STUDIES ON METHYL ETHYL KETONE AND n- PROPANOL MIXTURE USING THERMO – ACOUSTIC PARAMETERS

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Abstract: Ultrasonic velocities and densities of a binary mixture – methyl ethyl ketone + n-propanol were measured at temperatures 303.15K, 308.15K and 313.15K respectively. From the experimental values of velocity and density, thermo-acoustical parameters like adiabatic compressibility (β_S), specific acoustic impedance (Z_A), Rao's specific sound velocity (r) and intermolecular free length (L_f), which can complement the study of molecular interaction in a liquid mixture, are also determined. Deviation between experimental and ideal values in these acoustical parameters - β_S^E, Z_A^E, r^E and L_f^E have been calculated and examined as a function of composition of the mixture. An analysis of excess thermo-dynamic functions suggest the presence of molecular interaction in the binary mixture studied and is found to be useful in elucidating the nature of molecular interaction in the present mixture. The observed positive values of β_S^E and L_f^E and negative values of r^E and Z_A^E clearly indicate the presence of weak interaction due to dispersion forces between the component molecules of the system studied.

Index Terms: **Ultrasonic velocity, adiabatic compressibility, specific acoustic impedance, molecular interaction.**

I. INTRODUCTION

The unusual behaviour of binary mixtures has attracted considerable attention from early days [1-3].Ultrasonic investigations in liquid mixtures find numerous applications in characterizing the physico – chemical behaviour in them. The temperature dependence of acoustic parameters gives ample information about the molecular interaction between the components of liquid mixtures. Literature review on acoustic studies of solutions reveals that not much work is done in the binary system of ketones with lower alcohols [4-6].With this point of view, an ultrasonic study of methyl ethyl ketone in n-propanol has been conducted at temperatures 303.15K, 313.15K and 323.15K respectively. The mixture chosen are of polar + polar type and such a study throws light into the nature of molecular interaction existing between two polar molecules. From the measured values of ultrasonic velocity and density, thermo – acoustical parameters like adiabatic compressibility (β_s), specific acoustic impedance (Z_A), Rao's specific sound velocity (r), and inter molecular free length (L_f) were determined. These parameters compliment the study of molecular interaction in binary mixtures. Further the excess thermodynamic functions like β_s^E, Z_A^E, r^E and L_f^E were calculated and the deviations in these functions were explained on the basis of the nature of molecular interaction that exists between the component molecules in the mixture.

II. EXPERIMENTAL DETAILS

The ultrasonic velocity (U) and density (ρ) of the binary mixture – methyl ethyl ketone + n – propanol were measured at three different temperatures, viz, 303.15K, 308.15K and 313.15K. The temperature was maintained steady using a thermostatically controlled water circulating arrangement with an accuracy of ±0.1K. The highest temperature level was limited to 313.15K in order to avoid errors due to evaporation during the course of the experiment. Chemicals of AR/BDH grade and distilled water were used for the experimental purpose. The purity of the liquids was tested by comparing their densities with those in literature and is found to be in good agreement. The different concentrations of liquid mixture were prepared by varying the volumes of the components. The prepared mixtures were preserved using stoppered conical flasks and the flasks were left undisturbed to attain thermal equilibrium. The ultrasonic velocities of the liquid mixture were measured using a single - crystal ultrasonic interferometer [Mittal Enterprises- Model No: F 81] at a frequency of 2 MHz, having an accuracy of ± 0.1ms^{-1}. The working of the interferometer was checked by measuring the velocity of pure water at 303.15K. The measured value was 1513 ms^{-1}, which is in close agreement with the theoretical value [7] - 1515 ms^{-1} and confirms the accuracy of the instrument. Density measurements were performed using a 10 cm^3 double – stem pyknometer. Masses of the liquids were determined using a single – pan electronic balance having an accuracy of ±0.1mg.

III. RESULTS AND DISCUSSION

From the measured values of ultrasonic velocity (U) and density (ρ), various thermo – acoustical parameters were calculated using the formulae given below:

Adiabatic compressibility $\beta_s = 1/U^2\rho$ (1)

Specific acoustic impedance $Z_A = U\rho$ (2)

Rao's specific sound velocity $r = U^{1/3}/\rho$ (3)

Intermolecular free-length $L_f = K\beta_s^{1/2}$ (4)

where K is the Jacobson's constant[8].

