



Molecular Interaction Studies in Ternary liquid mixtures containing o-xylene at various Temperatures using Ultrasonic techniques

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ABSTRACT

The experimental data of ultrasonic velocity, density, viscosity have been measured for ternary liquid mixtures containing o-xylene and 1-propanol in n-hexane as solvent at 303K, 308K and 313K. The acoustic parameters like adiabatic compressibility, internal pressure, acoustic impedance, formation constant values, etc. have been computed using the above experimental data. The variation in ultrasonic velocity and other acoustical parameters are mainly due to the interactions between the donor and acceptor molecules. The stability of the complexes formed were also studied.

KEYWORDS : liquid systems, Ultrasonic velocity, Acoustic parameters, Molecular interactions, Formation constant.

I. INTRODUCTION

The molecular interactions in ternary liquids mixtures can be determined successfully using values of ultrasonic velocity. The experimental values of ultrasonic velocities in addition with density and viscosity were used to calculate the various acoustical parameters like Adiabatic compressibility, Free length, Free volume, Internal pressure, Acoustic Impedance, Absorption Coefficient, etc.¹⁻². The variation of these parameters with different temperatures for different concentrations provides information regarding the ions, dipoles like hydrogen bonding, multi-polar & dispersive forces³⁻⁵. The Ultrasonic investigations of liquid mixtures containing polar and non-polar components are of more important in analyzing intermolecular interactions between the liquid components⁶⁻⁹. Acoustic parameters help us for characterizing molecular association and dissociation^{10,11}. Here the ultrasonic velocity, density, viscosity of o-xylene and 1-propanol with n-hexane were measured at 303K, 308K and 313K to predict the possible molecular interactions between the liquid components.

II. THEORY AND CALCULATIONS

To prepare liquid mixtures of various concentrations the AR grade chemicals were purified and used¹². The ultrasonic velocity measurements were made using an ultrasonic interferometer (Mittal type: Model: F81) working at frequency 2 MHz with accuracy of $\pm 0.1 \text{ ms}^{-1}$. The density and viscosity were measured using a Pycnometer and an Ostwald's viscometer with an accuracy of $\pm 0.1 \text{ kg m}^{-3}$ and $\pm 0.001 \text{ Nsm}^{-2}$ respectively, at various temperatures 303K, 308K, 313K.

i. Ultrasonic Velocity (U): The expression used to determine the ultrasonic velocity is given by, $U = f\lambda \text{ ms}^{-1}$ Where **f** - Frequency of ultrasonic waves; **λ** - Wave length

ii. Densities Of The Mixture:

$$\rho_2 = (w_2/w_1) \rho_1$$

Where **w₁** = weight of distilled water; **w₂** = weight of experimental liquid; **ρ₁** = Density of water; **ρ₂** = Density of experimental liquid.

The viscosity was determined using the relation, $\eta_2 = \eta_1 (t_2/t_1) (\rho_2/\rho_1)$ Using the measured data, the following acoustical parameters can be calculated.

iii. Adiabatic Compressibility:

$\kappa = (1/U^2 \rho) \text{ kg}^{-1} \text{ ms}^{-2}$ Where **U** - Ultrasonic velocity; **ρ** - Density of the solution.

iv. Internal Pressure (π_i): $\pi_i = bRT (k\eta/U)^{1/2} (\rho^{2/3}/M_{\text{eff}})^{7/6}$ Where **T** - Absolute temperature; **ρ** - Density, R is the gas constant; **M_{eff}** - effective

molecular weight.

v. Free length: $L_f = (K/U\rho^{1/2}) \text{ m}$ Where **U** - Ultrasonic velocity of liquid; **ρ** - Density of liquid; **K** - Jacobson temperature $K = (93.875 + 0.345T) \times 10^{-8}$

vi. Free Volume: $V_f = (M_{\text{eff}} U / K\eta)^{3/2} \text{ m}^3$ Where, $M_{\text{eff}} = (X_1 M_1 + X_2 M_2 + X_3 M_3)$, **X** and **M** are mole fraction and molecular weight of the individual component in the mixture respectively. $K = 4.28 \times 10^9$.

vii. Lenard Jones Potential: $LJP = 6V_m/V_a$ Where **V_m** - the molar volume and **V_a** - the available volume

viii. Viscous Relaxation Time: $\tau = 4\eta/3\rho U^2$ Where **ρ** - Density; **η** - viscosity.

ix. Acoustic Impedance (Z): $Z = \rho U$ where **ρ** - density **U** - velocity.

