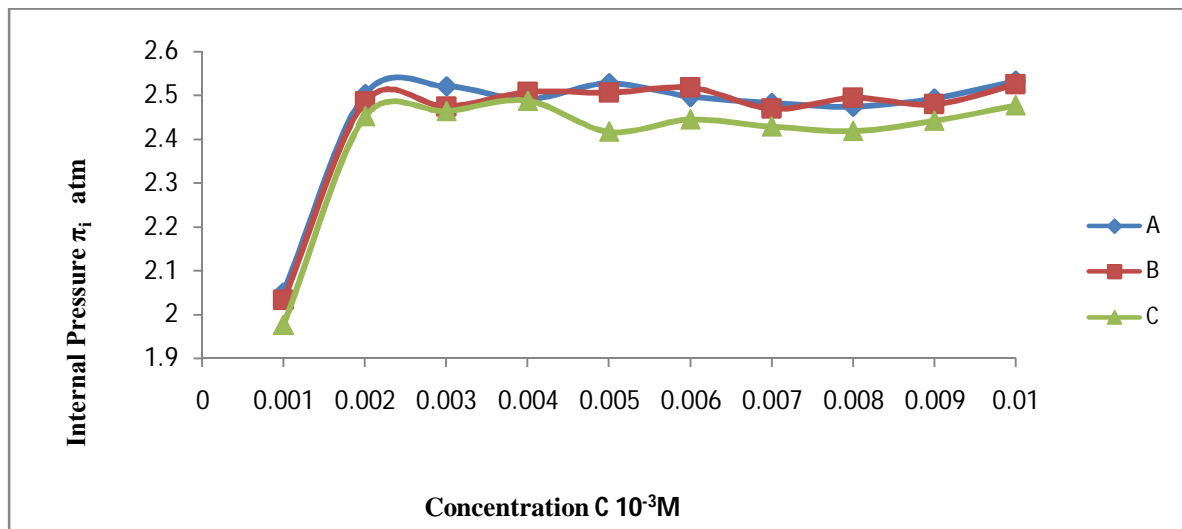
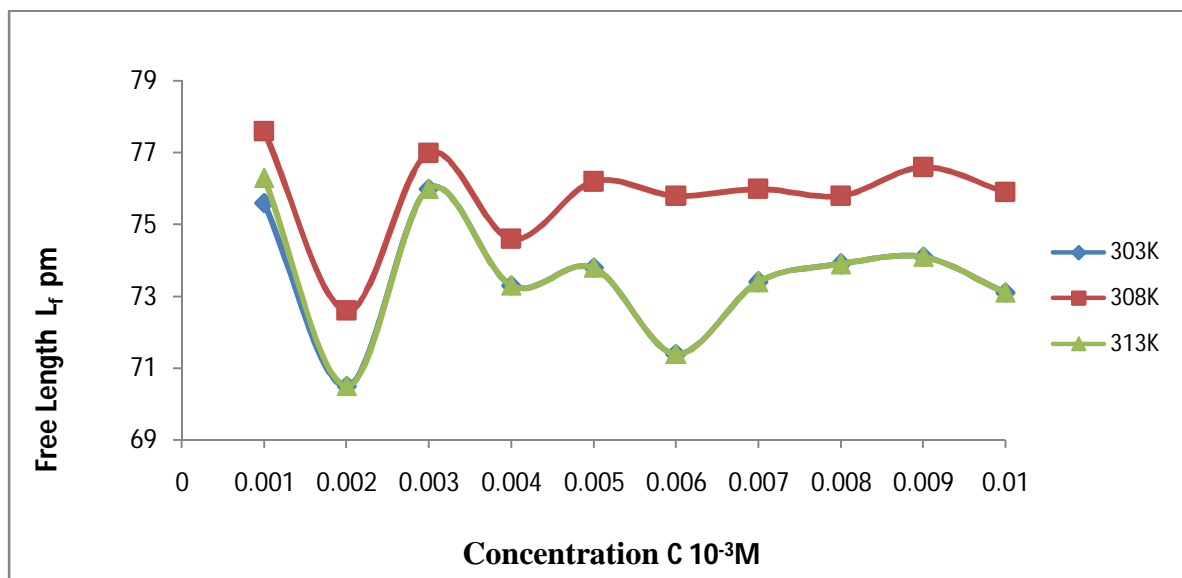


Fig 4: Variation of **Free length Vs Concentration** for the system: 4 methyl anisole + 1-propanol + n-hexane at different temperatures.



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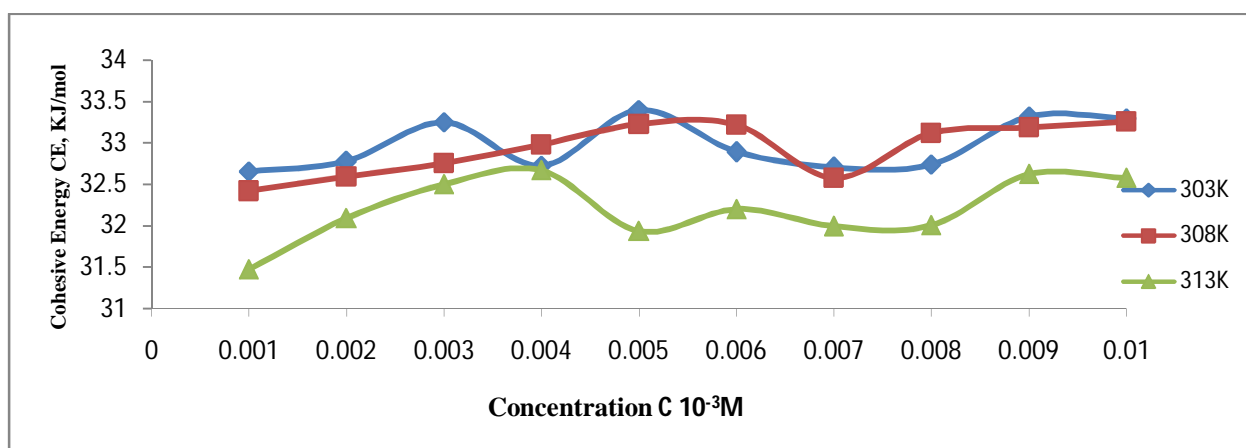
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Table 3: Values of Absorption Coefficient, Viscous Relaxation Time, Available Volume & Cohesive Energy for the system: 4 methyl anisole + 1-propanol + n-hexane at different temperatures.

