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Acoustical properties of binary liquid mixture at different temperature

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Abstract
The binary mixtures of propane -2-ol with CCl_4 containing various ultrasonic properties have been studied at different temperature at a fixed frequency of 2 MHz. The ultrasonic velocity, density and viscosity for pure samples such as propane -2-ol and CCl_4 were measured. From these other acoustical parameters like adiabatic compressibility, free length, free volume, internal pressure, impedance and their excess values are evaluated. These parameters provide the information regarding internal structure, molecular association and complex formation.

Keywords: ultrasonic velocity, isopropanol, carbon tetrachloride, excess parameters

Introduction
Ultrasonic investigations of liquid mixtures containing polar and non-polar components enable to understand the molecular interactions and structural behavior of molecules in the mixture [1]. The Ultrasonic velocity measurements find wide applications in characterizing physico-chemical behavior of the liquid mixtures and in the study of molecular interactions [2-4]. Ultrasonic velocity is related to binding forces between the atoms or the molecules. Ultrasonic velocities have been adequately employed in understanding the nature of molecular interaction in pure and liquid mixtures [5-8]. For a better understanding of the physico-chemical properties and molecular interaction between the components of the mixture, ultrasonic velocity together with density and viscosity are measured at different temperature and different concentrations of the components in the mixture keeping the frequency constant. Owing to these considerations, an attempt has been made to elucidate the molecular interactions in the mixtures of isopropyl alcohol with CCl_4 at 308,313,318,323 and 328K.

Materials and Methods
The chemicals used are of analytical grade and used without further purification. The liquid mixtures were prepared by mixing the calculated value of molar concentration in an air tight glass bottles to minimize the evaporation and contamination of the solvent. The velocities of ultrasonic waves in the liquid samples have been measured using an ultrasonic interferometer working at a fixed frequency of 2MHz supplied by Mittal Enterprises New Delhi. The temperature of the liquids in the measuring cell is stabilized by a water circulation thermostat which maintains the temperature within the accuracy of $\pm$ 0.2 ºC. The density is measured using a 5 ml specific gravity bottle with experimental liquid immersed in a temperature controlled water bath. The viscosity of the pure liquids and liquid mixtures are measured using an Ostwald's Viscometer. The time of flow of the liquid is measured using a stop watch.
The measured values of ultrasonic velocity, density and viscosity have been used to calculate the adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), enthalpy (H), molar volume (V_m), Acoustic impedance (Z), Relaxation time (τ), Gibb's free energy (G), using the following equations [9-11],

$\beta_a = 1/(U^2 \rho)$ ....(1)

$L_f = K_T (\beta_a)^{1/2}$ .... (2)

$V_f = (MU/\eta K)^{3/2}$ ……….(3)

$\pi_i = bRT (K\eta/U)^{1/2} (\rho^{2/3}/M^{7/6})$ ……... (4)

$H = \pi_i V_m$ ……... (5)

$V_m = M/\rho$ ……… (6)

$Z = \rho U$ ……… (7)

$\tau = \frac{4}{3}\beta\eta$ ……… (8)

$G = RT \ln(\eta V_m)$ ……… (9)

Results and Discussion
The experimental values of ultrasonic velocity, density and viscosity in solution of 2-propanol with CCl_4 measured over the entire composition range at 308K, 313K, 318K, 323K and 328K are listed in table 1. In order to understand the intermolecular interactions in the binary mixture, several acoustical and thermodynamic parameters such as adiabatic compressibility, free length, free volume, internal pressure, enthalpy, acoustic impedance, molar volume, relaxation time and Gibb's free energy have been computed using the measured values of U, η and ρ. The variations of these parameters with mole fraction and temperature are listed in table 2 to.3. The variation the above mentioned parameters and their excess values with mole fraction for this binary mixture at different temperature are graphically presented in the figures. In this binary mixture the interaction becomes weak with increase in temperature due to thermal agitation of component molecules and this is indicated by the decrease in velocity values [12].
From the variation of adiabatic compressibility (β_a) with mole fraction, it is observed that β_a decreases with increase of mole fraction which gives the information regarding the association and disassociation of the components. As a temperature increases β_a increases, may be because of

expansion of liquids. The fig. shows that the excess values of adiabatic compressibilities are positive and it varied nonlinearly with increasing the concentration as well as raising temperature.