III. RESULTS AND DISCUSSION Table 1: Values of Ultrasonic velocity, Density and Viscosity of the system: o-xylene + 1 propanol + n-hexane

CONC (M)	Ultrasonic Velocity (U) ms^{-1}			Density $\rho \text{ kg m}^{-3}$			Viscosity $\eta \times 10^{-4} \text{ Nsm}^{-2}$		
	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	1054.9	1034.1	1014	636	635	631	3.488	3.348	3.194
0.002	1055.7	1022.2	1010	633	631	630	3.471	3.327	3.189
0.003	1056.1	1026.2	1013.3	635	633	631	3.482	3.338	3.194
0.004	1059.1	1028.8	1014.1	635	633	630	3.482	3.338	3.189
0.005	1059.5	1031.4	1009.7	633	632	630	3.471	3.332	3.189
0.006	1057	1031.7	1008	638	636	631	3.499	3.353	3.194
0.007	1054.2	1032.4	1011.1	639	631	630	3.504	3.327	3.189
0.008	1053	1031.6	1011.9	636	633	630	3.488	3.338	3.189
0.009	1056.3	1034.1	1012	635	634	630	3.482	3.343	3.189
0.01	1052	1026.6	1011.5	634	630	628	3.477	3.322	3.179

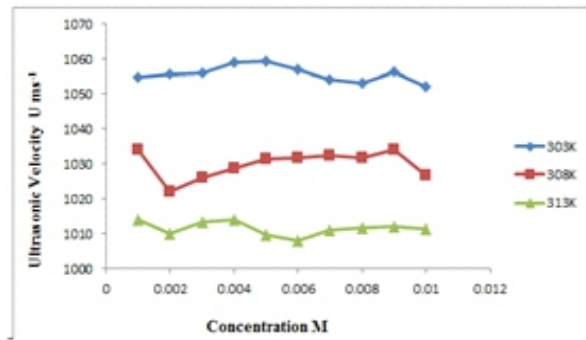
From the above table, it is observed that as the temperature increases the velocity, density, viscosity decreases.

Table 2: values of Adiabatic Compressibility (**κ**), Free Length (**L_f**), Free Volume (**V_f**) & Internal pressure (**π_i**) of the system: o-xylene + 1 propanol + n-hexane.

CON C (M)	Adiabatic Compressibility $\times 10^{-4} \text{ kg}^{-1} \text{ ms}^{-2}$			Free Length (L ₀) Pm			Free Volume (V ₀) $\times 10^{-7} \text{ m}^3$			Internal Pressure η , atm		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	1.41	1.47	1.54	7.46	7.62	7.79	6.313	6.514	6.789	2.019	2.029	2.025
0.002	1.42	1.52	1.56	7.41	7.66	7.76	8.081	8.205	8.588	2.51	2.533	2.532
0.003	1.41	1.5	1.54	7.39	7.62	7.73	9.886	10.09	10.58	2.519	2.537	2.533
0.004	1.4	1.49	1.54	7.37	7.6	7.73	11.9	12.14	12.72	2.515	2.534	2.527
0.005	1.41	1.49	1.56	7.38	7.59	7.76	14.05	14.35	14.85	2.505	2.526	2.533
0.006	1.4	1.48	1.56	7.37	7.56	7.77	16.01	16.45	17.09	2.531	2.545	2.540
0.007	1.41	1.49	1.55	7.38	7.59	7.75	18.16	19.02	19.65	2.539	2.52	2.531
0.008	1.42	1.48	1.55	7.41	7.58	7.75	20.62	21.36	22.22	2.527	2.531	2.530
0.009	1.41	1.47	1.55	7.39	7.55	7.74	23.24	23.94	24.87	2.518	2.532	2.530
0.01	1.43	1.51	1.56	7.43	7.63	7.76	25.71	26.54	27.73	2.519	2.523	2.521

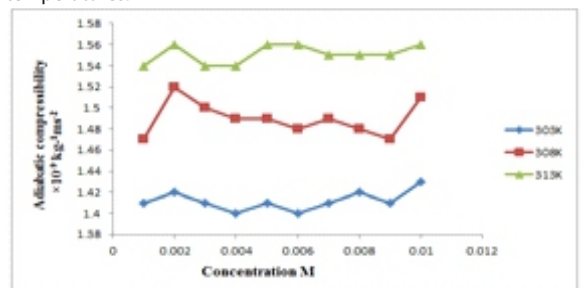
Free length is the distance between the surfaces of the neighboring molecules. Free length decreases when the ultrasonic velocity increases as the result of mixing the components. It is the magnitude of ion-ion or ion-solvent interaction or both. The increase in the free length shows weak molecular interactions and decrease in free length shows significant molecular interactions. The free Volume increases with increase in concentration shows expansion of volume. The decrease in free volume with increase in internal pressure leads to increase in intermolecular interactions and vice versa.

Fig 1: Variation of **Ultrasonic Velocity Vs Concentration** for system: o-xylene +1-propanol+n-hexane.