CONC (M)	Absorption Coefficient(α/f^2) $\times 10^{-14}$ $Npm^{-1}s^2$			Viscous Relaxation Time $\times 10^{-13}$ s			Available Volume V_a $\times 10^{-5} m^3$			Cohesive Energy CE $KJ mol^{-1}$		
	303 K	308 K	313 K	303K	308K	313K	303K	308K	313K	303K	308K	313K
	0.001	1.29	1.34	1.22	6.786	6.864	6.366	5.593	5.861	5.692	32.652	32.419
0.002	1.08	1.13	1.04	6.043	6.152	5.792	4.09	4.351	4.09	32.774	32.592	32.088
0.003	1.29	1.28	1.23	6.691	6.577	6.394	4.741	4.855	4.741	33.25	32.753	32.501
0.004	1.16	1.22	1.16	6.257	6.463	6.237	4.431	4.578	4.431	32.722	32.979	32.671
0.005	1.22	1.29	1.12	6.557	6.691	5.995	4.492	4.763	4.492	33.398	33.224	31.936
0.006	1.11	1.28	1.07	6.154	6.665	5.899	4.198	4.724	4.198	32.89	33.217	32.201
0.007	1.16	1.24	1.11	6.257	6.424	5.988	4.445	4.74	4.445	32.705	32.578	31.994
0.008	1.18	1.26	1.12	6.304	6.614	6.024	4.499	4.721	4.499	32.741	33.118	32.004
0.009	1.22	1.29	1.17	6.544	6.705	6.272	4.533	4.817	4.533	33.321	33.187	32.622
0.01	1.2	1.29	1.15	6.458	6.691	6.181	4.405	4.733	4.405	33.298	33.259	32.575

Fig-5: variation of Cohesive Energy Vs Concentration for the system: 4 methyl anisole + 1-propanol + n-hexane at different temperatures.



The Cohesive Energy is a measure of attraction between molecules of the components. The decrease in Cohesive Energy values with increase in concentration and temperature shows a weaker molecular interactions are present in this system. Molecular Interaction parameter values are computed and tabulated in Table 4.

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Table-4: Values of **Lenard Jones Potential:** 4 methyl anisole + 1-propanol + n-hexane at different temperatures. The below table values are positive or negative depending on the concentration. There is dipole – dipole interactions between 4- methyl anisole and 1 propanol, which acts as the donor and acceptor respectively

CONC (M)	Lenard Jones Potential			Free Energy of Activation			Molecular Interaction Parameter			Formation Constant		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	4.082	3.438	4.455	4.019	4.029	3.842	-4.115	-7.92	-1.972	105.6	103.1	90.4
0.002	6.200	9.305	12.60	3.698	3.251	3.581	7.672	3.146	3.965	89.4	85.6	74.6
0.003	3.696	3.696	3.354	3.98	3.867	3.854	-6.517	9.546	-1.403	49.6	52.4	61.6
0.004	4.778	3.552	3.027	3.794	4.007	3.786	-3.181	-3.72	1.349	33.2	34.5	45.3
0.005	4.647	3.41	2.868	3.924	4.034	3.676	-7.927	-1.024	-2.202	41.4	33	31.2
0.006	5.824	3.754	3.107	3.749	3.969	3.632	5.69	1.321	-2.016	33.8	28.2	24.3
0.007	4.778	3.696	3.134	3.794	3.867	3.673	-5.561	9.171	-1.829	21.1	24.6	20.4
0.008	4.647	3.872	3.189	3.815	3.948	3.689	-8.164	2.093	-1.447	24.6	22.4	19.7
0.009	4.68	3.667	3.134	3.918	3.985	3.801	-6.363	7.016	-1.847	25	20.8	16.4
0.01	4.91	3.696	2.936	3.882	3.98	3.761	6.762	8.89	-4.837			

Formation constant K:

System	Mean K Value
4 methyl anisole + 1-propanol + n-hexane at 303 K	47.07
4 methyl anisole + 1-propanol + n-hexane at 308 K	44.95
4 methyl anisole + 1-propanol + n-hexane at 313 K	42.65

The formation constant decreases with decrease in polarisability of donor molecules. Therefore, increase in polarisability of donor decreases the ease of complexation.

V.CONCLUSION

The results obtained from the present study indicates the weak dipole – dipole interaction between 4 methyl anisole and 1-propanol. Also it deals with the formation of donor – acceptor complexes between them. The study finally concludes that interaction and stability of the complexes decreases with increase of temperature.

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