The excess parameters were determined using the relation

$$Y^E = Y^{expt} - Y^{ideal} \quad (5)$$

where Y^{expt} represents the corresponding parameters β_s, Z_A, r and L_f of the liquid mixture determined experimentally and Y^{ideal} represents the value obtained by applying the ideal mixing rule.

The experimental values of ultrasonic velocity (U) and density (ρ), and the values of derived parameters like adiabatic compressibility (β_s), specific acoustic impedance (Z_A), Rao's specific sound velocity (r), and intermolecular free length (L_f) determined using equations (1 to 4), for the binary mixture of methyl ethyl ketone + n- propanol at different temperatures and concentrations were tabulated in Table1. The excess functions β_s^E, Z_A^E, r^E, and L_f^E were evaluated using equation (5) and are given in Table 2. It is evident from Table 1 that U, ρ and Z_A decreases with increase in temperature, whereas β_s, r and L_f increases with increase in temperature over the entire composition range. The pronounced increase or decrease in these parameters with temperature indicates the presence of molecular interaction in the mixture.

Table 1: Ultrasonic velocity (U), density (ρ), adiabatic compressibility (β_S), specific acoustic impedance (Z_A), Rao's specific sound velocity (r) and intermolecular free length (L_f) of Methyl ethyl ketone (X_1) + n-Propanol (X_2) at different temperatures and concentrations.

X_1	U (ms^{-1})	ρ (kgm^{-3})	$\beta_S \times 10^{10}$ (m^2N^{-1})	$Z_A \times 10^{-6}$ ($kgm^{-2}s^{-1}$)	$r \times 10^2$ ($kg^{-1}m^{10/3}s^{-1/3}$)	$L_f \times 10^{11}$ (m)
T = 303.15K						
0.0000	1233	852.9	7.7122	1.0516	1.2573	5.7641
0.1432	1222	852.4	7.8562	1.0416	1.2542	5.8177
0.2947	1219	852.2	7.8968	1.0388	1.2535	5.8327
0.4552	1215	852.0	7.9507	1.0352	1.2524	5.8526
0.6256	1213	850.4	7.9920	1.0315	1.2541	5.8677
0.8069	1208	848.8	8.0735	1.0254	1.2547	5.8976
1.0000	1205	847.2	8.1291	1.0209	1.2561	5.9179
T = 308.15K						
0.0000	1225	849.5	7.8445	1.0406	1.2595	5.8657
0.1432	1219	848.8	7.9284	1.0347	1.2585	5.8970
0.2947	1217	848.1	7.9611	1.0321	1.2589	5.9092
0.4552	1213	847.5	8.0193	1.0280	1.2584	5.9307
0.6256	1210	846.0	8.0734	1.0237	1.2596	5.9507
0.8069	1206	844.5	8.1415	1.0185	1.2604	5.9757
1.0000	1203	843.0	8.1967	1.0141	1.2616	5.9960
T = 313.15K						
0.0000	1223	847.1	7.8925	1.0360	1.2624	5.9365
0.1432	1218	846.3	7.9649	1.0308	1.2619	5.9636
0.2947	1216	845.5	7.9987	1.0281	1.2624	5.9763
0.4552	1212	844.8	8.0583	1.0239	1.2621	5.9985
0.6256	1209	843.3	8.1127	1.0196	1.2633	6.0187
0.8069	1205	841.9	8.1802	1.0145	1.2640	6.0437
1.0000	1202	840.5	8.2348	1.0103	1.2650	6.0638

Table 2: Excess values of adiabatic compressibility (β_S^E), specific acoustic impedance (Z_A^E), Rao's specific sound velocity (r^E) and intermolecular free length (L_f^E) of Methyl ethyl ketone (X_1) + n-Propanol (X_2) at different temperatures and concentrations.