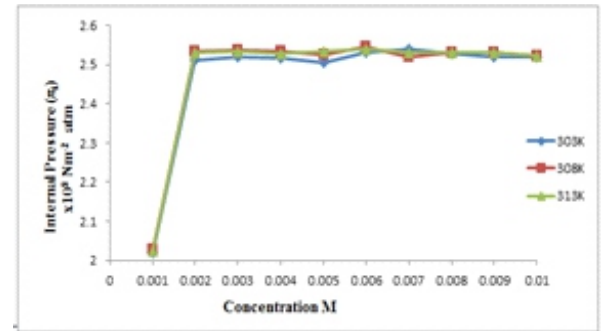
The plot shows the variation in the ultrasonic velocity with the increase in concentration is mainly due to the interactions between donor and acceptor molecules. On the basis of Kincaid and Eyring model (1938) proposed for propagation, the variation of ultrasonic velocity depends on the increase or decrease of intermolecular free length after mixing the components¹³.

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



Adiabatic compressibility shows a reverse trend to that of the ultrasonic velocity which indicates the extent of complexation.

Fig 3: Variation of **Internal pressure Vs Concentration** for the system: o-xylene +1-propanol+n-hexane.



Internal pressure reflects the cohesive or adhesive forces available in the medium. The variation in the internal pressure gives information regarding the nature and the strength of the forces existing between the molecules. Internal pressure gradually increases with increase in concentration shows the formation of donor-acceptor complexes.

The increasing values of acoustic impedance with concentration supports the possibility of molecular interactions between the unlike molecules. The positive and negative value of molecular interaction parameters shows strong and weak interaction between the components respectively.

Table 3: Values of **Acoustic Impedance, Lenard Jones Potential, Free Energy of Activation, Molecular Interaction Parameter, Formation Constant:** o-xylene + 1-propanol+ n-hexane at different temperatures.

CONC	Acoustic Impedance $\times 10^{-4}$			Lenard Jones Potential LJP			Free Energy of Activation			Molecular Interaction Parameter $\times 10^{-2}$			Formation Constant		
	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K	303K	308K	313K
0.001	6.71	6.57	6.4	4.611	3.965	3.302	3.929	4.042	4.149	-0.968	-0.368	-0.808	118.5	99.7	89.4
0.002	6.68	6.45	6.36	4.637	3.615	3.271	3.925	4.107	4.171	-0.826	-2.662	-0.804	80.2	58.8	81
0.003	6.71	6.5	6.39	4.65	3.751	3.363	3.925	4.085	4.153	-0.759	-1.907	-0.163	12.5	61.4	62.1
0.004	6.73	6.51	6.39	4.748	3.907	3.385	3.907	4.071	4.148	-0.203	-1.417	-0.014	49.7	50	25.2
0.005	6.71	6.52	6.36	4.761	3.884	3.263	3.965	4.056	4.173	-0.136	-0.925	-0.889	38.4	40.7	8.7
0.006	6.74	6.56	6.36	4.68	3.893	3.216	3.918	4.055	4.183	-0.061	-0.87	-1.221	30.2	31.1	29.2
0.007	6.74	6.51	6.37	4.589	3.913	3.202	3.913	4.051	4.165	-1.149	-0.749	-0.621	28.4	14.4	29.9
0.008	6.7	6.53	6.37	4.55	3.89	3.224	3.939	4.055	4.161	-1.283	-0.911	-0.402	22	10.3	27.6
0.009	6.71	6.56	6.38	4.657	3.965	3.227	3.922	4.042	4.16	-0.771	-0.432	-0.471	24.5	24.3	24.6
0.01	6.67	6.47	6.35	4.518	3.742	3.313	3.945	4.083	4.163	-1.586	-1.885	-0.579			

Formation constant K:

To calculate formation constant values of the charge transfer complexes, appreciable to weak complexes and in very dilute solutions. The stability constant is calculated using the relation

$$K = Y / (b - y)^2 \text{ dm}^3 \text{ mol}^{-1}$$

Where, $Y = [(a - k^{1/2}b) / (k - k^{1/2})]$; $k = x/y$

X = difference between U_{cal} and U_{obs} at lower concentration 'a'.

y = difference between U_{cal} and U_{obs} at lower concentration 'b'.

System	Mean K Value
O Xylene + 1-propanol + n-hexane at 303K	44.04
O Xylene + 1-propanol + n-hexane at 308 K	43.41
O Xylene + 1-propanol + n-hexane at 313 K	41.96

Formation constant is the measure of strength of the interaction between the components that come together to form a complex. It indicates the presence electron releasing group in the donor molecule, increases the tendency of complex formation. At high temperature thermal agitation of molecules takes place. Therefore at low temperature more stable complex is formed with high formation constant value.

IV. CONCLUSION

In this system the donor o-xylene is non-polar and the acceptor 1 propanol is polar in nature and thereby forming induced dipole - dipole interaction between the liquid components. The weak dispersive type of interaction occurs between 1 propanol and n-hexane, due to the non-polar nature of n-hexane. Alcohols are liquid associated through hydrogen bonding and in pure state they exhibit an equilibrium between multimer and monomer species. All these suggest the existence of different types of molecular interactions may present in this ternary liquid mixtures.

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