As 2-Propanol is hydrogen bonding liquid, the depolymerization of Isopropyl alcohol by CCl_4, intermolecular interactions result in the formation of large spices which cannot undergo closed packing. Hence the positive variation is observed in the β_a and L_f. Just it is concluded that, in hydrogen bonded solvent system, interstitial accommodation effect is more predominant, the dispersion forces are becoming dominant in mixed dipolar aprotic and non-polar are binary mixtures of non-polar solvents [13]. The intermolecular interaction seems to be stronger than intramolecular interaction, it leads to decrease of volume when the concentration of ccl_4 increases. When temperature increases, there is reduction in molecular interaction. This reduces the cohesive force or internal pressure and hence free volume increases [14].

The internal pressure is the measure of cohesive forces between the constituent molecules in liquids [15]. As the molar concentration increases, the internal pressure decreases. The decrease in π_i with increase in CCl_4 concentration is attributed to the decreasing magnitude of interaction and shows the absence of complex formation [16].

Enthalpy gets decreased when the molar concentration and temperature of the system increased. The change in enthalpy is used to explain whether the system under exothermic or endothermic reaction. In our case most positive values are observed in enthalpy. So it is concluded that the system is under endothermic that is heat was observed in that system.

The values of acoustic impedance and Gibb's free energy increase with molar concentration. The increase in acoustic impedance and Gibb's free energy with composition of the mixture indicates significant interaction between the component molecules [17].

In the present case, relaxation time decreases with increase in concentration and temperature. The former indicates the presence of molecular interaction in the mixture, when as the latter shows the instantaneous conversion of excitation energy to translational energy, when temperature is increased.

Gibbs free energy increases with increases in concentration and temperature. The increase in Gibbs free energy indicates the need for shorter time for the co-operative process to take place or for the rearrangement of molecules in the mixture. This indicates the easier flow of binary mixture compared with the behavior of pure components.

Thus we concluded that the weak molecular interactions occurring in the system.

Table 1: Values of ultrasonic velocity (U), density (ρ) and viscosity (η) for binary liquid mixture (Propane-2-Ol + Ccl_4) at different temperature

X	U(m/S)	ρ(KKg/m³)	ηx10⁻³ (Ns/m²)
T = 308 K			
0	1111	0.76	1.191
0.1	1073	0.864	0.96
0.3	969	1.033	0.843
0.5	916	1.198	0.804
0.7	889	1.333	0.767
0.9	887	1.479	0.77
1	884	1.542	0.808
T=313 K			
0	1087	0.761	1.13
0.1	1052	0.869	0.937
0.3	936	1.033	0.813
0.5	900	1.203	0.778
0.7	876	1.336	0.743
0.9	874	1482	0.771
1	861	1.541	0.798
T=318 K			
0	1069	0.761	1.06
0.1	1036	0.868	0.892
0.3	925	1.035	0.798
0.5	885	1.201	0.755
0.7	867	1.337	0.732
0.9	858	1.481	0.752
1	856	1.539	0.788
T=323 K			
0	1050	0.763	0.996
0.1	1020	0.867	0.848
0.3	912	1.036	0.773
0.5	871	1.201	0.721
0.7	857	1.335	0.707
0.9	847	1.483	0.731
1	842	1.535	0.767
T=328 K			
0	1038	0.76	0.916
0.1	1006	0.864	0.82
0.3	901	1.035	0.727
0.5	859	1.202	0.719

0.7	841	1.334	0.697
0.9	839	1.477	0.725
1	830	1.532	0.764

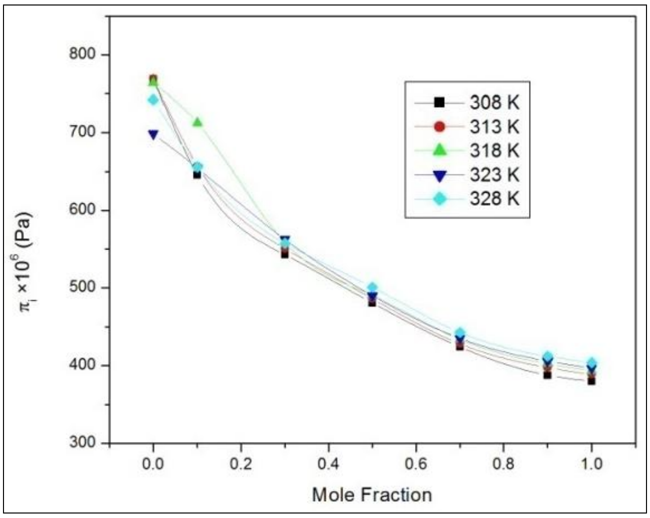
Table 2: Variation of β_a, L_f, V_f, Π_i and H with Mole Fraction at Different Temperature