X_1	$\beta_S^E \times 10^{10}$ (m^2N^{-1})	$Z_A^E \times 10^{-6}$ ($kgm^{-2}s^{-1}$)	$r^E \times 10^2$ ($kg^{-1}m^{10/3}s^{-1/3}$)	$L_f^E \times 10^{11}$ (m)
T = 303.15K				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1432	0.0843	-0.0056	-0.0030	0.0316
0.2947	0.0618	-0.0038	-0.0035	0.0233
0.4552	0.0487	-0.0024	-0.0044	0.0185
0.6256	0.0190	-0.0009	-0.0024	0.0074
0.8069	0.0249	-0.0015	-0.0016	0.0094
1.0000	0.0000	0.0000	0.0000	0.0000
T = 308.15K				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1432	0.0334	-0.0021	-0.0013	0.0127
0.2947	0.0128	-0.0007	-0.0012	0.0051
0.4552	0.0145	-0.0005	-0.0021	0.0057
0.6256	0.0085	-0.0003	-0.0013	0.0035
0.8069	0.0128	-0.0007	-0.0008	0.0049
1.0000	0.0000	0.0000	0.0000	0.0000
T = 313.15K				
0.0000	0.0000	0.0000	0.0000	0.0000
0.1432	0.0234	-0.0015	-0.0009	0.0089
0.2947	0.0053	-0.0003	-0.0008	0.0023
0.4552	0.0100	-0.0004	-0.0015	0.0041
0.6256	0.0060	-0.0003	-0.0007	0.0026
0.8069	0.0115	-0.0008	-0.0005	0.0045
1.0000	0.0000	0.0000	0.0000	0.0000

Intermolecular free length is defined as the distance between the surfaces of neighboring molecules. As temperature increases, due to thermal agitation, the molecules move apart resulting in an increase in L_f. This results in a decrease in velocity of sound waves through the mixture and a decrease in density which in turn causes an increase in adiabatic compressibility. This has been illustrated by Pandey *et.al* in his work [9]. According to Eyring and Kincaid[10], the variation of ultrasonic velocity in a solution depends on the increase or decrease of intermolecular free length after mixing the components. From the formula of intermolecular free length it is clear that L_f is directly proportional to adiabatic compressibility and inversely proportional to ultrasonic velocity. Hence L_f shows similar behaviour as that of β_s and opposite nature as that of sound velocity. A similar nature can be seen in the present mixture on analyzing Table1. Hence our observations are in agreement with the predictions of Pandey *et.al* and Eyring *et.al*. The natures of adiabatic compressibility and specific acoustic impedance reveal that they must exhibit opposite behaviour which is true in the mixture studied. Again, according to Kiyohara and Benson [11] and Nikam *et.al* [12], increase of β_s and L_f with temperature for a binary mixture indicates breaking of hetero- association and homo-association of component molecules. Such an effect can be seen in the present mixture also in the case of β_s and L_f which confirms that dissociation effect exists in the system under study.

The excess values of physical parameters play a vital role in determining the nature of interaction in a mixture. The excess value graphs of various acoustic parameters under study were plotted in Figures 1 to 4. The excess values occurring in a parameter may be due to the combination of several opposing factors, viz; chemical, physical and structural. The chemical or specific interactions include dipole-dipole, dipole-induced dipole interactions, charge transfer complexes and hydrogen bonding between component molecules, resulting in negative deviation in excess values. The physical or non-specific interactions include breaking of the structure of the component molecules in a mixture ie; molecular dissociation due to weak dispersion forces, steric hindrance of the molecules and breaking of hydrogen bonds. These factors cause positive deviation in excess values. The third one is the structural effect which arises from the interstitial accommodation and geometrical fitting of one component into another depending on the size and shape of the molecules and differences in free volume [13].