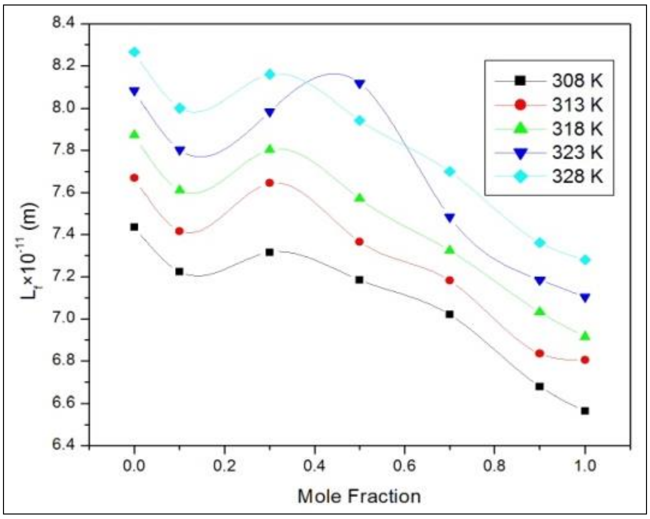
X	$\beta_a \times 10^{-10}$ (m²/N)	$L_f \times 10^{-11}$ (m)	$V_f \times 10^{-8}$(m³/mol)	$\pi_i \times 10^6$ (Pa)	H × 10⁴ J/mol
			T = 308 K		
0	10.649	7.436	4.738	768.762	6.073
0.1	10.051	7.224	7.727	645.555	5.189
0.3	10.308	7.316	11.518	542.84	4.635
0.5	9.942	7.185	15.201	480.597	4.288
0.7	9.492	7.02	19.838	423.857	3.997
0.9	8.592	6.679	24.219	387.464	3.784
1	8.298	6.564	24.661	379.713	3.763
T = 313 K					
0	11.118	7.67	4.963	769.533	6.076
0.1	10.396	7.417	7.774	657.226	5.253
0.3	11.045	7.645	11.592	550.546	4.7
0.5	10.257	7.367	15.544	486.071	4.32
0.7	9.748	7.182	20.352	427.894	4.024
0.9	8.828	6.835	23.67	397.419	3.871
1	8.753	6.805	24.152	388.418	3.851
T = 318 K					
0	11.493	7.872	5.327	763.705	6.028
0.1	10.739	7.61	8.186	712.398	5.704
0.3	11.292	7.803	11.681	558.497	4.761
0.5	10.631	7.571	15.834	490.105	4.365
0.7	9.95	7.325	20.505	433.689	4.077
0.9	9.17	7.032	23.882	402.277	3.923
1	8.868	6.915	24.394	392.936	3.902
T = 323 K					
0	11.891	8.082	5.693	698.803	5.506
0.1	11.084	7.803	8.627	654.302	5.241
0.3	11.603	7.984	12	562.645	4.79
0.5	10.978	8.112	16.579	490.157	4.366
0.7	10.199	7.485	21.234	434.975	4.096
0.9	9.399	7.185	24.446	405.766	3.952
1	9.187	7.104	24.787	396.374	3.945
T = 328 K					
0	12.209	8.266	6.342	742.4576	5.87
0.1	11.439	8.001	8.888	655.934	5.275
0.3	11.899	8.16	12.896	557.441	4.751
0.5	11.273	7.943	16.312	500.861	4.456
0.7	10.596	7.7	21.101	442.498	4.168
0.9	9.685	7.362	24.295	411.824	4.027
1	9.473	7.281	24.369	403.822	4.027

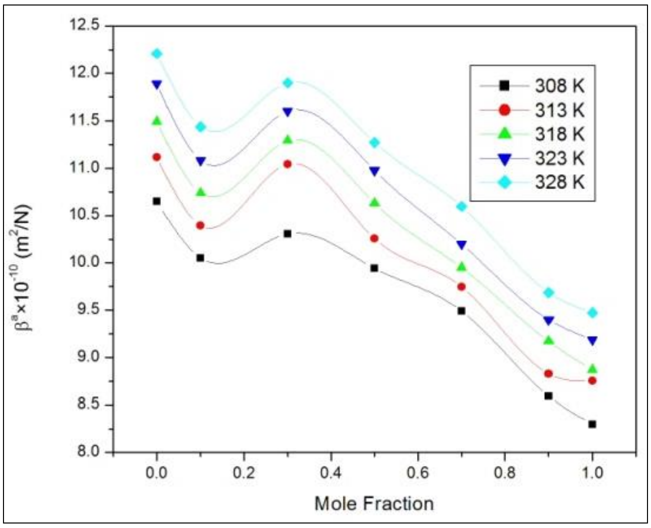
Table 3: Variation of Z, τ, G and V_m with Mole Fraction at Different Temperature

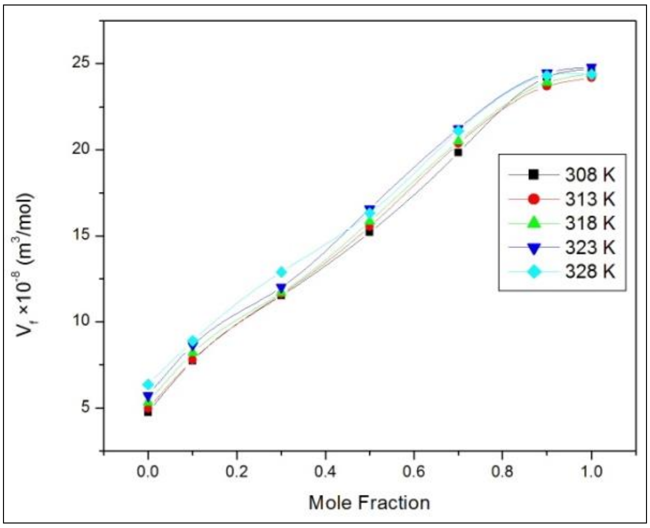
X	$Z \times 10^3$ (Kg/m²s)	$\tau \times 10^{-13}$ (s)	G (Kg/mol)	$V_m \times 10^{-5}$m³/mol)
		T = 308 K		
0	845.249	16.913	-41429.52	7.9
0.1	927.287	12.862	-41937.95	8.039
0.3	1001.171	11.593	-42114.21	8.539
0.5	1098.101	10.651	-42126.06	8.922
0.7	1185.037	9.712	-42102.05	9.43
0.9	1312.139	8.825	-42003.03	9.765
1	1363.216	8.937	-41843.85	9.91
T = 313 K				
0	827.424	16.752	-42240.72	7.895
0.1	914.398	12.99	-42695.77	7.992
0.3	967.262	11.948	-42899.66	8.537
0.5	1083.24	10.638	-42904.89	8.887
0.7	1171.037	9.662	-42875.62	9.403
0.9	1296.055	9.072	-42689.9	9.741
1	1326.973	9.309	-42554.04	9.916
T = 318 K				
0	813.937	16.243	-43085.23	7.893

0.1	898.834	12.767	-43504.53	8.007
0.3	957.375	12.01	-43633.74	8.524
0.5	1062.885	10.709	-43661.48	8.906
0.7	1159.179	9.713	-43601.43	9.406
0.9	1270.955	9.196	-43433.56	9.752
1	1317.384	9.315	-43263.07	9.93
T = 323 K				
0	800.94	15.793	-43934.58	8.879
0.1	884.544	12.529	-44322.89	8.011
0.3	945.014	11.951	-44409.13	8.514
0.5	1045.81	10.555	-44472.46	8.908
0.7	1144.095	9.614	-44376.67	9.416
0.9	1256.186	9.161	-44196.17	9.74
1	1292.807	9.391	-44009.92	9.953
T = 328 K				
0	789.088	14.916	-44833.1	7.906
0.1	841.821	12.502	-45090.19	8.042
0.3	932.715	11.541	-45258	8.522
0.5	1032.69	10.806	-45172.62	8.897
0.7	1122.23	9.843	-45102.39	9.42
0.9	1235.023	9.356	-44893.98	9.778
1	1271.892	9.655	-44694.04	9.973