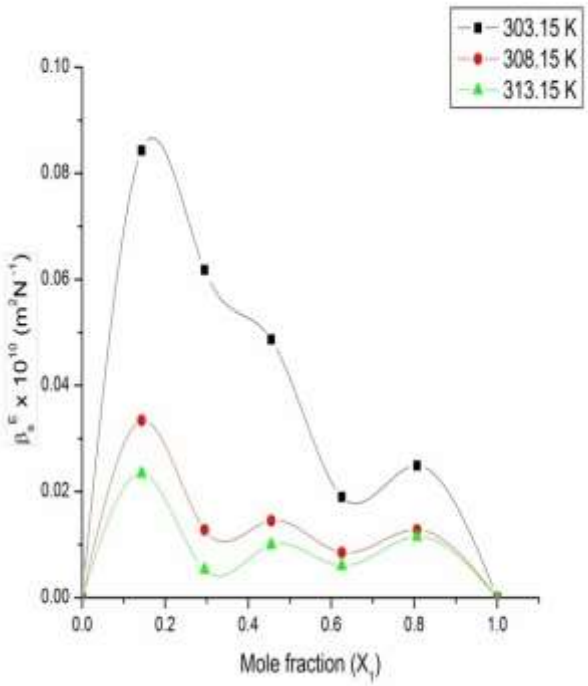

Fig 1: Variation of β_S^E with X_1 at different temperatures

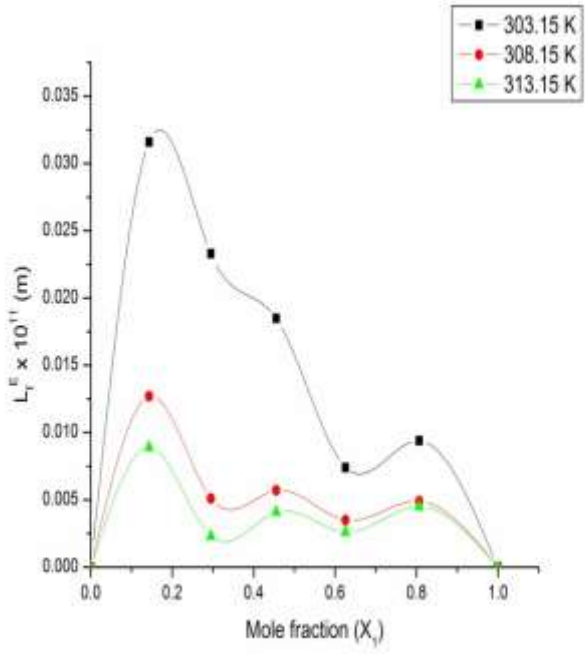

Fig 2: Variation of L_f^E with X_1 at different temperatures

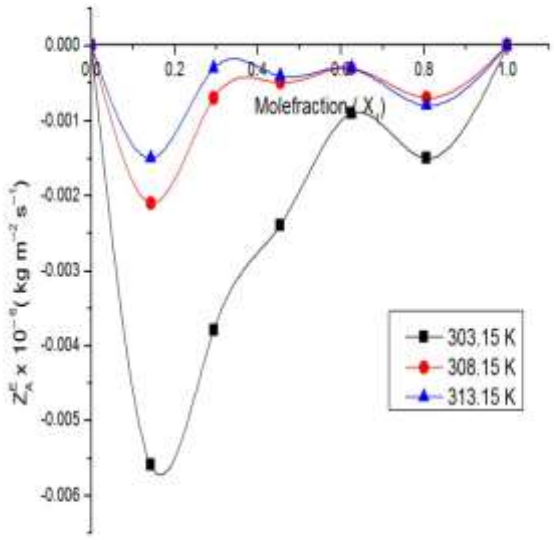

Fig 3: Variation of Z_A^E with X_1 at different temperatures

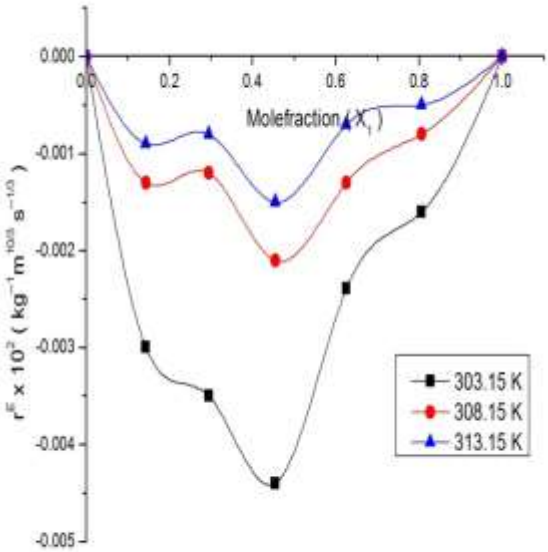

Fig 4: Variation of r^E with X_1 at different temperatures

X_1 – molefraction of methyl ethyl ketone

Fort and Moore [14] suggest that the negative excess compressibility in a mixture is an indication of strong hetero-molecular interaction which may be due to charge transfer, dipole-dipole, dipole-induced dipole interactions and H-bonding between component molecules, whereas positive deviation indicates weak interaction which is attributed due to dispersion forces. In the present study, β_s^E is positive over the entire composition range (Figure 1) showing the presence of weak molecular interaction due to dispersion forces (London forces) in the mixture. Moreover as temperature increases, the magnitude of excess adiabatic compressibility decreases. According to Fort and Moore [14], the magnitude of excess compressibility values indicates the strength of molecular interaction between unlike molecules. Hence it is clear from Figure 1 that the strength of weak interaction due to dispersion forces (London forces) decreases with increase in temperature.