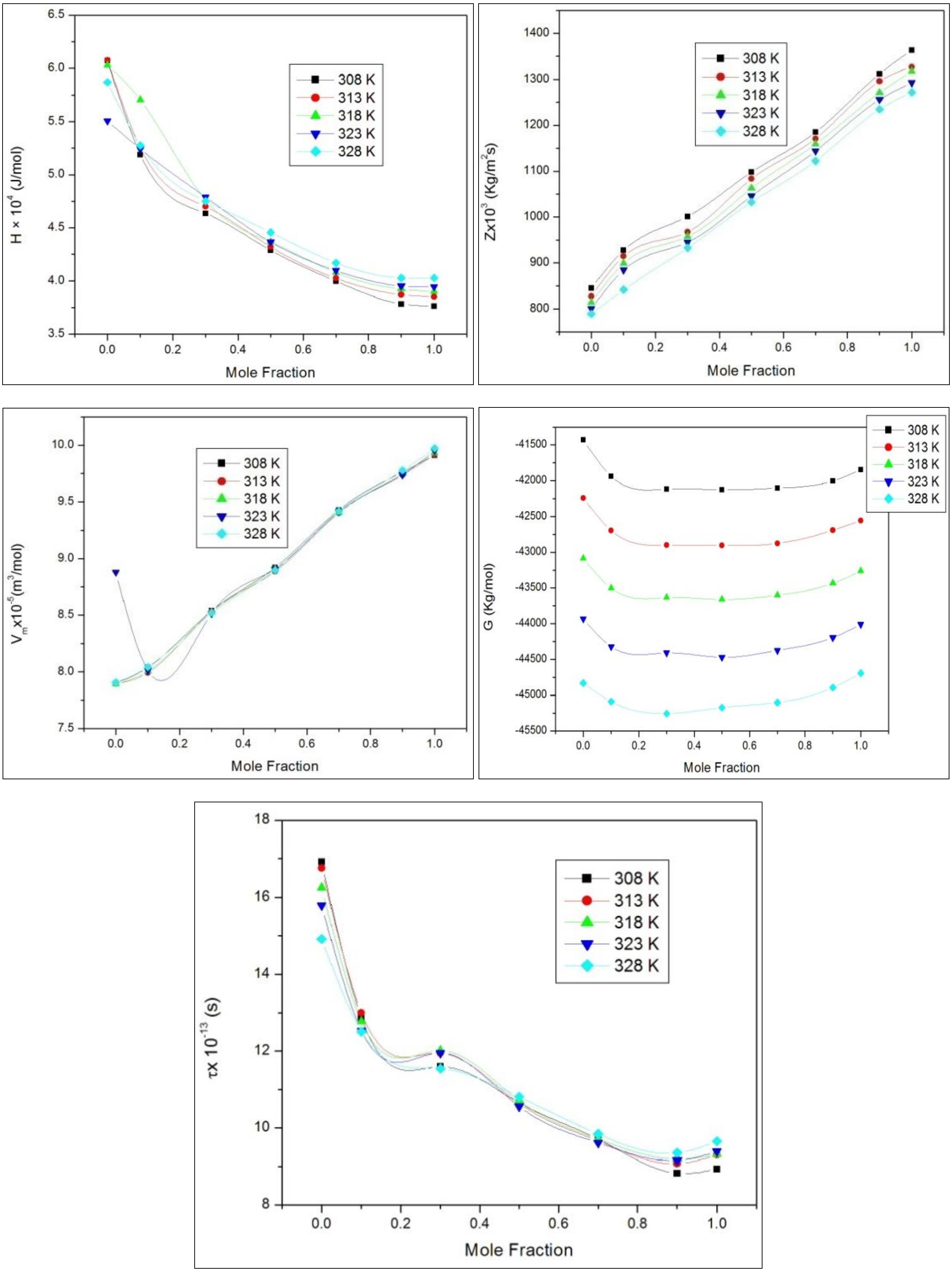


Fig 1: Variation of β_a, L_f, V_f, π_i, V_m, H, Z, τ and G with mole fraction at different temperature for the binary system of Propane-2-ol + CCl_4

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