Again Reddy *et.al* [15], have reported that negative values of excess compressibility in a mixture show molecular association and complex formation whereas positive values show molecular dissociation. In the present study, excess compressibility values were found to be positive for all temperatures and over the entire composition range indicating the presence of molecular

dissociation between unlike molecules. The positive nature of β_s^E in the present system may be due to breaking of hydrogen bonds in self associated propanol and structure breaking effect of methyl ethyl ketone in propanol due to steric hindrance.

Considering L_f^E and Z_A^E (Figure 2 and Figure 3) it can be seen that the values of L_f^E are positive for all temperatures and concentrations. As expected, the Z_A^E values are found to be negative at all temperatures and at entire composition range. It has been reported by Fort and Moore [14] and Kannappan [16] that dispersion forces tend to make positive contribution to L_f^E and negative contribution to Z_A^E. Thus dispersion forces are active in methyl ethyl ketone + n-propanol mixture which is in agreement with the result obtained in the case of adiabatic compressibility. Moreover the magnitude of interaction decreases with increase in temperature, which suggests that the strength of dispersion forces decrease with increase in temperature.

The sign and magnitude of sound velocity play an important role in determining the nature of solute-solvent interaction in a liquid mixture. Positive deviation in velocity indicates strong interaction between the component molecules. If strong interaction exists, it causes the formation of molecular aggregates, leading to a more compact structure for the system. Hence sound travels faster in such cases leading to positive deviation in velocity. On the other hand, if structure breaking effect predominates in the system, the molecules depart each other and due to expansion, sound travels at a slower rate through the mixture resulting in negative deviation in sound velocity [17]. Figure 4 shows the variation of r^E with molefraction for the system under study. An analysis of the graph reveals that r^E values are negative for all temperatures and over the entire composition range. This shows that structure breaking effect is predominant in methyl ethyl ketone + n-propanol mixture. Further, negative deviation in velocity is an indication of presence of weak interaction in a mixture [18]. According to Reddy *et.al* [15], positive deviation in velocity is attributed to molecular association and complex formation whereas negative deviation contributes to molecular dissociation of associated species. These findings again support the view point that the molecular interaction in methyl ethyl ketone + n-propanol mixture is weaker which is caused by weak dispersion forces which dissociates the molecules in the mixture. The result obtained in the case of r^E is in agreement with the results obtained in the case of β_s^E, L_f^E and Z_A^E. Moreover, the magnitude of excess velocity decreases with increase in temperature reveals that as temperature increases, the strength of dispersion forces decreases. This is clear from Figure 4.

IV. CONCLUSION

Ultrasonic study of an aliphatic ketone on an aliphatic alcohol was conducted experimentally at different temperatures and concentrations. From the measured values of density and ultrasonic velocity, various acoustic parameters were determined and their excess values were evaluated. These parameters and their excess values were used to interpret the nature of molecular interaction in the binary mixture. The present study reveals that velocity, density and specific acoustic impedance decrease with increase in temperature, whereas adiabatic compressibility, intermolecular free length and Rao's specific sound velocity increase with increase in temperature. Considering excess values, β_s^E and L_f^E are positive whereas Z_A^E, and r^E are negative at all temperatures and over the entire composition range. Analysis of derived parameters and their excess values suggest that there exists weak interaction in methyl ethyl ketone + n-propanol mixture which is due to dispersion forces. Such a weak force causes repulsive interaction between molecules and hence structure breaking effect is predominant in the present system. Further the experimental data clearly denotes that the strength of the molecular interaction decreases with increase in temperature.

V. ACKNOWLEDGEMENT

The author is thankful to the Post Graduate Department of Physics and Research Centre, Mahatma Gandhi College, Thiruvananthapuram, Kerala, India, for providing the facilities for doing the experiment. Sincere gratitude to Dr C R Rajasree, Department of Chemistry, VHSC, Thiruvananthapuram and Mr. Shaji Rajamony, Specialism Social Care Professional, Sheffield Hallam University, UK, for their constant encouragement, valuable suggestions and useful discussions.

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